

AD-A184 698

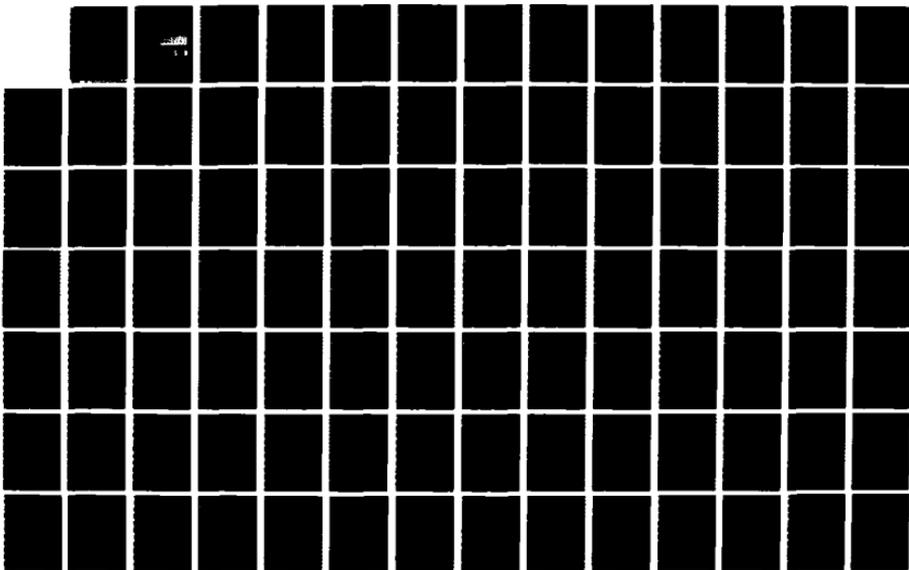
THE CONFERENCE ON THE DYNAMICS OF MOLECULAR COLLISIONS  
HELD IN OGLEBAY PA (U) JOHNS HOPKINS UNIV BALTIMORE MD  
P J DAGDIGIAN 17 JUL 87 ARO-24892 1-CH-CF  
DAAL83-87-G-8896

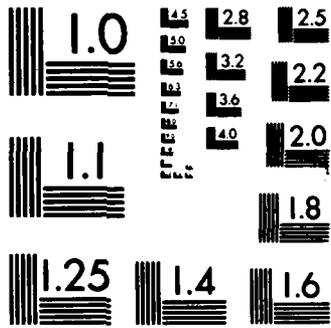
1/3

UNCLASSIFIED

F/G 7/4

NL





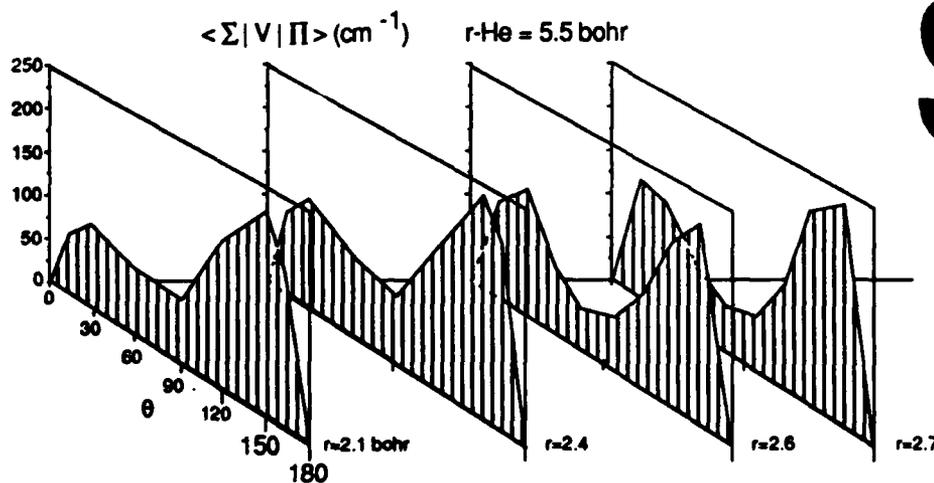
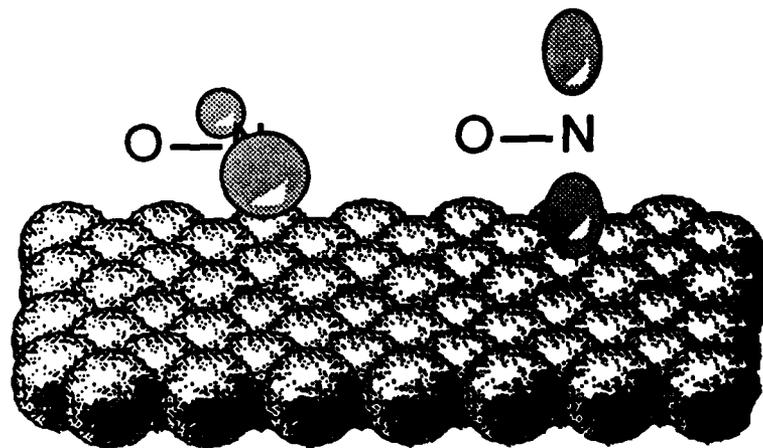
MICROCOPY RESOLUTION TEST CHART  
NATIONAL BUREAU OF STANDARDS-1963-A

2

AD-A184 690

# 1987 CONFERENCE ON THE DYNAMICS OF MOLECULAR COLLISIONS

July 12-17, 1987  
Oglebay Park  
Wheeling, West Virginia



DTIC  
ELECTE  
SEP 14 1987  
S D

**DISTRIBUTION STATEMENT A**  
Approved for public release  
Distribution Unlimited

Chairman: Paul J. Dagdigan  
Vice-Chairman: William H. Miller

# 1987 CONFERENCE ON THE DYNAMICS OF MOLECULAR COLLISIONS

July 12 - 17, 1987

Oglebay Park  
Wheeling, West Virginia

Chairman: Paul J. Dagdigan  
Vice-Chairman: William H. Miller  
Treasurers: Donald G. Truhlar and W. Ronald Gentry



Accession For	
NTIS CRA&I	<input checked="" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By _____	
Distribution/	
Availability Codes	
Dist	Avail and/or Special
A-1	

Sponsors: U.S. Army Research Office  
U.S. Air Force Office of Scientific Research  
Quantel International  
Research Corporation  
The Johns Hopkins University

**Cover Illustrations:** (a) Upper figure. Representation of the two possible orientations of the singly-filled  $\pi^*$  orbital on the NO molecule with respect to the (111) plane of a Ag surface. Since the interaction with the surface will depend on the orientation of the  $\pi^*$  orbital, the scattering of NO from the surface cannot be described by a single potential energy surface. Quantum interference between collisions occurring on these two potential surfaces will result in unequal population of the two  $\Lambda$ -doublet levels in the scattered NO molecules.

(b) Lower figure. Nonadiabatic coupling matrix element between the  $\text{CN}(X^2\Sigma^+)-\text{He}$  and  $\text{CN}(A^2\Pi)-\text{He}$  diabatic states of  $A'$  symmetry as a function of the orientation angle  $\theta$  and CN vibrational coordinate  $r$ , for a fixed  $\text{CN}\cdots\text{He}$  distance of 5.5 bohr (from MCSCF calculations of H.-J. Werner and M. H. Alexander). It is this coupling which gives rise to collision-induced transitions between the A and X states of CN. The bimodal angular dependence of this matrix element illustrates its near homonuclear character. Figures provided by Millard Alexander.

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER ARO 24892.1-GH-CF	2. GOVT ACCESSION NO. N/A	3. RECIPIENT'S CATALOG NUMBER N/A
4. TITLE (and Subtitle) 1987 Conference on the Dynamics of Molecular Collisions		5. TYPE OF REPORT & PERIOD COVERED Final Report - 1 May 87 - 30 Apr 88
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) Paul J. Dagdigian		8. CONTRACT OR GRANT NUMBER(s) DAAL03-87-G-0096
9. PERFORMING ORGANIZATION NAME AND ADDRESS The Johns Hopkins University 34th and Charles Streets Baltimore, MD 21218		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
11. CONTROLLING OFFICE NAME AND ADDRESS U. S. Army Research Office Post Office Box 12211 Research Triangle Park, NC 27709		12. REPORT DATE
		13. NUMBER OF PAGES
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report)  Approved for public release; distribution unlimited.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)  NA		
18. SUPPLEMENTARY NOTES  The view, opinions, and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy, or decision, unless so designated by other documentation.		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number)  Molecular collision dynamics, reactive collisions, molecular energy transfer, gas-surface interactions, photodissociation, van der Waals molecules.		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number)  The proceedings for the 1987 Conference on the Dynamics of Molecular Collisions, which was held in Oglebay Park, near Wheeling, WV, on July 12-17, is attached. There were formal sessions on both experimental and theoretical aspects of reactive collisions, inelastic energy transfer processes, and gas-surface interactions, as well as a special session on photodissociation and van der Waals molecules. There were 240 participants registered for the meetings, and 165 contributed papers were presented in several poster sessions.		

DD FORM 1 JAN 73 1473

EDITION OF 1 NOV 65 IS OBSOLETE

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

**Schedule of Presentations**  
**1987 Conference on the Dynamics of Molecular Collisions**  
 Oglebay Park, Wheeling, WV, July 12-17, 1987  
 Paul J. Dagdigan, Chairman; William H. Miller, Vice Chairman

Sunday, July 12

5:30 - 7:30 p.m. Registration and Reception

Monday, July 13

7:15 - 8:15 a.m.  
 8:30 - 12:00 noon

Breakfast  
 Session on Reactive Collisions (Experimental)  
 Chairman/Discussion Leader: S. L. Anderson  
 8:30 Announcements  
 8:40 S. R. Leone, "Overview."  
 9:30 Discussion  
 9:50 Break  
 10:10 Y. T. Lee, "Recent Crossed Molecular Beam  
 Studies on Elementary Chemical Reactions."  
 Discussion  
 11:05 C. Y. Ng, "State-to-State Electron Transfer  
 Reaction Dynamics."  
 Discussion  
 11:45 Discussion

12:15 - 1:15 p.m.  
 6:00 - 7:00 p.m.  
 7:20 - 10:10 p.m.

Lunch  
 Dinner  
 Session on Reactive Collisions (Theoretical)  
 Chairman/Discussion Leader: J. M. Bowman  
 7:20 D. G. Truhlar, "Overview."  
 8:10 Discussion  
 8:25 J. Manz, "Mode Selective Chemical  
 Reactions."  
 Discussion  
 9:05 Discussion  
 9:15 W. Meyer, "Theoretical Investigation of Electronic  
 Structures and Reactive Collisions Involving  
 Electronically Excited H<sub>2</sub>."  
 Discussion  
 9:55 Discussion

Tuesday, July 14

7:15 - 8:15 a.m.  
 8:30 - 11:55 a.m.

Breakfast  
 Session on Inelastic Energy Transfer (Experimental)  
 Chairman/Discussion Leader: C. A. Wight  
 8:30 U. Buck, "Overview."  
 9:20 Discussion  
 9:40 Break  
 10:05 K. Bergmann, "Rotational Rainbows in  
 Electron-Molecule Scattering."  
 Discussion  
 10:45 Discussion  
 11:00 G. W. Flynn, "Diode Laser Probing of Dynamic  
 Energy Transfer Events."  
 Discussion  
 11:40 Discussion

12:15 - 1:15 p.m.  
 2:00 - 2:30 p.m.  
 6:00 - 7:00 p.m.  
 7:30 - 10:00 p.m.

Lunch  
 Conference Business Meeting  
 Dinner  
 Poster Session I

Wednesday, July 15

7:15 - 8:15 a.m.  
 8:30 - 11:55 a.m.

Breakfast  
 Session on Inelastic Energy Transfer (Theoretical)  
 Chairman/Discussion Leader: F. R. McCourt  
 8:30 R. Schinke, "Overview."  
 9:20 Discussion

			9:40	Break
			10:05	D. J. Kouri, "Wavepacket Approach to Molecular Collisions."
			10:45	Discussion
			11:00	D. A. Micha, "Translational-to-Rovibrational Energy Transfer at Hyperthermal Velocities: Approaches Based on Collisional Time-Correlation Functions."
			11:40	Discussion
12:15	-	1:15		p.m. Lunch
6:00	-	7:00		p.m. Dinner
7:20	-	10:10		p.m. Session on Molecule-Surface Collisions (Experimental)
				Chairman/Discussion Leader: S. Bernasek
			7:20	S. J. Sibener, "Overview"
			8:10	Discussion
			8:25	M. Cardillo, "Hyperthermal Scattering from Surfaces: Electron Excitation, Ion Emission, and Rainbows."
			9:05	Discussion
			9:15	S. T. Ceyer, "Dynamics of Sticky Collisions with a Surface: Rotors, Splats, and Hammers."
			9:55	Discussion

Thursday, July 16

7:15	-	8:15		a.m. Breakfast
8:30	-	11:55		a.m. Session on Molecule-Surface Collisions (Theoretical)
				Chairman/Discussion Leader: J. W. Gadzuk
			8:30	J. C. Tully, "Overview."
			9:20	Discussion
			9:40	Break
			10:05	H. Metiu, "Time-Dependent Theory of Surface-Molecule Collisions: Gaussian Wave Packets and Fast Fourier Transform Methods."
			10:45	Discussion
			11:00	R. B. Gerber, "Atom Scattering from Surface Defects and from Disordered Surfaces."
			11:40	Discussion
12:15	-	1:15		p.m. Lunch
6:00	-	7:30		p.m. Banquet
8:00	-	10:00		p.m. Poster Session II

Friday, July 18

7:15	-	8:45		a.m. Breakfast
8:45	-	11:15		a.m. Session on Photodissociation/van der Waals Molecules
				Chairman/Discussion Leader: J. M. Lisy
			8:45	G. G. Ballint-Kurti, "Theory of Photodissociation Processes and Its Application to van der Waals Molecules."
			9:20	Discussion
			9:35	R. E. Miller, "The Structure and Photodissociation Dynamics of Binary and Tertiary van der Waals Complexes."
			10:10	Discussion
			10:25	D. Nesbitt, "Direct Absorption IR van der Waals Spectroscopy in Slit Supersonic Jets: Molecular Pinballs, Hinges, and Helicopters."
			11:00	Discussion
11:15	-	12:15		a.m. Lunch
12:30				p.m. Bus Departure for Greater Pittsburgh Airport

**ABSTRACTS  
OF  
PLENARY LECTURES**

## AN OVERVIEW OF EXPERIMENTAL REACTION DYNAMICS

Stephen R. Leone  
Joint Institute for Laboratory Astrophysics  
Department of Chemistry and Biochemistry  
National Bureau of Standards and University of Colorado  
Boulder, Colorado 80309

In the past several years the field of reaction dynamics has enjoyed the continued ingenuity and enthusiasm of many experimentalists who quest for the ultimate in specificity and detail in an attempt to unmask the underlying features of reacting systems. Studies range from the most fundamental tests for theoretical comparison, for example  $H + H_2$ , to the most subtle aspects of finely split spin orbit states, the effects of quantum mechanical resonances, lambda doublet populations, and mode selected ion chemistry. There is tremendous interest in the reactions of species trapped within van der Waals clusters and the possibilities of fixing molecular geometries before reaction by condensing molecules in clusters or on surfaces. The search for a full elucidation of the transition state continues.

This presentation will also investigate some of the rapid progress and news in spin orbit reactivity, alignment and orientation effects, resonances, vector correlations, rotational rainbows, reactions of hot atoms, and vibrationally, rotationally, and electronically state specific systems. Some new achievements with advancing techniques such as position sensitive detectors, coincidence methods, and ever powerful laser and molecular beam methods will be reviewed.

## RECENT CROSSED MOLECULAR BEAM STUDIES ON ELEMENTARY CHEMICAL REACTIONS

Yuan T. Lee

Materials and Molecular Research Division  
Lawrence Berkeley Laboratory and  
Department of Chemistry  
University of California  
Berkeley, California 94720 USA

This lecture will first briefly cover highlights of some of our recent investigations on the dynamics of elementary chemical reactions studied by the crossed molecular beams technique. The series of reactions which will be covered include endothermic substitution reactions involving bromine atoms and various chlorotoluene isomers, reaction of  $\text{CH}_3$  with  $\text{CF}_3\text{I}$  and  $(\text{CH}_3)_3\text{I}$  and the reaction of oxygen atom with  $\text{C}_2\text{H}_2$ .

The main part of the lecture will focus on the reaction dynamics of electronically excited sodium atoms with simple molecules. Special attention will be paid to the reaction of  $\text{Na}(4\text{D})$  with the  $\text{NO}_2$  molecule. This reaction does not seem to proceed unless the relative kinetic energy exceeds 18 kcal/mol. Two distinct reaction channels with vastly different dynamics are observed in the measurements of product angular and velocity distributions. Although these products only appear at  $m/e=23(\text{Na}^+)$  in mass spectrometric detection, they are likely to be  $\text{NaO}$  and  $\text{NaO}_2$ . The alignment of the excited orbital of  $\text{Na}(4\text{D})$  with respect to the relative velocity vector shows a dramatic effect on chemical reactivity. The rotation of the alignment of the  $\text{Na}(4\text{D})$  orbital also shows a very different effect whether the orbital is rotated in the scattering plane which contains both molecular beams and the detector or out of the scattering plane. The implication of these observations will be discussed in great detail.

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

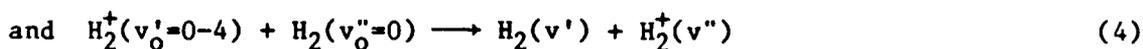
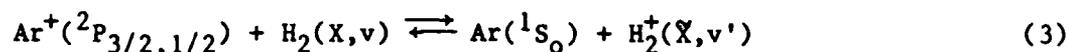
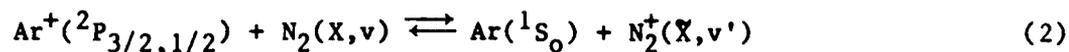
## State-to-State Electron Transfer Reaction Dynamics

C. Y. Ng

Ames Laboratory-USDOE and Department of Chemistry  
Iowa State University, Ames, Iowa 50011 USA

### Abstract:

The development of two new ion-molecule reaction apparatus for the study of state-selected and state-to-state ion-molecule reaction dynamics will be described. Using these apparatus, state-to-state cross sectional data for the electron transfer reactions<sup>1-4</sup>



have been obtained over wide kinetic energy ranges. These experiments provide detailed tests on the present theoretical understanding<sup>6-10</sup> of electron transfer processes. Valuable insight into the roles of vibronic coupling and energy resonance in electron transfer has been gained from the examination of state-to-state cross sections of reactions (2) and (3) in the forward and backward directions.

### References:

- (1) C.-L. Liao, C.-X. Liao, and C. Y. Ng, *J. Chem. Phys.* **81**, 5672 (1984); *ibid.* **82**, 5489 (1985).
- (2) C.-L. Liao, J.-D. Shao, R. Xu, G. D. Flesch, Y.-G. Li, and C. Y. Ng, *J. Chem. Phys.* **85**, 3874 (1986).
- (3) C.-L. Liao, R. Xu, and C. Y. Ng, *J. Chem. Phys.* **85**, 7136 (1986).
- (4) J.-D. Shao, G. D. Flesch, Y.-G. Li, and C. Y. Ng, *J. Chem. Phys.* **86**, 170 (1987).
- (5) C.-Y. Lee and A. E. DePristo, *J. Chem. Phys.* **80**, 1116 (1984).
- (6) M. R. Spalburg, J. Los, and E. A. Gislason, *Chem. Phys.* **94**, 327 (1985).
- (7) M. R. Spalburg and E. A. Gislason, *Chem. Phys.* **94**, 339 (1985).
- (8) G. Parlant and E. A. Gislason, *Chem. Phys.* **101**, 227 (1986).
- (9) P. Archirel and B. Levy, *Chem. Phys.* **106**, 51 (1986).
- (10) R. E. Johnson, *J. Phys.* **B3**, 539 (1970).

Abstract for 1987 Conference on the  
Dynamics of Molecular Collisions,  
Wheeling, WV, July 12-17, 1987

OVERVIEW LECTURE: THEORETICAL STUDIES  
OF REACTIVE COLLISIONS

Donald G. Truhlar  
Department of Chemistry and Supercomputer Institute,  
University of Minnesota, Minneapolis, MN 55455

There are several new approaches to the quantum mechanical reactive scattering problem, and I will review these as a major part of the overview. Other topics covered will include semiclassical approximations, comparisons to experiment, and potential energy surfaces for reactive scattering.

## Mode selective chemical reactions

Jörn Manz

Institut für Physikalische Chemie

Universität Würzburg

Marcusstr. 9-11

8700 Würzburg

Germany

Mode selective chemical reactions allow efficient investment of energy in educts, as well as control of products' distributions. Various dynamical effects are demonstrated using experimental results as well as theoretical models and movies. The bimolecular examples include the Polanyi rules of vibrational versus translational mode selectivity in hydrogen atom plus dihalogenic molecule reactions, the relations of mode specific energy release in forward reactions versus mode selective energy consumption in back reactions as implied by microscopic reversibility and detailed balance, Bernstein-Levine-type information theoretic surprisal analyses of non-statistical effects, and Baer's rule of approximate conservation of translational energy as well as oscillatory reactivity and resonances in elementary hydrogen transfer reactions. The unimolecular examples cover mode selective dissociations of van-der-Waals complexes, small and large polyatomic molecules, with particular consideration of local versus hyperspherical mode selective resonance decay of vibrationally excited water and formaldehyde molecules.

THEORETICAL INVESTIGATION OF ELECTRONIC STRUCTURES AND  
REACTIVE COLLISIONS INVOLVING ELECTRONICALLY EXCITED H<sub>2</sub>.

W. Meyer  
Fachbereich Chemie  
Universität Kaiserslautern  
D-6750 Kaiserslautern  
FED. REP. GERMANY

Problems encountered in the investigation of strongly changing electronic structures by advanced ab initio techniques will be discussed. They will be exemplified in particular by the small but nontrivial system H<sub>2</sub>-H<sub>2</sub>(B<sup>1</sup>Σ<sub>u</sub><sup>+</sup>). The entrance channel interaction potential and possible pathways for reactive quenching will be characterized. The quenching cross section obtained from rather simple dynamical calculations is in excellent agreement with the measured ones. Comparison will be made with systems involving H<sub>2</sub><sup>\*</sup> and noble gases.

## Inelastic Energy Transfer (Experimental)

U. Buck

Max-Planck-Institut für Strömungsforschung, D-3400 Göttingen,  
Fed.Rep. of Germany

The study of rotational and vibrational energy transfer in molecular collisions is still a very active field of research. The interest comes from a range of applications in chemistry, spectroscopy and astrophysics as well as from the general aim to understand the underlying mechanism and the intermolecular potential. Accordingly, the measured quantity of interest is either a rate constant or a differential cross section both at a state resolved level of detail. While the measurement of state-to-state rate constants has reached a highly sophisticated level using excitation and detection with pulsed lasers, the measurement of angular dependent state selective cross sections in a crossed molecular beam experiment is not an easy task. Therefore often two other quantities are used to extract information on the interaction potential in which one of the strict requirements has been relaxed: state selective integral cross sections and the differential energy loss cross sections.

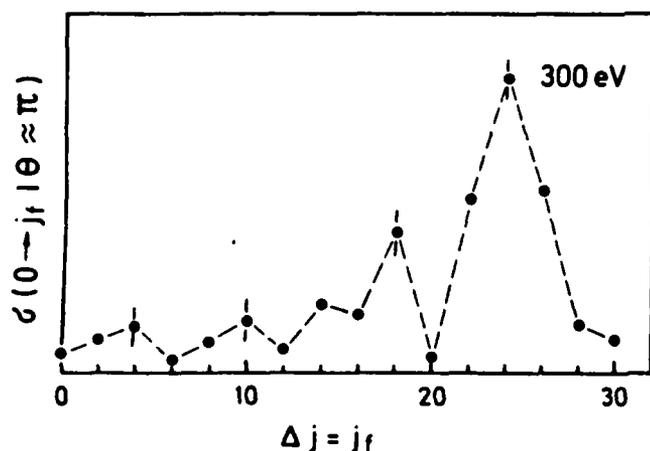
In the first part of this overview the experimental techniques for state preparation and state selection will be summarized and illustrated by typical examples both for cell experiments and molecular beam work. Then measured cross sections will be presented with particular emphasis on recent developments concerning diatomic open-shell molecules and vibrationally excited molecules as well as polyatomic molecules and small clusters. Finally the information content and the relation of the different measured quantities to the interaction potential will be discussed. This includes simple models for the interpretation of the data and the discussion of open questions in the field.

# ROTATIONAL RAINBOWS IN ELECTRON-MOLECULE SCATTERING

K. Bergmann

Fachbereich Physik der Universität, Postfach 3049,  
D-6750 Kaiserslautern, FRG

Rotational excitation of molecules in their electronic ground state by electron impact is one of the most important energy transfer processes in low temperature laboratory gas discharges and in low lying planetary ionospheric layers. Over the last few years, crossed beams experiments yielded total and differential cross sections and elucidated the mechanisms through which these processes proceed preferentially. No experimental nor theoretical investigations with state selection for other than hydrogen molecules or energies exceeding 100 eV have been reported. In particular, no experimental data are available for scattering in the backward direction. This angular range is not accessible in conventional electron scattering spectrometers. In this lecture state-to-state differential cross sections for scattering angles in the range  $90^\circ < \Theta < 180^\circ$  for collision



energies of 150, 225 and 300 eV, using the well established state selection technique /1/, are presented /2/. We find rotational transitions as large as  $\Delta j=28$  and pronounced rotational rainbow structures. This result is of fundamental importance because it is expected to be generally valid for high energy electron-molecule scattering.

Fig. 1: Rotational rainbow structure in  $\text{Na}_2$ -e scattering.

## REFERENCES

- 1 U. Hefter, P.L. Jones, A. Mattheus, J. Witt, K. Bergmann, and R. Schinke, Phys. Rev. Lett. **46**, 915 (1981)
- 2 G. Ziegler, M. Rädle, O. Pütz, K. Jung, H. Ehrhardt, and K. Bergmann, to be published

George W. Flynn  
Department of Chemistry  
and Columbia Radiation Laboratory  
Columbia University  
New York, NY 10027

DIODE LASER PROBING OF DYNAMIC ENERGY

TRANSFER EVENTS

Infrared diode lasers have been used to probe more than a dozen different carbon dioxide vibrational states and tens of rotational levels in each separate vibrational state produced as the result of collisions, photodissociation, and chemical reactions. Collisions between hot hydrogen or deuterium atoms (approximately 2eV translational energy) and cold CO<sub>2</sub> produce a wide distribution of excited vibrational and rotational states. Direct excitation of the CO<sub>2</sub> pure antisymmetric stretch levels 00<sup>0</sup><sub>1</sub> and 00<sup>0</sup><sub>2</sub> has been detected, and the rotational distribution produced in these vibrational states as a result of hot atom collisions is peaked at J=33. Relaxation of electronically-excited mercury atoms, NO<sub>2</sub> molecules, and azulene molecules due to collisions with a bath of room temperature CO<sub>2</sub> molecules has been studied. In these experiments, diodes are used to probe the energy of the vibrational modes of the CO<sub>2</sub> bath produced as a result of the relaxation of these electronically-excited donors. The low frequency CO<sub>2</sub> bending modes are produced more efficiently than the antisymmetric stretching modes for quenching of mercury atoms and azulene molecules, but the mechanism for relaxation of atoms, small and large molecules is clearly different in each case.

Inelastic Energy Transfer (Theoretical)

R. Schinke

Max-Planck-Institut für Strömungsforschung

D-3400 Göttingen, FRG

Recent developments of the theory of inelastic energy transfer will be reviewed. This includes new methods as well as applications to realistic systems. Of particular interest are rotational and vibrational excitation in atom-molecule and molecule-molecule collisions and the qualitative relation between the cross sections and the multi-dimensional potential energy surface. We will also consider electronic fine structure transitions in collisions with open shell molecules such as OH or NO. An appreciable amount of time will be allocated to direct photodissociation processes (half collisions) which are in many respects similar to atom-molecule collisions. The common features as well as significant differences will be discussed.

## WAVEPACKET APPROACH TO MOLECULAR COLLISIONS

Donald J. Kouri  
Department of Chemistry  
University of Houston  
Houston, TX 77004

The Schrödinger equation is a first-order linear partial differential equation and as a result, it is an initial value equation rather than a multipoint boundary value problem. This implies that one may obtain solutions corresponding to a single initial internal state when considering collision processes. An important consequence is that one may develop solution techniques which scale as the square of the number of quantum states involved in the collision. Further, most molecular beam experiments utilize a supersonic nozzle which leads to only a few initial internal states and therefore methods that only need calculate scattering for those may be very efficient. Time independent (close coupling) methods must calculate as many solutions to the scattering as there are coupled quantum states. As a result, they scale as the cube of the number of quantum states. Finally, wavepackets can contain components for many energies and thus the scattering information for all of the energies in the packet is obtained in a single wavepacket propagation. In this talk, the basic ideas of the wavepacket approach will be presented. The initial test calculations for the Lester-Bernstein model problem will be given to illustrate the method for gas phase collisions. These results include some obtained including 969 quantum states. In addition, sample applications to other scattering problems will be mentioned, including an exact quantum calculation done for  $N_2$  scattered off a LiF model corrugated surface, which included 18,711 rotation-diffraction states. The extension of the approach to treat reactive gas phase collisions will also be indicated.

Abstract for the 1987 Conference on the  
Dynamics of Molecular Collisions

TRANSLATIONAL-TO-ROVIBRATIONAL ENERGY TRANSFER AT HYPERTHERMAL  
VELOCITIES: APPROACHES BASED ON COLLISIONAL TIME-CORRELATION  
FUNCTIONS

David A. Micha  
Departments of Chemistry and of Physics  
University of Florida  
Gainesville, Florida 32611

Methods based on collisional time-correlation functions can be used to describe mechanisms of energy transfer in collisions of pairs of molecules with hyperthermal kinetic energies, and to calculate double differential cross sections for energy and angular distributions. Impulsive scattering, semi-classical and operator algebraic methods have been applied to the scattering of atoms with free and adsorbed molecules to calculate cross sections for usual experimental conditions.[1-3]

1. D. A. Micha, Intern. J. Quantum Chem. Symp.19, 443 (1986)
2. E. Vilallonga and D. A. Micha, J. Chem. Phys. 86, 750 and 760 (1987)
3. J. A. Recamier, D. A. Micha and B. Gazdy, J. Chem. Phys. 85, 5093 (1986)

## OVERVIEW: MOLECULE-SURFACE COLLISIONS (EXPERIMENTAL)

S. J. Sibener  
Department of Chemistry  
The University of Chicago  
Chicago, IL 60637

Recent experimental advances made in the areas of gas-surface and laser-surface interactions will be reviewed. Subjects examined will include elastic, inelastic, and reactive scattering experiments, as well as laser and electron induced desorption processes. Information obtained on topics such as interaction potentials, surface structure, adsorbate and defect properties, state-to-state interactions, energy transfer, surface phonon dispersion, reaction dynamics, and laser desorption mechanisms will be highlighted.

"Hyperthermal Scattering from Surfaces: Electron  
Excitation, Ion Emission, and Rainbows"

Mark J. Cardillo  
AT&T Bell Laboratories  
600 Mountain Ave.  
Murray Hill, N.J.

ABSTRACT

Nonadiabatic excitation processes have been directly measured in the scattering of 2-15eV rare gas atoms from single crystal semiconductor surfaces. These include: electron-hole pair excitations, ejection of ionic substrate and adsorbate atoms (neutrals are also observed), and incident particle ionization.

In addition, sharp rainbow maxima are observed in the scattered angular distributions which are sensitive to the surface topography yet insensitive to the massive energy loss of the incident particle. The energy loss for all surfaces scales with the energy of local normal motion.

Simple models will be developed which provide good explanations of the principal observations, the critical aspects of which are confirmed by classical trajectory calculations.

## Dynamics of Sticky Collisions with a Surface: Rotors, Splats and Hammers

S. T. CEYER  
Department of Chemistry  
Massachusetts Institute of Technology  
Cambridge, MA 02139

New and more direct evidence for the existence of a precursor molecule to molecular chemisorption will be discussed. We have found that there are two pathways through which CO chemisorbs on Ni(111): a pathway through which the CO molecule is initially adsorbed as a precursor to molecular chemisorption and a pathway through which adsorption into the molecular chemisorption state occurs directly from the gas phase. The precursor molecule is depicted as a tumbling rotor, still unhindered in its motion at 8K. These conclusions result from measurements of the effects of translational energy on chemisorption carried out in an apparatus combining molecular beam techniques with ultrahigh vacuum surface spectroscopies.

These techniques have also been used to show that there is a barrier to the dissociative chemisorption of CH<sub>4</sub> on Ni(111) and that the normal component of the translational energy of the incident CH<sub>4</sub> molecule is effective in surmounting it. The barrier arises from the energy necessary to deform the molecule to bring the carbon atom sufficiently close to the surface to form a Ni-C bond. Vibrational excitation of the incident CH<sub>4</sub> is similarly effective in promoting dissociative chemisorption. The large kinetic isotope effect and the exponential dependence of the dissociation probability on translational and vibrational energy indicate that tunneling also plays a role in the final C-H bond breaking step. The product of the dissociative chemisorption event is identified by high resolution electron energy loss spectroscopy as an adsorbed methyl radical and a hydrogen atom at a surface temperature of 130 K. The chemistry and stability of the methyl radicals are studied. The presence of this barrier presents a plausible explanation for an origin of the pressure gap in heterogeneous catalysis and provides a link between ultrahigh vacuum surface science and high pressure catalysis.

A new mechanism for dissociative chemisorption, collision-induced dissociation of adsorbates, will be discussed. We have shown that the dissociative chemisorption of CH<sub>4</sub>, molecularly adsorbed on a Ni(111) surface at 46 K, is induced by the impact of incident Ar atoms. The probability for dissociative chemisorption is exponentially dependent on the normal component of the kinetic energy of the Ar atoms. The impact of the Ar atom deforms the molecularly adsorbed methane molecule into the configuration for the transition state that leads to dissociation. The implications of collision-induced dissociative chemisorption of adsorbates for high pressure catalysis are immense. No reaction mechanism for heterogeneous catalysis under high pressure conditions can now be considered complete without assessing the importance of collision-induced chemistry. Collision-induced dissociative chemisorption of adsorbates is likely another contributor to the origin of the pressure gap in heterogeneous catalysis.

This work is supported by the National Science Foundation (CHE-8508734) and the Synthetic Fuels Center of the Energy Lab at MIT.

Overview: Molecule-Surface Collisions (Theory)  
John Tully, AT&T Bell Laboratories

Molecular collisions with surfaces have aspects in common with both gas-phase and liquid-phase dynamics. A gas-phase scattering picture is appropriate for initial and final states; i.e., questions concerning the efficacy of internal or translational energy in promoting reaction, the non-equilibrium disposal of energy in products, and the lifetime of the molecule-surface "collision complex" are relevant. During the time molecules are in close contact with the surface, however, the substrate plays a role similar to that of the solvent in solution chemistry. Interactions are mediated by the solvent, and frictional or stochastic elements are introduced. In addition, interesting dynamical effects emerge that, if not unique, are at least more prominent for gas-surface collisions. Among these are effects such as diffraction deriving from the crystal periodicity, continuous nesting of potential surfaces in metallic systems, and striking orientational effects imposed by the unique direction of the surface normal. Some current challenges in the theory of gas-surface interactions and recent progress toward surrounding these challenges will be summarized.

Time Dependent Theory of Surface-Molecule Collisions: Gaussian Wave Packets and Fast Fourier Transform Methods. Horia Metiu, Department of Chemistry, University of California, Santa Barbara, CA 93106.

We show results obtained by applying Gaussian wave packet and fast Fourier transform methods to study quantum processes occurring in molecule-surface collision problems. These cover He diffraction by a lattice in thermal motion, diffraction and rotational excitation of  $H_2$  colliding with a surface and  $H_2$  dissociation (in two dimensions!). If time permits we will discuss briefly simple model calculations pertinent to hydrogen diffusion on surfaces and adsorption-desorption processes in a system where desorption requires curve crossing.

## Atom Scattering from Surface Defects and from Disordered Surfaces

R.B. Gerber

Department of Physical Chemistry  
and The Fritz Haber Research Center  
The Hebrew University of Jerusalem  
Jerusalem 91904 Israel

### Abstract

Most recently, scattering of light atoms and molecules has emerged as a potentially powerful probe of imperfections on surfaces. Theoretical results are presented on the angular intensity distributions of atoms scattered from imperfect surfaces, which shed light on the relation between the measured intensity patterns and: The interaction between the defect and the scattered atom; Geometric parameters of the imperfection; The mutual (disordered) arrangement of the defects on the surface. Results are obtained also on the effects of defects on the diffractive scattering (from the crystalline part of the surface); Conditions for collapse of diffraction structure as disorder is increased; and new, non-Bragg intensity maxima due to scattering from the defects.

Calculations are presented for He scattering from vacancies on Pt(111), from CO adsorbates on Pt(111), and from mixtures of Xe and Ar in overlayers on Pt. Time-dependent quantum wavepacket techniques and the Sudden Approximation are used in different calculations. Specific findings include (1) Cross sections (measuring the attenuations of specular intensities) for scattering by adsorbates are sensitive to adsorbate location, but almost uninfluenced by interactions with the adsorbate image; (2) The energy and incidence angle dependence of the cross section suffice to determine an accurate He/defect potential; (3) New maxima in the scattering intensity are predicted associated with impurity-induced rainbows, and with impurity-induced selective adsorption; (4) Diffraction collapse in He scattering from mixed Xe + Ar overlayers is shown to occur as the "contamination" of the Xe by Ar is sufficiently increased.

It is argued that He scattering offers exciting possibilities for studying structural and dynamical properties of noncrystalline surfaces.

Theory of Photodissociation Processes  
and its Application to van der Waals Molecules

G.G. Balint-Kurti

School of Chemistry, University of Bristol,  
Bristol BS8 1TS, England

The theory of photodissociation and predissociation processes [1,2] is discussed and its application to van der Waals molecules reviewed. Results of applying the theory to the Ar-H<sub>2</sub> and Ar-HD van der Waals molecules are presented. The total integral photodissociation cross sections computed in the manner described correspond to the experimentally observed spectroscopic line shapes. Such line shapes for vibrational and rotational predissociation processes are presented and discussed [3]. Partial photodissociation cross sections, which tell us how the intermediate metastable predissociative complex decomposes into different fragment quantum states, are also given. For Ar-HD the results of the thermal averaging of many cross sections for individual elementary processes [4] to construct a simulated IR spectrum is presented [5]. New theoretical developments concerned with the application of multichannel quantum defect theory to such processes are discussed.

1. G.G. Balint-Kurti and M. Shapiro, Chem. Phys., 61, 137 (1981)
2. G.G. Balint-Kurti and M. Shapiro, Adv. Chem. Phys. 60, 403 (1985)
3. I.F. Kidd and G.G. Balint-Kurti, J. Chem. Phys. 82, 93 (1985)
4. I.F. Kidd and G.G. Balint-Kurti, Faraday Discuss. Chem. Soc. 82, (1986) (in press)
5. I.F. Kidd and G.G. Balint-Kurti, Chem. Phys. Letters, 105, 91 (1984).

THE STRUCTURE AND PHOTODISSOCIATION DYNAMICS OF BINARY AND  
TERTIARY VAN DER WAALS MOLECULES

R. E. Miller

Department of Chemistry

University of North Carolina

Chapel Hill, NC 27514

Recent advances in the field of infrared laser-molecular beam spectroscopy have made possible the detailed study of both the structure and photochemistry of a wide range of van der Waals and hydrogen bonded molecules. In our laboratory, we have made use of the optothermal detection method to study a number of these systems. In several cases, we have been able to obtain excited state lifetimes (from the homogeneous broadening of the observed transitions) for more than one vibrational state of the molecule. These results indicate that there is a strong mode specificity for vibrational relaxation which can be understood in terms of simple geometrical factors. For example, in the T-shaped  $C_2H_2$ -HF complex, excitation of the HF stretch, which is directly coupled to the van der Waals bond, gives rise to a shorter lifetime than that associated with the decoupled C-H stretch on the acetylene subgroup. This same effect has also been seen for the case of the "free" and "hydrogen bonded" C-H stretches of  $(HCN)_2$  and F-H stretches of  $(HF)_2$ .

Recently, we have made considerable advances in the study of tertiary complexes such as  $(CO_2)_3$  and  $(HCN)_3$ . In the case of the latter, both the linear and cyclic conformer have been observed. For the larger complexes, mode specific vibration relaxation is even more pronounced than in the dimers.

Direct Absorption IR van der Waals Spectroscopy in Slit Supersonic Jets:  
Molecular Pinballs, Hinges and Helicopters

David Nesbitt  
Joint Institute for Laboratory Astrophysics  
Bureau of Standards & University of Colorado  
Department of Chemistry & Biochemistry  
Boulder, Colorado 80309-0440

Abstract:

The combination of high resolution cw tunable difference frequency generation, high sensitivity ( $<10^{-6}/\sqrt{\text{Hz}}$ ) direct absorption methods and long path length (2.5cm) pulsed slit expansions provide a general method of spectroscopic investigation of weakly bound complexes in a cold molecular beam environment. The ability to probe both high frequency ("intramolecular") modes via fundamental absorptions as well as low frequency ("intermolecular") modes via hot band and combination band absorptions in these complexes permits investigation of the global features of the potential surface not sampled by rotational spectroscopic studies of the ground vibrational state. The floppy nature of the binding between the molecular constituents results in intramolecular dynamics (i.e. vibrationally averaged geometries, bond lengths, barriers to internal rotation, dissociation energies) that depend on internal quantum state. Since the intermolecular vibrational motion can occur on time scales comparable to end over end rotational motion, this results in a breakdown of traditional methods of spectroscopic analysis. These phenomena are discussed in the context of bimolecular complexes of HF with Ar, CO<sub>2</sub> and H<sub>2</sub> (D<sub>2</sub>), in which large amplitude motion in stretch, bend and nearly free internal rotation are evidenced in the spectra and fully analyzed.

## **CONTRIBUTED PAPERS**

### **Tuesday Evening Session**

Reactive Collisions - Theoretical (RT)

Reactive Collisions - Experimental (RE)

Molecule-Surface Collisions - Theoretical (ST)

Molecule-Surface Collisions - Experimental (SE)

### **Thursday Evening Session**

Inelastic Energy Transfer - Theoretical (ET)

Inelastic Energy Transfer - Experimental (EE)

Photodissociation, Photoionization (P)

van der Waals Molecules (V)

Quantum Chemistry by Random Walk:  
Application to the Potential Energy Surface for  $F + H_2 \rightarrow HF + H$

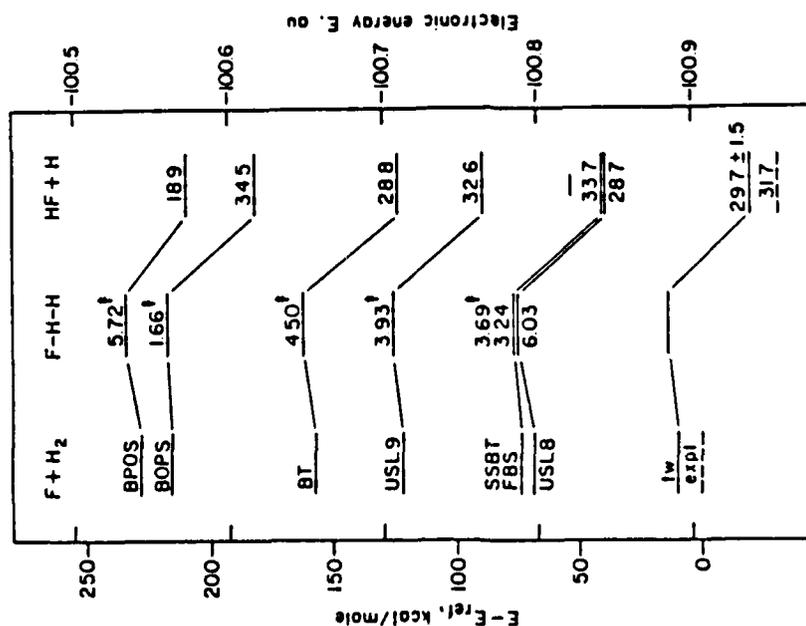
David R. Garmer and James B. Anderson

Department of Chemistry, The Pennsylvania State University  
152 Davey Laboratory, University Park, Pennsylvania 16802

We have applied the random walk method of solving the Schrodinger equation to determine energies of the following species: the fluorine atom F, the hydrogen fluoride molecule HF, and a number of F-H-H configurations of interest in determining the height and location of the saddle point for the reaction  $F + H_2 \rightarrow HF + H$  and the characteristics of the potential energy surface in the region of the barrier. Several of the F-H-H configurations examined correspond to those suggested as saddle points in past variational calculations.

In what may be "Paradise Regained" we obtain electronic energies for these species which are approximately 65 kcal/mol below those of the lowest-energy variational calculations and for F and HF are only about 9 kcal/mol above the relativity-adjusted experimental values. Recovery of correlation energy is 96 percent complete. Since there is little room left for error, differences in energies among  $F + H_2$ , F-H-H, and HF + H are expected to be relatively free of error.

Thus far, we have obtained potential energies for F-H-H with statistical uncertainties of about 1 kcal/mol. We will reduce these for the most important configurations so that questions of saddle point height and location can be resolved.



N.B.: Incomplete list; †Theoretical saddle point, determined by search. Others at saddle points indicated by earlier studies.

QUANTUM MECHANICAL STUDY OF CHEMICAL REACTION AND CHARGE TRANSFER  
PROCESSES IN THE  $(Ar+H_2)^+$  SYSTEM

Michael Baer, Soreq Nuclear Research Center, Yavne 70600, Israel

and Hiroki Nakamura, Division of Theoretical Studies, Institute for  
Molecular Science, Myodaiji, Okazaki 444 JAPAN

Abstract

A quantum mechanical study within the Reactive Infinite Order Sudden Approximation for the ion-molecule system  $(Ar^+ + H_2, ArH_2^+, ArH^+ + H)$  is carried out.<sup>(1)</sup> All three arrangement channels for exchange and charge transfer were treated simultaneously. Steric factors, opacity functions, angular distributions and integral cross sections were calculated. The results whenever possible were compared with both, with experimental results<sup>(2)</sup> and with trajectory surface hopping results.<sup>(3)</sup> In general a reasonable agreement was obtained for both integral cross sections and differential cross sections. The main discrepancy is found for the integral cross section of the reaction  $Ar + H_2^+(v_1=0) \rightarrow ArH^+ + H$  and a gratifying result is the nice fit between the experimental<sup>(4)</sup> and quantum mechanical differential cross sections for the reaction  $Ar^+ + H_2(v_1=0) \rightarrow Ar + H_2^+$ . As mentioned, also steric factors were calculated and they seem to reveal the existence of a new mechanism not entirely understood.

References

1. M. Baer, H. Nakamura and A. Ohsaki, Chem. Phys. Lett. 131, 468 (1986); M. Baer and H. Nakamura (sent for publication).
2. K. Tanaka, J. Durup, T. Kato and I. Koyano, J. Chem. Phys. 74, 5561 (1981); 75, 4941 (1981); F.A. Haule, S.L. Anderson, D. Gerlich, T. Turner and Y.T. Lee, J. Chem. Phys. 77, 748 (1982); K.M. Ervin and P.B. Armentrout, J. Chem. Phys. 83, 166 (1985).
3. S. Chapman, J. Chem. Phys. 82, 4033 (1985).
4. P.M. Hierl, V. Pacak and Z. Hermann, J. Chem. Phys. 67, 2678 (1977).

## SOLUTION OF DISSOCIATIVE STATE IN SHIFTED CHEBYSHEV SERIES

Lue-yung Chow Chiu and Edward E. LaFleur  
 Department of Chemistry, Howard University  
 Washington, D. C. 20059

The solution in shifted Chebyshev series has been derived for the following dissociative state radial equation:

$$\frac{d^2R}{dr^2} + \frac{\Lambda^2 - N(N+1)}{r^2} R + [k^2 - U(r)] R = 0 \quad (1)$$

where  $U(r) = B_1/r + B_2/r^2$ . For  $r \geq 1$ , substitution of

$R(r) = (2s)^S \exp(ik/z + iplnz) F(z)$  into Eq.(1), where  $z=1/r$ ,

$s = 1/2 + [1/4 + N(N+1) + B_2 - \Lambda^2]^{1/2}$  and  $p = B_1/2k$ , yields

the following confluent hypergeometric equation:

$$z^2 F''(z) + [(2 + 2ip)z - w] F'(z) + (s+ip)(1-s+ip) F(z) = 0 \quad (2)$$

where  $w=2ik$ . Substituting a shifted Chebyshev polynomial expansion<sup>1,2</sup>, i.e.  $F(z) = \sum_n G_n(w) T_n^*(z)$ , into Eq.(2), and integrating Eq.(2) two times, we obtain a five-term recurrence relation as follows:

$$\begin{aligned} & \left[ 1 + \frac{(a_1-1)(a_2-1)}{n(n-1)} + \frac{a_1 + a_2 - 3}{n} \right] G_{n-2} \\ & + \left[ 4 + \frac{2(a_1 + a_2 - 3)}{n} + \frac{4w}{n} \right] G_{n-1} \\ & + \left[ 6 - \frac{2(a_1-1)(a_2-1)}{(n-1)(n+1)} \right] G_n + \left[ 4 - \frac{2(a_1 + a_2 - 3)}{n} - \frac{4w}{n} \right] G_{n+1} \\ & + \left[ 1 + \frac{(a_1-1)(a_2-1)}{n(n+1)} - \frac{a_1 + a_2 - 3}{n} \right] G_{n+2} = 0 \end{aligned} \quad (3)$$

Where  $a_1 = s + ip$  and  $a_2 = 1 - s + ip$ . The expansion coefficients  $G_n(w)$  can then be evaluated through the backward recursions.<sup>3</sup> The above recurrence relation can be reduced to the four-term recurrence relation derived previously<sup>3</sup>. The new method developed here can be extended to solve the differential equations of different potential function  $U(r)$ .

- 
- 1) Y.L.Luke, "The Special Functions and Their Approximations (Academic New York 1969) Vols I and II.
  - 2) C.W. Clenshaw, Proc. Cambridge Phil. Soc. 53,134 (1957).
  - 3) E.E.LaFleur and L.-Y.Chow Chiu, J.Chem.Phys.84,2150(1986).

## A New Approach for the Determination of Addition Rate Constants from the Analysis of Relaxation Measurements

Ronald J. Duchovic and Albert F. Wagner  
Chemistry Division, Argonne National Laboratory, Argonne, IL 60439

David M. Garner and Donald G. Fleming  
TRIUMF, University of British Columbia, Vancouver, B. C. V6T 2A3 Canada

A variety of relaxation techniques has been applied to study the reaction rates of chemical processes in which extremely short-lived intermediate species play a fundamental role. E. B. Gordon, et al. [*Chem. Phys. Lett.* **35**, 79(1978)] have determined addition rate constants using a hydrogen maser to measure spin shifts and broadening in the hyperfine transition of atomic hydrogen. The technique of muonium spin relaxation, pioneered by the research group at TRIUMF [see D. G. Fleming, et al. *Muonium Chemistry--A Review*, in *Positronium and Muonium Chemistry*, H. J. Ache, ed., American Chemical Society, 1979], has been utilized to measure rate constants for a number of muonium addition and abstraction reactions in the presence of a buffer gas.

Previously, the results of relaxation experiments have been analyzed using an *abstraction* model. In this work we report the development of a new *addition* model which includes the competing processes of unimolecular decomposition and pressure stabilization. Both the unimolecular decomposition and the pressure stabilization rate constants included in the new model can be related directly to RRKM theory. The new model allows the determination of the high-pressure limit rate constant from data collected in relaxation experiments performed at *any* pressure.

This model is applied to a set of synthetic data (including a randomly generated noise component) designed to simulate the results of a muonium spin relaxation experiment. These calculations suggest that it is possible to extract both the high-pressure limit addition rate constant and the unimolecular decomposition rate constant, provided the noise component is well-controlled. Secondly, the new model is used to analyze actual data from a muonium spin relaxation experiment, permitting a comparison of the previous *abstraction* analysis with the current *addition* analysis.

**ACKNOWLEDGEMENT:** Work supported by the U. S. Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences, under contract W-31-109-ENG-38.

NUMERICAL INTEGRATION OF DIFFERENTIALLY COUPLED EQUATIONS:  
APPLICATION TO THE STUDY OF NON-ADIABATIC INTERACTIONS IN MOLECULES

by

T. Tung Nguyen-Dang, Sylvain Durocher  
Université de Sherbrooke  
Département de Chimie  
Sherbrooke, Québec, Canada

J1K 2R1

and

Osman Atabek  
Laboratoire de Photophysique Moléculaire  
Université de Paris-Sud  
Orsay, France  
91405

ABSTRACT

It is shown that coupled differential equations involving derivative channel couplings, as arise in collision problems formulated in terms of adiabatic basis, can be solved numerically by a three points recurrence formula. This recurrence formula exhibits a structure similar to the well known Numerov formula for potential multiplicative coupled channels problems.

Introduction of differential couplings results in a lowering in the order of the integrator with respect to the step size 'h'. Nevertheless, this is expected to be compensated by the reduction in the number of coupled channels as a result of using an adiabatic basis. Indeed, it is known that non-adiabatic couplings of adiabatic states are generally more localized on the energy scale than the corresponding potential adiabatic couplings of equivalent diabatic states.

The above property is illustrated by results of the numerical integrations of coupled equations for the Hénon-Heiles hamiltonian in an adiabatic basis, using the present algorithm, and in the usual diabatic basis of zeroth order harmonic oscillator states, using the usual Numerov formula.

The Onset of Non-Rotating Wave Effects for  
Reactive Collisions in a Laser Field

RT6

James C. Peploski and Larry Eno  
Clarkson University  
Potsdam, NY 13676

A number of aspects of the breakdown of the rotating wave approximation (RWA) in laser modified reactive collision processes are examined. An analysis is presented into the factors which are responsible for the breakdown and our conclusions are similar to those in a recent article by Last, save with regard to the effect of varying laser field strength. We also consider ways in which one can correct for the onset of RWA breakdown. The schemes considered, all depend upon suppression (by matrix transformation) of low order couplings to the non-RWA channels. Application of the schemes and general investigation of non-RWA behavior is made for a simple model problem involving a single nuclear degree of freedom. We find that the results of the calculations lend support to our identified breakdown factors. Of the correction schemes, one is clearly to be preferred, although a second may also have merit. Finally, we discuss a number of complicating features of the theoretical description of laser modified collisions which may be expected to frequently accompany the appearance of non-RWA effects.

The Sensitivity Approach to the Analysis of  
Parameter Dependencies in Reactive Collision Theory

Thomas R. Horn and Larry Eno  
Clarkson University  
Potsdam, NY 13676

New working expressions are given for the first derivatives or elementary sensitivity coefficients of reactive and non-reactive scattering matrices with respect to an arbitrary input parameter. The expressions, as in our earlier work, are constructed for collinear reaction but within now a less restricted representation of the electronic-vibrational degrees of freedom. Application is made to two simple test problems. The first deals with the collision energy dependence of transmission and reflection on a one dimensional potential curve. We examine the relative convergence behavior of values and energy derivatives of the scattering elements with the steplength in our procedure for integrating the dynamical equations. The second test problem adds on a closed potential curve which is non-adiabatically coupled to the potential curve of the first (test problem). We examine the effectiveness of sensitivity and non-sensitivity calculations in describing how the scattering elements behave through the space of a parameter which centers the non-adiabatic coupling envelope. We find that for the single parameter variation, sensitivity and half-spaced non-sensitivity calculations using a common steplength, yield essentially equal quality descriptions of the parameter dependence. When this finding is projected into a multi-parametric context and we roughly estimate the relative work involved in the two approaches, a minimum order for the parameter space, i.e. 2, is identified such that the sensitivity approach may be expected to be the more efficient.

**Application of variational transition state theory  
to the isomerization reaction  $\text{HONO} \rightarrow \text{HNO}_2$ \***

Bruce C. Garrett  
Chemical Dynamics Corporation  
Upper Marlboro, Maryland 20772

Marcy E. Rosenkrantz<sup>†</sup> and Byron H. Lengsfeld III  
Ballistics Research Laboratory  
Aberdeen, Maryland 21005

Unimolecular hydrogen migration reactions are important in gas-phase combustion processes. The isomerization of HONO is a prototypical example which is thought to be important in the combustion of nitro containing compounds. Although the  $\text{HNO}_2$  species has not been seen directly under combustion or flame conditions, it has been postulated to explain experimental results. One possible route for production of  $\text{HNO}_2$  is the isomerization of HONO, however, the barrier for this reaction is known to be high. One of the goals of this study is to obtain an estimate of the order of magnitude of the rate for this reaction.

High pressure thermal rate constants are computed for the  $\text{HONO} \rightarrow \text{HNO}_2$  reaction using variational transition state theory with multidimensional transmission coefficients. The rates are computed using potential energy information obtained from *ab initio* electronic structure calculations. The potential energy and analytic first and second derivatives along the reaction path are calculated using the multiconfiguration self consistent field (MCSCF) method.

The barrier for this reaction is quite high (approximately 60 kcal/mol) which leads to very small computed rates when quantum mechanical tunneling effects are neglected. For temperatures from room temperature up to about 600K the reaction is dominated by tunneling; the tunneling correction factor varies over several orders of magnitude for this temperature range. Thus, although the barrier is very high, the reaction is facilitated by quantum mechanical tunneling. Preliminary results indicate that the reaction rate is appreciable for temperatures characteristic of combustion conditions.

A major concern in calculations based upon *ab initio* potential energy information is the effective use of the computed potential information. We examine the dependence of the computed rates on the amount of potential information available along the reaction path. The dependence of the rates on the level of accuracy of the *ab initio* potential energy information is also addressed.

\* Work supported by the Army Research Office under contract DAAG-29-84-C-0011.

<sup>†</sup> Permanent address: Department of Chemistry, SUNY at Binghamton, Binghamton, New York, 13901

A new decomposition of the S-matrix for  
multichannel resonant collisions<sup>a</sup>

Bela Gazdy and Joel M. Bowman

Department of Chemistry

Emory University, Atlanta, GA 30322

The usual decomposition of a multichannel scattering matrix near an isolated, narrow resonance is given as a sum of a direct and resonant part. The direct part which describes the background scattering is regular and unitary. The resonant part features a pole at the complex resonance energy, and both its magnitude and phase change rapidly as the energy varies. Given the S-matrix, it is often a cumbersome task to extract resonance parameters from it. We propose a new decomposition that overcomes this difficulty, and derives from the standard one. The new resonant part is a complete analog of the single channel S-matrix. Its magnitude is constant, and its phase jumps by  $2\pi$  as the energy increases. The resonant time-delays for each state-to-state transition are independent of the channel indices, and exhibit a Lorentzian shape from which the resonance energy and width are readily obtained. The square of the magnitude of the resonant S-matrix elements are the state-to-state transition probabilities of the resonant scattering, and are expressed in terms of the channel partial widths. The applicability of the proposed decomposition is demonstrated in a coupled-channel study of multichannel resonances and unimolecular decay in H-CO collisions using a global *ab initio* potential energy surface.

---

<sup>a</sup>Work partly supported by the Department of Energy under Grant No. DE-FG05-86ER13568

## **Intramolecular Energy Transfer and Cis-Trans Isomerization of HONO**

Yuhua Guan, Gillian C. Lynch and Donald L. Thompson  
Department of Chemistry, Oklahoma State University,  
Stillwater, OK 74078

Classical trajectories have been used to investigate intermolecular energy transfer and unimolecular reaction in nitrous acid. The influence of various initial normal mode excitations has been investigated. Power and coherence spectra are used to examine the intramolecular dynamics. The rate of cis-trans conversion is strongly dependent on site of initial excitation. The results show that the OH stretching mode is only weakly coupled to the other modes. Energy transfer out of excited states of the OH mode is slow and preferential partitioning of energy into that mode leads to reduced rate of isomerization.

Abstract of a paper for the Conference  
on the Dynamics of Molecular  
Collisions, Wheeling, WV, July 12-17,  
1987

$\Psi^2$  Amplitude Density Method for  
Atom-Molecule Rearrangement Collisions

K. Haug, D. W. Schwenke,<sup>1</sup> Y. Shima,<sup>2</sup> and D. G. Truhlar  
Department of Chemistry and Supercomputer Institute,  
University of Minnesota, Minneapolis, MN 55455

Y. Sun, J. Z. H. Zhang,<sup>3</sup> Y. Zhang, and D. J. Kouri  
Departments of Chemistry and Physics  
University of Houston, Houston, TX 77004

A new method has been developed for the quantum mechanical calculation of chemical reaction rates, and it is being applied to reactive collisions of H, D, O, F, Cl, and Br with H<sub>2</sub> in either the ground or first excited vibrational state. The method involves solving a set of coupled integral equations equivalent to the Schroedinger equation with scattering boundary conditions by expanding the amplitude density describing the chemical system in a square-integrable basis set. This method reduces the computational work involved in the problem to two steps: the numerical evaluation of multidimensional integrals and the solution of large sets of linear equations. Our program is designed for and run on a Cray-2 computer, and it takes advantage of its large memory and vector processing ability. The results obtained so far are very encouraging and have already helped to clarify disagreements between more approximate theoretical results and experimental results.

This work was supported in part by the National Science Foundation, the Minnesota Supercomputer Institute, and the Control Data Corporation.

---

<sup>1</sup>Present address: NASA Ames Research Center, Moffett Field, CA 94035.

<sup>2</sup>MSI Visitor, 1986. Permanent Address: Israel Atomic Energy Commission, Soreq Nuclear Research Centre, 70600 Yavne, Israel.

<sup>3</sup>Present address: Department of Chemistry, University of California, Berkeley, CA 94720.

Monte Carlo simulation of RRKM unimolecular decomposition in molecular beam experiments.

Product OX angular and energy distributions from  $O(^3P) + X_2$  ( $X = Br, I$ )

Per Anders Elofson, Kjell Rynefors<sup>†</sup> and Leif Holmlid

Department of Physical Chemistry GU

University of Göteborg and Chalmers University of Technology

S-412 96 Göteborg, Sweden

<sup>†</sup> Deceased Dec. 31, 1986

### Abstract

Statistical simulation was applied to the unimolecular decomposition of the collision complexes formed in the crossed beam experiments on  $O(^3P) + Br_2$  [1] and  $O(^3P) + I_2$  [2]. The simulation procedure [3-5] used the fundamentals of RRKM theory and included exact angular momentum conservation. The impact parameter distributions were varied to obtain the best fits. Good agreement with experimental laboratory angular distributions measured with O atoms seeded in both He and Ne was found for impact parameter distributions which were peaked at quite small values, in most cases between 2 and 3 Å. Product OX molecules were found to be rotationally excited and inverted with a mean rotational energy close to twice the value expected without angular momentum restrictions. The differences found between the calculated and the experimental angular distributions do not support any assumptions about osculating or shortlived complexes. The normal exoergicity  $\Delta D_0$  of 27 kJ/mol for the  $O + I_2$  reaction agrees well with the experiments in Ref. [2].

### References

1. D.P. Fernie, D.J. Smith, A. Durkin and R. Grice, Mol. Phys. 46 (1982) 41.
2. A. Durkin, D.J. Smith and R. Grice, Mol. Phys. 46 (1982) 1251.
3. L. Holmlid and K. Rynefors, Chem. Phys. 60 (1981) 393.
4. K. Rynefors, Computer Phys. Commun. 27 (1982) 201.
5. P.A. Elofson, K. Rynefors and L. Holmlid, Chem. Phys. 100 (1985) 39.

Dynamical tests of RRKM unimolecular decomposition on a simplified potential energy surface

Gunnar Nyman, Kjell Rynefors<sup>†</sup> and Leif Holmlid

Department of Physical Chemistry GU

University of Göteborg and Chalmers University of Technology

S-412 96 Göteborg, Sweden

<sup>†</sup> Deceased Dec. 31, 1986

Abstract

The unimolecular decomposition of a model triatomic system similar to an excited water molecule was studied with the classical trajectory method. Energy term values for the different degrees of freedom were recorded for various product separation distances, using total angular momentum as a parameter, in the range 10-80  $\hbar$ . Results for the same type of system were also found from our RRKM-type statistical algorithm which has previously been applied to the unimolecular decomposition of excited H<sub>2</sub>O formed in crossed beams experiments [1] (experiments by Y.T. Lee et al. [2]), and in LIF experiments [3] (experiments by Luntz et al. [4]). The available energy is there distributed in an RRKM fashion between the degrees of freedom, observing strict conservation of total angular momentum. By comparing the two sets of results, a dynamical test of the fundamental assumptions in RRKM-type statistical theories is found. The comparison indicates good agreement between dynamical and statistical results for high but not for low values of total angular momentum. The main reason for this discrepancy appears to be dynamical effects close to the centrifugal barrier due to the asymmetry in the potential. These results will be used for further improving of the statistical simulation method for studies of unimolecular decomposition.

References

1. P.A. Elofson, K. Rynefors and L. Holmlid, Chem. Phys. 100 (1985) 39.
2. R.J. Buss, P. Casavecchia, T. Hirooka, S.J. Sibener and Y.T. Lee, Chem. Phys. Letters 82 (1981) 386.
3. K. Rynefors, P.A. Elofson and L. Holmlid, Chem. Phys. 100 (1985) 53.
4. A.C. Luntz, J. Chem. Phys. 73 (1980) 1143, 5393.

ANHARMONIC VIBRATIONAL PARTITION FUNCTIONS FOR  
POLYATOMIC MOLECULES AND TRANSITION STATES

Alan D. Isaacson and Xing-Guo Zhang

Department of Chemistry  
Miami University  
Oxford, OH 45056

The calculation of accurate anharmonic vibrational energy levels for a given potential energy surface has recently become possible through the development of, e.g., vibrational SCF-CI programs. However, the application of such methods to the calculation of a sufficient number of vibrational levels for the evaluation of vibrational partition functions in polyatomic molecules is a major undertaking, and would be impractical for the calculation of partition functions for the bound vibrational modes of a reacting complex along a reaction path, as is needed in generalized transition state theory. One practical alternative in such cases is provided by second-order perturbation theory. While this approach is not in general as reliable for excited state energies as it is for the ground state, we have found in preliminary calculations that the individual excited state energies may not be very important in determining the partition function, as long as vibrational resonances are treated properly. In this talk, we will compare the results for partition functions computed from levels obtained by accurate methods and by perturbation theory for water and for the saddle point of the  $\text{OH} + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{H}$  reaction. Further conclusions using perturbation theory for this reaction will also be discussed.

COMPLETE AB INITIO REACTION DYNAMICS STUDY FOR  $\text{Ca} + \text{HF} \rightarrow \text{CaF} + \text{H}$ 

R. L. Jaffe, NASA Ames Research Center, Moffett Field, CA 94035, M. D. Pattengill, Department of Chemistry University of Kentucky, Lexington, KY 40506, and F. G. Mascarello and R. N. Zare, Department of Chemistry, Stanford University, Stanford, CA 94305

## ABSTRACT

A comprehensive first principles theoretical investigation has been carried out for the gas phase reaction  $\text{Ca} + \text{HF} \rightarrow \text{CaF} + \text{H}$ . The overall study involves three distinct elements: (a) generation of an accurate ab initio potential energy surface for the ground electronic state of the Ca-F-H system, (b) careful fitting of the computed surface to an analytical form suitable for three dimensional reactive scattering calculations, and (c) execution of classical trajectory calculations for Ca + HF collisions using the fitted potential surface.

The potential energy surface is dominated by a deep well corresponding to a stable linear H-Ca-F intermediate with an extremely small bending force constant. The preferred geometry for Ca attack on HF is markedly non-collinear with the saddle point for both the F atom exchange reaction and Ca atom insertion into the H-Ca-F well occurring for a Ca-F-H angle of  $75^\circ$ . The saddle point energy is 16.1 kcal/mol relative to Ca + HF (the barrier for the collinear reaction path is 30.0 kcal/mol). The analytical representation of the ab initio potential energy surface is based on a polynomial expansion in the three diatomic bond lengths and reproduces the values of the compute energies to within a root mean square deviation of 1.2 kcal/mol.

Classical trajectory calculations for  $\text{Ca} + \text{HF}(v=1)$  utilizing the fitted surface establish the fact that the H-Ca-F potential well dominates the collision dynamics, thus qualifying Ca + HF as a bona fide example of a chemical insertion reaction. This finding is consistent with the interpretation of results from previous experimental studies on  $\text{Ca} + \text{HF}(v=1)$ . Due to the extensive sampling of the H-Ca-F well, many trajectories formed rather long-lived intermediate complexes before proceeding to diatomic end products. The results obtained support a number of generalizations relating to microscopic features of Ca + HF collisions. Among these are: (1) at fixed total collision energy, excitation of HF to  $v=1$  is much more effective in promoting reaction than is placing the corresponding amount of energy in Ca, HF translation, (2) at fixed initial translational energy, reaction cross sections increase with increasing value of the HF rotational quantum number J, (3) for trajectories which enter the H-Ca-F well, escape to form products is favored by increasing initial HF J and escape back to reactants is favored by increasing initial relative translational energy, and (4) the CaF fractional product energy disposals are remarkably independent of initial collision conditions. These findings are compatible with the observation that significant intermode vibrational energy does not occur in the H-Ca-F intermediate on the collision time scale (1-2 ps).

-----  
MDP was partially supported by a Guggenheim Fellowship, FGM was supported by a fellowship from the Swiss National Foundation and RNZ acknowledges support from the National Science Foundation.

Ralph Jaquet

Lehrstuhl für Theoretische Chemie, Universität Siegen

D5900-Siegen, West-Germany

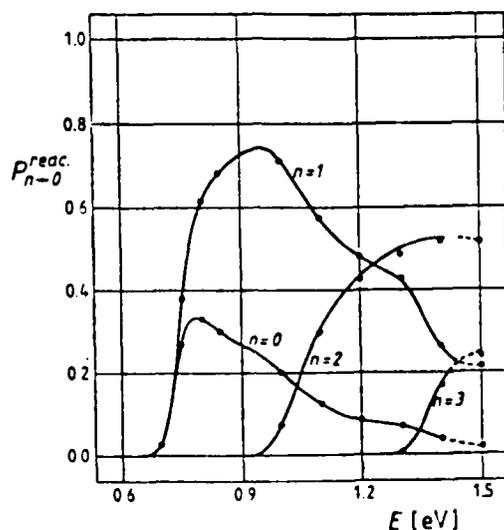
**Abstract.** We are investigating systematically the use of the finite element method ( FEM ) for solving the Schrödinger equation. The following work is devoted to the calculation of vibrational transition probabilities for the collinear reactive system  $A + BC$  ( i.e.  $H + H_2$  and their isotopes and  $F + H_2$  ). The calculations are full two-dimensional as in the early work of Askar et al. /1/ and the results are compared with the conventional basis set expansion methods using the R-matrix or S-matrix propagation.

We made extensive analysis of FEM on the vector-computer Cyber 205 and developed a vector code for the efficient use in two dimensions, so that in the near future applications even in three dimensions will be possible.

For the hydrogen isotope reactions we investigated the following combinations: a)  $H + H_2$  b)  $H + DH, D + HD$  and  $H + \mu H$  symmetric reaction c)  $D + HH, H + DD$  and  $\mu \mp DD$  asymmetric reaction. We calculated the transition probability for five open vibrational channels and found excellent results compared to the known "exact" values.

The details of our FEM calculations are the following /2/: The symmetry of the potential surface was not used in case of a symmetric reaction in order to have a good comparison to the values of an asymmetric reaction. This results naturally into a larger number of grid points. The integration area was discretized into triangles where we defined quadratic polynomials for the local wavefunction. With this simple ansatz convergent results can be reached for most reactions with  $\approx 10000$  grid points and in the case of  $F + H_2$  with  $\approx 32000$  grid points.

As an example in fig.1 we show our results for the reaction probability of  $\mu + D_2$  ( $n = 0, 1, 2, 3$ )  $\rightarrow \mu D$  ( $n' = 0$ ) + D. The lines are results of Bondi et al. /3/ and the dots are the present results.



## References:

- /1/ A. Askar, A. Cakmak and H. Rabitz, Chem. Phys. 33 (1978) 267
- /2/ R. Jaquet, Theor. Chim. Acta, xxxx (1987)
- /3/ D. K. Bondi, D. C. Clary, J. N. L. Connor, B. C. Garrett and D. G. Truhlar, J. Chem. Phys., 76 (1982) 4986

TIME DEPENDENT SEMI-CLASSICAL REACTION DYNAMICS  
VIA GAUSSIAN WAVEPACKETS

Joel D. Kress and Andrew E. DePristo  
Department of Chemistry and Ames Laboratory, USDOE  
Iowa State University Ames, IA 50011

A time dependent solution for a one dimensional atom-diatom exchange reaction is presented based upon a modification of Heller's semi-classical propagation of gaussian wavepackets (GWP's) scheme<sup>1</sup>. The full scattering wavefunction, initialized as a product of an incoming plane wave times an internal oscillator state, is expanded in terms of GWP's in both translational and vibrational variables. We have found that a multiple GWP expansion in translations is crucial for providing an adequate final scattering wavefunction in both the reactant's and product's arrangement channels.

The time dependent quantum dynamics is treated within the interaction picture (IP) where the channel Moeller operators<sup>2</sup> are used explicitly. The propagation of the GWP's within the IP is a two step process: 1. all GWP's are propagated forward in time from  $t_0$  using the full Hamiltonian until the translational center of each and every GWP resides in either the reactant's or product's channel asymptotically; 2. the forward propagation is then stopped (at  $t_{asp}$ ) and all the GWP's are propagated backwards in time back to  $t_0$  using the channel Hamiltonian appropriate for the asymptotic translational center of each GWP at  $t_{asp}$ .

The GWP's are propagated by solving the differential equations for the GWP parameters derived from the various Hamiltonians. Each GWP trajectory consists of the integration of Hamilton's equations of motion plus an accumulation of the classical action integral. Truncation of the Taylor expansion for the potential energy function at first order provides an analytic solution to the GWP width equation of motion. This analytic solution along with the IP propagation procedure provides a time dependent justification to the Frozen (width) Gaussian Approximation.

Scattering information is extracted by constructing wavefunction overlaps in each of the arrangement channels. Numerical results for the exchange reaction  $H + H_2$  on the Porter-Karplus (II) potential energy surface<sup>3</sup> are presented.

1. E. J. Heller, J. Chem. Phys. 62 (1975) 1544;  
R. Skodje and D. G. Truhlar, J. Chem. Phys. 80 (1984) 3123.
2. Scattering Theory, J. R. Taylor, (Wiley and Sons, 1972).
3. R. Porter and M. Karplus, J. Chem. Phys. 40 (1964) 1105.

## ORIENTATION EFFECTS IN H REACTIVITY

J.M. Alvaríño, Dep. de Química Física, Universidad, Salamanca(E)  
A. Lagana', Dip. Chimica, Università', Perugia(I)

The study of reaction paths associated to collisions starting at a given value of the angle of attack is usually based on the analysis of exact and model classical trajectory results. A recent classical trajectory study of the  $H + H_2$  system/1/ has shown that reaction can occur either by exchange of the hydrogen atom with the nearest molecular end or (especially at higher collision energy) through its insertion into the hydrogen molecule. A tight correlation between the angle of attack of the incoming atom and the reactive outcome was found. According to these results, one can define a reaction cone inside which the large majority of trajectories react with the atom located on its apex.

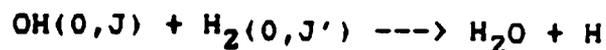
We are currently investigating the dynamics of  $M + HY$  ( $M = \text{alkali and alkaline earth, } Y = \text{halogen}$ ) and  $H + XY$  ( $X = \text{halogen}$ ) families of reactions. During our investigation we found that in the  $Li HF$  reaction where the  $H$  atom is bound to a significantly heavier partner and the transition state has a bent geometry, reorientation mechanisms influence reactivity. In particular, it was found that especially when  $H$  is substituted by  $Mu$  attacks from the  $F$  side are scarcely or no reactive whereas attacks on the  $Mu$  side are highly reactive even if the final product is  $LiF$ . Such a reorientation effect disappears when  $H$  is substituted by heavier isotopes.

Orientational effects have been found to be important also for reaction of  $H$  with  $ICl$ . In fact, for  $H$  initially pointing toward  $I$ , 3.5% of events led to  $HCl$ . At the same time, 0.5% of collisions initially pointing toward  $Cl$  led to  $HI$  product. Reactive collisions ending with  $H$  bound to the atom towards which it was originally pointing are respectively 5.8% and 4.9% for  $I$  and  $Cl$ . A graphical study of these trajectories has evidenced the role played by migration of the impinging  $H$  atom around the target molecule for determining the final outcome.

### References

1/ I. Schechter, R. Kosloff, and R.D. Levine, *J.Phys.Chem.* 90,1006(1979).

## EFFECT OF REAGENT ROTATION ON THE REACTION



Howard R. Mayne and Judith A. Harrison

Department of Chemistry  
University of New Hampshire  
Durham, NH 03824

Classical trajectory calculations on the reaction  $\text{OH}(0, J) + \text{H}_2(0, J') \longrightarrow \text{H}_2\text{O} + \text{H}$  have been carried out for  $J$  up to 30 and  $J'$  up to 15 at several values of the collision energy. Both the Schatz-Elgersma<sup>1</sup> and Rashed-Brown<sup>2</sup> potential surfaces have been used.

Rotation in the  $\text{H}_2$  bond shows reactivity trends similar to those seen in recent studies on  $\text{H} + \text{H}_2$ .<sup>3</sup> Generally the reaction cross section increases as  $J'$  increases; however, near threshold this increase is preceded by a decrease for  $J'=0-4$ . Model calculations<sup>4</sup> have succeeded in explaining the effect for  $\text{H} + \text{H}_2$ , and seem to be also useful for  $\text{OH} + \text{H}_2$ .

Rotation in OH produces different effects for different collision energy regimes. At high translational energy OH rotation tends to increase reaction cross sections, often after an initial decrease. At low translational energy, the reaction cross section increases up to a maximum near  $J=20$ , after which it decreases. Possible explanations for this behavior will be discussed.

1. G.C. Schatz and H. Elgersma, Chem. Phys. Lett. 73(1980)21.
2. O. Rashed and N.J. Brown, J. Chem. Phys. 82(1985)5506.
3. C.A. Boonenberg and H.R. Mayne, Chem. Phys. Lett. 108(1984)67.
4. H.R. Mayne, Chem. Phys. Lett. 130(1986)249.

Quasiclassical and Semiclassical Approaches to  
Molecular Collision Dynamics

J.T. Muckerman, S. Kanfer, J. Logan and R.D. Gilbert  
Chemistry Department  
Brookhaven National Laboratory  
Upton, NY 11973  
and  
G.D. Billing  
Panum Institute  
University of Copenhagen, Denmark

Research elucidating the details of molecular collision phenomena, especially reactive scattering and electronically nonadiabatic behavior, using one of several types of classical trajectory approach as the principal tool will be presented. These various "types" of classical trajectories range from the standard quasiclassical trajectory method, in which all degrees of freedom are treated classically after the imposition of a single quantum condition or constraint, to "quantum trajectories", which resemble classical trajectories only in form, but arise from an approximate solution to the time-dependent Schrödinger equation. The thrust of this research is two-fold: one aspect deals with developing concepts and methods, the other with their applications to chemical problems. The major "applications" project concerns the reaction of  $O(^1D)$  with isotopes of  $H_2$ . It and several "methods" projects will be summarized.

These "methods" projects include a fully three-dimensional application of a semiclassical (classical path) reactive scattering method employing hyperspherical coordinates. In this application, the "hyperradius" and the Euler angles specifying the overall orientation and rotation of the system are treated classically; the two "internal angles" that specify the arrangement of the system are treated using time-dependent quantum mechanics. No angular momentum decoupling approximations are made.

A "quantum trajectory" method which arises from a quantum mechanical treatment employing an approximate, separable time-dependent wavefunction of the form  $X(x,t)Y(y,t)$ , where  $x$  is the "relative" coordinate,  $y$  the "internal" coordinates, and  $X(x,t)$  a Gaussian wavepacket that is constrained to remain Gaussian throughout the course of the collision, will also be discussed. An expression for "semiclassical T-matrix" elements in this theory and the sensitivity of computed transition probabilities to the initial values of the "free" parameters, which revealed a startling result, will be presented. In all cases in which the momentum transfer in the collision was "not too large", there appeared to be a unique value of the initial momentum for which wavepackets of all initial breadths gave exactly the same result. A formal explanation of this behavior, which follows from the basic assumptions of the theory, not only shows that such a "stationary point" should occur when the initial momentum is near the average of the initial and final asymptotic channel momenta for the transition in question, but also explains the shift in the value of the unique momentum away from the average of the asymptotic channel momenta, and why the theory breaks down for large magnitudes of momentum transfer in the "quantum trajectory".

## EFFECTS OF DIATOMIC REAGENT ALIGNMENT ON THE A + BC REACTION

M. D. Pattengill, Department of Chemistry, University of Kentucky, Lexington, KY 40506, R. N. Zare, Department of Chemistry, Stanford University 94305 and R. L. Jaffe, NASA Ames Research Center, Moffett Field, CA 94035

## ABSTRACT

Effects of diatomic reagent alignment on the prototype reaction  $A + BC \rightarrow AB + C$  have been investigated by running classical trajectories on a modified version of the LEPS potential which permits the minimum energy path for reaction to be varied from collinear to broadside attack. Preliminary calculations on both exothermic (early barrier) and endothermic (late barrier) potentials have been performed for mass combinations of the class  $H + H'L \rightarrow HH' + L$ , where H and H' are heavy atoms and L is a light atom. Separate calculations have been performed for alignments in which the initial BC rotational angular momentum vector is either asymptotically parallel (or equivalently antiparallel) or asymptotically perpendicular to the direction of the A,BC initial relative velocity vector.

In all cases, initial BC rotational energies were chosen from a 300 K Boltzmann distribution and for each mass combination and potential surface utilized, BC(v=0) and BC(v=1) collisions have been studied at constant relative translational plus vibrational energies. Thus, for each case, the BC(v=0) and BC(v=1) average total collision energies were virtually identical.

For endothermic surfaces, a distinct reagent alignment effect [for both BC(v=0) and BC(v=1)] on the extent of product vibrational excitation is observed. Although the present studies are clearly model ones, the observed effect is in qualitative agreement with results obtained in alignment experiments on  $Sr + HF(v=1)$ . A similar but weaker effect is observed for BC(v=0) on exothermic surfaces, but is absent for BC(v=1).

Beyond product energy disposals, results obtained also demonstrate a marked effect, both for endothermic and exothermic potentials, of diatomic reagent alignment on reactive cross sections. Analysis of the observed trends suggests a possible underlying steric basis of the Polanyi rules which, for elementary bimolecular gas reactions, relate mode specific excitation to extent of reactivity. Results obtained are also suggestive of generalizations relating to the applicability of the Polanyi rules to reactions which favor non-collinear collisions.

-----  
MDP expresses his thanks to the NASA Ames Research Center and RNZ thanks the National Science Foundation NSF CHE 84-07270 for support.

QUANTUM REACTIVE SCATTERING IN THREE DIMENSIONS  
USING HYPERSPHERICAL (APH) COORDINATES.

TESTS ON  $H+H_2$  AND  $D+H_2$ \*

Gregory A. Parker,\*\* Russell T Pack,  
Billy Joe Archer,\*\* and Robert B. Walker  
Theoretical Division (T-12, MS J569)  
Los Alamos National Laboratory  
Los Alamos, NM 87545

ABSTRACT

Accurate OC calculations of 3D quantum reactive scattering using hyperspherical (APH) coordinates are reported for both zero and nonzero total angular momentum  $J$  and for both symmetric ( $H+H_2$ ) and unsymmetric ( $D+H_2$ ) mass combinations. Accurate 3D reactive scattering calculations are now possible for heavier systems and higher energies than ever before.

\*Work performed under the auspices of the U S Department of Energy.

\*\*Department of Physics and Astronomy, University of Oklahoma, Norman, OK

73019, USA

by

Michael J. Redmon  
Chemical Dynamics  
9560 Pennsylvania Avenue  
Upper Marlboro, MD 20772

and

J. Stephen Binkley  
Sandia National Laboratories  
Livermore, CA 94550

A calculation of the potential energy surface for HF-HF is reviewed.<sup>1</sup> The surface consists of 1,332 points computed with the GAUSSIAN 82 program<sup>2</sup> using a standard 6-311G\*\* basis set. In addition to both molecules at equilibrium, several hundred points correspond to one molecule displaced from its equilibrium geometry. The MP4 data was fit to within 1 kcal/mole rms error using a modified London formula augmented by many-body polynomial terms<sup>3</sup>. A fit to a triple product of spherical functions was also investigated,<sup>4</sup> and was found to be deficient at shorter internuclear separations, although satisfactory at separations larger than 6 a<sub>0</sub>.

In this work the electron correlation energy is studied at several levels of perturbation theory in addition to the full MP4 level. The SCF, MP2, MP3 and MP4 levels are accurately fit and compared. It is shown that the most significant effect on the energy occurs at the MP2 level, with the next most significant change occurring at the full SDTQ-MP4 level. The global variation of the various surfaces is examined graphically to illustrate the effect of geometry on correlation energy.

---

<sup>1</sup> M. J. Redmon and J. S. Binkley, "Global Potential Energy Hypersurface for Dynamical Studies of Energy Transfer in HF-HF Collisions", J. Chem. Phys., in press.

<sup>2</sup> W. J. Hehre, L. Radom, P. v.R. Schleyer and J. A. Pople, *Ab Initio Molecular Orbital Theory* (Wiley & Sons, New York, 1986).

<sup>3</sup> K. S. Sorbie and J. N. Murrell, Mol. Phys. **29**, 1387 (1975).

<sup>4</sup> M. H. Alexander and A. E. DePristo, J. Chem. Phys. **65**, 5009 (1976)

by

Michael J. Redmon, C. S. Murthy, and P. K. Swaminathan,  
Chemical Dynamics, 9560 Pennsylvania Avenue,  
Upper Marlboro, MD 20772

The Intel iPSC computer is composed of a number of independent processors operating asynchronously and communicating via message passing over a hypercube network.<sup>1</sup> In an  $n$ -cube configuration consisting of  $2^n$  processors, each processor, or node, is connected to  $n$  other nodes and forms an  $n$ -dimensional hypercube, or binary  $n$ -cube. Rather than sharing a common memory, each node has its own local memory, and is a self contained computational unit running a Unix-like operating system called XENIX. For compute-intensive applications, using algorithms that adapt well to a concurrent architecture, such a machine offers the possibility of low cost supercomputer performance.

We report our experience in adapting two types of calculations to the hypercube, namely molecular dynamics simulation of a liquid, and quantum mechanical close-coupling calculations. Both types of calculation present a high degree of parallelism, and present the opportunity to investigate the efficiency of various algorithms. Since interprocess communication is the obvious bottleneck that must be overcome, some balance is needed between optimization of the numerical algorithms and the need to pass data between the nodes in an effective manner. The availability of vector boards that increase each processor's power a hundredfold for some applications makes this even more critical.

Since the nodes operate asynchronously, many novel applications can be envisioned, such as concurrent graphical analysis of a simulation, leading to new horizons in interactive modelling. Since several manufacturers are implementing the hypercube approach, it is worthy of study to anticipate some of the problems to be encountered in adapting our traditionally sequential algorithms to this highly parallel architecture.

---

\* Work Supported by the National Science Foundation under Grant ISI-8661037.

<sup>1</sup> Charles L. Seitz, "The Cosmic Cube", *Comm ACM* **28**, 22 (1985)

## Combining Transition State Theory and Quasiclassical Trajectory Calculations for 3-Dimensional Reactive Collisions

R.J. Frost and I.W.M. Smith, Department of Chemistry, University of Birmingham, Birmingham B15 2TT, England

A major disadvantage of the conventional quasiclassical trajectory technique of investigating reactive collisions is its inefficiency. Often a very large proportion of the trajectories fail to react and are hence 'uninteresting'. This drawback can be overcome by starting the trajectories at the transition state so that almost all the trajectories reach the strong interaction region of the potential energy surface. Following earlier work<sup>1</sup> using purely classical methods and our own quasiclassical studies<sup>2</sup> of collinear systems, this paper reports the first 3-dimensional, quasiclassical calculations which combine transition state and trajectory techniques.

3-D vibrationally adiabatic transition states have been constructed using the adiabatic periodic reduction method.<sup>3</sup> These transition states are sampled from a classical, thermal distribution over the bending, rotational and translational (i.e., reaction coordinate) motions. Trajectories are then run 'forwards' in time towards products or 'backwards' in time towards reagents. The forward trajectories give product state distributions, whilst the backward trajectories yield information about the extent of vibrational adiabaticity between reagents and transition state and the properties of the colliding reagents which lead to reaction. The trajectory procedure produces relative values for state-to-state rate constants. These are converted to absolute rate constants using adiabatic reactive sudden transition state theory.<sup>3</sup>

The method has been applied to  $H + H_2(v)$  collisions occurring on the accurate LSTH potential energy surface<sup>4</sup> with  $0 \leq v \leq 9$ . The results will be described and comparisons made with the results obtained in conventional trajectory calculations.<sup>5</sup>

<sup>1</sup>e.g., R.L. Jaffe, J.M. Henry and J.B. Anderson, *J. Chem. Phys.*, **59**, 1128 (1973).

<sup>2</sup>I.W.M. Smith, *J. Chem. Soc. Faraday 2*, **77**, 747 (1981);  
R.J. Frost and I.W.M. Smith, *Chem. Phys.*, **111**, 389 (1987).

<sup>3</sup>E. Pollak and R.E. Wyatt, *J. Chem. Phys.*, **78**, 4464 (1983).

<sup>4</sup>D.G. Truhlar and C.J. Horowitz, *J. Chem. Phys.*, **68**, 2466 (1978) and **71**, 1514 (1979).

<sup>5</sup>E. Garcia and A. Lagana, *Chem. Phys. Letters*, **123**, 365 (1986).

Abstract of a paper for the 1987  
Conference on the Dynamics of  
Molecular Collisions, Wheeling,  
WV, July 12-17, 1987

Completely  $\Psi^2$  Golden Rule Method for  
Resonance Energies, Widths and Branching Ratios

Susan C. Tucker and Donald G. Truhlar  
Department of Chemistry and Supercomputer Institute  
University of Minnesota, Minneapolis, MN 55455

Abstract. We have calculated resonance energies and widths for both one- and two-dimensional scattering resonances by a general method involving only Hamiltonian and overlap integrals in a single square-integrable basis set containing a scale parameter. We use a stabilization method with a compactness criterion to find the resonance energies and a generalization of the golden rule formalism to calculate the widths. For one-channel resonances we have found good agreement with accurate resonance energies and widths obtained by Breit-Wigner fits. Preliminary results on two-channel resonances indicate that we can calculate branching ratios to similar accuracy.

This work was supported in part by the National Science Foundation, by the Minnesota Supercomputer Institute, and by an NSF Graduate Fellowship to S.C.T.

**A COMPARISON OF LOCAL AND GLOBAL SINGLE  
GAUSSIAN APPROXIMATIONS TO TIME DYNAMICS:  
ONE DIMENSIONAL SYSTEMS**

**Ralph Eric Turner and R.F. Snider  
Department of Chemistry  
University of British Columbia  
Vancouver, British Columbia  
Canada V6T 1Y6**

The detailed calculation of the dynamics of a chemical system is usually not considered due to the size and cost of the computation. It is thus useful to examine various approximation methods. Such methods first need to be tried out on simple systems, like one dimensional motion. Here two approaches to approximating the solutions of the Schrodinger and von Neumann equations by single time dependent Gaussians are explored and contrasted, explicitly for one dimensional barrier penetration. The first approach, in which no tunnelling occurs, is local in nature and characterized by an expansion of the equations of motion to second order about the average position of the Gaussian wavepacket or about the average position and momentum of the Gaussian Wigner function. This approach was first introduced by Heller [E.J. Heller, J. Chem. Phys. **62**, 1544 (1975)]. Here both Heller's approach and a more general truncation method are considered. Indeed tunnelling can be incorporated if second order terms in the quantal von Neumann equation are included. However, the resulting dynamics is unstable for kinetic energies where the exact wavepacket (and Wigner function) splits into non-negligible parts that represent reflection and transmission. In contrast, the second approach is a global method which is obtained by applying appropriate closure approximations to the equations of motion for the first and second order position and momentum expectation values. This method allows tunnelling and is stable at all kinetic energies. It is also possible to approximate the global equations in such a way that the local equations are obtained.

THE APPLICATION OF THE TIME DEPENDENT HARTREE FOCK METHOD  
TO THE STUDY OF LOW-ENERGY, COLLINEAR ION-MOLECULE REACTIONS;  
AN EXAMPLE:  $H^+ + H_2 \rightarrow H_2 + H^+$

Detlev H. Tiszauer and K. C. Kulander

Dept. of Applied Science, and Lawrence Livermore National Lab  
University of California, Livermore, California

Application of the Time Dependent Hartree Fock (TDHF) method to the problem of low energy ion-on-molecule scattering presents an opportunity to study non adiabatic processes dynamically (1). The electronic state is expressed as a single time dependent determinantal wave function with the motion of the nuclei evaluated classically. The electronic and nuclear motions and interactions are determined self consistently. A report of the application of this method to the highly reactive collinear collision of  $H^+$  on  $H_2$  is given. This collision is studied for two scattering energies, and for two different target  $H_2$  vibrational levels. The resulting reaction and charge exchange probabilities are compared with two-state quantum mechanical calculations of Top and Baer (2). It is found that this method accurately predicts the reaction probability but gives charge exchange probabilities that agree only qualitatively with those calculated by Top and Baer.

Charge density contours of the  $H_3^+$  system at selected time points during the collision are shown, as also are phase plane plots of the nuclear coordinates and the temporal progression of the net charge on the scattering proton. These plots show an interesting interplay between the electronic, vibrational, and translational energies during the collision.

A short description of the use of the TDHF method in reactive molecular scattering will be given including a discussion of the dynamic coupling terms that are implicitly included in this type of calculation. These dynamic terms are absent in the standard two-step approach of calculating the electronic potential energy surface and then calculating the classical trajectories on that surface.

#### References

- (1) D. Tiszauer and K. C. Kulander, Phys. Rev. A 29, 2909 (1983)
- (2) Z. H. Top and M. Baer, Chem. Phys. 25, 1 (1977)

## Comparison between Theory and Experiment for the Recombination



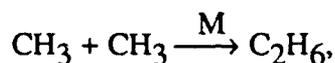
Albert F. Wagner

Chemistry Division, Argonne National Laboratory, Argonne, IL 60439

David M. Wardlaw

Department of Chemistry, Queens University, Kingston, Ontario, K7L 3N6 Canada

The recombination of methyl radicals to ethane in the presence of a buffer gas M,



is of interest in combustion applications and in theoretical studies of loose transition state reactions. A microcanonical variational RRKM rate constant calculation, based on the flexible transition state theory of Wardlaw and Marcus (*J. Phys. Chem.* **1986**, *90*, 5383) and an adjustable empirical potential energy surface, is compared to recent measurements of this reaction in both Ar and He buffer gas. The calculations contain two adjustable parameters: a potential parameter  $\alpha$ , which influences the tightness of the transition state and  $\langle \Delta E \rangle_{\text{tot}}$ , the total average energy change in metastable  $\text{C}_2\text{H}_6^*$  per collision with the buffer gas. For Ar buffer gas, the parameters are optimized to obtain the best agreement with the only directly measured high pressure limit (Hippler, et al. *Z. Phys. Chemie Neue Folge* **1984**, *142*, 1) and with pressure dependent measurements by Gutman, et al. or Pilling, et al. (*J. Phys. Chem.* **1985**, *89*, 2268 ) at 296, 474, 577, 700, 810, or 900 K. The resulting calculated rate constants have a 10.7% rms error with the measurements. The final value of  $\langle \Delta E \rangle_{\text{tot}}$  is  $-240 \pm 70 \text{ cm}^{-1}$  if temperature independent. However the data will permit a wide variety of temperature dependencies for  $\langle \Delta E \rangle_{\text{tot}}$ . The final value of  $\alpha$  is  $0.64 \pm 0.07 \text{ \AA}^{-1}$ . With these two parameters fixed, additional calculated rate constants for Ar buffer gas at 407, 513, 539, and 1350 K are in good agreement with other measurements by either Pilling, et al., or Glanzer, et al. (*J. Comb. (Int.) Symp.* **1977**, *XVI*, 949). The calculated rate constants for Ar buffer gas have been extended up to 2000 K and accurately fit to a functional form recommended by Gilbert, et al. (*Ber Bunsenges. Phys. Chem.* **1983**, *87*, 169). This fit is an accurate representation of the calculations for the temperature range 300 - 2000 K and for all pressures where the rate constant is larger than  $10^{-12} \text{ cc/molec-sec}$ .

The calculations for He buffer gas can be compared to a small set of measurements by Gutman, et al. The agreement is good but not as good as with Ar buffer gas unless  $\langle \Delta E \rangle_{\text{tot}}$  is made strongly temperature dependent. More extensive measurements are required before this result can be confirmed.

**ACKNOWLEDGEMENT:** Work supported by the U. S. Department of Energy under Contract W-31-109-Eng-38 and by the Natural Sciences and Engineering Research Council of Canada.

### Time Delay in a Chaotic Quantum Scattering System

Wojciech Jaworski and David M. Wardlaw  
Department of Chemistry  
Queen's University  
Kingston, Ontario K7L 3N6

The quantum treatment of a two degree of freedom scattering system originally studied by Gutzwiller<sup>†</sup> is re-examined and new results for the time delay obtained. Although apparently not corresponding to any known physical system, this system is exceptional in that its scattering can be solved analytically yet its behaviour, as indicated by the role of the Riemann zeta function, is inherently chaotic. It is hoped that this simple, albeit somewhat abstract, system will provide insights into the nature and manifestations of quantum chaos in the scattering regime. In order to make the model more intuitive, we have recast the mathematical treatment, dropped Gutzwiller's curved space interpretation, and have explained the meaning of the phase shift and time delay in terms of plane waves and wave packets.

Plots of phase shifts (which are identical to Gutzwiller's) and time delays as a function of the "velocity" are presented. The chaos in the phase shift is evident. The chaotic contribution to the time delay fluctuates smoothly between positive and negative values, displaying fairly sharp positive peaks reminiscent of resonances in conventional scattering systems. At the time of writing an analysis of these "resonances" was underway; some results of this analysis will be included in the poster.

<sup>†</sup>M.C. Gutzwiller, *Physica* 7D, 341 (1985).

Ab Initio Potential Energy Surfaces of the Electronically  
Excited Na atom with the O<sub>2</sub> and HCl molecules

Koichi Yamashita and Keiji Morokuma

Institute for Molecular Science, Myodaiji, Okazaki 444, Japan

The potential energy surfaces of the reactive scattering processes between the Na(3S, 3P and 3D) atom with the O<sub>2</sub> and HCl molecules are investigated by ab initio configuration interaction (CI) calculations. The MRSD-CI method is applied with the DZP basis set. The effective core potential is used for the Na and Cl atoms. The mechanism of the Na atom quenching, the electronic state selectivity of reactions, and the internal energy distribution of the products are discussed based on the characteristics of the potential energy surfaces such as the barrier heights along reaction paths and of the surface crossing between several states.

Theoretical Studies of Nonadiabatic Processes  
and Spin-Forbidden Radiative Processes

RT32

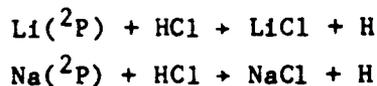
David R. Yarkony  
Department of Chemistry  
The Johns Hopkins University

Nonadiabatic processes involve, in an adiabatic states approach, motion on two or more Born-Oppenheimer potential energy surfaces (PES's) which are coupled by terms including

$$g(J, I, R_\alpha, R) = \langle \Psi_J(\underline{r}; R) | \frac{\partial}{\partial R_\alpha} \Psi_I(\underline{r}; R) \rangle_{\underline{r}}$$

where the  $\Psi_J(\underline{r}; R)$  are the electronic wavefunctions for the adiabatic states. A recently developed method for determining  $g(J, I, R_\alpha, R)$  for large scale MCSCF/CI wavefunctions<sup>1</sup> using analytic gradient techniques now permits efficient evaluation of these coupling matrix elements.

We will use this methodology to consider the nonadiabatic chemical quenching reactions<sup>2,3</sup>



and (if results are available) the charge transfer reaction



For the  $\text{Na}(^2\text{P}) + \text{HCl}$  reaction the  $g(2^2\text{A}', 1^2\text{A}', R_\alpha, R)$  will be determined for three internal coordinates,  $R_\alpha$ , in several regions of coordinate space,  $R$ , including the vicinity of a saddle point on the  $1^2\text{A}'$  PES and two minima on the  $2^2\text{A}'$  PES in order to examine where the propensity for quenching might be significant and which degrees of freedom facilitate this process.

We will also discuss the radiative decay of the  $a^1\Delta$  state of  $\text{CH}^-$ , i.e., the spin-forbidden dipole-allowed transition  $a^1\Delta \rightarrow X^3\Sigma^-$ . This transition is particularly difficult to treat theoretically since it derives its intensity by coupling to  $^3\Pi$  and  $^1\Pi$  states embedded in the  $\text{CH} + e^-$  continuum. An approach will be presented which circumvents this difficulty.<sup>4</sup>

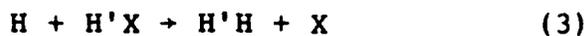
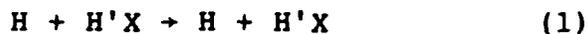
#### References

1. P. Saxe, B. H. Lengsfeld and D. R. Yarkony, Chem. Phys. Lett. 113, 159 (1985).
2. D. R. Yarkony, Int. J. Quant. Chem. 31, 91 (1981).
3. M. M. Gallo and D. R. Yarkony, J. Chem. Phys. in press.
4. B. H. Lengsfeld, J. O. Jensen and D. R. Yarkony, work in progress.

## Abstract for 1987 Dynamics of Molecular Collisions Poster

Energy Partitioning in the H + HX Reactions  
at 1.6 eV Collision EnergyP.M. Aker, K.D. Tabor, G. Germann and J.J. Valentini  
University of California, Irvine, CA 92717

Coherent anti-Stokes Raman Spectroscopy has been used to probe the initial vibrational and rotational distributions arising in the HX and H<sub>2</sub> products from reaction of translationally excited H-atoms with HX (where X = I, Br, Cl, F).



The conditions of the experiment are such that the distributions are probed after virtually only one collision of the fast H atom with the HX molecule. The use of isotopic labelling has allowed us to distinguish between inelastic energy transfer (1) and reactive exchange energy transfer (2). We also report the first measurements of the total vibrational and rotational distributions in the H<sub>2</sub> product of the H-atom abstraction reaction (3).

Pulsed Crossed Molecular Beam Measurements of Vibrationally  
State-Resolved Differential Cross Sections for the Reaction  
 $D + H_2(v=0) \rightarrow HD(v') + H$

Steven A. Buntin, Clayton F. Giese and W. Ronald Gentry  
Chemical Dynamics Laboratory, University of Minnesota  
Minneapolis, MN 55455

By using pulsed molecular beam scattering methods coupled with laser photolysis we have measured, for the first time, vibrationally state-resolved differential cross sections for the hydrogen exchange reaction,  $D + H_2 \rightarrow HD + H$ .

Translationally hot D atoms (Etrans = 2.2 eV) are generated by ArF\* (193 nm) laser photolysis of D<sub>2</sub>S. A low pressure expansion of D<sub>2</sub>S from a pulsed beam source is intersected by the mildly focused output of an excimer laser so that the D atoms are formed under nearly collisionless conditions. This results in the very narrow D atom velocity distribution ( $\Delta v/v \approx 0.07$ ) necessary for this high resolution crossed beam experiment. The collimated D atom beam then intersects a skimmed pulsed supersonic beam of H<sub>2</sub>. The reactively scattered HD product is ionized by electron impact in a differentially pumped ion source and detected by a quadrupole mass spectrometer followed by a particle counter. Internal state selectivity is achieved by time-of-flight (TOF) velocity analysis of the scattered product.

Results at a collision energy of 0.95 eV show clearly resolved peaks in the TOF spectrum for the slow laboratory HD products formed in  $v=0$  and  $v=1$  (scattering  $\sim 180^\circ$  relative to the D atom center-of-mass direction). In addition, details concerning the rotational state distribution can be extracted from the shape of the TOF feature for each vibrational state. The translational energy dependence of the state-resolved differential cross sections has been investigated by varying the D,H<sub>2</sub> intersection angle. Under the current conditions, collision energies from about 0.8 eV to 1.1 eV are accessible. The results of these experiments and their implications concerning dynamical features of the reaction will be presented.

This research is supported by the Chemical Physics Program of the National Science Foundation, Grant No. CHE-8205769.

SPIN-ORBIT EFFECTS IN CHEMICAL REACTIONS:  
Investigation of Ground State Products from Reactions of Ba( $^3D$ )

Mark L. Campbell  
Department of Chemistry  
U.S. Naval Academy  
Annapolis, Maryland 21402

Paul J. Dagdigian  
Department of Chemistry  
The Johns Hopkins University  
Baltimore, Maryland 21218

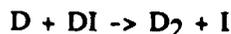
An optical-pumping state selection technique<sup>1,2</sup> has been employed to determine the dependence of the cross sections for the production of ground-state barium halide products on incident spin-orbit state for the reaction of metastable Ba(6s5d  $^3D$ ) with HX and CH<sub>3</sub>X (X = Cl, Br). In addition, cross sections for the metastable  $^1D$  state were related to those of the  $^3D_J$  multiplet by optical pumping on an intercombination line. Ground-state products were detected by laser-induced fluorescence using the C - X transition. For the reactions studied, the spin-orbit dependence for the production of electronic ground-state barium halide molecules (X  $^2\Sigma$ ) in which the product is highly vibrationally excited was substantial with the magnitude of the J-dependent cross sections having an ordering J = 1 > J = 2 > J = 3. This is an opposite ordering to that previously observed for the chemiluminescence channels in analogous reactions.<sup>2</sup> The magnitude of the spin-orbit effect depends upon both the halide reactant and product vibrational state monitored. However, for all the reactions in which the product was highly vibrationally excited, the lower energy J = 1 state was at least two times and up to four times more reactive than the J = 3 state. A significantly diminished variation of reactivity with incident J was observed for lower v in the hydrogen halides. Arguments will be presented which support that the variation of spin-orbit effect with product vibrational level is due to the dependence of the reaction dynamics on incident impact parameter.

1. H.-J. Yuh and P. J. Dagdigian, J. Chem. Phys. 81, 2375 (1984).
2. M. L. Campbell and P. J. Dagdigian, J. Chem. Phys. 85, 4453 (1986).

## Deuterium Atom Abstraction Reactions

Robert E. Continetti, Gary N. Robinson, and Yuan T. Lee  
Materials and Chemical Sciences Division  
Lawrence Berkeley Laboratory and  
Department of Chemistry, University of California  
Berkeley, California 94720 USA

Photolytic production of monoenergetic deuterium atoms via the excimer laser photolysis of deuterium iodide at 248 and 193 nm has given us information concerning the dynamics of the deuterium atom abstraction reaction:



at collision energies of 42 and 76 kcal/mole. A pulsed excimer laser was crossed with a continuous beam formed by the expansion of neat DI through a 0.5 mm nozzle at low pressures. Some of the deuterium atoms then react with unphotolyzed DI before they escape from the molecular beam and produce  $D_2$  molecules whose translational energy distribution is then measured by the time of flight method.

The time of flight data obtained may be directly inverted to yield the translational energy distribution due to the skewed kinematics of the deuterium atom abstraction reactions. In general, the observed energy distributions indicate that the  $D_2$  is produced in highly excited vibrational states. This shows that a large fraction of the energy available, which includes the 33 kcal/mole exothermicity, ends up in the internal energy of the  $D_2$  molecule. Features are also observed which indicate that a momentum conserving spectator stripping mechanism may be important at these collision energies.

Moderation effects were observable at the highest target pressures, however, the data at the lowest pressures allows us to make these initial conclusions concerning the nascent translational energy distribution. Further experiments involving a polarized excimer laser and lower target densities will enable us to obtain a clearer picture of the dynamics of numerous isotopic hydrogen atom abstraction reactions in the near future.

### ACKNOWLEDGEMENT

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract No. DE-AC-03-7600098.

Absolute Rate Coefficient for  $\text{NH}_2 + \text{NO}_2$  from 274 to 364 KDavid A. Dolson<sup>†</sup> and Robert D. StephensEnvironmental Science Department, General Motors Research  
Laboratories, Warren, Michigan 48090-9055

The interest in reactions of amidogen radicals ( $\text{NH}_2$ ) is largely due to the pivotal role that they play in the atmospheric chemistry of ammonia and in the reduction of NO in post-combustion gases. Although the reaction of amidogen with nitric oxide has received much attention recently,  $\text{NH}_2 + \text{NO}_2$  may be of equal importance in the atmospheric chemistry of ammonia. Accurate measurements of rate constants and product yields are required for atmospheric modeling efforts and to aid the understanding of the reaction dynamics of the amidogen radical.

We report the results of an experimental measurement of the  $\text{NH}_2 + \text{NO}_2$  reaction rate between 274 and 364 K using a laser photolysis - laser excited fluorescence technique. Our experimental results can be summarized by  $k(T) = 5.7 \times 10^{-8} (T)^{-1.35} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over this temperature range. No pressure dependence of the reaction rate was detected with up to 40 Torr of helium.  $\text{N}_2\text{O}$  and  $\text{H}_2\text{O}$  were detected as stable reaction products with a modulated-beam mass spectrometer coupled to a fast flow tube reactor.

The many similarities between the reactions of  $\text{NH}_2$  with  $\text{NO}_2$  and with NO suggest that similar mechanisms may apply to both reactions. The experimental observations are consistent with the view that products are formed by rapid intramolecular rearrangements of an energetic collision complex ( $\text{H}_2\text{NNO}_2$ )<sup>‡</sup>. Further theoretical treatment of this reaction would improve our understanding of amidogen reaction dynamics.

---

<sup>†</sup> present address: Laser Spectroscopy Facility, Department of Chemistry, Ohio State University, Columbus, Ohio 43210

A Reinvestigation of the Laser-Initiated Cl<sub>2</sub>/HBr Chain Reaction:  
 Absolute Rate Constants and the v=2/v=1 Ratio from Cl + HBr → HCl(v) + Br

David A. Dolson<sup>†</sup> and Stephen R. Leone<sup>‡</sup>

Joint Institute for Laboratory Astrophysics, National Bureau of Standards,  
 and Department of Chemistry, University of Colorado, Boulder, Colorado  
 80309-0440

The Cl<sub>2</sub>/HBr chain reaction has been reinvestigated using realtime state-selected observations of Δv = -1 chemiluminescence from the HCl(v) products following pulsed laser photolysis of Cl<sub>2</sub>. These state-selected observations have been analyzed with a more complete kinetic treatment to obtain room temperature rate constants for the chain propagation steps and the vibrational deactivation of HCl(v=1,2) by HBr. The chain propagation rate constants are  $k_{R1} = (1.02 \pm 0.15) \times 10^{-11}$  and  $k_{R2} = (1.1 \pm 0.4) \times 10^{-15}$  cm<sup>3</sup>

molecule<sup>-1</sup> s<sup>-1</sup>, respectively, for Cl + HBr  $\xrightarrow{k_{R1}}$  HCl(v) + Br and Br + Cl<sub>2</sub>  $\xrightarrow{k_{R2}}$  BrCl + Cl. Rate constants for vibrational deactivation of HCl(v=1) and HCl(v=2) by HBr are  $k_{V1} = (1.06 \pm 0.16) \times 10^{-12}$  and  $k_{V2} = (2.09 \pm 0.50) \times 10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. Relative intensity measurements of the HCl v=2→1 and 1→0 vibrational fluorescence are used to obtain an HCl(v) product branching ratio,  $N_{v=2}/N_{v=1} = 0.40 \pm 0.06$ . The kinetic analysis indicates that broadband observations of infrared chemiluminescence may lead to erroneous rate constant determinations because of vibrational cascade, whereas the detection of individual vibrational states leads to correct results.

---

This work was supported by the Department of Energy.

<sup>†</sup> NRC-NBS Postdoctoral Fellow 1981-1982. Present address: Laser Spectroscopy Facility, Department of Chemistry, Ohio State University, Columbus, Ohio 43210

<sup>‡</sup> Staff Member, Quantum Physics Division, National Bureau of Standards, Boulder, Colorado 80302

## Reactive Scattering from Double Minimum Potentials

William R. Creasy<sup>a</sup> and James M. FarrarDepartment of Chemistry  
University of Rochester  
Rochester, NY 14627

We present a crossed ion beam-molecular beam study of dehydration and dehydrohalogenation reactions of alcohols and alkyl halides with  $\text{Li}^+$  at collision energies between 20 and 50 kcal mol<sup>-1</sup>. The kinetic energy and angular distributions for the olefin- $\text{Li}^+$  and  $\text{HX-Li}^+$  or  $\text{H}_2\text{O-Li}^+$  products measured as a function of relative collision energy provide detailed information about the partitioning of energy in these complex reactions. As the relative collision energy increases, the intermediate complexes break up in a fraction of a rotational period, establishing the time scale for the reactive process as a few hundred femtoseconds. Like many low energy ion-molecule reactive processes, these systems are hypothesized to occur on a double minimum potential energy surface. The first well on the surface arises from the initial encounter complex formed by the approaching reagents, while a sizable barrier for isomerization to a second ionic complex prior to product formation plays a critical role in determining the overall rate and dynamics of the elimination process. This isomerization barrier lies below the asymptotic reactant or product energy levels, but serves as an entropic bottleneck to reaction. Encounter complexes formed as the reagents approach have a large probability for decaying back to reactants, with a very large transfer of initial translational energy to internal excitation of the neutral reagent. Direct observation of this non-reactive flux leads to an assessment of energy partitioning in both wells of the double-minimum potential energy surface. The energy dependent branching ratios for this non-reactive scattering relative to the reactive flux yield very precise ( $\pm 1$  kcal mol<sup>-1</sup>) estimates of the intermediate isomerization barriers. The experimental results provide tests of current double minimum potential models for ion-neutral reaction rates and their statistical foundations.

<sup>a</sup> Present address: Naval Research Laboratory  
Chemistry Division  
Washington, D.C. 20375

Exchange Reactions of  $^{18}\text{OH}$  with Various Oxygen Containing Molecules

Gary D. Greenblatt and Carleton J. Howard  
Aeronomy Laboratory, National Oceanic and Atmospheric  
Administration, Boulder, CO 80303 and  
Cooperative Institute for Research in Environmental  
Sciences, University of Colorado, Boulder, CO.

Oxygen atom exchange reactions of isotopically labeled  $^{18}\text{OH}$  with various molecules of atmospheric importance were studied in a flow tube at room temperature. Laser magnetic resonance was used to measure the removal of the  $^{18}\text{OH}$  and the appearance of the  $^{16}\text{OH}$  product. Results showed that NO and  $\text{NO}_2$  undergo rapid O-atom isotope exchange ( $\approx 2 \times 10^{-11}$  and  $\approx 1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , respectively) No significant exchange was observed for CO,  $\text{CO}_2$ ,  $\text{SO}_2$ , OCS,  $\text{H}_2\text{O}$ ,  $\text{O}_2$ , and  $\text{N}_2\text{O}$ . The experimental results will be discussed in terms of possible reaction mechanisms.

## Why Radioactivity Must Be Used in Crossed Molecular Beam Reactive Scattering Experiments

J. R. Grover

Dept. of Chemistry, Brookhaven Natl. Lab., Upton NY 11973

The study of reactive collisions in crossed molecular beams has reached a plateau in qualitatively new capabilities because for more than a decade the sensitivity of the general techniques presently in use has been only incrementally improved. Among the alternative techniques that have been explored, only one combines the possibility of wide generality with the orders-of-magnitude increase in sensitivity that is necessary to bring about further major advances: the use of reagent molecules that incorporate short-lived radioactive nuclides generated on-line at a nuclear accelerator<sup>1</sup>. Many of the necessary techniques have already been developed for nuclear studies and for crossed-beam feasibility demonstration experiments using radioactive precursors in place of nuclear beams<sup>2</sup>. Recently there has been a spectacular proliferation of small accelerators for use in analysis, materials processing, isotope production, nuclear medicine, etc., so the time is now right for their application to the study of reactive collisions between molecules.

A possible experimental program will be presented in sufficient detail to highlight the problems that can be foreseen. For specificity the study of the reaction  $^{12}\text{NH}_3 + \text{Cl} \rightarrow ^{12}\text{NH}_2 + \text{HCl}$  is considered. Nitrogen-12, half life = 0.011 sec, is generated by the reaction  $^{10}\text{B}(^3\text{He},n)^{12}\text{N}$  using a multiple thin target and a 50- $\mu\text{A}$  beam of 12.5-Mev  $^3\text{He}$  ions from a minicyclotron (cost  $\sim$  \$250,000). The  $^{12}\text{N}$  recoils from the target, is stopped in flowing gaseous helium, converted to  $^{12}\text{NH}_3$  by reaction with hydrogen donors, and expanded from a nozzle to form a molecular beam of  $10^7$  molecules  $\text{sec}^{-1}$ . Each  $^{12}\text{N}$  atom will disintegrate with the emission of a positron of median energy 8 Mev, which can be detected by known techniques with 100% efficiency and essentially zero background. The  $^{12}\text{NH}_2$  can be very selectively detected in the presence of unreacted  $^{12}\text{NH}_3$  with nearly unit efficiency via differential sticking coefficients or thermal chromatography. Pulsed nuclear beams from a post-acceleration storage ring plus detector timing techniques will allow the measurement of final state velocity distributions without sacrificing the nuclear beam intensity. Hodoscopic detector arrays will greatly increase overall data acquisition rates. In favorable systems doubly-differential cross sections as small as  $10^{-4}$   $\text{A}^2$  per steradian per kcal  $\text{mol}^{-1}$  should be measurable.

<sup>1</sup>J. R. Grover, C. R. Iden, H. V. Lilenfeld, F. M., Kiely, and E. Lebowitz, Rev. Sci. Instr. 47, 1098 (1976).

<sup>2</sup>J. R. Grover, C. R. Iden, and H. V. Lilenfeld, J. Chem. Phys. 64, 4657 (1976).

Work performed at Brookhaven National Laboratory under contract DE-AC02-76CH00016 with the U. S. Department of Energy and supported by its Division of Chemical Sciences, Office of Basic Energy Sciences.

Crossed-Beam Reactive Scattering of  $F_2 + C_6H_6$ :  
Heat of Formation of ipso- $C_6H_6F^\cdot$

RE10

J. R. Grover<sup>a</sup>, Y. T. Lee<sup>b</sup>, and K. Shobatake

Institute for Molecular Science, Myodaiji, Okazaki 444, Japan

<sup>a</sup> Chem. Dept., Brookhaven Natl. Lab., Upton, NY 11973

<sup>b</sup> Chem. Dept., Univ. of Calif., Berkeley, CA 94720

Angular distributions and relative total cross sections were measured for products of the collisions of  $F_2$  with  $C_6H_6$  at relative collision energies of 14 to 26 kcal mol<sup>-1</sup>. For this work the Lee-design crossed beam scattering apparatus at the Institute for Molecular Science, Okazaki, Japan, was used. The most conspicuous product is the ipso-fluorocyclohexadienyl radical  $\underline{1}$ - $C_6H_6F^\cdot$ , which displays a rather narrow peak very near the laboratory center-of-mass angle at all collision energies studied. This suggests that the reaction  $C_6H_6 + F_2 \rightarrow C_6H_6F^\cdot + F$  proceeds preferentially by a statistical or quasi-statistical mechanism. Product fluorobenzene,  $C_6H_5F$ , is masked at  $M/e = 96$  by dissociative ionization of  $C_6H_6F^\cdot$  near the center-of-mass angle but becomes clearly observable at smaller angles to which little or no  $C_6H_6F^\cdot$  is scattered. This means that the reaction  $C_6H_6 + F_2 \rightarrow C_6H_5F + HF$  occurs, and does so in such a way that the products acquire high translational energies. The dependence on collision energy of the total cross section for the production of  $C_6H_6F^\cdot$  was measured, and displays a well-marked onset at  $13.6 \pm 0.4$  kcal mol<sup>-1</sup>. The mean final state translational energy as a function of collision energy was obtained from the angular distributions and also displays an apparent onset near 13-15 kcal mol<sup>-1</sup>, meaning that the onset is most likely a true threshold. Improved measurements to confirm this observation are underway. The average final state translational energy asymptotically approaches 3.7 kcal mol<sup>-1</sup> as the collision energies are increased, which is so large that only a few vibrational modes of  $C_6H_6F^\cdot$  can be involved in the energy partitioning. Therefore the reaction is not completely statistical. This conclusion is confirmed by the center-of-mass angular distribution, which favors backward scattering of product F atoms, but only by about 10-30%.

Our tentative value of the heat of formation of the ipso-fluorocyclohexadienyl radical is  $14.6 \pm 0.4$  kcal mol<sup>-1</sup>. This work shows that the crossed beam method can be used to make precision thermochemical measurements of polyatomic free radicals. It is also an outstanding example of a polyatomic-polyatomic reaction, for which type of reaction very few crossed beam reactive scattering studies have been reported.

J. R. G. supported in part by U. S. Department of Energy.

Properties and Reactivity of Thermalized, Mass-Selected  
Aluminum and Boron Cluster Ions

Luke Hanley, Stephen A. Ruatta, and Scott L. Anderson  
Department of Chemistry  
State University of New York at Stony Brook  
Stony Brook, N.Y. 11794-3400

Aluminum and boron cluster ions produced by ion or laser sputtering are thermalized in multiple collisions with helium inside a radio frequency ion trap. The cooled boron clusters are then mass selected by a Wien filter and injected into a radio frequency ion guide. Interactions with a scattering gas inside this ion guide occur under single collision conditions at well defined collision energies. Collision induced dissociation with xenon yields quantitative dissociation energies and qualitative ionization potentials and structural information for the clusters. Clusters of aluminum have dissociation energies ranging from  $0.85 \pm .40$  eV for  $Al_4^+$  to  $2.25 \pm .70$  eV for  $Al_7^+$ . Reactions with  $O_2$  are exoergic for both boron and aluminum clusters with the atomic ion being the main reaction product. The aluminum reactions with oxygen possess a small energy threshold ( $<0.30$  eV) which increases up to  $Al_7^+$  and drops again at  $Al_8^+$ . The boron clusters appear to have no threshold for reaction with oxygen. Reactions with  $D_2O$  and  $O_2$  are also examined.

LASER-INITIATED HALF REACTION. VIBRATIONAL-ROTATIONAL STATE DISTRIBUTION OF NO PRODUCED FROM THE REACTANT PAIR,  $O(^1D) \cdot N_2O$ .

Kenji Honma, Yoh Fujimura, Okitugu Kajimoto, and Gen Inoue\*

Department of Pure and Applied Sciences, University of Tokyo, Meguro, Tokyo, Japan

\*The National Institute for Environmental Studies, Tsukuba, Ibaraki, Japan

Vibrational and rotational states distribution of NO produced from the reactant pair  $O(^1D) \cdot N_2O$  was measured by the laser-induced fluorescence. The  $N_2O$  dimer was generated by the supersonic expansion of the mixture of  $N_2O$  in He or Ar through the pulse nozzle (0.4mm diam., 10 Hz), and it was converted to the reactant pair by the 193nm(ArF) laser irradiation. Frequency doubled tunable dye laser irradiated the jet with short delay behind the ArF laser to measure the laser-induced fluorescence of NO.

The formation of the  $N_2O$  dimer was confirmed by the quadrupole mass spectrometer. Intensities of the  $N_2O$  monomer, dimer, and trimer signals were measured as functions of the nozzle pressure and compared with the pressure dependence of the LIF signal of NO to identify the source of the NO product. The parallelism between the LIF signal and the dimer ion intensity was excellent and we concluded that the NO was produced from the  $N_2O$  dimer by the ArF laser irradiation.

The rotational distribution was measured for  $v=0$  to 7 levels. At all vibrational levels, the distribution was almost Boltzmann-like with the temperature of 80-100 K.

The population of the vibrational levels were determined up to  $v=7$ . The distribution was bimodal, i.e. one maximum is  $v=0$  and the other maximum is  $v=3$  to 4. This distribution implies the formation of two kinds of NO. The Doppler widths of the LIF lines were measured for  $v=0$  and  $v=3$ . The widths of  $v=0$  lines are limited by the laser line width, i.e. narrower than  $0.1 \text{ cm}^{-1}$ , whereas those of  $v=3$  lines are fairly broad,  $0.2 \text{ cm}^{-1}$ . These results indicate that two NO are formed by the reaction and one is vibrationally and translationally cool, and the other is hot.

The comparison will be made with the study of same reaction in the bulk condition and the details of the reaction mechanism will be discussed.

O(<sup>1</sup>D<sub>2</sub>) Reaction Dynamics Studies by Time-Resolved Fourier Transfer Spectroscopy.

E.J. Kruus, B.I. Niefer and J.J. Sloan  
National Research Council of Canada  
and  
Department of Chemistry  
Carleton University, Ottawa K1S 5B6 Canada.

Since the presentation of our new algorithm for time-resolved Fourier transform spectroscopy at the Dynamics of Molecular Collisions meeting in Utah two years ago, the parameters of the experiment have been improved substantially and several new energy distribution studies have been carried out using low-pressure infrared emission spectroscopy. In its present form, the apparatus is capable of simultaneously recording up to 128 time-delayed spectra of an excitation event, spaced at a minimum of 10 nanoseconds with respect to each other and with subnanosecond time uncertainty. The minimum time delay is arbitrarily short and corrections for variable baseline and excitation amplitude are automatically included. The parameters of the system will be described, and several reaction dynamics studies carried out using the instrument will be reported.

The results to be reported will include studies of the dynamics of O(<sup>1</sup>D<sub>2</sub>) atom reactions with hydrogen halides and with several halogenated methanes. The energy partitioning into the diatomic products of these reactions (OH and HX, X a halogen atom) have been measured in experiments based on low-pressure infrared emission techniques; and in all cases, considerable vibrational excitation is found. It is generally believed that O(<sup>1</sup>D<sub>2</sub>) reactions proceed largely via insertion mechanisms involving the formation of a strongly-bound singlet intermediate species, hence the degree of product vibrational excitation created by these reactions is somewhat surprising. The dynamical features responsible for this result will be discussed in terms of the relevant potential energy surfaces. Where available, energy transfer information derived from the time-resolved measurements will be reported as well. In particular, state-specific rate data on processes of the kind OH(v) + HX(v=0) → OH(v-N) + HX(v') have been obtained.

## Steric and Rotational Effects in the Reaction



M.Hoffmeister, R.Schleysing, and H.J.Loesch

Fakultät für Physik der Universität Bielefeld  
4800 Bielefeld 1, W.-Germany

The effect of both the approach geometry and the initial reagent rotation on direct reactions is tightly related to the angular dependence of the potential energy of the system along the reactant valley as well as of the critical distance [1]. Experimental data on the influence of both types of reagent preparation provide direct qualitative evidence about these potential attributes and represent sensitive probes for theoretical predictions.

The title reaction has been investigated using the crossed molecular beam method. Preparation of the reagent molecules is achieved optically. For this purpose the beam of a colour center laser tuned to one of the R- or P-lines of the  $v = 0 \rightarrow v = 1$  transition of HF is radiated perpendicularly through the HF beam and excites a fraction of the molecules ( $\sim 3\%$  of the coupled ground state population at 10 mW laser power) to the desired  $v = 1, j$ -state. As the laser light is linearly polarized the final state is aligned [2]. Depending on the angle between the polarization vector  $\vec{E}$  and the mean relative velocity  $\vec{v}$  the angle of attack is roughly  $90^\circ$  for  $\vec{E} \perp \vec{v}$  while it is broadly distributed for  $\vec{E} \parallel \vec{v}$ .

Integral reaction cross sections  $\sigma_r(j; E_{tr})$  have been measured for fixed  $E_{tr}$  as a function of  $j$  ( $j = 0, 1, 2$  and  $3$ ) at collision energies  $E_{tr} = 0.49, 0.75,$  and  $1.21$  eV. With rising  $j$  the cross section increases monotonously by 16% at  $E_{tr} = 1.21$  eV while at  $E_{tr} = 0.49$  eV it drops initially by 20% and reaches a flat minimum at  $j = 2$ . At  $E_{tr} = 0.75$  eV it is constant till  $j = 2$  and grows then by 12%. For  $j = 2$  (R(1)-line)  $\sigma_r$  has been measured for the two approach geometries obtained with  $\vec{E} \parallel \vec{v}$  ( $\sigma_{\parallel}$ ) and  $\vec{E} \perp \vec{v}$  ( $\sigma_{\perp}$ ) at various  $E_{tr}$  ranging from 0.43 eV to 1.23 eV. The steric effect  $(\sigma_{\parallel} - \sigma_{\perp})/\bar{\sigma}$  ( $\bar{\sigma} = (\sigma_{\parallel} + \sigma_{\perp})/2$ ) amounts to 17% at  $E_{tr} = 0.46$  eV; it decreases with rising  $E_{tr}$  and reaches zero near 1.2 eV.

All findings are consistent with the assumption that the potential energy surface features weak angular dependence within a wide range, insignificant steric hindrance and a collinear transition state.

[1] H.J.Loesch, Chem.Phys. 104, 213 (1986) and 112, 85 (1987)

[2] R.N.Zare, Ber.Bunsenges.Phys.Chem. 86, 422 (1982)

Vibrationally State-Selected Ion-Molecule Reactions with  
Resonance Enhanced Multiphoton Ionization Generated Ions

E. S. McGinley, S. Opitz, and D. Proch  
Max-Planck-Institut für Quantenoptik  
D-8046 Garching bei München  
Federal Republic of Germany

Due to the large number of ions produced and the possibility of a high degree of vibrational quantum state selectivity, resonance enhanced multiphoton ionization (REMPI) of a pulsed free jet can be an excellent source of ions for vibrationally state-selected ion-molecule reaction studies, as has recently been shown<sup>1,2</sup>. In a new apparatus of beam-gas geometry, such a REMPI ion source will be used to investigate the the role of internal excitation in determining the rates and branching ratios of ion-molecule reactions, particularly those of astrophysical importance. Photoelectron energy spectroscopy and especially laser induced fluorescence of the nascent ions provide a means to follow the disposition of energy in the REMPI process.

Ions formed in the focus of the REMPI laser beam(s) are extracted, accelerated, injected into a 90 degree magnetic sector for mass analysis, and then decelerated by an exponential field lens down to the chosen collision energy before entering a differentially pumped scattering gas cell containing the neutral reagent. Products are collected by a quadrupole mass analyser mounted downstream. Collinear with the scattering chamber ion beam axis is another laser beam axis with fluorescence collection optics for diagnostic LIF of the ion beam. The separate 50 cm time-of-flight photoelectron spectrometer has triple mu-metal shielding and an all molybdenum enclosed flight path.

1. S.T. Pratt, P.M. Dehmer, and J.L. Dehmer, J. Chem. Phys. **81**, 3444 (1986)
2. R.J.S. Morrison, W.E. Conaway, T. Ebata, and R.N. Zare, J. Chem. Phys. **84**, 5527 (1986)

Dynamics of the Reaction  $O(^3P) + HBr \rightarrow OH(X^2\Pi) + Br$ 

K. G. McKendrick, D. J. Rakestraw and R. N. Zare  
Department of Chemistry, Stanford University, Stanford, CA 94305

The nascent product state distribution of  $OH(X^2\Pi)$ , produced by hydrogen atom abstraction by  $O(^3P)$  from  $HBr$ , with full resolution of  $v''$ ,  $N''$ , spin-orbit and  $\Lambda$ -doublet sublevels was determined using LIF spectroscopy. The  $OH$  product was found to be highly internally excited with strongly inverted vibrational and rotational distributions. We observe no  $OH(v''=0)$  and determine the vibrational branching ratio of  $P(v''=1):P(v''=2)$  to be approximately 9:1. The rotational distributions for  $OH(v''=1)$  and  $OH(v''=2)$  show maxima at  $N''\approx 12$  and  $N''\approx 5$ , respectively. The most highly excited states observed were  $OH(v''=1, N''=16)$  and  $OH(v''=2, N''=9)$ , very close to the energetic limit imposed by the collision energy, internal excitation of reagents and exothermicity.

Independent quasiclassical trajectory studies on a LEPS<sup>1</sup> potential-energy surface have been carried out by Broida et al<sup>1</sup> for the  $O(^3P) + HBr$  system. They were able to fit well the previous kinetic measurements on reaction rate as a function of temperature. Moreover, their calculations correctly predict the dominance of the  $OH(v''=1)$  channel as well as high rotational excitation. We have performed further calculations using the same LEPS surface, allowing a quantitative comparison of results generated using initial conditions designed to match those of our experiment. We find that this LEPS surface is unable to reproduce the detailed internal state distribution.

Our observations are consistent with a  $H + LH' \rightarrow HL + H'$  reaction which is dominated by kinematic effects. Similar behavior has been observed in hydrogen atom abstraction by halogen atoms where the product  $HX$  is found to be highly internally excited. This differs substantially from the dynamical behavior observed in hydrogen abstraction reactions of  $O(^3P)$  from organic molecules, the only systems to have previously been studied, which exhibit very little rotational excitation. This has been argued to be the result of a very collinear reaction geometry. The dramatic dynamical differences in behavior of  $O(^3P)$  abstraction of hydrogen from different classes of molecules will be discussed.

[1] M. Broida, M. Tamir and A. Persky, Chem. Phys. 110 (1986) 83.

We wish to thank the National Science Foundation for support of this work under grant number NSF CHE 84-07270.

REACTION OF BARIUM ATOMS WITH N<sub>2</sub>O CLUSTERS

J.P. Visticot, J.M. Mestdagh, J. Cuvellier, and J. Berlande

Service de Physique des Atomes et des Surfaces  
C.E.N. Saclay, 91191 Gif sur Yvette cedex, France

The chemiluminescence of the reaction of barium atoms and N<sub>2</sub>O molecules is observed in a crossed molecular beam experiment. The conditions of the molecular N<sub>2</sub>O beam are varied so that this beam contains no or many large N<sub>2</sub>O clusters. No additional chemiluminescence occurs when the cluster concentration is increased. The large difference in electronic structure between monomers and polymers, which has been shown by measurement of electron attachment, suggests that a different reaction channel yielding BaO solvated in a N<sub>2</sub>O cluster could explain these results.

## ABSTRACT

An experimental study of the dynamics of  $H+H_2$  with total energy from 0.9 - 1.4 eV.

Jong-Chen Nieh and James.J.Valentini  
Department of Chemistry, University of California, Irvine

Both  $H+(\text{para})H_2$  and  $H+(\text{normal})H_2$  with total energy from 0.9 - 1.4 eV were studied by time resolved CARS. Two resonance structures were observed which agreed with the theoretical prediction. With para  $H_2$  we are able to distinguish the reactive scattering from the inelastic scattering. A surprisal parameter of 5 is found for the reactive scattering while 9 for the inelastic scattering. The resonances are more pronounced in  $H+(\text{para})H_2$  than in the  $H+(\text{normal})H_2$  indicated the parent molecule's rotational motion is coupled to the quasi-bound state.

*The effect of reagent excitation on reactions of acetylene cations.*

Thomas M. Orlando, Baorui Yang and Scott L. Anderson  
Department of Chemistry  
State University of New York at Stony Brook  
Stony Brook, New York 11794

Vibrationally and electronically state selected acetylene cations have been produced via multiphoton ionization and the electronic and vibrational identity of the resultant ions have been probed using photoelectron kinetic energy analysis. Ionization via good Rydberg states follow a strict  $\Delta v=0$  propensity rule resulting in ions with > 90% vibrational purity. Ionization via mixed or valence states results in PES involving both stretching and bending modes. Excitation of bending vibrations in the excited state manifold has been found to generally lead to rapid non-radiative decay.

The reactions of the vibrationally 'pure' ions are being studied using radio frequency guided ion beam techniques. The effect of excitation of both the bending and stretching modes on the collision induced dissociation channels observed using various rare gas collision partners have been studied and the absolute cross sections for these channels are presented.

## Chemiluminescent Reactions of Beams of Excited States of Cu and Ge with Halogens

J. M. Parson, E. J. Wall, and C. C. Fang  
Department of Chemistry, Ohio State University, Columbus, OH 43210

Studies of chemiluminescent (CL) reactions of Cu ( $^2S$ ) and Ge ( $^3P$ ) with  $F_2$ <sup>1,2</sup> have been extended to include reactions of the lowest excited states, Cu ( $^2D$ ) and Ge ( $^1D$ ), with halogen molecules. These metastable states were generated in an electric discharge at the beam source orifice, and were monitored by fluorescence excited by a lamp or dye laser. Attenuation of the Ge beam by  $H_2$  was used to attribute reaction to the  $^1D$  state rather than a higher metastable  $^1S$  state, as in a previous study of Sn.<sup>3</sup> The effect of initial translational energy has been explored by a TOF beam-gas method for the total cross sections, and by using a crossed nozzle beam for some of the spectra. Cross sections for forming electronically excited metal fluorides are much larger relative to ground state reactions than predicted by statistical models, while the CL reactions with the heavier halogens are only allowed from the excited atomic states. After the first electron of the metal atom is largely transferred to the halogen molecule, the orbital symmetry of the other high-lying valence electron is thought to play a major role in determining the favored reaction pathways. In the case of Cu ( $^2D$ ) this electron is in a 4s orbital which is repelled from broadside approach to the halogen. For Ge ( $^1D$ ) the  $\sigma$  or  $\pi$  character of the 4p orbital determines whether the metal halide is in a  $\Sigma$  or  $\pi$  electronic state. In general, excited atom reactions studied appear to be direct, as evidenced by inverted vibrational populations. Some of the spectra have been successfully simulated using a least-squares fitting procedure, but for others (particularly CuI and GeCl) too little is known about the spectroscopic constants to achieve good fits.

- <sup>1</sup>R. W. Schwenz and J. M. Parson, *J. Chem. Phys.* **73**, 259 (1980).
- <sup>2</sup>W. J. Rosano and J. M. Parson, *J. Chem. Phys.* **79**, 2696 (1983).
- <sup>3</sup>W. J. Rosano and J. M. Parson, *J. Chem. Phys.* **85**, 2644 (1986).

Energy Disposal in the Reaction of  $\text{Mg}(^1\text{S}) + \text{Cl}_2 \rightarrow \text{MgCl}(^2\Sigma^+) + \text{Cl}$

B. Bourignon\*, J. Rostas, N. Shafizedeh,

Laboratoire de Photophysique Moleculaire du C. N. R. S., Batiment 213,  
Universite de Paris-Sud, Orsay, FRANCE

G. Taleb,

U. E. R., Claude Bernard, Universite de Rennes I, Rennes, FRANCE

and M. G. Prisant†

Department of Chemistry, University of California, Berkeley, Ca. 94720 USA

The reaction of  $\text{Mg} + \text{Cl}_2$  yielding ground-state  $\text{MgCl}(X^2\Sigma^+)$  product has been studied under single collision beam-gas conditions. The spectroscopy and internal state distribution of  $\text{MgCl}$  product were probed by laser induced fluorescence of the  $\Delta v=0$   $X^2\Sigma^+-A^2\Pi$  band system. The form of the spectrum showed rotational population up to the exoergicity limit of  $7500 \text{ cm}^{-1}$  or  $j=195$  for  $v=0$ ; in contrast, the highest populated vibrational state ( $v=9$ ,  $f_v \approx .55$ ) was well below that permitted by the reaction exoergicity. Extension of the spectroscopic constants to the above limits for both the X and A state was accomplished by analysis of the spectrum obtained in this work in conjunction with reanalysis of the results of Morgan<sup>1</sup> and Barrow<sup>2</sup>. An inversion procedure incorporating the extended set of spectroscopic constants was used to determine the internal energy disposal of the reaction. This yielded values of  $.19 \pm .02$  for the average product vibrational energy,  $\langle f_v \rangle$  and  $.35 \pm .05$  for the average scaled rotational energy,  $\langle g_{jv} \rangle$ . The form of the extracted population distribution was consistent with a direct interaction mechanism in which repulsive energy release in the ionic complex  $\text{Mg}^+ \cdots \text{Cl}^- \cdots \text{Cl}$  formed at the electron jump crossing radius of  $\approx 3\text{\AA}$  determines product angular momentum and is thus uncoupled from attractive energy release in  $\text{Mg}^+ \cdots \text{Cl}^-$  product formation.

1 F. Morgan, Phys. Rev. 50 603 (1936)

2 R. F. Barrow, Nature 192 1182 (1961) and private communication

\*Present address: JILA, University of Colorado, Boulder, Co.

†Author to whom correspondance should be addressed

**Line Broadening as a Measure of the Extent of Laser-Assisted  
Chemistry in the Reaction  $\text{Mg } ({}^1\text{S}) + \text{CO}_2 \rightarrow \text{MgO } (\text{B } {}^1\Sigma^+) + \text{CO}$**

George A. Raiche and Joseph J. BelBruno  
Department of Chemistry, Dartmouth College, Hanover NH 03755

Evidence of laser-assisted chemistry in the gas phase reaction of  $\text{Mg } ({}^1\text{S})$  with carbon dioxide has been observed. In this experiment, energy to overcome the substantial reaction endoergicity ( $\sim 35\,000\text{ cm}^{-1}$ ) for production of the excited  $\text{B } {}^1\Sigma^+$  state of  $\text{MgO}$  is provided by a laser photon which is nonresonant with any reactant or product. The endoergicity nearly matches the energy of the  ${}^1\text{P} \leftarrow {}^1\text{S}$  UV transition in atomic magnesium, through which the driving laser is tuned. Broadening of the atomic absorption line is observed, by resonance fluorescence, in the presence of small amounts of carbon dioxide, and production of excited  $\text{MgO}$  is detected by its visible fluorescence. Extended wing emission is observed in both the resonance and visible channels. Pressure broadening and other non-reactive effects have been ruled out.

Laser-assisted reactions have been considered in the context of a kinetic model which treats the absorbing species as a collisional "quasimolecule"<sup>1</sup>. The model predicts that the cross section for absorption will depend on the energy defect between the driving photons, supplying the endoergicity of the reaction, and a resonance in a reactant. In our system, this energy defect is small. Additionally, the drive-energy dependence of the cross section should provide insight to the attractive nature of the intermolecular potential for this collision. This analysis, based on the quasi-static theory of line broadening as employed by Gallagher<sup>2</sup>, is proceeding.

Support: Research Corporation.

<sup>1</sup>J.J. BelBruno, Chem. Phys. Lett., 117, 592 (1985).

<sup>2</sup>R.E.M. Hedges, D.L. Drummond, and A. Gallagher, Phys. Rev. A6 (1972) 1519.

## REACTIONS OF METHYL RADICALS WITH HALOALKANES

Gary N. Robinson, Gilbert M. Nathanson, Robert E. Continetti, and Yuan T. Lee  
Materials and Chemical Science Division, Lawrence Berkeley Laboratory and  
Department of Chemistry, University of California  
Berkeley, CA 94704 USA

We have carried out the first molecular beam reactive scattering studies of a radical with a polyatomic reagent. A supersonic beam of methyl radicals, generated by passing a dilute mixture of ditertiary butyl peroxide through a heated quartz nozzle, is crossed with a seeded haloalkane reagent beam. The nearly thermoneutral iodine abstraction reactions,  $\text{CH}_3 + \text{RI} \rightarrow \text{CH}_3\text{I} + \text{R}$  for  $\text{R} = \text{CF}_3$  and  $(\text{CH}_3)_3\text{C}$ , have been observed at collision energies around 14 kcal/mol. In both reactions, the  $\text{CH}_3\text{I}$  product is entirely backward scattered with respect to the incident  $\text{CH}_3$  beam indicating that the radical must collide with the iodine atom within a narrow steric cone of acceptance in order for reaction to occur. The product angular distribution from  $(\text{CH}_3)_3\text{CI}$  is somewhat narrower than that from  $\text{CF}_3\text{I}$  as a result of the larger number of vibrational modes in the t-butyl product. The cross section for bromine abstraction from  $\text{CF}_3\text{Br}$  is evidently much smaller since we detect no  $\text{CH}_3\text{Br}$  from the reaction  $\text{CH}_3 + \text{CF}_3\text{Br} \rightarrow \text{CH}_3\text{Br} + \text{CF}_3$ . This may result from both the smaller target area of the Br atom and a higher barrier to reaction. Other reactions are currently being investigated.

Reactive Scattering of  $O(^3P)$  with Unsaturated Hydrocarbons

A. M. Schmoltner, P. Chu, Y. T. Lee  
Materials and Chemical Sciences Division, Lawrence Berkeley Laboratory  
and Dept. of Chemistry, Univ. of California, Berkeley CA 94720

We are currently investigating reactive scattering of ground state oxygen atoms with unsaturated hydrocarbons using the crossed molecular beam method with mass spectrometric detection.

In the reaction of  $O(^3P)$  with ethylene most investigators have found evidence for  $CH_3 + CHO$  as products<sup>1</sup>. Experiments in our laboratory<sup>2</sup> have clearly shown that the formation of  $C_2H_3O + H$  is an important channel. Today there is still a controversy about the relative cross-sections for those two channels. We are reinvestigating the reaction using  $^{18}O$  in order to be able to distinguish between  $CHO$  product, at mass 31 and elastic scattering contributions from ethylene at mass 29. No determination of the relative cross sections has been done previously under true single collision conditions. This is important since this pathway can occur in a single step only if intersystem crossing to a singlet surface takes place or if the barrier for hydrogen migration in the triplet addition complex is lower than theoretical calculations<sup>3</sup> indicate. Preliminary results indeed show no evidence for this channel under our experimental conditions.

For the reaction of  $O(^3P)$  with cis- and trans-2-butene we are investigating the relative cross sections of the channels leading to  $H + C_4H_7O$  and  $CH_3 + C_3H_5O$ , respectively, as well as the different reactivities of the two isomers.

## References:

1. R. J. Cvetanovic, D. L. Singleton, Rev. of Chem. Int. 5, 183 (1984)
2. R. J. Buss, R. J. Baseman, G. He and Y. T. Lee, J. Photochem. 17, 389 (1981)
3. C. F. Melius, unpublished results

## Acknowledgement:

This work is supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the Department of Energy under Contract No. DE-AC-3-76SF00098.

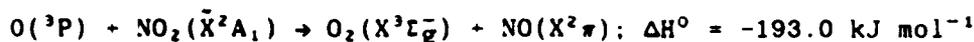
Product State Distributions from  $\text{H} + \text{NO}_2 \rightarrow \text{OH} + \text{NO}$  Studied by Laser-Induced Fluorescence

Alistair M.L. Irvine, Brian J. Orr, I.W.M. Smith and R.P. Tuckett,  
Department of Chemistry, University of Birmingham, P.O. Box 363,  
Birmingham B15 2TT.

Bimolecular reactions between free radicals may proceed via a transitory collision complex, since the formation of a bond between the radicals can lead to a deep minimum on one of the potential energy surfaces which correlate with both the reagents and products. Such reactions proceed with essentially zero activation energy and measurements of the rovibrational product state distributions can indicate the extent to which the dynamics of reactive collisions are dominated by the formation of collision complexes. We are investigating several such reactions which produce NO and expect to report detailed results on the reaction:



and preliminary results on



and



The reactions take place in a low pressure chamber under 'arrested relaxation' conditions. The output of an excimer-pumped dye laser is Raman-shifted into the appropriate spectral range to induce fluorescence from NO (and OH) product molecules, and laser excitation spectra are recorded.

The  $\text{H} + \text{NO}_2$  reaction is sufficiently exothermic to populate  $v'' \leq 3$  in OH and  $v'' \leq 3$  in NO. The OH product state distributions have been studied by other groups<sup>1-3</sup> and our results essentially confirm their data. The earlier work indicates that ca 25% of the energy released in the reaction should cause internal excitation of the NO. However, we detect no vibrational excitation of the NO ( $[N_{v=1}/N_{v=0}] < 10^{-2}$ ). Experiments are now being performed at increasingly low total pressure in order to eliminate, as far as possible, any collisional relaxation. At the meeting we shall report the results of these measurements yielding spin-orbit,  $\Lambda$ -doublet and rotational state populations, as well as those for vibrational level populations.

<sup>1</sup>R.P. Mariella, B. Lantzsch, V.T. Maxson and A.C. Luntz,  
1978, J. Chem. Phys., 69, 3411.

<sup>2</sup>J.A. Silver, W.L. Dimpfl, J.H. Brophy and J.L. Kinsey,  
1976, J. Chem. Phys., 65, 1811.

<sup>3</sup>J.C. Polanyi and J.J. Sloan,  
1975, Int. J. Chem. Kinet. Symp., 1, 51.

Investigations of Ion-Molecule and Electron-Molecule Dynamics  
Using a New Laser Ionization Free Jet Flow Reactor

Michael Hawley, A. H. L. K. Randeniya and Mark A. Smith  
Department of Chemistry  
University of Arizona  
Tucson, AZ 85721

ABSTRACT

A new kinetic technique has been developed to study mechanisms of intrabeam ion-molecule reactions in free jet expansions. Using multiple laser photoionization, it is possible to study reaction rates of state selected ions with a variety of neutral molecules at collisional temperatures in the 1 to 30<sup>0</sup>K regime. Results will be presented describing the kinetics of NO<sup>+</sup> clustering reactions with NO and other small molecules. Using the same ionization technique, we demonstrate the ability to produce monoenergetic electrons with a distribution width of less than 3meV. The electron kinetic energy is continuously variable from 0 to 120 meV. The attachment dynamics of these electrons with cold beam molecules is investigated. Attachment to van der Waals clusters is found to proceed with extremely large cross sections and produces predominantly open shell parent anions of the parent monomer and its higher VDW homologs.

Direct Evidence for Multiple Entrance Channels in the  
Thermal Energy Ion-Molecule Reactions:  $\text{Ne}^*(^3\text{P}_2) + \text{N}_2$  and  
 $\text{Ar}^+ + \text{N}_2$  by Rotationally Resolved LIF

David M. Sonnenfroh and Stephen R. Leone

Joint Institute for Laboratory Astrophysics, National  
Bureau of Standards and University of Colorado, and  
Department of Chemistry and Biochemistry, University of  
Colorado, Boulder, Colorado 80309

Bimodal rotational distributions have been observed in the  $\text{N}_2^+$  products of the Penning ionization reaction:  $\text{Ne}^*(^3\text{P}_2) + \text{N}_2$  and in the charge transfer reaction:  $\text{Ar}^+ + \text{N}_2$  at thermal energies. These results are interpreted as evidence for multiple entrance channels in both systems. In the Penning system, the rotational distributions are well fit by a bimodal Boltzmann distribution having a low temperature ranging from 45 to  $60\text{K} \pm 10\text{K}$  and a high temperature varying between 200 and  $500\text{K} \pm 50\text{K}$  depending on  $v$  level. In this system, the two major entrance channels arise from the relative orientation of the  $\text{Ne}^*$  core  $p$  orbital with respect to the relative velocity. The degree of rotational excitation can be modeled by "hard-sphere", inelastic collisions with an ellipsoidal potential of different ellipticity for each channel.

The rotational distributions for the charge transfer system can also be fit by a two component Boltzmann distribution. The two components have temperatures of  $115 \pm 50\text{K}$  and  $630 \pm 50\text{K}$  for  $v = 0$  and  $215\text{K} \pm 50\text{K}$  and  $660\text{K} \pm 50\text{K}$  for  $v = 1$ . The two entrance channels in this case arise from an avoided crossing between the ground and excited surfaces of the system. Reactant flux that follows the adiabatic entrance channel misses the curve crossing on the incoming leg of the trajectory. This flux then samples a repulsive wall, and ultimately forms the rotationally cooler products by making the curve crossing to the charge-exchanged surface on the outgoing leg of the trajectory. In comparison, reactive flux that follows the diabatic entrance channel makes the curve crossing on the incoming leg and samples a potential well. A transient complex can then form with sufficient lifetime to permit partitioning of the available energy into the internal degrees of freedom. This channel, then, leads to the rotationally hotter products.

The observation of these rotational subtleties critically depends on quenching the initial rotation of the  $\text{N}_2$  using a supersonic expansion.

" Spectroscopic Investigation of the Transition State:  $K + NaCl \rightarrow KCl + Na$  "

James H. Spence, Philip R. Brooks, R. F. Curl,  
Stefan Kaesdorf, T. C. Maguire, and Sydney J. Ulvick

Department of Chemistry and Rice Quantum Institute, Rice University, Houston, TX 77001

We are using photo-excitation to investigate the nature of transition states, i.e. states *in transition* between reagents and products. Specifically, we utilize a triple-beam configuration where effusive molecular beams of K and NaCl cross in the presence of a tunable dye laser. Previous work<sup>1</sup> involved laser wavelengths 735-590nm, which although not resonant with either reagent, nevertheless gave rise to excited Na\* emission ( 589nm). We take this as evidence of photon absorption by the transition state. In order to preclude possible artifact processes involving the slight impurity K<sub>2</sub> (which can be resonant with our probe laser) we passed the atomic beam through an inhomogeneous magnetic field, which focussed the atom but not the dimer. Na\* emission was found<sup>2</sup> to correlate with atomic K intensity, thus supporting our original interpretation of the photo-excitation spectrum.

However, the spectrum is featureless, obscuring conclusions about the fundamental forces involved with transition states. With an eye towards observing structure, we are reducing the number of initial states by seeding both molecular beams in rare gases. Concurrently, preliminary data suggests it is possible to excite the transition state with near infra-red frequencies and populate the first (bound) excited state of the quasi-molecule KCINa. This state can fluoresce back into a ground state well associated with certain nuclear geometries. This emission may exhibit structure, and toward that end we have developed a low light level f/2 spectrograph for multichannel data acquisition. This poster will present a summary of work to date on the project.

- 1) T. C. Maguire, Philip R. Brooks, R. F. Curl, James H. Spence, Sydney J. Ulvick, *J Chem Phys* **85** (2), 844-855 (1986).
- 2) Stefan Kaesdorf, Philip R. Brooks, R. F. Curl, James H. Spence, Sydney J. Ulvick, *Phys Rev A* **14** (5), 4418-4420 (1986).

LIF STUDY OF THE  $F + I_2 \rightarrow IF + I$  REACTION

B. GIRARD, N. BILLY, G. GOUEDARD, J. VIGUÉ

Laboratoire de Spectroscopie Hertzienne de l'E.N.S.

(associé au CNRS : UA n° 18)

24, rue Lhomond, 75231 PARIS CEDEX 05 - France

The  $I_2 + F \rightarrow IF + I$  reaction has been studied in a crossed beam experiment and the product IF is detected by laser induced fluorescence. The exoergicity of the reaction (1.23 eV) and the initial energy (kinetic collision energy  $\sim 0.1$  eV, iodine internal energy, fluorine atom fine structure energy) make that the total energy available in the center of mass frame is between 1.33 and 1.45 eV. This is enough to populate IF ( $X, v$ ) up to  $v = 21$  if I is in the ground  $^2P_{3/2}$  state or up to  $v = 6$  if I is in the excited  $^2P_{1/2}$  state.

With c.w. single frequency dye laser in the near infrared, we have detected about ten thousand lines of IF in the spectral ranges 700-790 and 836-873 nm. These lines have been identified and they give measurements of the relative population of the rovibrational levels of IF with  $v = 9$  to 19 and  $J = 0$  to 150. The population of about 1300 levels has been measured in this way :

- \* For each vibrational level, the highest rotational level detected has an energy close to 1.40 eV, in agreement with the total available energy.
- \* The rotational distribution presents, for most of the vibrational levels, a strong peak near highest values of the rotational quantum number  $J$ . This bimodal rotational distribution may be due to the existence of two types of trajectories, namely migratory and direct trajectories as observed in other  $L + HH$  systems (e.g.  $H + IC_2$  studied by J. Polanyi et al). Moreover migration was found important by Fletcher and Whitehead in their trajectory calculation of the  $F + I_2$  reactive collision.
- \* The vibrational distribution presents a broad peak around  $v = 13$ .

We have also detected the  $v'' = 0$  level population with a c.w. single frequency dye laser in the blue (near 490 nm). Trickl and Wanner have detected a very intense population in this level ( $P(v'' = 0) \sim 100 P(v'' = 13)$ ) and they interpreted this population as associated to the production of Iodine  $^2P_{1/2}$  atoms, and this should have been the major branch of this reaction. However, direct detection of these excited Iodine atoms is in strong contradiction with this interpretation.

We have detected a considerably (50x) weaker population of the  $v'' = 0$  level and we have shown by modulating the Fluorine beam that this population was not directly due to the reactive collisions in the beam. As a consequence, the production of low  $v''$  levels and of excited iodine atoms appears to be a minor branch of the  $F + I_2$  reaction.

## FREE RADICAL CHAIN REACTIONS IN LOW-TEMPERATURE SOLIDS

A. J. Sedlacek, E. S. Mansueto and C. A. Wight\*  
Department of Chemistry  
University of Utah  
Salt Lake City, UT 84112

Photoinitiated reactions of chlorine with propane and cyclopropane have been studied in frozen thin films to investigate some of the effects of the solid state environment on the reaction mechanism. The experiments are conducted by depositing a pre-mixed sample of the halogen and hydrocarbon onto a CsI optical window at 10-77 K. Excimer laser photolysis of the thin films at 308 nm dissociates some of the chlorine molecules to initiate the reactions. Product yields and branching ratios are determined from transmission infrared spectra of the films recorded before and after photolysis.

In the propane system we find that radical-radical recombination dominates the reaction mechanism, resulting in very low product yields. Chlorine atoms may abstract H atoms at either primary or secondary sites in the propane molecule. The branching ratio between these two channels provides an interesting probe of hot atom effects in the solid.

Attack of chlorine atoms on cyclopropane occurs by addition and ring opening. This mechanism effectively separates radical pairs in the solid, inhibiting recombination. As a result, true chain reactions propagate through the solid and up to 30 product molecules are formed per UV photon absorbed by the sample. Interestingly, the sole product of the reaction is an unstable anti-anti conformer of 1,3-dichloropropane. Detection of specific conformers of reaction products is unique to solid-state studies and provides important clues to the details of the reaction mechanism on a molecular scale.

PRODUCTION AND LOSS OF  $CF_2(^3B_1)$  IN THE  $O + C_2F_4$  REACTION

R. A. Young, J. Blauer, R. Bower, and C. L. Lin  
Rocketdyne Division, Rockwell International  
6633 Canoga Avenue, FA38  
Canoga Park, California 91303

## ABSTRACT

Low pressure fast flow measurements of the emission from  $CF_2(^3B_1)$  generated in mixtures of O with  $C_2F_4$  in Ar and similar measurements using the air afterglow to follow oxygen atoms were made. From measurements of the exponential decay of air afterglow emission, it is concluded that the reaction proceeds through a  $C_2F_4O^*$  intermediary. From the intensity and time evolution of the  $CF_2(^3B_1)$  emission it is found, contrary to existing belief, that the yield of  $CF_2(^3B_1)$  is small (less than 1%) and its radiative lifetime is much shorter than 1s (~10 ns). The overall loss of O atoms at low  $C_2F_4$  densities is characterized by rate constant of  $1.2 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ . Both NO and  $O_2$  strongly quench the  $CF_2(^3B_1)$ , while quenching the precursor much less effectively.  $C_2F_4$  quenches the precursor regenerating O, but does not quench  $CF_2(^3B_1)$  significantly.

Edward J. Boyle and Thomas J. O'Brien  
U.S. Department of Energy, Morgantown Energy Technology Center  
Morgantown, West Virginia 26505

The hydrodynamic behavior of flowing granular material is of considerable economic and scientific interest. An accurate representation of the stress tensor for granular material is central to successfully treating it as a continuum. Representations of such a stress tensor can be developed from either a continuum mechanics approach or a kinetic theory approach. Hopefully, these two approaches would yield similar forms for the stress tensor.

The continuum model approach considers the granular material to be isotropic and isothermal and postulates a linear stress tensor that depends on the void fraction, the gradient of the void fraction, the velocity, and the gradient of the velocity. Then by requiring the stress tensor to be frame indifferent, the stress tensor is restricted to depend on the void fraction, the gradient of the void fraction, and the symmetric part of the rate of deformation tensor. The resulting stress tensor is similar to that of a Navier-Stokes fluid except that an extra term appears, containing the dyadic formed from the gradient of the void fraction. This term is necessary because it predicts a stress in the direction normal to the plane of a one dimensional Couette flow of granular material as observed experimentally. In principle, the stress tensor for granular material derived by the continuum model approach is valid from extremely slow flows, in which the particles are in enduring contact, to very rapid flows in which the particles move chaotically and suffer only binary collisions. The major drawback to this approach is the large number of undetermined parameters which are introduced.

In this paper, an expression for the stress tensor for flowing granular material which contains no undetermined coefficients has been developed from Enskog's kinetic theory for dense gases. This approach supposes that the zeroth order approximation to the distribution of granule velocities is described by a Gaussian function, the variance of which is related to the degree of chaos in the movement of the granular particles. A granular temperature can be introduced analogous to the temperature of a gas. The stress tensor is determined by averaging the flux of momentum from the first order approximation to the velocity distribution, as given by Enskog's dense gas theory. This approximation is assumed to depend on the gradients of granular temperature, average velocity, and number density. The forms of the two terms in which the gradient of granular temperature and gradient of average velocity appear are determined by analogy with the Enskog approach as applied to gases. The third term, which describes the effect of the density gradient, does not appear in the Enskog development for gases. It appears in the development for granular material, because the particles suffer energy dissipating collisions. The importance of inelastic collisions is what distinguishes granular material from monatomic gases. In the past, this term was chosen in a manner that produced no dependence of the granular stress tensor on the dyadic of the density gradient. This is inconsistent with the form of the stress tensor as developed from continuum mechanics. Furthermore, the resulting stress tensor is limited to granular flows in which the granule velocities are chaotic enough to obey a Gaussian distribution and dilute enough so that only binary collisions occur. We propose an alternative choice which causes the granular stress tensor to be dependent on the dyadic of the density gradient. In so doing, the range of granular flows over which the stress tensor is applicable is increased, and the undetermined parameters which appear in the continuum model approach can be evaluated.

DYNAMICS OF MOLECULAR STEREOCHEMISTRY VIA ORIENTED MOLECULE  
SCATTERING

H. Jalink, M. Jarissen and S. Stolte  
Department of Molecular and Laser Physics, University of Nijmegen  
Toernooiveld, 6525 ED Nijmegen, The Netherlands

D.H. Parker  
Department of Chemistry, University of California Santa Cruz  
Santa Cruz, CA 95064, USA

In a crossed molecular beam machine the steric dependence of the reaction  $\text{Ba} + \text{N}_2\text{O} \rightarrow \text{BaO}^* + \text{N}_2$  has been investigated at variable translational energy,  $E_{tr}$ , as a function of the angle of attack of the  $\text{N}_2\text{O}$ -axis, which has been selected in the  $(J_1, n_2, M) = (1, 1, 1)$  or  $(2, 1, 2)$  state by means of a hexapole focuser. A strong orientational dependent reactive opacity function has been found and the alignment of the angular momentum of the  $\text{BaO}^*$  product molecule was found to depend on the orientation of the  $\text{N}_2\text{O}$  molecule. The implications of these observations for the dynamics of the chemical reaction will be discussed and compared with those obtained for the reaction  $\text{Ca}(^1\text{D}) + \text{CH}_3\text{F}(1, 1, 1) \rightarrow \text{CaF}^*(\text{A or B}) + \text{CH}_3$ .

Molecular Dynamics Study of the Diffusion Induced Rearrangement of the

Silicon {100} Surface, Donald W. Brenner<sup>\*</sup> and Barbara J. Garrison,

Department of Chemistry, The Pennsylvania State University, University  
Park, PA 16802.

Many semiconductor surfaces are known to exhibit large rearrangements of atoms in the surface region from the bulk configurations. The reconstruction of the silicon {100} surface, for example, involves the rebonding of surface atoms which would be second neighbors in the crystal into rows of dimers. In order to grow epitaxially on these surfaces, the reconstruction must somehow be rearranged so that surface atoms occupy bulk lattice sites. Molecular dynamics simulations of the silicon adatom induced rearrangement of the silicon {100} symmetric dimer reconstructed surface have been performed. A surface diffusion induced rearrangement of the reconstruction plays a critical role in the reordering of this surface which leads to good epitaxial growth. It will also be shown that diffusion plays much less of a role in the reordering induced by an amorphous overlayer. These results will be used to provide an atomic scale understanding of the high-energy ion channelling/blocking studies by Gossman and Feldman of the initial stages of silicon growth on this surface.<sup>1</sup>

<sup>1</sup> H.-J. Gossman and L.C. Feldman, Phys. Rev. B 32, 6 (1985).

<sup>\*</sup> Current address: Naval Research Laboratory, Washington, D.C. 30275-5000

**A VELOCITY-RESET METHOD FOR INCORPORATING A  
THERMAL RESERVOIR INTO MOLECULAR DYNAMICS  
SIMULATIONS OF LATTICE MOTION\***

Michael E. Coltrin and Merle E. Riley

Sandia National Laboratories

Albuquerque, NM 87185

Dennis J. Diestler

Department of Chemistry

Purdue University

West Lafayette, IN 47907

The molecular dynamics simulation of gas-surface collisions or adspecies-lattice dynamics requires the partitioning of the solid into an active P zone (described by the equations of motion) and a reservoir. The approximation generated by this partitioning is improved if the damping and thermal motion caused by the reservoir are included in the P-zone dynamics. Here we present a new partial velocity reset method of accounting for damping and thermal agitation. The partial velocity reset method allows the simulation of dynamic processes in the systems of interest to us, namely, classical surface collisions and lattice dynamics. The partial velocity reset method becomes a robust computational procedure allowing for: (1) relaxation dynamics which are equivalent to the first-order damping theories, (2) inclusion of non-zero temperature effects on damping and dissipation, (3) rapid generation of initial states selected from a canonical ensemble, (4) preparation of individual collisions with the surface, and (4) approximate heat transport within the dynamic subset.

---

\*This work was performed at Sandia National Laboratories, a part of the U.S. Department of Energy, under contract No. DE-AC04-76-OR-21400.

AD-A184 690

THE CONFERENCE ON THE DYNAMICS OF MOLECULAR COLLISIONS  
HELD IN OGLEBAY PA (U) JOHNS HOPKINS UNIV BALTIMORE MD  
P J DAGDIGIAN 17 JUL 87 ARO-24892 1-CH-CF

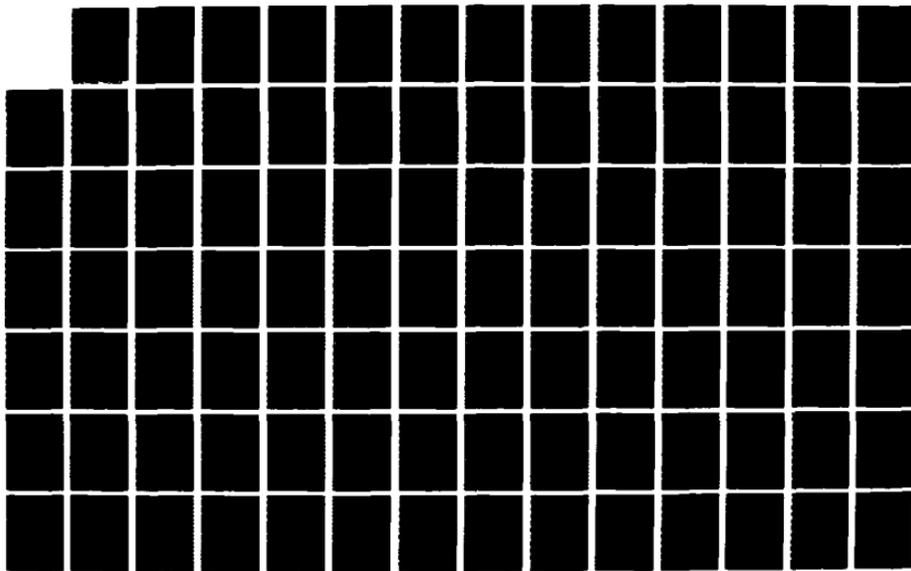
2/3

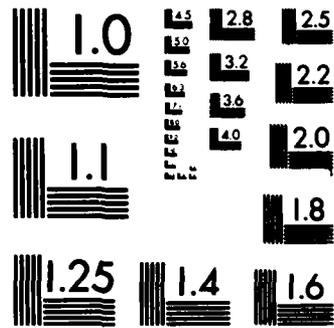
UNCLASSIFIED

DAAL03-87-G-0096

F/G 7/4

NL





MICROCOPY RESOLUTION TEST CHART  
NATIONAL BUREAU OF STANDARDS-1963-A

Selectivity of Elementary Molecular  
Processes in Molecule-Surface Collisions

J.W. Gadzuk  
National Bureau of Standards  
Gaithersburg, MD 20899

The theoretical basis for an experiment involving the scattering of polyatomic molecules from metal surfaces in which selective control of the fragmentation products is possible<sup>1</sup>, will be presented. The current proposal is based on an adaptation of ideas put forth by Tannor and Rice<sup>2</sup> in which they "show that selectivity of reactivity is possible if an excited electronic state is used as an intermediary to assist chemistry on the ground electronic state surface". Selectivity can be attained by controlling the time structure of a coherent, two-photon process in which initial excitation to the excited state intermediary is followed by stimulated decay to the electronic ground state.

From the point of view of intra-molecular dynamics, a similar sequence of electronic transitions occurs in molecule-surface collisions involving charge transfer/harpooning<sup>3,4</sup>. For an event in which a molecule picks up an electron on its incident trajectory and returns it to the surface on its outward leg, a temporary negative molecular ion is formed for the time duration between electron hops. This time scale is of the order of molecular vibrational times and can be controlled by varying the incident translational energy. While existing as a molecular ion, the polyatomic can distort into new geometrical configurations which, when returned to the electronic ground state potential surface, lead to fragmentation. The geometrical structure of the distortion, as controlled by the potential energy surface and the lifetime of the negative ion, determines the fragmentation distribution and hence selectivity in this elementary molecular process. Relative merits of the 2-photon versus surface collision mechanisms will be presented.

1. J.W. Gadzuk, Chem. Phys. Letters (In press).
2. D.J. Tannor and S.A. Rice, J. Chem. Phys. 83, 5013 (1985).
3. J.W. Gadzuk, Comments on Atomic and Mol. Phys. 16, 219 (1985).
4. P. Haochang, T.C.M. Horn, and A.W. Kleyn, Phys. Rev. Letters 57, 3035 (1986).

Dynamics of diffusion and desorption processes of Cs on pyrolytic graphite basal surfaces: a new way to get into the bulk

Kenneth Möller and Leif Holmlid

Department of Physical Chemistry GU

University of Göteborg and Chalmers University of Technology

S-412 96 Göteborg, Sweden

Abstract

Molecular beams have been used to study the interaction between Cs and graphite (or metal) surfaces. Using the so called field reversal, surface ionization kinetic method, a time resolution of 30 ns can be reached at present. Variations of this method have been applied to surface diffusion and desorption processes [1-3], as well as to the diffusion processes into, out from and through the bulk [4,5]. In the present study, an analytical diffusion model has been matched to the variation of the peak of the ion signal with the length of the retarding field period. Surface diffusion processes are observed, as well as the very rapid diffusion into the bulk. The new experiments give a barrier towards diffusion into the bulk of around 5.8 eV with a very large preexponential factor of the order of  $10^{22} \text{ s}^{-1}$ . This rapid process has been proposed [3] to be caused by very highly excited cesium atoms, presumably in the form of a Rydberg state. They are probably coupled to the existence of at least two separate binding states of Cs on the crystallite faces [3].

References

1. L. Holmlid and K. Möller, Surface Sci. 149 (1985) 609.
2. K. Möller and L. Holmlid, Surface Sci. 163 (1985) L635.
3. K. Möller and L. Holmlid, Surface Sci. 173 (1986) 264.
4. L. Holmlid, K. Möller and E. Sanchez, Surface Sci. 173 (1986) L627.
5. K. Möller and L. Holmlid, Surface Sci. 179 (1987) 267.

Jan B.C. Pettersson, Gunnar Nyman and Leif Holmlid  
Department of Physical Chemistry GU  
University of Göteborg and Chalmers University of Technology  
S-412 96 Göteborg, Sweden

Abstract

In the past few years, experimental investigations of NO scattering from various surfaces have yielded distributions of several quantities. In the present Monte Carlo trajectory study the aim has been to calculate angular and rotational distributions for NO/graphite surface scattering, simulating conditions used in experiments [1].

NO was modeled as a rigid rotor, each end interacting with a smooth vibrating surface through a Lennard-Jones 12-6 potential. In the model, the surface moved in one dimension under a linear restoring force. The same surface model has previously been successfully used for Br<sub>2</sub>/graphite surface scattering [2]. We have also reported on the angular distributions for NO on graphite [3].

NO approached the graphite surface with a momentum large enough to require at least two hits from the carbon atoms before the NO molecule could leave the surface. Further, NO often made extended jumps on the surface before definitely leaving it, resulting in interaction times around or above 10<sup>-12</sup> s.

In the experiments [1] on NO/graphite scattering it had been found that the rotational state population could be approximated by a Boltzmann distribution. The rotational temperature  $T_{rot}$  was found to equal the surface temperature  $T_s$  up to about 190 K, while at higher surface temperatures,  $T_{rot}$  approached a constant value of about 250 K. In the trajectory calculations, this behaviour was found using only the most populated rotational states. At higher energies, rotational rainbow structure was found, similar to the behaviour observed in experiments on NO/Ag(111) [3].

References

1. F. Frenkel, J. Häger, W. Krieger, G. Ertl, J. Segner and W. Vielhaber, Chem. Phys. Lett. 90, 225 (1982).
2. G. Nyman and L. Holmlid, J. Chem. Phys. 85, 6163 (1986).
3. G. Nyman and J.B.C. Pettersson, J. Chem. Phys. (1987).
4. G.D. Kubíak, J.E. Hurst, Jr., H.G. Rennagel, G.M. McClelland and R.N. Zare, J. Chem. Phys. 79, 5163 (1983).

## TIME DEPENDENT THEORY OF GAS-SURFACE ENERGY TRANSFER

Bret E. Jackson  
Dept. of Chemistry  
University of Massachusetts  
Amherst, MA 01003

Several time dependent studies have been made of gas-surface scattering in recent years, using both discrete<sup>2,3c,4</sup> and Gaussian wave packet<sup>1,3a,3b</sup> representations of the molecular wave function. All attempts to introduce finite surface temperature have involved a classical propagation of the surface atoms<sup>2,3a</sup>, which is invalid for gas species of low mass or energy. We present a fully quantum mechanical theory of gas-surface energy transfer, which can be easily applied to any of these time dependent approaches. Using perturbation theory, the reduced density matrix for the gas atom/molecule is written in terms of three wave function-like objects, which obey Schrödinger-like equations of motion. Thus, the time evolution of the reduced density matrix requires only about three times the computational effort of the zero temperature calculation. The theory allows one to compute thermally averaged properties of the scattering molecular system at all times.

Results are presented for the scattering of He and Ne from various metal surfaces. The influence of coupling to bulk phonons and Raleigh modes is examined. Extensions to time dependent studies of dissociative adsorption<sup>3c</sup> and rotationally inelastic diffraction<sup>3b,4</sup> are considered.

1. G. Drolshagen and E. Heller, J. Chem. Phys. 79, 2072 (1983), Surf. Sci. 139, 260 (1984).
2. R. Kosloff and C. Cerjan, J. Chem. Phys. 81, 3722 (1984).
3. B. Jackson and H. Metiu, J. Chem. Phys. (a) 83, 1952 (1985); (b) 84, 3535 (1986); 85, 4129 (1986); (c) 86, 1026 (1987).
4. R. C. Mowrey and D. J. Kouri, J. Chem. Phys. 84, 6466 (1986).

Classical Trajectory Method and Generalized Langevin Equation:  
Atomic Motions on Solid Matrix

Xing-Guo Zhang\*, Alex Boeglin, and S. H. Lin  
Department of Chemistry  
Arizona State University  
Tempe, AZ 85287, USA

Because of the wealth of details about the atomic motions provided by the classical trajectory simulation, i.e., the step by step variation in atomic momentum and position that make it possible to study the mechanism by which a process occurs. The classical trajectory method has obtained considerable development.

Using the newest program on the classical trajectory method (QCPE program No. 453), on the two-dimensional system up to 50 particles, we studied the vibrational relaxation of impurity molecules in solid matrices. However, we also did several preliminary studies on the reactions  $C + CH_4$ ,  $C + C_3H_8$  etc., in preparation for the above work. But we put emphasis on phase transition and atomic missing on 50 particles solid matrix to simulate some electron microscope-observed results recently (1). Some phase transition and atomic missing have been simulated.

However, comparing our results with the experimental data from electron microscopy, we found that there is a time scale problem between calculations and observations. By means of the generalized Langevin equation, it was concluded that the origin of this time scale difference is caused by the interaction of the system with the heat bath. Also we got some numeral comparison.

Reference

- (1) Bovin, J. O., Seminar in Arizona State University, Oct. 18, 1985.  
Iijima, S. and Ichihashi, T., Japan, J. Appl. Phys. 24, 125 (1985).  
Kang, Z. C., Smith, D. J., and Eyring, L., (Scripture, 1985).

---

\*Permanent address: Shanghai Institute of Metallurgy, Academy of Sciences of China, Shanghai, China.

# DYNAMICS OF ADSORPTION/SCATTERING OF ATOMIC HYDROGEN ON PARTIALLY COVERED Si(111) SURFACES\* ST8

Betsy M. Rice, Lionel M. Raff, and Donald L. Thompson

Department of Chemistry  
Oklahoma State University  
Stillwater, Oklahoma 74078

The adsorption and scattering of atomic hydrogen from a partially covered Si(111) surface has been investigated using classical trajectory methods.

The potential energy surface used in this study is expressed as the sum of a lattice potential, a lattice-atom interaction potential, and an atom-atom potential. The lattice interaction is Keating's potential [1] for the unreconstructed Si(111) lattice, as modified by Weber [2]. The atom-atom interaction is repulsive. There is experimental evidence that more than one binding site exists on the Si(111) surface for hydrogen interactions. There is no disagreement about the position of one of these sites, located directly above each surface silicon atom. The location of a second site is less well understood; however, several studies have suggested that this site is located in an interstitial position on the surface [3]. We have developed a lattice-atom interaction potential function with parameters fitted to available experimental data and theoretical information [4] for two types of binding sites for hydrogen on a Si(111) surface, a top binding site, and an interstitial or open binding site.

Adsorption of hydrogen has been studied as a function of hydrogen coverage on the Si(111) crystal face. Translational energy and scattered azimuthal angle distributions for scattering of a beam of hydrogen atoms will be presented. Sticking probabilities as a function of incident azimuthal angle, the mechanism of adsorption, and the effect of the heterogeneity of the binding sites on sticking and scattering will also be presented.

- [1] P. N. Keating, *Phys. Rev.* **145**, 637 (1966).
- [2] W. Weber, *Phys. Rev. B* **15**, 4789 (1977).
- [3] G. Schulze and M. Henzler, *Surf. Sci.* **124**, 336 (1983);  
B. A. Joyce and J. H. Neave, *Surf. Sci.* **34**, 401 (1973);  
P. Klimesch, G. Meyer and M. Henzler, *Surf. Sci.* **137**, 79 (1984);  
M. Seel and P. S. Bagus, *Phys. Rev. B* **23**, 5464 (1981); and  
W. S. Verwoerd, *Surf. Sci.* **125**, 575 (1983).
- [4] See, for example,  
H. Froitzheim, U. Kohler, and H. Lammering, *Surf. Sci.* **149**, 537 (1985),  
and references therein;  
H. Kobayashi, K. Edamoto, M. Onchi, and M. Nishijima, *J. Chem. Phys.*  
**78**, 7429 (1983), and references therein.

\* Supported by the Air Force Office of Scientific Research

## Variable-step stochastic dynamics in gas-surface and condensed phase simulations\*

Bruce C. Garrett, P. K. Swaminathan,  
C. S. Murthy, and Michael J. Redmon  
Chemical Dynamics Corporation  
Upper Marlboro, Maryland 20772

Two variable-step integration procedures are presented for solving the stochastic equations of motion describing the dynamics of chemical processes in condensed phases. The generalized Langevin equation (GLE) provides a convenient framework for studying explicitly the nuclear dynamics of a 'primary' or 'chemically-crucial' few-body region in which the effects of the heat bath are modeled by time-dependent memory and random force terms<sup>1</sup>. Traditionally these equations of motion are solved using a low-order fixed-step integration scheme which requires small step sizes throughout a trajectory even though larger steps are acceptable for parts of the trajectory. A general variable-step integrator has not been previously developed for stochastic equations of motion because of the presence of the random force term which complicates the determination of the error in a given step of the integration which in turn is used to predict the next step size. We show how a variable-step integrator can be properly adapted for stochastic equations to yield an efficient yet reliable method.

The methods have been tested for a simple model of electronically inelastic collisions with an insulator surface in which the phonon manifold acts as a heat bath and the electronic states are localized. The semiclassical equations of motion are obtained from a formalism<sup>2</sup> based on the selfconsistent Eikonal method (SCEM) of treating the electronic inelasticities combined with the the GLE for the heat bath. The variable step algorithms are particularly well suited to the numerical task of following the much faster, and at the same time important, molecular electronic degrees of freedom along with the slower nuclear variables.

Two approaches are considered, one based upon the molecular timescale GLE (MTGLE)<sup>3</sup> which is applicable to arbitrary memory kernels, and one based upon the Brownian harmonic-oscillator (BHO) form for the memory kernel<sup>4</sup>. In the MTGLE approach the heat bath is model as a white noise source and the white noise random force is sampled randomly leading to complications in use of high-order predictor-corrector algorithms. With the BHO form the random force is sampled from an exact conditional probability function which tends to smooth out the random fluctuations and make the approach amenable to the use of a high-order predictor-corrector algorithm. A new method which combines the BHO form for the memory function with the MTGLE equivalent chain representation permits modeling of arbitrary memory kernels and provides for a more justifiable implementation of the variable step method.

Applications of these methods will be presented for electronic excitation and quenching of atoms at insulator surfaces (such as oxygen atoms colliding with silica) and for the quenching of electronically excited species in condensed phases (such as metastable helium atoms in a rare gas condensed phase). In applications to the gas-surface collisions the variable step integration provides up to an order of magnitude increase in efficiency over fixed-step integration methods.

\* Work supported by NASA under contract NAS2-12356 and the Air Force Rocket Propulsion Laboratory under contract F04611-86-C-0068.

<sup>1</sup> J. C. Tully, *Ann. Rev. Phys. Chem.* **31**, 319 (1980); S. A. Adelman, *Adv. Chem. Phys.* **44**, 143 (1980), **53**, 611 (1983).

<sup>2</sup> P. K. Swaminathan, see abstract for contributed papers in this volume.

<sup>3</sup> S. A. Adelman, *J. Chem. Phys.* **71**, 4471 (1979).

<sup>4</sup> J. C. Tully, *J. Chem. Phys.* **73**, 1975 (1980).

## The Influence of Condensed Phase on Electronically Excited Metastables

P. K. Swaminathan and C. S. Murthy  
Chemical Dynamics Corporation  
9560 Pennsylvania Avenue  
Upper Marlboro, MD 20772

Excited  $\text{He}^*$  atoms in normal liquid  $^4\text{He}$  ( $1^1\text{S}$ ) environment exist<sup>1</sup> inside "bubbles" that have sizes and shapes characteristic of the electronic state of  $\text{He}^*$  as well as the thermodynamic state (pressure, temperature etc.) of the liquid. The bubbles are stabilized by the repulsive interaction of the Rydberg-like excited electron with bath He atoms.

In a large classical [room temperature with high pressure (gigapascals)] regime, where classical computer simulation methods (Monte Carlo, and Molecular Dynamics) can be employed to characterize these "bubble states", we assess the influence of the liquid in affecting the metastability of the  $\text{He}^*$  ( $2^3\text{S}$ ) species. Due to the large size of the bubble (of diameter 5-10 angstroms), the trapped excited species undergo almost gas-surface-like collisions, with the inner surface of the bubble, that are responsible for nonradiative quenching. Computer simulations provide the data (frequency moments of the heatbath spectral density) necessary to parameterize a Generalized Langevin Equation (GLE) model<sup>2</sup> of the condensed phase dynamics involved in the quenching process and the electronic inelasticity is described by the Self-Consistent Eikonal Method (SCEM)<sup>3</sup> in a merged semiclassical formal framework<sup>4,5</sup>.

The  $\text{He}^*$  along with the He atoms on the bubble's inner surface behave like a single-shell solventberg at lower pressures, whereas, a two-shell structure emerges in the high pressure regime. The simulated bubble radius varies between 5-3 angstroms in the pressure range, 1-15 GPa. The heatbath parameters are found to be very sensitive to pressure and temperature since these variables change the bubble radius and hence the solvent effect.

This work was supported by the  
Air Force Rocket Propulsion Laboratory under contract F04611-86-C-0068

<sup>1</sup> (a) W. S. Dennis, E. Durbin, Jr., W. A. Fitzsimmons, O. Heybey, and G. K. Walters *Phys. Rev. Lett.* **23**, 1083 (1969); (b) J. C. Hill, O. Heybey, and G. K. Walters, *ibid.* **26**, 1213 (1971); (c) A. P. Hickman and N. F. Lane *Phys. Rev. Lett.* **26**, 1216 (1971); (e) A. P. Hickman, W. Steets, and N. F. Lane *Phys. Rev.* **B12**, 3705 (1975).

<sup>2</sup> J. C. Tully, *Ann. Rev. Phys. Chem.* **31**, 319 (1980); S. A. Adelman, *Adv. Chem. Phys.* **44**, 143 (1980); **53**, 611 (1983).

<sup>3</sup> D. A. Micha *J. Chem. Phys.* **78**, 7138 (1983).

<sup>4</sup> P. K. Swaminathan, see abstracts for contributed papers in this volume.

<sup>5</sup> B. C. Garrett, P. K. Swaminathan, C. S. Murthy, and M. J. Redmon, "Implementation of Variable Timestep Stochastic Dynamics for Electronically Inelastic Gas-Surface Collisions", *J. Chem. Phys.*, In Press, also see abstracts for contributed papers in this volume.

## **Eikonal Treatment of Electronically Inelastic Processes in the Condensed Phase**

**P. K. Swaminathan**  
Chemical Dynamics Corporation  
9560 Pennsylvania Avenue  
Upper Marlboro, MD 20772

A practical route towards the dynamical description of localized electronic inelasticity in a condensed phase environment (gas-surface collisions, reactions in liquids etc.) is achieved by merging two powerful formulations. (1) the Self Consistent Eikonal Method (SCEM)<sup>1</sup> and (2) the Generalized Langevin Equation (GLE)<sup>2</sup> formalism.

Within the SCEM, electronic amplitudes are selfconsistently coupled to nuclear trajectories by employing an Ehrenfest effective potential and the short-wavelength approximation. The GLE framework provides effective few-body representation of many-body dynamics from heatbath-like influence of the condensed phase. Since the SCEM framework leads to Hamilton's equations, the GLE framework readily mixes with it to allow inclusion of nuclear variables such as the phonon manifold from a solid. The GLE is particularly well suited because it provides an accurate short-time description of many-body dynamics - exactly the feature sought in identifying condensed phase dynamical features that couple strongly to fast-varying electronic variables.

The combined formalism is quite versatile and computationally tractable. It is particularly efficient when implemented by adapting a variable step integration scheme<sup>3</sup>. Applications being pursued or already achieved include atom-insulator electronic quenching studies and electronic quenching in liquid Helium bubbles<sup>4</sup>. The resultant electronically inelastic stochastic dynamics formalism may be extended and employed for a variety of new applications such as laser-induced gas-surface chemistry and the influence of electron-hole pair creations in a metallic condensed phase.

This work was supported by NASA under contract NAS2-12356 and the Air Force Rocket Propulsion Laboratory under contract F04611-86-C-0068

---

<sup>1</sup> D. A. Micha, *J. Chem. Phys.* **78**, 7138 (1983).

<sup>2</sup> J. C. Tully, *Ann. Rev. Phys. Chem.* **31**, 319 (1980); S. A. Adelman, *Adv. Chem. Phys.* **44**, 143 (1980); **53**, 611 (1983).

<sup>3</sup> B. C. Garrett, P. K. Swaminathan, C. S. Murthy, and M. J. Redmon, "Implementation of Variable Timestep Stochastic Dynamics for Electronically Inelastic Gas-Surface Collisions", *J. Chem. Phys.*, In Press; also see abstracts for contributed papers in this volume.

<sup>4</sup> P. K. Swaminathan and C. S. Murthy, see abstract for contributed papers in this volume

DYNAMICS OF CLUSTER SCATTERING FROM SURFACES. Guo-Qin Xu, R.J. Holland, J. Levkoff, A. Robertson, Steven L. Bernasek, Department of Chemistry, Princeton University, Princeton, New Jersey 08544 and John C. Tully, AT&T Bell Laboratories, 600 Mountain Avenue, Murray Hill, New Jersey 07974

We have studied nitrogen cluster beam scattering from Fe(111), Fe(110) and Ag(111) surfaces. The angular distributions and rotational energies of scattered species were measured by the electron beam induced fluorescence technique. The angular distributions show that the maximum density of the scattered fragments is near the surface tangent, essentially independent of the incident angles. The rotational energy measurements show that the fragments scattered near the surface normal direction have a higher rotational temperature than those near the surface tangent. This is the reverse of what is seen for diatomic molecules scattering from crystal surfaces.

In order to interpret these experimental results, theoretical calculations of argon cluster scattering from Pt(111) have been carried out by using the stochastic trajectory method. The results of this study show that the angular distributions of the fragments depend on the size of incident cluster,  $Ar_n$ . When  $n_1 = 26$ , the angular distributions have only one peak which is near the surface tangent angle for both  $\theta_i = 30^\circ$  and  $60^\circ$ . It is found that the average energy of the scattered monomers increases with the scattered angle, which is the reverse of the trend for atoms scattering from surfaces. It is very interesting to note that cluster-surface collisions tremendously enhanced the trapping probability and the mobility of the trapped species in comparison to the atomic-surface collisions. A binary collision model is suggested to explain these results.

Mr. Guo-Qin Xu  
Professor Steven L. Bernasek  
Department of Chemistry  
Princeton University  
Princeton, NJ 08544  
(609) 452-4121

QUASICLASSICAL TRAJECTORY STUDY OF ROTATIONAL  
AND VIBRATIONAL ENERGY TRANSFER  
IN  $\text{NH}_3$  / GOLD GAS-SURFACE SCATTERING\*

Michael E. Coltrin and Bruce D. Kay

Sandia National Laboratories

Albuquerque, NM 87185

Quasiclassical trajectories are used to study rotational energy transfer in the collision of a rigid-rotor  $\text{NH}_3$  molecule with a flat, rigid gold surface. The anisotropic dipole-image dipole term in the long-range attractive potential causes the  $\text{NH}_3$  to preferentially reorient with its dipole moment normal to the surface plane as it approaches surface. This reorientation decreases the rotational energy transfer and gives rise to a sharp rotational rainbow at zero rotational energy. The molecule preferentially scatters into low  $K$  rotational states (tumbling) rather than the  $J = K$  states (spinning), in qualitative agreement with recent molecular beam/surface scattering experiments. These calculations have been extended to include the "umbrella" vibrational mode of the ammonia molecule to explain the high degree of vibrational energy transfer observed experimentally. Up to three quanta of excitation is transferred into this vibrational mode. The model predicts the threshold for the onset of vibrational excitation and the average final vibrational energy as a function of the incident normal translational energy in good agreement with experiment. These results indicate that a simple "mechanical" collision excitation mechanism can account for the facile vibrational excitation seen experimentally.

---

\*This work was performed at Sandia National Laboratories, supported by the U.S. Department of Energy, under contract No. DE-AC04-76DP00789.

ROTATIONALLY AND VIBRATIONALLY INELASTIC SCATTERING  
OF NH<sub>3</sub> FROM Au(111)\*

Bruce D. Kay, T. D. Raymond, and Michael E. Coltrin  
Sandia National Laboratories  
Albuquerque, NM 87185

Employing molecular beam scattering and multiphoton laser ionization spectroscopy we have measured the rotational, vibrational, velocity, and angular distributions of NH<sub>3</sub> scattered from a Au(111) single crystal surface. The scattering is characterized by markedly non-equilibrium rotational, vibrational, and velocity distributions indicating a direct inelastic scattering mechanism. The rotational state distributions indicate that the NH<sub>3</sub> is preferentially scattered into the lowest K rotational states; these are states in which the molecule is tumbling normal to its symmetry axis as opposed to spinning about it. This is the first observation of a dynamical propensity in rotationally inelastic gas-surface scattering. In addition to the anomalous rotational distributions we observe up to three quanta of vibrational excitation in the NH<sub>3</sub> "umbrella" mode. Both the rotational and vibrational inelasticity scale linearly with incident normal kinetic energy and are insensitive to surface temperature. The detailed results and their implications will be presented.

---

\*This work was performed at Sandia National Laboratories, supported by the U.S. Department of Energy, under contract No.DE-AC04-76DP00789.

A Comparison of Rotational Energy Accommodation  
in Catalytically Produced OD and OH Radicals  
Desorbing from a Smooth Pt(111) Single Crystal

David S.Y. Hsu and M.C. Lin

Chemistry Division, Naval Research Laboratory  
Washington, D.C. 20375-5000

Abstract

Rotational energy distributions of OD and OH radical reaction products desorbing from a smooth Pt(111) single crystal have been measured by using the laser-induced fluorescence technique in conjunction with an UHV apparatus. The measured distributions are Boltzmann-like and the rotational temperatures scale with the surface temperatures over the temperature ranges studied. For OD, the average rotational to surface temperature ratio,  $T_r/T_s$ , is  $0.95 \pm 0.06$  over the temperature range 1230-1440K. For OH, the average  $T_r/T_s$  ratio is somewhat lower, at  $0.87 \pm 0.05$ , over the temperature range 1200-1470K.

For both OD and OH the rotational energy distributions over both the  $^2\Pi_{3/2}$  and  $^2\Pi_{1/2}$  spin-orbit states have been measured by using Q, P, and R branch transitions. We have found the spin-orbit temperature to be the same as the rotational temperature in each of the OD and OH systems. The lack of preference for the P and R branch transitions over the Q branch transitions indicates a lack of preference for any lambda-doublet state and suggests that no rotational angular momentum polarization was present in our experiments.

This work examines the effect of the rotational constant on rotational energy accommodation under the influence of the same interaction potential between the surface and the two species. A rationalization will be given on the observed rotational energy accommodation for OD and OH.

## FINAL STATE DISTRIBUTIONS IN MOLECULES SPUTTERED FROM SOLIDS.

JOSEPH E. MORYL, DAVID WM. CULLIN, AND PATRICK L. JONES,  
DEPARTMENT OF CHEMISTRY, THE OHIO STATE UNIVERSITY,  
120 WEST 18TH AVE., COLUMBUS, OH 43210.

To understand the dynamics of molecule production during the physical erosion of surfaces by fast particles requires knowledge of the energy partitioning among the possible final states of the system. Laser-induced fluorescence of sputtered molecules is a sensitive means of obtaining these data and has been employed in the present experiment to provide high angular resolution final state distributions of sodium dimers formed by ion bombardment of metallic sodium surfaces. The results from this new experiment will be presented and discussed in terms of various possible models of the erosion process and how the results might be used to choose among them. In addition, preliminary efforts on chemical erosion studies will be presented.

Plated Graphite

P. Rowntree\*, C. Ruiz\*, G. Scoles\*\* and J. Xu\*\*

We have recently observed the first ordered monolayers of polar molecules ( CH<sub>3</sub>F, CH<sub>3</sub>Cl ) on single crystal surfaces ( C(0001), Xe(111)/C(0001) ), and have studied their structural characteristics using He atom diffraction.

When a CH<sub>3</sub>F monolayer is deposited on graphite, the unit cell is  $\sqrt{3} \times \sqrt{3}$  R30° with respect to the graphite substrate, with real space lattice parameters of 4.26 Å. The diffraction intensities suggest that the corrugation of this layer is approximately 0.6 Å. When this monolayer of CH<sub>3</sub>F is physically separated from the graphite by an adsorbed spacer layer of xenon, ( ~4 Å ), it is seen that the centre-of-mass positions of the CH<sub>3</sub>F molecules are exactly those described above. The unit cell, however, is now  $\sqrt{3} \times 2\sqrt{3}$  R30°, and corresponds to a striped arrangement of oriented dipoles, such that the repeat distance across the stripes is now twice the CH<sub>3</sub>F-CH<sub>3</sub>F nearest neighbour distance. This orientational order is apparently made possible by decreasing the array of dipoles' interactions with the polarizability of the graphite substrate.

Monolayers of CH<sub>3</sub>Cl on C(0001) and on Xe(111)/C(0001) both show a rectangular unit cell which is uniaxially incommensurate, with real space lattice parameters of 4.26 Å and 6.38 Å. We believe that the increased polarizability of chlorine ( with respect to fluorine ) increases the lateral interactions within the layer such that the dipole-graphite interactions are not dominant; this is consistent with the unit cell of the CH<sub>3</sub>Cl layer being smaller than the unit cell of the CH<sub>3</sub>F layer, despite the larger volume of the CH<sub>3</sub>Cl molecule.

\* University of Waterloo, Waterloo, Ontario, Canada

\*\* Princeton University, Princeton, New Jersey, USA

Millard H. Alexander and Didier Lemoine

Department of Chemistry, University of Maryland, College Park, Maryland 20742

Hans-Joachim Werner

Fachbereich Chemie der Universität Frankfurt/M, D-6000 Frankfurt, West Germany

There has been considerable past interest in the dynamics of electronically inelastic collisions involving excited states of small molecules and radicals. Recently Dagdigan has used optical-optical double resonance (OODR) to investigate transitions between individual rotational and fine-structure levels of the  $A^2\Pi$  and  $X^2\Sigma^+$  states of CN. In these experiments initial CN A state levels were prepared by excitation in the A-X band system, while collisionally populated levels in the initial A state vibrational level and the nearly isoenergetic X state vibrational manifold were interrogated by detection of B-X fluorescence upon B-A and B-X probe laser excitation, respectively. Last year, Alexander and Corey developed the exact, fully quantum treatment of collision induced transitions between a  $\Pi$  and a  $\Sigma^+$  electronic state.

Electronically inelastic collisions result from a mixing between the  $\Pi$  and  $\Sigma$  electronic states of the isolated molecule which is provoked by the approach of the collision partner. To describe this effect, qualitatively as well as quantitatively, it is necessary to understand the dependence on geometry of the matrix elements of this electrostatic potential in a diabatic (isolated molecule) basis. In order to transform to this diabatic basis, one must determine the non-adiabatic coupling matrix elements  $\langle\Pi/(\partial/\partial q)/\Sigma\rangle$ , where  $q$  designates the internal coordinates of the triatomic (molecule + perturber) system.

We shall report progress on state-averaged multiconfiguration self-consistent-field (SA-MCSCF) and multireference configuration-interaction (MCSCF-CI) calculations of the interaction of CN in both the excited  $A^2\Pi$  and ground  $X^2\Sigma^+$  states with He. The three adiabatic potential energy surfaces have been calculated for several values of the CN bond distance. A fit to this surface has then been used in Coupled-States calculations of the cross sections for inelastic collisions *within* the  $A^2\Pi$  state. These results will be compared with the experimental cross sections, for collisions with Ar, obtained in Dagdigan's laboratory. In addition we have begun the calculation of the electronically nonadiabatic (first derivative) coupling matrix elements which are responsible for the  $A\rightarrow X$  electronically *inelastic* transitions.

---

<sup>1</sup> Research supported in part by the National Science Foundation under grant CHE84-05828.

THE EXPANSION OF ANGULAR-ENERGY PROBABILITY DISTRIBUTIONS FROM  
TRAJECTORY CALCULATIONS IN 2-D FOURIER SERIES\*

F. E. Budenholzer and S. C. Hu

Department of Chemistry, Fu Jen Catholic University  
Hsinchuang 24205, Taipei, Taiwan ROC

E. A. Gislason

Department of Chemistry, University of Illinois at Chicago  
Chicago, IL 60680 U. S. A.

Angular and energy distributions from classical trajectory calculations were expanded in one and two dimensional Fourier series. The method gives smooth, continuous "maps" of the product angle-energy distribution,  $P(x,y)$ . To test the method we calculated 9,200  $F+H_2$  trajectories at an initial energy of 3.0 kcal/mol using the Muckerman<sup>2</sup> potential energy surface. (1) Of these trajectories, 2,471 were reactive. The figure shows the 2-D product distribution for scattering angle  $\phi$  versus vibrational energy of product HF.

$$x = E_{\text{vib}}/ET$$

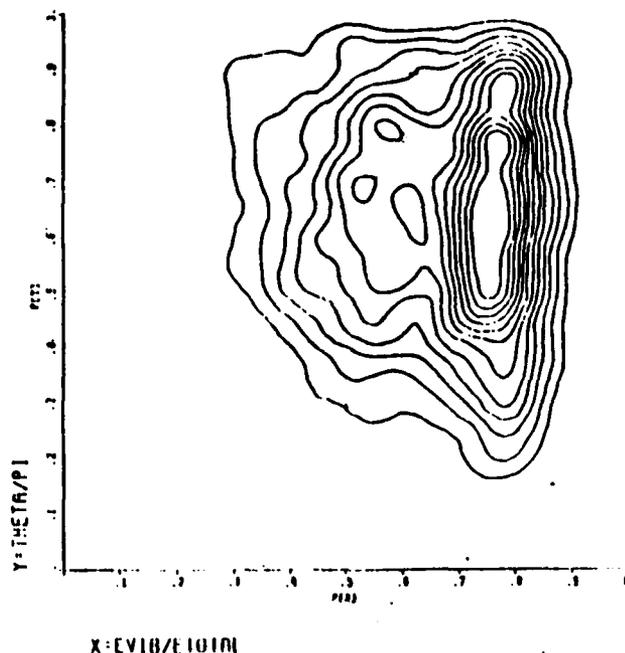
$$y = \phi/\pi$$

$$P(x,y) = \sum_{n=1}^{\infty} \sum_{m=1}^{\infty} A_{nm} \sin(n\pi x) \sin(m\pi y) \exp[-(k^2 n^2 + l^2 m^2)]$$

Here ET is the total energy available to products,  $A_{nm}$  are Fourier coefficients calculated analogously to those for one dimensional series (2), and  $k$  and  $l$  are smoothing parameters determined from the statistics of the trajectory calculation. Countours indicate relative probability and are normalized such that integration over  $x$  and  $y$  gives unity. Countour intervals are 0.5.

Various angle-energy and energy-energy contour maps will be displayed. We believe this method provides the optimal way to display the results of such trajectory calculations.

\*Work supported by the National Science Council of the ROC.



(1) J. T. Muckermann, Theoretical Chemistry: Advances and Perspectives 6A(1981)1.

(2) A. Kosmos, E. A. Gislason and A.D. Jorgensen, J. Chem. Phys., 75(1981)2884.

## H+NO TRANSLATION-TO-VIBRATION/ROTATION ENERGY TRANSFER:

## A CLASSICAL TRAJECTORY STUDY\*

F. E. Budenholzer, S. C. Hu, L. M. Hwang, and M. Song

Department of Chemistry, Fu Jen Catholic University  
Hsinchuang 24205, Taipei, Taiwan ROC

In 1983 and 1985 Wight, Donaldson and Leone (1) published two papers describing the results of experiments in which translation-to-vibration/rotation energy distributions were measured. After publication of the initial experimental study we began a classical trajectory study of the H+NO scattering process using only the 'A' surface. In 1985 Colton and Schatz (2) published a classical trajectory study in which trajectories were run over all four surfaces that correlate with ground state H+NO. We here present the results of our trajectory calculations over the single 'A' surface. They compliment in several interesting ways the study of Colton and Schatz.

The semiempirical surface of Carter, Mills and Murrell (3) was used. The initial vibration energy was set to the zero point energy of NO. The initial translation energy was 3.0 kcal/mol and the initial rotation energy was set to zero. 2000 trajectories were run over this surface of which 886 gave excitation to the  $v=1$  or higher state. Since the initial rotation energy was zero we were able to use the orientation of the initial N-NO velocity vector to distinguish H--NO from H--ON collisions. Some results are tabulated below. (All theoretical results are for the 'A' surface only.)

energy level	vibrational distributions			fraction of exciting col. at O or N side of mol.		
	v	traj. calc. this work	traj. calc. ref. 2.	experiment ref. 1.	H--ON	H--NO
1		0.38	0.36	0.55	0.41	0.59
2		0.22	0.19	0.24	0.45	0.55
3		0.15	0.19	0.07	0.47	0.53
4		0.09	0.13	0.05	0.58	0.42
5		0.07	0.05	0.04	0.92	0.08
6		0.04	0.04	0.03	0.92	0.08

We also added features to record the number of "nearly direct hits" and "complex formation." We will discuss the dynamics of rotational and vibrational excitation in relation to features of the potential energy surface.

\* Supported by the National Science Council of the ROC.

- (1) C. A. Wight and S. R. Leone, J. Chem. Phys. 79(1983)4823; C. A. Wight, D. J. Donaldson, and S. R. Leone, J. Chem. Phys. 83(1985) 660.
- (2) M. C. Colton and G. C. Schatz, J. Chem. Phys. 83(1985)3413.
- (3) S. Carter, I. M. Mills, and J. N. Murrell, J. Chem. Soc.: Faraday Trans., 275(1979)148.

VIBRONIC SYMMETRY CORRELATION THEORY FOR THE PROTON SCATTERING FROM  
HYDROCARBONS WITH DEGENERATE VALENCE ORBITALS

Ying-Nan Chiu

Center for Molecular Dynamics and Energy Transfer  
Department of Chemistry, The Catholic University of America  
Washington, D.C. 20064 U.S.A.

and

Max-Planck Institut für Strömungsforschung, Bunsenstrasse 10,  
3400 Göttingen, Federal Republic of Germany

A vibronic symmetry correlation theory<sup>1</sup> is proposed for the unusual results of proton-energy loss spectroscopy of J. Peter Toennies, M. Noll, G. Niedner and B. Friedrich.<sup>2</sup> The theory is based on protonated complex formation and charge transfer. Methane and acetylene are chosen as examples, both have degenerate highest occupied molecular orbitals. While the  $\text{CH}_5^+$  complex may assume different configurations, it is shown that vibronic interaction promotes a conical-type intersection. This guides the proton to a path of lower potential in which the proton interacts mainly with one of the degenerate orbitals and minimally with the rest of orbitals that are orthogonal to this one, e.g. attack along the center of one tetrahedral edge results mainly in proton interaction with one of the  $t_2$  component of  $T_d$  and yields a trigonal bipyramid complex  $\text{CH}_5^+(D_{3h})$ . In this, the second-order Jahn-Teller effect between the ground  $^1A_1$  state and the excited  $^1E'$  state promotes  $\nu_6, \gamma (E')$  vibrations. The latter modes can correlate to the  $\nu_4 (E)$  mode of the  $\text{CH}_4$  - a mode that is observed<sup>2</sup> but is not accountable by the usual I.R. excitation. These  $E'$  vibrations are precisely those causing the Berry pseudorotation. In case of acetylene, the complex may assume the non-classical structure  $\text{H}-\text{C} \equiv \text{C}-\text{H}$  or the classical vinyl cation structure  $\text{H}_2\text{C}=\text{C}^+-\text{H}$ . It is shown that the attack of proton along one of the  $\pi_u$  - orbital will promote  $\nu_2^+(\Sigma_u^+)$  and  $\nu_4^-(\pi_g)$  vibrations which may start the three protons off in a merry-go-round motion that interconverts the two isomeric forms in a two-dimensional planar elliptical 'orbit'. This is in lieu of a three-dimensional ellipsoidal orbit, even though acetylene initially has "cylindrical" symmetry. We consider such preferential interaction with one degenerate orbital to be a chemical reactional Jahn-Teller effect. We believe it to be especially prominent when charge transfer takes place resulting in degenerate cations with Renner-Teller<sup>3</sup> or Jahn-Teller effect. The symmetry of the  $\text{H}^+$  and  $(\text{H}_2 (T_d, ^1A_1))$  reactants may be different from that of the charge-transfer product  $\text{H} (^2S)$  and  $(\text{H}_2^+ (T_d, ^2T_2))$  and the potential curves will cross. But, a preferential approach will give rise to a conical-intersection and result in an avoided intersection and charge-transfer. The center of tetrahedral edge attack resulting in  $\nu_4^-(E')$  vibration of  $\text{CH}_4$  also promotes the Jahn-Teller distortion from a  $^2T_2$  state in  $T_d$  geometry to a  $^2B_2$  state in  $D_{2d}$  geometry. The non-rigid molecular aspects of scattering and isomerization will be discussed in terms of complete nuclear permutation inversion group theory<sup>4-6</sup>.

1. Y.-N. Chiu, J. Chem. Phys. 64, 2997 (1976); Y.-N. Chiu, M.S.F.A. Abidi, J. Phys. Chem. 86, 3288 (1982).
2. U. Gierz, M. Noll, J. Peter Toennies, J. Chem. Phys. 82, 217 (1985); M. Noll, Ph.D. Thesis, Göttingen 1986.
3. C.F. Chang and Y.-N. Chiu, J. Chem. Phys. 53, 2186 (1970); C.F. Chang, Ph.D. Thesis, The Catholic University of America, 1972.
4. M. Quack, Mol. Phys. 34, 477 (1977).
5. A. Metropoulos and Y.-N. Chiu, J. Chem. Phys. 68, 5607 (1978). A. Metropoulos, Ph.D. Thesis; The Catholic University of America, 1978.
6. P.R. Braker, "Molecular Symmetry and Spectroscopy" (Academic Press, NY, 1979).

CALCULATION OF ROVIBRATIONAL SPECTRA OF WATER USING AN  
ADIABATIC SEPARATION OF STRETCHING AND BENDING MOTIONS.

Gerardo Delgado-Barrio and Pablo Villarreal  
Instituto de Estructura de la Materia, CSIC.  
Serrano 123, 28006 Madrid, SPAIN  
and

Grigory A. Natanson\*, David Leitner, and R. Stephen Berry  
Department of Chemistry, The University of Chicago  
Chicago, Illinois 60637

\*Department of Chemistry, Northwestern University, Evanston,  
Illinois 60201.

We use an adiabatic separation of fast stretching modes from bending and overall rotational modes to calculate the spectrum of the water molecule<sup>1,2</sup>. The potential used was that of Sorbie and Murrell<sup>3</sup> as modified by Lawton and Child<sup>4</sup>. After freezing the bending angle, the stretching modes were solved by two different ways, 1) expanding the two-dimensional wavefunctions in a basis formed by products of harmonic oscillator eigenfunctions, and 2) using the numerical solutions of the OH bond. Both representations yield similar frequencies to those previously reported<sup>4</sup>, at least for excitations  $\nu_1, \nu_2 \leq 8$ . However, large differences were found from the values obtained in an one-dimensional calculation<sup>5</sup>. In order to get the necessary effective potentials for the bending motion, the stretching calculations were carried out a) at each bending angle, and b) extending in a perturbative way the quantities at the equilibrium angle. Finally, a body-fixed frame with one OH bond as the Z-axis was used to obtain the spectrum. In Table I, a few frequencies (in  $\text{cm}^{-1}$ ) for JTOT=0 and low excitations are compared with "exact" theoretical values<sup>5,6</sup> and also experimental data<sup>7</sup>.

Table I

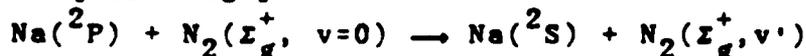
$\nu_1$	$\nu_2$	$\nu_3$	Exp	Ref. 5	Ref. 6	This work
1	0	0	3657.054	3662.7	3671.73	3654.7
0	0	1	3755.930	3764.9	3764.11	3752.5
1	1	0	5234.977	5225.5	5226.59	5167.6
0	1	1	5331.269	5329.2	5325.35	5269.9
1	2	0	6775.094	6756.3	6734.34	6657.3
0	2	1	6871.522	6861.2	6841.42	6762.3

- G.A. Natanson, G.S. Ezra, G. Delgado-Barrio, and R.S. Berry, *J. Chem. Phys.* **81**, 3400 (1984)
- G.A. Natanson, G.S. Ezra, G. Delgado-Barrio, and R.S. Berry, *J. Chem. Phys.* **84**, 2035 (1986)
- K.S. Sorbie and J.N. Murrell, *Mol. Phys.* **29**, 1387 (1975)
- R.T. Lawton and M.S. Child, *Mol. Phys.* **40**, 773 (1980)
- M.S. Child and R.T. Lawton, *Chem. Phys. Lett.* **87**, 217 (1982)
- B.R. Johnson and W.P. Reinhardt, *J. Chem. Phys.* **85**, 4538 (1986)
- J.M. Fland and C. Camy-Peyret, *Mol. Phys.* **26**, 811 (1973).

ELECTRONIC QUENCHING OF Na(<sup>2</sup>P) BY COLLISION WITH  
N<sub>2</sub> (Σ<sub>g</sub><sup>+</sup>, v=0) IN THE PERPENDICULAR CONFIGURATION

Jose Campos-Martinez, Gerardo Delgado-Barrio  
and Pablo Villarreal  
Instituto de Estructura de la Materia, CSIC,  
Serrano 123, 28006 Madrid, SPAIN

We apply a close-coupling approach to study the  
electronic quenching process



assuming a perpendicular configuration. The potential energy  
surfaces used were those reported by Archirel et al<sup>1</sup>. Instead  
of the interelectronic coupling previously employed<sup>2</sup>, we have  
taken a gaussian expression

$$U_{\text{PS}}(R, r) = B \exp\{-\beta[R - R_c(r)]^2\}$$

where R is the atom-diatom distance r is the diatomic bond  
length, R(r) is the crossing curve between both diabatic  
electronic surfaces and B, β are adjustable parameters. This  
coupling is able to reproduce the main features of the  
collision, i.e., the inversion of the final diatomic  
vibrational population and the high efficiency of the  
quenching process. For thermal energies only one channel in  
the initial state and eight in the final one are open. In  
Table I we present the partial quenching probabilities at a  
collision energy E=810 cm<sup>-1</sup>. They were calculated taking into  
account 9 channels in the final state and 2,4,...etc in the  
initial state, using the values B=0.002 and β=8 (atomic  
units). Convergence was achieved in a 9x10 calculation.

Table I

	P <sub>0→0</sub>	P <sub>0→1</sub>	P <sub>0→2</sub>	P <sub>0→3</sub>	P <sub>0→4</sub>	P <sub>0→5</sub>
9 x 2	6.41(-1)	6.30(-2)	4.09(-2)	3.57(-1)	5.22(-4)	5.05(-6)
9 x 4	7.07(-4)	1.99(-2)	3.77(-1)	7.76(-2)	1.44(-3)	1.93(-5)
9 x 6	4.88(-2)	2.33(-1)	1.76(-1)	4.67(-2)	7.06(-3)	2.24(-4)
9 x 8	4.87(-2)	2.91(-1)	1.46(-1)	3.61(-2)	5.56(-3)	9.98(-3)
9 x 9	4.25(-2)	3.05(-1)	1.14(-1)	2.02(-2)	1.49(-2)	6.26(-2)
9 x 10	5.72(-2)	2.70(-1)	6.47(-2)	9.51(-3)	2.52(-2)	6.28(-2)
9 x 11	5.95(-2)	2.64(-1)	6.66(-2)	1.20(-2)	2.38(-2)	6.32(-2)

Finally, partial quenching probabilities averaged by a  
Boltzmann distribution of the temperature are presented in  
Table II. The inversion of the final diatomic vibrational  
population, in this temperature range, can be seen from  
inspection of this table.

Table II

T(°k)	P̄ <sub>0→0</sub>	P̄ <sub>0→1</sub>	P̄ <sub>0→2</sub>	P̄ <sub>0→3</sub>	P̄ <sub>0→4</sub>
200	1.50(-3)	1.04(-2)	5.20(-2)	1.48(-2)	4.58(-4)
400	3.16(-3)	1.67(-2)	4.61(-2)	1.36(-2)	5.20(-4)
600	4.95(-3)	2.20(-2)	4.09(-2)	1.22(-2)	6.05(-4)
800	6.48(-3)	2.61(-2)	3.68(-2)	1.12(-2)	6.69(-4)
1000	7.65(-3)	2.90(-2)	3.39(-2)	1.03(-2)	7.17(-4)

1 P. Archirel and P. Habitz, Chem. Phys. **78**, 213 (1983)

2 J. Campos-Martinez, S. Miret-Artés, P. Villarreal, and G.  
Delgado-Barrio, J. Mol. Struct. **142**, 517 (1986).

Collision Complex Model Predictions for Electronic Transitions  
in a Diatomic Molecule

A. V. DENTAMARO and D. H. KATAYAMA, Air Force Geophysics  
Laboratory (LIU), Hanscom AFB, MA 01731

While much work has been done on collision-induced rotational and vibrational energy transfer, electronic transitions in molecules due to atomic collisions remains a relatively new topic. Alexander and Corey<sup>1</sup> have recently developed a quantum formulation which they applied to  $2\Pi-2\Sigma$  transitions in a diatomic molecule that yield good qualitative results when compared to experiment. Previously, we applied this model to our QODR data<sup>2</sup> for the specific transitions  $A^2\Pi_u(v=4)-X^2\Sigma_g^+(v=7,J)$  in  $N_2^+$  due to collisions with helium atoms. We now extend this theoretical model by inserting an explicit interaction potential into Alexander and Corey's expression for the transition matrix, thereby removing the dependence on quantities they define as the base cross sections,  $\sigma_0$ . Based on our previous work demonstrating the importance of the attractive force, we assume the  $N_2^+$  and He form a metastable collision complex which predissociates, resulting in E→T energy transfer. By using a phenomenological potential to generate initial and final wavefunctions for the atom-molecule system, we are able to make predictions for relative cross sections precluding previous knowledge of the data.

- 1 M.H. Alexander and G.C. Corey, J. Chem. Phys. 84, 100 (1986).
- 2 D.H. Katayama and A.V. Dentamaro, J. Chem. Phys. 85, 2595 (1986).

Nonadiabatic Reaction Dynamics Studies of  
Li, Na ( $^2P$ ) + H<sub>2</sub>, D<sub>2</sub> Quenching

Charles W. Eaker  
University of Dallas

We have constructed diatomics-in-molecules (DIM) potential energy surfaces which have been optimized to agree with ab initio surfaces for Li, Na ( $^2P$ ) + H<sub>2</sub>, D<sub>2</sub> quenching reactions. On the Na + H<sub>2</sub> surfaces we have used two different nonadiabatic classical trajectory methods to predict surface hopping: (1) transformation of the multidimensional surface intersection to a local one-dimensional curve crossing and calculation of the Landau-Zener transition probability (Muckerman-Stine method), and (2) integration of the coefficients of the adiabatic electronic states to determine transition probability (Blais-Truhlar method). For Na + H<sub>2</sub> we have compared nonadiabatic coupling terms calculated by DIM to ab initio values and find them to be in good agreement.

We report the results of over 5000 trajectories run at a variety of initial conditions using the two methods to describe surface hopping. We find method 2 in all cases gave significantly larger quenching cross sections than method 1. We find that the magnitudes of the quenching cross sections to be very sensitive to the details of the interacting potential energy surfaces.

Theoretical State-to-State Charge Transfer Cross Sections  
for  $\text{Ar}^+ + \text{N}_2$  and  $\text{Ar}^+ + \text{CO}$  Collisions

Eric A. Gislason  
Department of Chemistry, University of Illinois at Chicago

Pierre Archirel and Gérard Parlant  
University of Paris - South at Orsay

Theoretical state-to-state cross sections have been calculated for charge transfer in collisions of  $\text{Ar}^+ ({}^2P_J) + \text{N}_2$  and  $\text{Ar}^+ ({}^2P_J) + \text{CO}$ . Our semiclassical theoretical method<sup>1</sup> computes the classical trajectory for each collision and solves the time-dependent Schrodinger equation along the trajectory for the vibronic states of the system. The potential energy surfaces and couplings have been calculated using the procedure of Archirel and Levy.<sup>2</sup>

Although  $\text{N}_2$  and  $\text{CO}$  are isoelectronic, the ionization potentials of the two molecules differ by 1.6 eV. As a consequence, the charge transfer cross sections with  $\text{Ar}^+$  are quite different. At  $E_{\text{cm}} = 2$  eV, the total cross section for  $\text{Ar}^+ + \text{N}_2$  is large, and the product states nearest in energy to the reactant state are primarily populated, even when this violates the Franck-Condon principle.<sup>3</sup> For  $\text{Ar}^+ + \text{CO}$  the reactant state is nearly resonant with  $\text{Ar} + \text{CO}^+ (n' = 7)$ , but the Franck-Condon factor for the transition  $\text{CO} (n = 0) \rightarrow \text{CO}^+ (n' = 7)$  is zero. As a consequence, the total charge transfer cross section is small. The product state populations appear to represent a compromise between energy resonance and Franck-Condon factors. The calculations show that the  $\text{CO}^+ (\text{A})$  state plays an important role in this system, even at low collision energies. We shall discuss these results in our poster.

---

<sup>1</sup> G. Parlant and E. A. Gislason, Chem. Phys. **101**, 227 (1986).

<sup>2</sup> P. Archirel and B. Levy, Chem. Phys. **106**, 51 (1986).

<sup>3</sup> E. A. Gislason and G. Parlant, Comments At. Mol. Phys. **19**, 157 (1987).

Low-Energy Collision-Induced Vibrational Energy Transfer in the HeI<sub>2</sub> System

Young Sik Kim  
Department of Chemistry  
University of Rochester  
Rochester, New York 14627

Thomas F. George  
Departments of Chemistry and Physics & Astronomy  
239 Fronczak Hall  
State University of New York at Buffalo  
Buffalo, New York 14260

An investigation<sup>1</sup> is made of vibrational energy transfer in low-energy collisions between He and vibrationally excited I<sub>2</sub>(B).<sup>2</sup> Taking into account the open-channel as well as closed-channel (Feshbach-type) resonances and the coupling between the rotational and the vibrational motions, it is shown that the dynamics is not sensitive to the resonance position,<sup>3</sup> and that the enhancement of the vibrational relaxation cross section at low collision energies is due to resonances (both closed- and open-channel), the anharmonicity of the I<sub>2</sub> molecule, and the long-range attractive force of the intermolecular potential.<sup>4</sup>

1. Y. S. Kim, M. Hutchinson and T. F. George, J. Chem. Phys., submitted.
2. J. Tusa, M. Sulkes and S. A. Rice, J. Chem. Phys. 70, 3136 (1979).
3. S. Gray and S. A. Rice, J. Chem. Phys. 83, 2818 (1985).
4. D. W. Schwenke and D. G. Truhlar, J. Chem. Phys. 83, 3454 (1985).

FULLY QUANTUM STUDIES OF COLLISIONS OF  $\text{Li}_2(\text{B}^1\Pi_u)$  WITH He and Ne<sup>1</sup>Didier Lemoine, Gregory C. Corey<sup>2</sup>, and Millard H. Alexander

Department of Chemistry, University of Maryland, College Park, Maryland 20742

Jacques Derouard

Laboratoire de Spectrométrie Physique, Université Scientifique et Médicale de Grenoble

B.P. 87, 38402 Saint-Martin d'Hères Cedex, France

More than a decade ago several experimental groups began the investigation of inelastic collisions within the excited  $\text{B}^1\Pi_u$  electronic states of the alkali dimers. In these open-shell systems the relative motion of the collision partners can couple not only with the rotational motion of the molecule but also with the orbital motion of the electron in the singly filled  $\pi$  orbital of the alkali dimer. Motivated by this work a number of authors developed general frameworks for the treatment of the collisions of molecules in  $^1\Pi$  electronic states. In several early treatments the interaction of the  $\Pi$  state molecule with a perturber atom was described in terms of a *single* potential energy surface which depended explicitly on the orientation of the singly filled  $\pi$  orbital. A less confusing description invokes the *two* potential energy surfaces which arise when the electronic degeneracy of a  $^1\Pi$  electronic state is lifted by the approach of a collision partner. Much of the early experimental work, and the interpretation thereof, was devoted to the observed inequalities in the cross sections for *upward* ( $J \rightarrow J + \Delta J$ ), as compared to *downward* ( $J \rightarrow J - \Delta J$ ) transitions.

We report close-coupled (CC), coupled-states (CS), and infinite-order-sudden (IOS) cross sections for collisions of  $\text{Li}_2(\text{B}^1\Pi_u)$  with He and Ne, a system currently under experimental study. Two choices were made for the relevant potential energy surfaces, both based on functional forms introduced by Poppe. Since these surfaces are simplistic, our goal will not be the determination of quantitative cross sections to compare with experiment. Rather we shall concentrate on exploring the range of validity of the CS and IOS approximations and investigating and interpreting quantum interference effects in the integral cross sections. These interference effects are clearly manifested, for example, in the variation with initial  $\Lambda$ -doublet level of the cross sections for  $J \rightarrow J + \Delta J$  transitions.

<sup>1</sup> Research supported in part by the National Science Foundation under grant CHE85-506502.

<sup>2</sup> NSERC of Canada University Research Fellow. Present address: Département de Chimie, Université de Montréal, C.P. 6128, Succursale A, Montréal, Québec, Canada H3C 3J7.

ABSTRACT FOR CONFERENCE ON  
DYNAMICS OF MOLECULAR COLLISIONS

A Calculation of the Second Virial Coefficient  
of Equilibrium and Normal Hydrogen

G. T. McConville<sup>†</sup>  
MRC-Mound\*

Niblett and Takayanagi set up a formalism to solve coupled Schrodinger equations for hydrogen which they considered a mixture of J=0 and J=1 molecules where the J=0 molecules are spherical and the J=1 molecules are eleptical. We have used this formalism to calculate phase shifts and amplitudes in an energy grid from 1 to 1000 K. The J=0, J=0 interaction was determined from the HFD potential function of McConville and the phase shifts were found from a single Schrodinger equation. The angular part of the J1 interaction was taken as an additional P<sub>2</sub>(cosθ) repulsive term and a 1/r<sup>5</sup> quadrupolar attractive term. The J=0, J=1 interaction leads to three coupled equations for J-j=0, ±1 and the J=1, J=1 interaction leads the nine coupled equations for J-j=0, ±1, ±2. The Takayanagi selection rules allow the latter set to be broken into four sets of 4, 2, 2 and 1 equations which are coupled in each set. The code uses the deVogelaere scheme for simultaneous numerical integration of the coupled equations. Then the R rotation done to satisfy the asymptotic boundary condition is accomplished by a matrix inversion in complex notation. The resultant phases and amplitudes are then stored according to E, J, J-j, and μ. The second virical and viscosity can be obtained from combinations of the phases and amplitudes. The second virial was found from an average of the amplitudes of the form

$$(2j+1) \delta \ln^2 \delta_j = \frac{1}{n} \sum_{\mu} \sum_J (E_{J \mu}^j)^2$$

where n = 3 fo, J=0, J=1 and n=5 for J=1, J=1.

The calculation for equilibrium hydrogen was obtained from B<sub>00</sub> and that for normal hydrogen from .06 B<sub>00</sub> + .375 B<sub>10</sub> + .56 B<sub>11</sub> agrees quite well with the experimental values tabulated in Dymond and Smith.

<sup>†</sup>Work was in collaboration with American Institute of Physics Summer Interns: Stephen Allegero, Michael Cavagnero, Joseph Dimarco, and Jonathan Luke.

\*MRC-Mound is operated by Monsanto Research Corporation, a subsidiary of Monsanto Company for the U. S. Department of Energy, under Contract Number DE-AC04-76-DP00053.

Higher-order adiabatic approximations for coupled systems,  
by T. Tung Nguyen-Dang, Département de chimie, Université de Sherbrooke,  
Sherbrooke, Québec, Canada, J1K 2R1.

It is shown that a higher-order adiabatic representation for any interacting system may be constructed via a proper unitary transformation of the system's hamiltonian. This transformation physically corresponds to a phase shift describing a retardation in the fast subsystem's response to the slow subsystem's motions. In this higher-order representation, the two subsystems are still adiabatically separated, even though first-order non-adiabatic interactions had been implicitly resummed, yielding residual second-order non-adiabatic couplings. The systematic search for the above phase-shift transformation is illustrated for simple two-body systems, ranging from dressed and free hydrogen atoms, to the Hénon-Heiles anharmonically coupled oscillator system. For this last non-integrable system, it is shown that the dynamics of the system appears, in the new adiabatic representation, to mimic closely the dynamics of the integrable anti-Hénon-Heiles system.

## Spectroscopy and Dynamics of Alkali-Halide Charge Transfer States

S.-H. Pan and F. H. Mies  
National Bureau of Standards, Gaithersburg, MD 20899

Near the dissociation threshold in a given isolated diatomic charge-transfer state, we can expect a dramatic change in the properties of the vibrational levels. The usual  $^1\Sigma^+$  electronic state, with total angular momentum  $J$ , is well represented, in atomic units, by a Rittner-type potential [1,2]

$$V(R) = A \exp(-aR) - C/R^6 - \alpha/2R^4 + J(J+1)/2mR^2 - Z/R$$

Except for being rather anharmonic due to the skewness introduced by the soft  $-Z/R$  term, we expect the spacings of the lowest vibrational levels to be reasonably normal. However, since the large amplitude vibrational levels just below the dissociation limit predominantly experience this coulombic interaction, we expect an infinite number of rotational-vibrational levels to be supported by the Rittner potential, with vibrational spacings given by the typical perturbed Rydberg expression

$$E_{J,v} = -Z^2 m/2(v+J+1-\mu_J)^2,$$

where  $m$  is the reduced mass of the diatomic molecule. The vibrational quantum number,  $v$ , measures the number of nodes in the given vibrational state and simply replaces the radial quantum number  $n$  we normally associate with electronic Rydberg states. We have used accurate numerical algorithms, based on the Milne's quantum number function [3], to evaluate the vibrational quantum defect  $\mu_J(m)$ . The exact transition from harmonic-like to Rydberg-like behavior depends in detail on the rotational angular momentum  $J$  and mass  $m$ , but typically for vibrational quantum numbers  $v \geq \text{Order}(10^3)$  we achieve a reasonably exact Rydberg limit, with  $\mu_J(m)$  approaching a constant, independent of  $v$ .

Even in the simplest  $^1\Sigma^+$  alkali-halide charge-transfer system,  $M^+X^-$ , the Rittner potential is crossed by the potential curves originating from neutral, ground state  $M(^2S)+X(^2P)$  collisions. This induces predissociation of the coulombic vibrational levels [1]. In previous studies of the charge-transfer dynamics only the diabatic coupling between the neutral and charge-transfer  $^1\Sigma^+$  electronic states were included [2]. In our close-coupled calculations of the predissociation, we also include a coupling to the neutral  $^3\Pi_0^+$  state. Using these three pure case(c) molecular states, with appropriate radial, rotational and spin-orbit couplings, we can evaluate the partial widths for predissociation into the specific  $j=1/2$  and  $j=3/2$  fine-structure states of the  $X(^2P)$ . Utilizing a rigorous analytic multichannel quantum defect representation of the resonance scattering [4], we attempt to isolate the effect of varying fine-structure splitting on the charge-transfer spectra for different alkali-halogen systems.

- [1] R.S. Berry, in Alkali Halide Vapors, Academic Press, N.Y., 77 (1979).
- [2] M.B. Faist and R.D. Levine, J. Chem. Phys. 64, 2953 (1976).
- [3] B. Yoo and Ch.H. Greene, Phys. Rev. A 34, 1635 (1985); H.J. Korsch and H. Laurent, J. Phys. B 14, 4213 (1981).
- [4] F.H. Mies, J. Chem. Phys. 80, 2514 (1984); F.H. Mies and P.S. Julienne, J. Chem. Phys. 80, 2526 (1984).



COLLISIONAL ENERGY TRANSFER IN POLYATOMICS.  
VIBRATIONAL EFFECTIVE HAMILTONIAN FOR CO<sub>2</sub>-Ar

G. JOLICARD\*, M.Y. PERRIN\*\*

\* Faculté des Sciences et Techniques de Besançon  
Laboratoire de Physique Moléculaire, ERA n° 834  
25030 BESANCON Cedex, France

\*\* Laboratoire E.M2.C d'Energétique Moléculaire et  
Macroscopique, Combustion du CNRS et de l'ECP  
92295 CHATENAY-MALABRY Cedex, France

In the processes of collision induced energy transfers between translation, rotation and vibration, the perturbations seen by the different vibration modes frequently vary adiabatically. The use of an adiabatic formulation enables to reduce considerably the coupling strengths while opening indirect transition paths. Then a perturbative approach, even at the first order, can give reliable results. The major difficulties occur in the construction of the adiabatic basis and non adiabatic coupling terms. We propose a new approach in the framework of the effective Hamiltonian for the CO<sub>2</sub>-Ar system.

The Hamiltonian can be written as :

$$\mathcal{H} = \frac{1}{2} \mu (\dot{\vec{R}})^2 + \frac{1}{2} m (\dot{\vec{r}})^2 + \mathcal{H}_0^{\text{vib}} + V_1 + V(R, \cos\gamma, q) + \Delta \mathcal{H}$$

$\mathcal{H}_0^{\text{vib}}$  is the zero order vibrational Hamiltonian.  $V_1$  is the anharmonic part of the vibrational Hamiltonian (limited to the fourth order).  $V(R, \cos\gamma, q)$  is the interaction potential used in ref 1.  $\Delta \mathcal{H}$  represents the rovibrational couplings limited to the first order, i.e. Coriolis and centrifugal terms.

The static part of the vibrational Hamiltonian

$$\mathcal{H}_{\text{sta}} = \mathcal{H}_0^{\text{vib}} + V_1 + V(R, \cos\gamma, q)$$

is bloc diagonalized using intermediate representations<sup>2, 3</sup>. The basis set of 70 vibrational states is partitionned in 7 blocs of 1,2,4,6,1,9,47 states respectively. The procedure is repeated in about a hundred coordinates points, nodes of elliptical coordinates.

The dynamical equations are then expressed. The part corresponding to the adiabatic dynamics between quasi degenerated states-blocs and that corresponding to the internal dynamics in each bloc are clearly separated.

- 1 G.D. BILLING, Chem. Phys. 91, (1984) 327
- 2 G. JOLICARD, A. GROSJEAN, Rev. Phys. A 32 (1985) 2051
3. G. JOLICARD, to be published in Chem. Phys.

## **Cis-Trans Isomerization of Methyl Nitrite\***

**Aleksandra Preiskorn\*\* and Donald L. Thompson**

**Department of Chemistry, Oklahoma State University, Stillwater, Oklahoma 74078**

The unimolecular dynamics of methyl nitrite has been investigated by using quasiclassical trajectory methods. The rates of intramolecular cis-trans conversion have been calculated as a function of various initial excitations of CH bonds and selected normal modes. Also, the energy flow from CH overtones has been examined. Mode specificity of the internal conversion will be discussed.

\* Work supported by the U.S. Army Research Office.

\*\* On leave from the Institute of Physics, N. Copernicus University, Toruń, Poland.

THEORETICAL STUDY OF ENERGY TRANSFER IN COLLISIONS OF ALIGNED  $\text{Ca}(4s5p^1P)$   
ATOMS WITH NOBLE GASES<sup>1</sup>

Jean Michel Robbe

Laboratoire de Spectroscopie des Molécules Diatomiques UA 779, Université de Lille  
Flandres-Artois, Bâtiment P5, 59655 Villeneuve d'Ascq cedex, France

Brigitte Pouilly and Millard H. Alexander

Department of Chemistry, University of Maryland, College Park, Maryland 20742

The investigation of alignment effects in atomic and molecular collisions is presently emerging as a field of considerable interest. The present study was motivated by the recent experiment of Bussert, Neuschäfer and Leone where polarized laser excitation in a crossed beam was used to investigate the dependence on orbital alignment of the cross section for the  $\text{Ca}(4s5p^1P) \rightarrow \text{Ca}(4s5p^3P)$  spin-changing transition. With He, Ne and Ar, the observed cross sections were larger when the Ca 5p orbital is aligned initially *perpendicular* to the direction of the relative velocity of the two partners. However, with Xe as the collision partner, the opposite result is found: the  $^1P \rightarrow ^3P$  cross section is larger for *parallel* excitation. Lastly, in the case of Kr, no preferential alignment effect is observed.

In the full quantum theory of this process the  $^1P \rightarrow ^3P$  spin changing transition occurs by means of the spin-orbit mixing between the  $^1P$  and  $^3P_{j=1}$  states of the Ca atom. It is, furthermore, facilitated by the crossing between the  $^1\Pi$  and  $^3\Sigma$  potential curves which at long range correlate respectively, to the  $^1P$  and  $^3P$  states of the Ca atom.

As an extension of previous work on  $\text{Ca}^+ \text{-He}$  collisions [B. Pouilly and M. H. Alexander, J. Chem. Phys. **86**, xxxx (1987)], we shall present the results of close-coupled calculations for the collision of  $\text{Ca}(4s5p^1P)$  with the other noble gases (Ne, Ar, Kr, Xe). In addition we have studied the polarization dependence of the *reverse* ( $^3P \rightarrow ^1P$ ) process, for which some experimental cross sections have also been obtained. Since the electrostatic potential curves for the relevant highly excited states of the Ca+rare gas systems are unknown, we modelled these curves using a flexible Morse-Spline-Van der Waals function. We have paid particular attention to the influence of the shape of the electrostatic curves on the polarization dependence of the cross sections.

---

<sup>1</sup> Research supported in part by the U.S. Army Research Office under grant DAAG29-85-K-0018.

Energy Transfer and Reaction in Collisions  
of Fast H Atoms with CO<sub>2</sub>

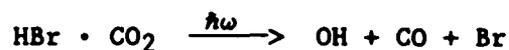
George C. Schatz

Department of Chemistry, Northwestern University

Evanston, IL 60201

In this paper we present the results of a state resolved quasiclassical trajectory study of the H + CO<sub>2</sub> collision system using a potential surface that we have developed by fitting ab initio calculations for all the HCO<sub>2</sub> minima and saddle points. Both reactive and nonreactive collisions are studied, with the nonreactive results being compared with recent measurements due to Flynn, Weston and coworkers, and the reactive results compared with measurements due to Kleinermanns and Wolfrum. Sensitivity of the results to features of the potential surface is considered, and it appears that rather tight bounds on the addition barrier to form HOCO can be inferred from the data.

We will also present results of a trajectory simulation of the photoinduced reaction



Comparisons with measurements due to Wittig and coworkers will be made, along with an analysis of the orientation dependence of the OH product state distributions.

DISSOCIATION OF  $H_2^+$  BY He

M. SIZUN, E.A. GISLASON\* and G. PARLANT†

L.C.A.M., Bât. 351, Université Paris-Sud, 91405 ORSAY Cedex (France)

\*Department of Chemistry, University of Illinois, CHICAGO IL 60680 USA

†L.R.E.I., Bât. 350, Université Paris-Sud, 91405 ORSAY Cedex (France)

The collision induced dissociation CID process  $H_2^+ + He \rightarrow He + H^+ + H$  has been studied over a wide range of kinetic energies and once more very recently (1) at low energies. Gislason and Guyon (2) discussed these experimental results and went deeper into the study of the mechanism of C.I.D. :

There are two potential energy surfaces which are relevant to the system  $HeH_2^+$ . The ground surface is correlated to two diatomic bounds fragments  $H_2^+ \Sigma_g^+ + He$  and  $HeH^+ + H$ , the excited surface to dissociative fragments  $H_2^+ \Sigma_u^+ + He$  and  $HeH + H^+$ . Among these asymptotes, one can distinguish, first  $H_2^+ \Sigma_g^+$  and  $\Sigma_u^+$  where the one electron is shared equally between the two nuclei,  $HeH^+ + H$ , where it is located on the proton which is farther from the He atom,  $HeH + H^+$  where it is on the proton the nearest the He. So the position of the proton relative to the atom (or its velocity) can be used to distinguish the two states which are nearly degenerate when all three nuclei are far apart. We are interested into the distribution of CID products between these two states.

To study the dynamics of the reaction, the adiabatic energies of the system were expressed in terms of diabatic terms relevant to the two electronic configurations  $H_A^+ - H_B^+ - He$  and  $H_A - H_B^+ - He$  : in  $C_{2v}$  the two  ${}^2A_1$  diabatic states can cross and a Landau-Zener transition is possible but the transitions are in majority Demkov transitions.

The trajectories were carried out on adiabatic potential energy surfaces given by Whitton and Kuntz (3) and the surface hop was treated as localized Demkov and Landau-Zener transitions. The initial vibrational state of  $H_2^+$   $v$ , is varied between 0 and 10 and the relative kinetic energy,  $E_{rel}$ , between 3. and 1000 eV. The preliminary results show that the dissociation cross section on the excited surface is in the order of 7 % of the dissociation cross section on the ground surface

if ( $v=0$   $E_{rel}=3eV$ ), 10% if ( $v=10$   $E_{rel}=3eV$ ), 70% if ( $v=0$   $E_{rel}=1000eV$ ). More detailed results will be presented at the Conference.

(1) T. Govers and P.M. Guyon (to appear in Chem.Phys.)

(2) E.A. Gislason and P.M. Guyon ; J. Chem.Phys. 86, 677 (1987)

(3) W.N. Whitton and P.J. Kuntz ; J. Chem. Phys. 64,3624 (1976)

## Secondary Encounters in Collinear, Dissociative Atom-Diatom Collisions

Neil Snider

Department of Chemistry, Queen's University, Kingston, Ontario

Canada K7L 3N6

Classical trajectory simulations of dissociative collisions between a diatomic molecule  $A_2$  and an atom  $M$  have shown that the correction  $\kappa_3$  for recrossing of an appropriately chosen phase space dividing surface is independent of temperature  $T$  when collisions are dominated by  $A-M$  repulsion. Recrossing in this case is thought to be due to secondary  $A-M$  encounters in the course of a collision, but the physical basis of the  $T$ -independence of  $\kappa_3$  has been unclear. As a first step toward providing such a basis, collinear classical trajectories were run for several of the same three body potentials and mass ratios that had been studied in the three dimensional simulations. Recrossing corrections derived from the collinear trajectories show a  $T$  behavior similar to that of  $\kappa_3$ . The collinear results can be interpreted in terms of the single encounter impulsive collision model with a simple modification to account for secondary encounters.

Breakdown of the Phenomenological Rate Law  
for the Dissociation of Diatomic Molecules

Heshel Teitelbaum  
Department of Chemistry  
University of Ottawa

We have solved the master equation describing the rates of change of vibrational level populations during the steady dissociation of a diatomic gas, AB, in mixtures of finite composition. V-T energy transfer processes among neighbouring levels as well as collision induced dissociation from the top-most level are considered. This simple model presents most of the features of real systems. Although more detailed models have been treated in the past and their corresponding rate equations solved numerically, none of those studies give the insight which the present analytical treatment affords and at the same time make predictions concerning the validity of the so-called linear mixture rule (LMR) for specific examples. This rule states that if  $k_{AB}$  is the rate coefficient for  $AB + AB \rightarrow AB + A + B$  and  $k_M$  is the rate coefficient for  $M + AB \rightarrow M + A + B$  (M is inert), then the overall rate coefficient,  $k$ , for the effective process  $AB \rightarrow A + B$  is

$$k = k_{AB} x_{AB} + k_M x_M \quad (1)$$

It is well known that the LMR is not generally valid when non-equilibrium vibrational population distributions persist. This has been shown for unimolecular dissociation of polyatomic molecules [1], and theorems have been developed for the maximum size and direction of the deviation from the LMR [2]. In previous theoretical and experimental work we have shown that deviations can be severe for the vibrational relaxation of diatomic molecules [3] and of polyatomic molecules [4,5].

Eq. (1) implies the validity of the phenomenological rate law.

$$-\frac{d[AB]}{dt} = k[AB]([AB] + [M]), \quad (2)$$

with  $k$  independent of concentration. Because of the fundamental importance and universal use of eq. (2) we investigate the conditions for validity of eq. (1) as applied to the dissociation of diatomic molecules. We find that deviations can indeed be very serious. The deviations are most serious when (1) the relative AB:M efficiency for collisional induced dissociation differs most from the relative AB:M efficiency for collisional de-excitation, and (2) when the temperature is high. Deviations manifest themselves at low mole fractions of the least efficient collision partner.

We identify previously unrecognized examples of the phenomena from published research.

- [1] J. Troe, Ber. Bunsenges. Phys. Chem. 84, 829 (1980).
- [2] J.E. Dove, S. Halperin, S. Raynor, J. Chem. Phys. 81, 799 (1984).
- [3] C. Carruthers, H. Teitelbaum, Can. J. Chem. 63, 381 (1985).
- [4] Z. Baalbaki, H. Teitelbaum, J.E. Dove, W.S. Nip, Chem. Phys. 104, 107 (1986).
- [5] Z. Baalbaki, H. Teitelbaum, Chem. Phys. 104, 135 (1986).

## ROTATIONAL ENERGY TRANSFER WITHIN THE $B^3\Pi_g$ $v=3$ MANIFOLD OF MOLECULAR NITROGEN

Ashraf Ali and Paul J. Dagdigian  
Department of Chemistry  
The Johns Hopkins University  
Baltimore, MD 21218, USA

An optical-optical double resonance experiment has been carried out to study rotationally inelastic collisions of  $N_2$   $B^3\Pi_g$   $v=3$  by argon with initial and final rotational state resolution. This experiment is similar to that recently performed by Katayama,<sup>1</sup> but with higher spectral resolution here. Nitrogen molecules in the metastable A state are generated by collisional excitation transfer from metastable argon atoms. Specific B state rotational levels are prepared in a flow system by pulsed pump laser excitation of isolated rotational lines in the  $B^3\Pi_g - A^3\Sigma^+$  (3,0) band near 688 nm. After a short delay (ca. 20 nsec), a probe laser interrogates the rotational populations in the B state by fluorescence excitation in the  $C^3\Pi_u - B^3\Pi_g$  (0,3) band near 406 nm. Collisional transfer from incident levels in all 3 spin-orbit manifolds of the B state was investigated. For molecules initially in the  $F_1$  ( $\Omega=0$ ) manifold, a preference for conservation of fine-structure label with even  $\Delta J$  changes was observed. This propensity is very pronounced for the  $J=0$  level but is considerably relaxed by  $J=6$ . By contrast, inelastic collisions involving the  $F_2$  ( $\Omega=1$ ) and  $F_3$  ( $\Omega=2$ ) manifolds do not exhibit a significant propensity to conserve fine-structure label. A slight residual preference for even  $\Delta J$  changes is observed in collisional transitions within the  $F_2$  manifold. These experimental results will be compared to the propensity rules derived for homonuclear  $^3\Pi$  rotationally inelastic collisions, both in the case (a)<sup>2</sup> and case (b) limits. The reduction of the predicted propensities by the transition to intermediate case coupling and "orbital-correlated" scattering will be discussed. The latter term refers to the difference potential for the  $N_2$ -Ar interaction where the  $N_2$  unfilled  $\pi$  orbital is in or perpendicular to the triatomic plane.

1. D. H. Katayama, *J. Chem. Phys.* **84**, 1477 (1986).
2. M. H. Alexander and B. Pouilly, *J. Chem. Phys.* **79**, 1545 (1983).

A NEW CROSSED BEAM EXPERIMENT FOR STUDY OF VIBRATIONALLY INELASTIC SCATTERING WITH NEUTRAL POLYATOMICS. GLYOXAL.

K.W. Butz, H. Du, D.J. Krajnovitch, and C.S. Parmenter, Chemistry Department, Indiana University, Bloomington, IN 47405

The laser pump-dispersed  $S_1 \rightarrow S_0$  fluorescence probe method commonly used in bulb studies of rotational and vibrational energy transfer has been adapted to crossed molecular beams. These new experiments extend the state-resolved energy transfer studies to conditions of low rotational temperatures and controlled collision energies. We intend to use the method primarily with large polyatomics.

Our first polyatomic study involves collisions between  $S_1$  glyoxal and each of several partners ( $H_2$ , He, Ar, Kr and cyclohexane). Data are now available from five initial  $S_1$  glyoxal vibrational levels ( $v_{7b} = 0$  to about  $700\text{ cm}^{-1}$ ). The experiments prove quite feasible with respect to signal-to-noise levels, even when rotational resolution is imposed on the inelastic scattering observations.

Features reminiscent of bulb studies as well as very new aspects of energy transfer have emerged. For example  $H_2$  scattering from the  $0^0$  glyoxal level excites only the lowest fundamental (the CHO-CHO torsion  $v_7 \approx 233\text{ cm}^{-1}$ ) even though four other levels lie within the  $600\text{ cm}^{-1}$  collision energy range. Thus the high state selectivity seen in many bulb experiments (and also  $S_0$  beam experiments) appears once again. Scattering from other initial glyoxal levels behaves similarly. Single-collision rotationally inelastic scattering can be followed with resolution of the  $\Delta K$  angular momentum change and the total rotational energy change. These data have been transformed into relative cross sections for scattering from  $0^0$  glyoxal initially with  $J < 10$  and  $K = 0$ . When we compare the total cross section for rotational excitation to the total cross section for rovibrational excitation, we obtain results that are familiar from many other studies. Rotational excitation is about an order of magnitude more likely than rovibrational excitation. If, however, we plot the cross section as a function of energy transferred, we observe a completely different picture of the competition. Rotational and vibrational cross sections both fall off exponentially. The important point, however, is that the fall-off curves merge when placed on the same plot. In other words, for sufficiently large energy transfers (i.e., large enough to excite mode 7), equal probability exists for excitation of the torsional vibration mode and molecular rotations. In this case, there is no molecular distinction what-so-ever between rotational and vibrational excitation.

## SPECTROSCOPY AND DYNAMICS OF HIGHLY VIBRATIONALLY EXCITED ACETYLENE

E. Carrasquillo M., A. L. Utz, and F. F. Crim

Department of Chemistry, University of Wisconsin, Madison, WI 53706

A new technique enables the collisional relaxation of a highly vibrationally excited polyatomic molecule to be studied in previously unattainable detail. Direct overtone excitation of  $3\nu_{\text{CH}}$  prepares acetylene in an initial state with  $\sim 9600 \text{ cm}^{-1}$  excitation energy. Time resolved laser induced fluorescence (LIF) detection via excitation to the  $\tilde{A}^1A_u$  electronic state provides a monitor of the collisional relaxation pathways with rovibrational state resolution. The technique is also a potentially powerful spectroscopic tool. It accesses high-lying vibrational states whose symmetry and Franck-Condon overlap with the upper electronic surface can differ from thermally populated levels. Therefore, the technique provides new spectroscopic information about both collisionally accessed levels and the rovibrational structure of the excited electronic state.

Preliminary results demonstrate the value of this technique as a probe of collisional relaxation and as a spectroscopic tool. Temporal data show rapid collisional population of several rovibrational states followed by relaxation at a rate similar to gas kinetic. The symmetry of the overtone state allows  $\tilde{A}$  state vibrational levels of  $B_u$  symmetry to be reached in the LIF probe step. The initially prepared state is monitored via excitation to  $\nu_6$  (asymmetric in-plane bend) and to  $\nu_5$  (asymmetric C-H stretch), a previously unobserved vibration in the  $\tilde{A}$  state. Analysis of the spectrum indicates that the previous  $\nu_4$  and  $\nu_6$  vibrational assignments in the  $\tilde{A}$  state are reversed and must be reassigned. Weak couplings between vibrational states on the ground electronic surface are also evident in these experiments.

HIGH RESOLUTION CROSSED MOLECULAR BEAM STUDIES OF SPHERICAL AND  
NON-SPHERICAL INTERMOLECULAR FORCES

Laura Beneventi, Piergiorgio Casavecchia, and Gian Gualberto Volpi

Dipartimento di Chimica, Università di Perugia, 06100 Perugia, Italy

Much experimental and theoretical interest is currently being shown in the study of intermolecular potential energy surfaces (PES) for non-spherical interactions.<sup>1</sup> Once the PES is known to a sufficient accuracy, all the necessary data on rotational energy transfer can be calculated.

In our laboratory we have recently exploited the very detailed information content of diffraction scattering for the determination of interaction potentials for both spherical (atom-atom)<sup>2,3</sup> and non-spherical (atom-molecule)<sup>3,4</sup> systems. While for spherical systems the determination is very accurate and conclusive<sup>2</sup>, for non-spherical systems its validity remains confined within the limits of the approximate scheme of analysis employed<sup>4</sup>, since it is still impracticable to perform exact quantum scattering calculations for potential fitting purposes.

We will report on high resolution elastic differential cross section (DCS) measurements for Ne-Ne, Ar, Kr and Xe, in which the diffraction quantum oscillations superimposed on the rainbow structure are for the first time clearly resolved at collision energies corresponding to room temperature beams.<sup>2,3,5</sup> These new high quality data have allowed us to refine or assess, with high precision (better than 1%), the interatomic potentials for these systems, whose knowledge is considered<sup>6</sup> to be the less accurate among the like and unlike rare gas pairs.

We will also report on precise measurements of total DCS for some simple atom-molecule systems (He-N<sub>2</sub>, O<sub>2</sub> and NO,<sup>4</sup> Ne-N<sub>2</sub>, O<sub>2</sub> and NO,<sup>7</sup> and He-CO<sub>2</sub><sup>8</sup>) in which an accurate evaluation of the phase and amplitude of the diffraction structure has brought to rather reliable potential energy surfaces within a multiproperty analysis in the infinite-order-sudden approximation. For instance, for the prototype (beyond the rare gas atom-H<sub>2</sub> cases) He-N<sub>2</sub> system a potential surface which predicts correctly a wide variety of scattering and bulk data and whose spherical part has an accuracy (<1% on R<sub>m</sub> and <5% on ε) comparable to that achieved for the corresponding isotropic He-Ar system was recently derived.<sup>4</sup>

REFERENCES

1. U.Buck, *Comments At.Mol.Phys.* 17, 143 (1986); M.Faubel, *Adv.At.Mol.Phys.* 19, 345 (1983).
2. L.Beneventi, P.Casavecchia and G.G.Volpi, *J.Chem.Phys.* 84, 4828 (1986).
3. L.Beneventi, P.Casavecchia and G.G.Volpi, in *Structure and Dynamics of Weakly Bound Molecular Complexes*, edited by A.Weber (Reidel, Dordrecht, 1987), in press.
4. L.Beneventi, P.Casavecchia and G.G.Volpi, *J.Chem.Phys.* 85, 7011 (1986).
5. L.Beneventi, P.Casavecchia and G.G.Volpi, to be published.
6. R.A.Aziz, in *Inert Gases*, edited by M.L.Klein (Springer, Berlin, 1984).
7. L.Beneventi, P.Casavecchia and G.G.Volpi, to be published.
8. L.Beneventi, P.Casavecchia, F.Vecchiocattivi, G.G.Volpi, U.Buck, H.Meyer, M.Tolle and R.Schinke, to be published.

## MOLECULAR BEAM STUDIES OF THE INTERACTION OF OXYGEN ATOMS WITH RARE GASES AND METHANE

V.Aquilanti, R.Candori, G.Liuti, E.Luzzatti, F.Pirani and G.G.Volpi  
Dipartimento di Chimica dell'Università, 06100 Perugia, Italy.

To study intermolecular potential energies we measure integral cross sections as a function of the collision velocity. The apparatus used for the present experiments is that operating in our laboratory since a number of years and already described in several papers.<sup>1,2,3</sup>

The main problems in these experiments are the production of an intense and stable oxygen atom beam and the control of the electron states and of the relative population of the involved magnetic sublevels. An inhomogeneous magnetic field is used to defocus from the beam direction those atoms which show a non zero effective magnetic moment, characterizing the electronic state and varying the relative population of magnetic sublevels. For the analysis of the present scattering data, we were guided by the consideration about angular momentum coupling schemes described in refs. 4,5,6. For the O-He system, for which a comparison is possible with accurate quantum chemical calculations of open shell interactions, it is found that van der Waals forces are still underestimated by theory.<sup>7</sup>

In addition we have performed experiments, using the same apparatus, to obtain integral cross sections for rare gas-methane systems.<sup>8</sup> The presence of fully developed glory oscillations indicates that the anisotropy of methane plays only a minor role. Therefore these data can be treated in terms of a central field assumption. The substantially isotropic behaviour of methane under the present experimental conditions allows a significant understanding of integral cross sections measurement involving O atoms, where, then, anisotropy effects originate only from the non zero angular momentum of the atoms.

#### References

- 1) V.Aquilanti, G.Liuti, F.Pirani, F.Vecchiocattivi and G.G.Volpi, *J. Chem.Phys.* **65**, 4751 (1976).
- 2) V.Aquilanti, E.Luzzatti, F.Pirani and G.G.Volpi, *Chem.Phys.Letters* **90**, 382 (1982).
- 3) V.Aquilanti, G.Grossi and F.Pirani, in "Electronic and Atomic Collisions", Invited Papers, XIII ICPEAC (North Holland 1984) 441.
- 4) V.Aquilanti and G.Grossi, *J.Chem.Phys.* **73**, 1165 (1980).
- 5) V.Aquilanti, P.Casavecchia, G.Grossi and A.Laganà, *J.Chem.Phys.* **73**, 1173 (1980).
- 6) V.Aquilanti, F.Pirani and F.Vecchiocattivi, in: "Structure and Dynamics of Weakly Bound Molecular Complexes" A.Weber Ed. (Plenum, New York) 1987 to be published.
- 7) V.Aquilanti, R.Candori, E.Luzzatti, F.Pirani and G.G.Volpi, *J.Chem. Phys.* **85**, 5377 (1986).
- 8) G.Liuti, E.Luzzatti, F.Pirani and G.G.Volpi, *Chem.Phys.Letters*, **135**, 387 (1987).

STATE-TO-STATE ENERGY TRANSFER MEASUREMENTS  
OF  
VIBRATIONALLY EXCITED DIATOMIC MOLECULES WITH THERMAL COLLISION PARTNERS

David W. Chandler, Eric A. Rohlfing, and Roger L. Farrow  
Sandia National Laboratories  
Combustion Research Facility  
Livermore California, 94550

and

David H. Parker<sup>\*</sup>  
Department of Chemistry  
University of California, Santa Cruz, Ca.

We present recent results on the state-to-state energy transfer rate measurements of vibrationally excited diatomic molecules. The technique of stimulated Raman scattering is used to prepare a single rotational level of the first vibrational level of a diatomic molecule, in this case HD, H<sub>2</sub>, or HCl. State-selective multiphoton ionization is used to monitor populations in a specific ro-vibrational state in order to monitor the collisional transfer of energy from the initially prepared state to other states. By controlling the time delay between the Raman lasers and the Multiphoton Ionization laser, as well as the pressure, the collisional energy transfer rates are determined. This is done at sufficiently low pressures that the shape of the energy transfer function is directly determined. Rotational energy transfer has been studied in the systems of HD and HCL. In the H<sub>2</sub> system, in addition to rotational energy transfer, direct observation of vibration-vibration energy transfer between ortho and para hydrogen is measured.

<sup>+</sup> Work supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences

<sup>\*</sup> Summer Faculty Fellow (DHP) at the Combustion Research Facility during the period of work

STATE SELECTIVE STUDIES OF T + R,V ENERGY TRANSFER:  
THE H + CO SYSTEM

G. K. Chawla, G. McBane, and P. L. Houston  
Department of Chemistry, Cornell University  
Ithaca, New York 14853

Energy transfer in inelastic H + CO collisions is investigated by measuring the quantum state distributions of the scattered, rovibrationally excited CO product.

The experiment is performed using a 1:10 coexpansion of a hydrogen atom precursor, such as H<sub>2</sub>S, and CO in a pulsed supersonic beam. Pulsed laser photolysis of H<sub>2</sub>S at  $\lambda=222\text{nm}$  is the technique used to generate fast, monoenergetic hydrogen atoms with  $E_{\text{trans}}=1.6\text{eV}$ . The hydrogen atoms, thus produced, participate in a nominally single collision event with beam-cooled CO( $v_i=0, J_i=2$ ). The resulting CO( $v_f, J_f$ ) distribution is determined from VUV laser induced fluorescence excitation spectra, recorded using the CO  $\Lambda^1\Pi + X^1\Sigma^+$  band system.

The qualitative features of the observed CO  $v_f=0$  and  $v_f=1$  rotational distributions appear to be consistent within the framework of a classical, sudden collision occurring on a sharply repulsive potential surface. Comparisons are made with the predictions of an hard ellipse scattering model<sup>1</sup> as well as with the quasiclassical trajectory calculations of Schatz<sup>2</sup> on an *ab-initio* HCO ground state potential surface.

1. J. A. Serri, R. M. Bilotta and D. E. Pritchard, J. Chem. Phys. 77, 2940 (1982).
2. G. C. Schatz, private communication; L. C. Geiger, G. C. Schatz and L. B. Harding, Chem. Phys. Lett. 114, 520 (1985).

ROTATIONAL LEVEL VARIATION OF VIBRATIONAL ENERGY TRANSFER  
IN OH(A<sup>2</sup>Σ<sup>+</sup>, v' = 1)

Richard A. Copeland, Michael L. Wise, and David R. Crosley  
Molecular Physics Department  
SRI International  
Menlo Park, CA 94025

Rate constants for the collisional removal of v' = 1 vibrational level of the A<sup>2</sup>Σ<sup>+</sup> first excited electronic state of OH have been measured for specific rotational levels N' of the radical and a variety of collision partners. In these experiments, the output of a frequency-doubled excimer-pumped dye laser excites the molecules to an individual rotational level in v' = 1, and a transient digitizer and boxcar integrator record the time and wavelength dependence of the fluorescence. The excited OH radical can be removed from the initially excited level via reaction, quenching to X<sup>2</sup>Π<sub>1</sub>, vibrational energy transfer to v' = 0, rotational energy transfer within v' = 1, or spontaneous emission. We observe a significant decrease of the total collisional removal rate from v' = 1 (the sum of reaction, quenching, and vibrational energy transfer) with increasing rotational quantum number. For N<sub>2</sub>, CO<sub>2</sub>, CF<sub>4</sub>, and SF<sub>6</sub> the total removal rate is about a factor of two slower in N' = 4 compared to N' = 0. The electronic quenching for all but CO<sub>2</sub> is extremely slow and this difference in v' = 1 removal must be attributed to a decrease in vibrational energy transfer with rotational level.<sup>1</sup> This rotational level effect is similar to that observed for the total collisional removal rates of OH(A<sup>2</sup>Σ<sup>+</sup>, v' = 0)<sup>2</sup> and NH(A<sup>3</sup>Π<sub>1</sub>, v' = 0)<sup>3</sup> indicating that similar processes may be operating in both kinds of collisions.

From the wavelength dependence of the fluorescence we also obtain the relative amounts of vibrational energy transfer versus electronic removal for several colliders. The species studied fall into three categories. In the first there are two molecules, H<sub>2</sub>O and NH<sub>3</sub>, which remove the electronic state rapidly but cause little vibrational energy transfer. Both of these have large dipole moments; perhaps this causes rapid Σ-Π state mixing, leading to quenching and not transfer as the outcome of the collisional encounter. In the second are molecules for whom the removal and vibrational transfer are of similar magnitude: CO<sub>2</sub>, N<sub>2</sub>O, and CH<sub>4</sub>. In the third are the poor quenchers, CF<sub>4</sub>, SF<sub>6</sub>, and N<sub>2</sub>. They cause relatively rapid vibrational transfer although they quench each vibrational state quite slowly. This indicates that they interact at long range but do not mix the excited and ground states well during the collision lifetime. How this is related to the electronic structure remains a mystery.

We acknowledge support from the National Aeronautics and Space Administration (Contract NAS1-16956) and the Air Force Office of Scientific Research (Contract F49620-85-K-0010) for this work.

<sup>1</sup>R. K. Lengel and D. R. Crosley, J. Chem. Phys. 68, 5309 (1978).

<sup>2</sup>R. A. Copeland, M. J. Dyer, and D. R. Crosley, J. Chem. Phys. 82, 4022 (1985).

<sup>3</sup>N. L. Garland and D. R. Crosley, in preparation.

ELECTRONIC QUENCHING AND FLUORESCENCE LIFETIME  
OF THE TRIATOMIC RADICAL  $\text{NCN}(A^3\Pi_u)$ Gregory P. Smith, Richard A. Copeland, and David R. Crosley  
Chemical Physics Laboratory  
SRI International  
Menlo Park, California 94025

Laser-induced fluorescence of NCN has been detected for the first time via the  $A^3\Pi_u-X^3\Sigma_g^-$  electronic transition near 329 nm. The NCN radical was detected downstream of a 1.5 Torr He discharge containing about 10 mTorr of  $\text{CF}_4$  and less than 5 mTorr of  $\text{N}_2$ . From the time dependence of the fluorescence, we find a zero pressure fluorescence lifetime for the 0,0,0 and 0,1,0 vibrational levels of  $183 \pm 6$  ns ( $2-\sigma$ ). In addition to the strong 0,0,0 - 0,0,0 vibrational band, excitation spectra, fluorescence spectra, and lifetimes were also obtained for several previously unobserved, weak off-diagonal bands. The spectroscopic identification of some features is currently uncertain. Quenching cross sections were measured for the vibrationless level of the A-state for 13 different gases at 300 K. Values range over more than two orders of magnitude, from  $< 0.1 \text{ \AA}^2$  for He and  $\text{N}_2$  to values  $> 50 \text{ \AA}^2$  for NO, Xe, and  $\text{CCl}_4$ . The variation of the quenching cross section with collider cannot be correlated with the attractive part of the potential as was relatively successful for  $\text{OH}(A^2\Sigma^+)$  quenching.<sup>1</sup> For example, the isoelectronic species  $\text{N}_2\text{O}$  and  $\text{CO}_2$  show significantly different cross sections with  $\text{N}_2\text{O}$  quenching NCN about seven times faster than  $\text{CO}_2$ . Possible explanations for the large variation in the magnitude of the quenching with collision partner will be presented.

We acknowledge support from the U.S. Army Research Office under Contract DAAG29-84-K-0092 for this work.

1. G. P. Smith and D. R. Crosley, J. Chem. Phys. 85, 3896 (1986) and references therein.

**CARS Studies of Nonadiabatic Collision Processes:****"Vibrational Energy Distribution of H<sub>2</sub> after Red Wing Excitation of the Na(3p)-H<sub>2</sub>-Collision Pair"**

P.Hering, S.L.Cunha and K.L.Kompa

Max-Planck Institut für Quantenoptik  
D-8046 Garching  
Federal Republic of Germany

**ABSTRACT:**

Nonadiabatic collisions between atoms and molecules have drawn a large amount of attention in theoretical and experimental studies. In particular, the transfer of electronic energy of an atom to the vibrational, rotational and translational energy of a diatomic molecule (also called electronic quenching) can be considered an important fundamental process of this type and is thus extensively investigated. /1/

We study Na + H<sub>2</sub> as a model collision system for experimental and theoretical reasons. Ab initio potential surfaces are currently available, enabling comparison of experimental results with theoretical calculations. /2/

We apply a new experimental technique in the field of nonadiabatic processes to obtain a more detailed understanding of these energy transfer processes. We use Coherent Anti-Stokes Raman Spectroscopy (CARS) to measure directly the internal energy distribution of H<sub>2</sub> molecules produced by quenching of Na in the first excited state (3 P<sub>1/2</sub>).

Furthermore, we analysed the internal state distribution of H<sub>2</sub> after nonresonant, red wing excitation of the Na(3p)-H<sub>2</sub> collision pair dependant on excitation wavelength. The detuning range was 600 cm<sup>-1</sup> to the red starting with excitation at 589 nm. /3/ We observed a marked change in the H<sub>2</sub> vibrational distribution compared to resonant excitation of sodium. To interpret this behaviour one needs detailed knowledge about potential energy surface crossings with scattering dynamical calculations.

**References:**

- /1/ I.V.Hertel, Adv. Chem. Phys., "Dynamics of the Excited State", ed. by K.Lawley, p.475, (1982)  
W.H.Breckenridge, H.Umemoto, Adv. Chem. Phys., "Dynamics of the Excited State", Ed. by K.P.Lawley, p.325, (1982)
- /2/ P.Botschwina, W.Meyer, I.V.Hertel, W.Reiland, J.Chem. Phys. V75, p.5438, (1981);
- /3/ P.Hering, S.L.Cunha and K.L.Kompa, accepted for publication in J. of Phys. Chem., 1987, special issue on "dynamical stereochemistry"

## Isotope Effects in Excitation of CO<sub>2</sub> 00<sup>0</sup><sub>1</sub> by Hot Atoms

John F. Hershberger, Scott A. Hewitt\*, and George W. Flynn  
Department of Chemistry and Columbia Radiation Laboratory,  
Columbia University, N.Y., N.Y. 10027,  
Ralph E. Weston, Jr.  
Department of Chemistry, Brookhaven National Laboratory, Upton N.Y. 11973

Tunable diode laser spectroscopy has been used to probe the internal state distribution of CO<sub>2</sub> after collision with H and D atoms produced by excimer laser photolysis of H<sub>2</sub>S and D<sub>2</sub>S, respectively. Time-resolved infrared absorption signals of carbon dioxide spectral lines provided nascent rovibrational distributions before collisional relaxation. H atoms are roughly twice as efficient as D atoms at exciting CO<sub>2</sub> to the 00<sup>0</sup><sub>1</sub> asymmetric stretch vibrational level, in qualitative agreement with Landau-Teller arguments. Measurement of the rotational distribution of the 00<sup>0</sup><sub>1</sub> state shows a peak in the distributions at about J=33 for both H and D atoms. Deuterium, however, shows a small but distinct preference for higher rotational excitation as compared to hydrogen, as revealed by a decreasing H\* / D\* excitation ratio as J increases. This result can be explained by angular momentum considerations. The D and H atoms are formed with nearly the same energy (2.16 eV for D, 2.30 eV for H), so for a collision of fixed impact parameter, deuterium will have more angular momentum by a factor of roughly 1.4, causing more rotational excitation.

\*AT&T Bell Laboratories Ph.D. Scholar

# ISOTOPE EFFECTS IN THE HOT ATOM COLLISIONAL EXCITATION OF ISOENERGETIC STATES OF CO<sub>2</sub>

Scott A. Hewitt\*, John F. Hershberger, and George W. Flynn  
Department of Chemistry and Columbia Radiation Laboratory, Columbia  
University, N.Y., N.Y. 10027,

Ralph E. Weston, Jr.  
Department of Chemistry, Brookhaven National Laboratory, Upton, N.Y. 11973

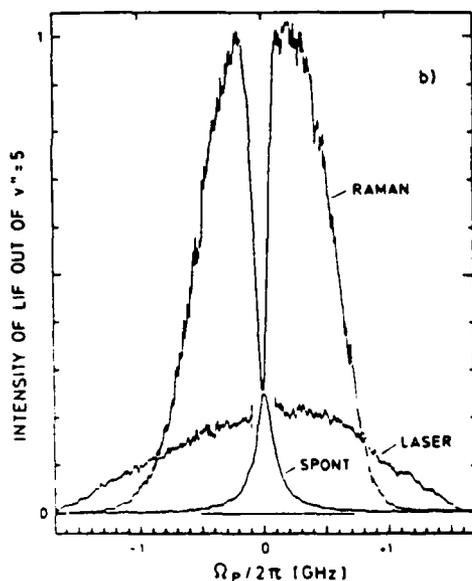
High resolution diode laser spectroscopy is used to probe specific rovibrational states of CO<sub>2</sub> molecules which are collisionally excited by translationally hot hydrogen or deuterium atoms. Time-resolved changes in the transmitted IR intensity are detected while monitoring the antisymmetric stretch  $00^01 \rightarrow 00^02$  P(13) and ground state  $00^00 \rightarrow 00^01$  P(78) isoenergetic transitions in CO<sub>2</sub> after UV photolysis of H<sub>2</sub>S or D<sub>2</sub>S. The low pressures ( $P_{\text{tot}} = 25$  mtorr) employed permit direct measurement of nascent rotational populations. The measurements show that whereas the excitation of CO<sub>2</sub>  $00^01$  P(13) by hot H atoms is approximately 2.5 times as efficient as excitation by hot D atoms, the hot D atoms are about twice as efficient as hot H atoms in exciting CO<sub>2</sub>  $00^00$  P(78). These differences in excitation probabilities are accounted for by the different trajectories required to excite a stretch versus a highly rotationally excited ground state. In order to excite a pure stretch the collision must be end-on, whereas hot atoms may approach from almost any angle to collisionally excite high rotational levels of the ground state.

\*AT&T Bell Laboratories Ph.D. Scholar

EFFICIENT AND SELECTIVE POPULATION OF HIGH VIBRATIONAL LEVELS  
BY STIMULATED NEAR RESONANCE RAMAN SCATTERING

M.Becker, U.Gaubatz, P.L.Jones and K.Bergmann  
Fachbereich Physik der Universität, Postfach 3049  
D-6750 Kaiserslautern, FRG

We report the successful application of an optically pumped molecular beam laser for efficient and selective population transfer from  $v''=0$  to high lying vibrational levels of  $\text{Na}_2$  in the electronic ground state [1]. The molecular beam itself acts as an active medium in an optically pumped laser, the gain of which is dominated by near resonance stimulated Raman scattering [2,3]. More than 50% of the molecules in a thermally populated rotational level of  $v''=0$  can be transferred to a state  $v_f \gg 1$ . The level  $v_f$  is chosen by



appropriate adjustment of an intracavity tuning element (birefringent filter). With sufficiently intense pump lasers dynamic Stark splitting occurs and the maximum population transfer is observed for off resonant tuning of the pump laser (see Fig.1). Consequently spontaneous emission is significantly reduced. This ensures a high selectivity of the transfer.

Typically  $>75\%$  of the molecules are found in the level  $v_f$  while  $<25\%$  are distributed over other vibrational levels. The applicability of this technique for the study of collision processes involving vibrationally highly excited states is demonstrated. This technique is expected to be particularly valuable for the investigation of electronic and reactive processes.

- 1) M.Becker, U.Gaubatz, P.L.Jones, K.Bergmann J.Chem.Phys. subm.
- 2) P.L.Jones, U.Gaubatz, U.Hefter, K.Bergmann, B.Wellegehausen Appl.Phys.Lett. 42, 222 (1983)
- 3) U.Hefter, J.Eichert, and K.Bergmann Opt.Comm. 52, 330 (1985)

Collision Dynamics of the SiCl Radical in the B'<sup>2</sup>Δ State

Jay B. Jeffries  
 Chemical Physics Laboratory  
 SRI International  
 Menlo Park, CA 94025

Collisions with rare gases rapidly deactivate SiCl radicals in the B'<sup>2</sup>Δ electronic state via a significant near-resonant electronic-to-electronic energy transfer pathway to the B<sup>2</sup>Σ<sup>+</sup> state. Either the v' = 0 or 1 vibrational level of the B'<sup>2</sup>Δ is excited with tunable laser light; in the presence of rare gas quenchers fluorescence from the B<sup>2</sup>Σ<sup>+</sup> is observed in the wavelength resolved data. The nascent vibrational distribution in B<sup>2</sup>Σ<sup>+</sup> depends dramatically upon the rare gas collider, He, Ne, and Ar, and also varies with the initial vibrational level v' in B'<sup>2</sup>Δ. For v' = 0 the final state distribution from He collisions includes v = 0-2 and peaks in v = 1 of B<sup>2</sup>Σ<sup>+</sup>, whereas for Ne collisions only the v = 2 final state is observed. The fluorescence lifetime of the B-state is < 25 ns, significantly faster than the B' fluorescence lifetime of near 1 μs. When B<sup>2</sup>Σ<sup>+</sup> is directly excited, no vibrational relaxation of the B-state is observed under the conditions used. Thus after exciting the B'<sup>2</sup>Δ, the collision induced fluorescence from the B<sup>2</sup>Σ<sup>+</sup> provides the nascent vibrational distribution of the B<sup>2</sup>Σ<sup>+</sup> resulting from the electronic-to-electronic energy transfer. Analysis of the branching ratio to these and other dark channels is currently underway.

In addition to this state-specific electronic-to-electronic energy transfer, total collisional removal rates from the v' = 0 and 1 levels of the B'<sup>2</sup>Δ are measured. Laser-induced fluorescence of the SiCl radical is observed in the afterglow of a microwave discharge in rare gas with a trace of added SiCl<sub>4</sub>. The initial excitation to the B'<sup>2</sup>Δ state uses light from a frequency doubled, excimer pumped, dye laser tuned to the Q<sub>11</sub> band head of either the (0,0) or (1,0) vibrational bands of the B'<sup>2</sup>Δ - X<sup>2</sup>Π electronic transition. The resulting fluorescence is time resolved at various rare gas concentrations to obtain collisional removal rate constants; preliminary results are given in Table 1.

This work is supported by internal research and development funds of SRI International.

Table 1. Total Removal Cross Sections ( $\sigma = k/\langle v \rangle$ , Å<sup>2</sup>) for B'<sup>2</sup>Δ SiCl.

	He	Ne	Ar
v' = 0	4.3	5.7	16
v' = 1	5.0	1.4	8.4

### Quenching of Infra-Red Fluorescence in NO<sub>2</sub>\*

J. J. McAndrew, R. E. Weston, and J. M. Preses  
Department of Chemistry, Brookhaven National Laboratory, Upton, NY 11973

and

G. W. Flynn  
Department of Chemistry and Columbia Radiation Laboratory,  
Columbia University, New York, NY 10027

The first excited electronic state (<sup>2</sup>B<sub>2</sub>) of NO<sub>2</sub> is strongly mixed with high vibrational levels of the ground state. NO<sub>2</sub> was promoted to this state by irradiation with 505 nm light from an excimer-pumped dye laser. The rise and subsequent decay of infrared fluorescence involving single quantum changes in the ν<sub>1</sub>, ν<sub>2</sub>, ν<sub>3</sub> and ν<sub>1</sub> + ν<sub>3</sub> vibrational modes was monitored, using appropriate filters and solid state detectors. The pressure ranged from 0.1 to 40 torr.

The fluorescence at the asymmetric stretch (ν<sub>3</sub>) frequency shows markedly slower rise and decay times than the other modes. The combination ν<sub>1</sub> + ν<sub>3</sub> band is very intense and does not appear to be in equilibrium with ν<sub>1</sub> or ν<sub>3</sub>.

Our results so far indicate the following approximate rate constants.

Mode	Rise Rate Constant (x 10 <sup>-11</sup> cm <sup>3</sup> sec <sup>-1</sup> )	Decay Rate Constant (x 10 <sup>-11</sup> cm <sup>3</sup> sec <sup>-1</sup> )
ν <sub>1</sub>	3.0 ± 1.2	3.0 ± 1.2
ν <sub>2</sub>	> 10.	3.0 ± 1.5
ν <sub>3</sub>	1.1 ± 0.1	0.2 ± 0.2
ν <sub>1</sub> + ν <sub>3</sub>	> 10.	0.6 ± 0.2

A second, slower decay component of order 10<sup>-13</sup> cm<sup>3</sup> sec<sup>-1</sup> is clearly apparent for ν<sub>1</sub> and ν<sub>2</sub> at higher pressures (> 12 torr).

Work is still in progress on the interpretation of these results and further experiments are planned.

\*This research was carried out at Brookhaven National Laboratory under contract DE-AC02-76CH00016 with the U.S. Department of Energy and supported by its Division of Chemical Sciences, Office of Basic Energy Sciences. Support to G. W. Flynn provided by the U.S. Department of Energy under contract DE-AC02-78ER04940.

## DISSOCIATIVE RECOMBINATION IN ARGON

R. G. Macdonald\* and F. C. Sopchyshyn  
 Atomic Energy of Canada Limited  
 Chalk River Nuclear Laboratories  
 Chalk River, Ontario

Inert gases are characterized by two important features which make them attractive candidates for the development of high energy laser systems, either directly as VUV laser devices or as energy storage media. These two features are 1) a large fraction of the energy lost by an energetic particle interacting with the inert gas, such as a high energy electron, leads to ionization and 2) upon neutralization a large fraction of the electron-ion recombination energy is channeled into the excitation of only a few atomic levels. The reaction governing the ion neutralization process has long been recognized to be the dissociative recombination reaction



where  $X^*$  is an excited atomic energy level of the inert gas,  $X$ . In the present work dissociative recombination of argon was studied over the pressure range 20 to 200 kPa at a temperature of 291 K. Reaction (1) has been investigated by several workers for all the inert gases at low pressures. Because all high power inert gas laser systems operate at pressures of 100's kPa it is important to be able to predict the influence of pressure on Reaction (1) and to explore the effect of 3 body processes on electron-ion recombination. In the present work pulse radiolysis and laser photoionization were combined to measure  $\alpha$ , the dissociative recombination rate constant, in pure Ar. A pulse of 1 MeV electrons was used to create a small concentration of  $Ar_2(^3\Sigma_u^+)$  excimer. After a selected delay time from the initial electron beam pulse,  $Ar_2(^3\Sigma_u^+)$  was photoionized by a pulse of 308 nm laser radiation thus creating a small excess of  $Ar_2^+$  ions directly. The dissociative recombination of  $Ar_2^+$  was followed by monitoring emission from  $Ar(3p^54p)$  atomic states, created directly in Reaction (1), or by monitoring the time dependence of  $Ar(3p^54s)$  atomic states by absorption spectrophotometry.

\*Present address: Chemistry Division, Argonne National Laboratory, Argonne, IL

## Ro-Vibrational State Mixing in the C-H Stretch Region of Norbornadiene

T.K. Minton, H.L. Kim, and J.D. McDonald

School of Chemical Sciences

University of Illinois

Urbana, Illinois 61801

Infrared laser induced fluorescence has been used to probe the extent of state mixing, as well as its rotational dependence, in the C-H stretch region of norbornadiene in the electronic ground state. Both total and dispersed IR fluorescence were collected from molecules, cooled and isolated in a molecular beam, after excitation with an infrared optical parametric oscillator. The *dilution factor*, which is inversely related to the number of coupled states, has been measured for four C-H stretch bands, and in addition, the rotational dependence of the dilution factor has been investigated by exciting different positions, or average  $J$  values, within a single ro-vibrational band. The relative energy contents of various vibrational modes, whose fluorescence was observed, have also been determined. An approximate average coupling width of  $0.1 \text{ cm}^{-1}$  can be derived from the dilution factors and the calculated state density of the ro-vibrational bath states  $|l_i\rangle$  that are permitted by symmetry and angular momentum to couple to the zero order optically active ro-vibrational state  $|s\rangle$ . The rotational dependence of the dilution factor shows that the number of mixed states is proportional to  $2J + 1$ , where  $J$  is the total angular momentum quantum number for the  $|s\rangle$  state. Allowing for both Coriolis and Fermi type couplings within a width of  $0.1 \text{ cm}^{-1}$ , we can adequately predict the distribution of the excitation energy among the modes of the molecule by using a straightforward statistical model, which assumes equal coupling between all the zero order ro-vibrational states that have the correct energy, symmetry, and  $J$  to couple. This study of norbornadiene and other recent work in our laboratory on a variety of molecules illustrate the strong correlation between the extent of state mixing and ro-vibrational state density regardless of molecular structure.

LASER DOUBLE RESONANCE MEASUREMENTS OF THE VIBRATIONAL  
ENERGY TRANSFER RATES AND MECHANISMS OF DEUTERIUM  
FLUORIDE ( $v = 1,2,3$ )

M. A. Muyskens, J. M. Robinson, K. J. Rensberger and F. F. Crim

*University of Wisconsin, Madison, Wisconsin 53706*

Overtone vibration-laser double resonance measurements determine the self-relaxation rate constants for DF( $v=1,2$ ) to be  $k_1 = (0.37 \pm 0.03) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ,  $k_2 = (22.0 \pm 0.6) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . Preliminary work demonstrates a total relaxation rate of DF( $v=3$ ) that is slower than that for DF( $v=2$ ). These experiments show that DF( $v=2$ ) relaxes solely by vibration-to-vibration (V-V) energy transfer; in contrast, the fraction of HF( $v=2$ ) molecules that relax by V-V energy transfer is 59%.

The results demonstrate that the magnitude of the energy defects for the available pathways plays a significant role in determining the energy transfer mechanism for the relaxation of DF( $v \geq 2$ ) and HF( $v \geq 2$ ). A comparison of the  $v=1$  rate constants for DF and HF indicates that rotational degrees of freedom are the primary receptor modes for the vibration-to-translation, rotation energy transfer process.

# Vibrationally resolved Charge Transfer in $H^+ + H_2$ , $CO_2$ , and $N_2O$ at $E_{coll} = 30eV$

Gereon Niedner, Martin Noll, and J.Peter Toennies  
Max Planck Institut für Strömungsforschung, D-3400 Göttingen  
Federal Republic of Germany

Little is known about vibrational excitation in charge transfer collisions involving molecules, since in most previous scattering experiments individual vibrational states could not be resolved. Recently we were able to resolve the vibrational state distributions for the exoergic charge transfer reaction of  $H^+$  with  $O_2$  in a crossed beam experiment at an energy of 23eV in the angular range of  $0^\circ \leq \Theta \leq 10^\circ$  [1].

In the present work the same apparatus has been used to study the charge transfer reactions of  $H^+$  with  $H_2$  ( $\Delta E=1.83eV$ ),  $CO_2$  ( $\Delta E=0.19eV$ ), and  $N_2O$  ( $\Delta E=-0.71eV$ ). Angular distributions as well as energy loss spectra have been measured for both the (in)elastically scattered protons and the charge transfer product H-atoms at a laboratory energy of 30eV and scattering angles up to  $12^\circ$ . For both endoergic systems ( $H_2$ ,  $CO_2$ ) the results give clear evidence for a two step mechanism, in which the neutral target molecule is vibrationally excited by the strong interaction with the proton in the first part of the collision followed by charge transfer to the near-resonant vibrational states of the molecular ion in the second part. Nevertheless, an important difference should be pointed out between  $H_2$  and  $CO_2$ . The charge transfer process in  $H^+ + H_2$  takes place by conversion of the vibrational excitation into electronic energy to overcome the large endoergicity. In contrast, in the only slightly endoergic  $H^+ + CO_2$  system we observe a conservation of vibrational distributions, which for both  $CO_2$  and  $CO_2^+$  consists of predominant excitation of the asymmetric stretch mode  $\nu_3$ . The more exoergic  $H^+ + N_2O$  charge transfer looks similar to  $CO_2$  but there is some evidence that charge transfer may also occur in the incoming part of the collision.

## References

- [1] M.Noll, and J.P.Toennies, J.Chem.Phys. 85, 3313 (1986)

ROTATIONAL EXCITATION OF AMMONIA COLLIDING  
WITH H<sub>2</sub> AND He.

M. Broquier, H. Aroui and A. Picard-Bersellini

\*Laboratoire de Photophysique Moléculaire du CNRS Bât 213  
Université de Paris-Sud 91405 ORSAY CEDEX FRANCE.

Y. Blanchard, DPC Bât 21 CEA SACLAY FRANCE.

G. Billing, Department of Chemistry  
Panum Institute, University of Copenhagen  
DK. 2200 COPENHAGEN, DANEMARK.

I) We have studied the ammonia absorption profile in the near infrared (6 $\mu$ m and 3 $\mu$ m) and far infrared using laser spectroscopy (diode and colour center lasers) and a FT spectrometer. We are interested by NH<sub>3</sub>-H<sub>2</sub> and NH<sub>3</sub>-He collisions with two aims :

- The study of interference effects in the infrared.
- The access to new experimental results at room and at low temperatures because there are relatively few measurements of lines broadening in the  $\nu_4$  band and the  $\nu_3$  band. More these systems have an astrophysical interest.

In the case of NH<sub>3</sub>-He, the cross relaxation rates are found to be negligible. These results are different from NH<sub>3</sub>-H<sub>2</sub>. In this case the cross relaxation rates are larger. More we have put in evidence a vibrational effect (the results in the  $\nu_3$  band are different from the  $\nu_4$  band).

We have compared our experimental results to the calculation done by G. Billing. He has done extensive calculations of cross sections and the rate coefficients for rotational excitation of ammonia colliding with helium on ab initio potential energy surfaces. He has used a semi classical collision model. Our results are in a good agreement with his calculations.

The first results with the parahydrogen show that these cross-sections are 30% smaller from the normal hydrogen and are completely different from He. These results tremendous change the theoretical hypothesis. Indeed it has been currently admitted that the collisions with helium are the same than collisions with the parahydrogen.

II) We have undertaken time resolved infrared infrared double resonance using two tunable infrared laser. The pump laser is a high pressure CO<sub>2</sub> laser and the probe laser is a diode laser. Preliminary results are discussed here.

† Laboratoire associé au CNRS.

## State-to-State Vibrational Relaxation in ${}^1B_{2u}$ Benzene- $d_6$ Induced by Low Energy Collisions with He, $H_2$ , $N_2$ and Ar.

Mark W. Rainbird, Brian S. Webb and Alan E.W. Knight  
School of Science, Griffith University, Nathan, Queensland, 4111.

Time-resolved dispersed fluorescence spectroscopy has been used to study very-low-energy collision-induced vibrational relaxation in  ${}^1B_{2u}$  benzene- $d_6$  expanded in a supersonic free jet. Several expansion gases have been used to enable the rate coefficients for vibrational relaxation to be obtained as a function of collision partner in the very low energy collision regime. Benzene- $d_6$  is found to undergo vibrational deactivation with each of the chosen collision partners He,  $H_2$ ,  $N_2$  and Ar. This study focuses on measuring state-to-state relaxation rates and branching ratios for vibrational relaxation from the  $S_1$  vibrational level  $6^1$  ( $\epsilon_{\text{vib}} = 498 \text{ cm}^{-1}$ ) to all energetically accessible  $S_1$  vibrational levels, namely  $10^1$  ( $\epsilon_{\text{vib}} = 454 \text{ cm}^{-1}$ ),  $16^2$  ( $\epsilon_{\text{vib}} = 414 \text{ cm}^{-1}$ ),  $11^1$  ( $\epsilon_{\text{vib}} = 382 \text{ cm}^{-1}$ ),  $16^1$  ( $\epsilon_{\text{vib}} = 208 \text{ cm}^{-1}$ ) and  $0^0$  ( $\epsilon_{\text{vib}} = 0 \text{ cm}^{-1}$ ) as well as two as yet unidentified channels. Argon and nitrogen are found to be most efficient collision partners ( $\sigma_{\text{obs}}/\sigma_{\text{hs}} \sim 1-2$ ) in inducing relaxation, whereas hydrogen and helium are found to be an order of magnitude less efficient. The relaxation channels  $6^1 \rightarrow 10^1$  and  $6^1 \rightarrow 11^1$  are the dominant deactivation pathways for all the gases studied. The relative importance of other relaxation pathways changes with collision partner. There appears to be a light or small collision partner effect, whereby the propensity of transfer for the channel  $6^1 \rightarrow 10^1$  ( $\Delta\epsilon_{\text{vib}} = 44 \text{ cm}^{-1}$ ) seems to be redistributed among other channels, involving a greater energy or momentum gap, as the collision partner becomes lighter.

## Scattering of High Vibrationally Excited Molecules: $\text{Li}_2(v \leq 21) + \text{Na}$

Gerd Gundlach, Horst-Günter Rubahn, and J.Peter Toennies  
Max Planck Institut für Strömungsforschung, D-3400 Göttingen  
Federal Republic of Germany

A beam of vibrationally hot  $\text{Li}_2$ -molecules with a vibrational state distribution with  $v \leq 21$  has been generated via Franck-Condon pumping by use of an actively stabilized CW ring dye laser. After scattering from a secondary beam of Na atoms the remaining intensity in the forward direction in a specific vibrational state has been measured by laser induced fluorescence with a second ring dye laser. In this way it is possible to measure the integral total cross section as a function of the vibrational state. Since the collision time is longer than the vibrational period we are justified in assuming vibrationally adiabatic collisions in which the internuclear distance is given by the vibrational expectation value. The measured cross sections show a dramatic increase of the total state selective integral cross section of about 110% as the mean internuclear distance of  $\text{Li}_2$  increases from 2.7 Å to 3.6 Å. This is to be compared with only 15% in analogous experiments on He and Kr [1]. The large difference in Na collisions is attributed to a transition from a weakly attractive van der Waals potential at small  $v$  to covalent Li-Na potential at high  $v$ . The use of linearly polarized light from the probe laser has made it possible to observe a large increase in the anisotropy of highly vibrationally excited molecules compared to the ground state molecules.

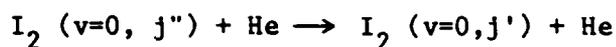
### References

- [1] M.Fuchs and J.P.Toennies, *J.Chem.Phys.*85, 7062 (1986)

State-to-State Rotational Excitation of  $I_2$  in Collisions with He

Vasgen A. Shamamian, David L. Catlett, Jr., Clayton F. Giese and  
W. Ronald Gentry  
Chemical Dynamics Laboratory, University of Minnesota  
Minneapolis, MN 55455

Our work has focused on the behavior of the state-to-state integral cross sections for the rotationally inelastic process:



where the initial distribution spans  $j'' = 0-5$ .

The apparatus incorporates two pulsed molecular beams, which cross at a variable intersection angle,<sup>1,2</sup> and a laser-induced fluorescence detector. An intracavity etalon in the dye laser provides resolution sufficient to observe discrete  $I_2$  rotational states.

We obtain data in two complementary experiments. First, the excitation probability for a final rotational state is  $j' = 30, 52, \text{ and } 53$  over a collision energy range 25-225 meV. In addition, cross sections are determined as a function of the angular momentum transfer  $j$ , at a fixed collision energy  $E_0$ . We show results for  $E_0 = 75$  meV and  $E_0 = 87$  meV.

Comparison of the data to a simple, classical rigid ellipsoid model allows for the extraction of an anisotropy of the repulsive character of the scattering potential energy surface.<sup>3</sup> The anisotropy parameter, defined as the difference between the major and minor axes of the ellipsoid, has been determined to be 1.6 angstroms.

Research supported by the U. S. Department of Energy, Division of Chemical Sciences, grant no. DE-AC02-86ER13515.

## References:

1. G. Hall, K. Liu, M. J. McAuliffe, C. F. Giese and W. R. Gentry  
J. Chem. Phys. 81, 5577 (1984).
2. G. Hall, K. Liu, M. J. McAuliffe, C. F. Giese and W. R. Gentry  
J. Chem. Phys. 84, 1402 (1986).
3. M. A. Hoffbauer, S. Burdinski, C. F. Giese and W. Ronald Gentry  
J. Chem. Phys. 78, 3832 (1983).

RESTRICTED PHASE SPACE MODELS APPLIED  
TO THE ENERGY DEPENDENCE OF ISOTOPE  
BRANCHING IN  $\text{He}^*(2^1\text{S}, 2^3\text{S}) + \text{HD}$  IONIZATION

P. E. Siska  
Department of Chemistry,  
University of Pittsburgh, Pittsburgh, PA 15260, USA

The usual phase space theory (PST) gives equal weight to all possible angular momentum vectorial combinations consistent with the conservation laws, while it is well known, for example, from the trajectory studies of Polanyi and coworkers that on a repulsive potential energy surface, combinations of  $L'$  (orbital) and  $J'$  (rotational) product angular momenta with  $L'$  antiparallel to  $J'$  are favored. We suggest that this represents one side of a coin whose reverse is the case of an attractive, angle-dependent surface that favors  $L' \parallel J'$ . Thus we can partition angular phase space into "attractive" and "repulsive" halves for which, if we take  $m_{l'} > 0$ , then  $m_{j'} > 0$  and  $m_{j'} < 0$ , respectively. We refer to the attractive coupling as a slingshot model, in which the pebble (ejected atom) and slingshooter (remaining molecule) spin in the same direction. We apply full PST and both forms of restricted PST (RPST), in combination with a modified turning point model to predict the energy dependence of  $\text{HeD}^+/\text{HeH}^+$  isotope branching in the ionization of HD by  $\text{He}^*(2^1\text{S}, 2^3\text{S})$ . Attractive RPST, the slingshot model, is found to give the best agreement with experiment, as suggested by the features of the  $\text{HeH}_2^+$  potential energy surface.

## NEAR RESONANT CHARGE EXCHANGE OF FAST MOLECULAR IONS WITH CESIUM: AN EXPERIMENTAL STUDY.

W.J. van der Zande, W. Koot, S. Otte and J. Los  
FOM-institute for Atomic and Molecular Physics, Amsterdam, NL

In near resonant charge exchange (NRCE) collisions between keV molecular ions with Cesium atoms highly excited molecular states (I.P.= 3.8 eV) are formed. Using translational spectroscopy, as developed by De Bruijn and Los (1) we are able to study in detail all dissociative processes following the CE process. The kinetic energy release spectra have high resolution for ion optical standards and reveal information on the spectroscopy (position of the levels) and the dynamics (decay mode, lifetimes).

We will present data on the  $H_2^+/Cs$  system and the  $HeH^+/Cs$  and  $Mg$  systems and their isotopes. In NRCE of  $H_2^+$  with Cesium vapor the  $c^3\Pi_u$  state is one of the dominantly populated states. The  $c^3\Pi_u^+$  (2) state decays via an allowed predissociation to the repulsive  $b^3\Sigma_u^+$  state coupled by rotational coupling. The  $c^3\Pi_u^-$  state is metastable and undetected in our experiments. We measured and calculated (within a pure precession model for the electronic coupling) the lifetimes of the first  $c^3\Pi_u^+$  levels for  $H_2$  (3), HD and  $D_2$ . The lifetimes strongly increase with increasing mass.

In collisions of  $HeH^+$  with Cesium Rydberg states of HeH converging to the stable  $HeH^+$  ion are formed ( $A^2\Sigma^+$ ,  $B^2\Pi$  and to a less extent  $C^2\Sigma^+$ ) (4). Coupling with the repulsive ground state of the (excimer) HeH molecule is the fate of all formed molecules. The experiments show the decay route of the populated levels to be predissociation for the A-, radiation for the B-state. The C-state decays via radiation for  $^3HeD$  and via predissociation for  $^4HeH$ . Calculations have been made using SCF-HF electronic wavefunctions and the Fermi Golden rule. These confirm the experimental results (5).

The NRCE collisions of  $HeH^+/Mg$  favors population of the repulsive ground state which enables a study of anisotropy in the  $HeH^+-Mg$  potential (He versus H forward). The results of these experiments will be shown on the conference.

### References

- 1 D.P. de Bruijn and J. Los, Rev.Sci. Instrum., **52**(1982)1020
- 2 G. Herzberg in Spectra of Diatomic Molecules (1950)
- 3 G. Comtet and D.P. de Bruijn, Chem.Phys., **94**(1984)365
- 4 G.Theodorakopoulos, S.C. Farantos, R.J. Buenker and S.D. Peyerimhoff, J.Phys.B **17**(1984)1453
- 5 W.J. van der Zande, W. Koot, C. Kubach and D.P. deBruijn, Phys.Rev. Lett., **57**(1986)1219

MAGNETIC DEFLECTION ANALYSIS  
OF EXCITED ATOM BEAMS

C. Weiser and P. E. Siska

Department of Chemistry,  
University of Pittsburgh, Pittsburgh, PA 15260, USA

Spatially resolved Stern-Gerlach deflection patterns have been obtained for electronically excited, supersonic metastable beams of  $\text{He}^*(2^3\text{S})$ ,  $\text{Ne}^*(3s^3\text{P}_2)$ ,  $\text{Ar}^*(4s^3\text{P}_2)$ ,  $\text{Kr}^*(5s^3\text{P}_2)$  and  $\text{Xe}^*(6s^3\text{P}_2)$ . Electron impact excitation energy was varied between 100 and 400 eV, the magnet used was of the classic two-wire-field geometry,<sup>1</sup> and the detector was a cold Ta wire surrounded by a grounded shield and a pair of positively biased collector plates to remove stray surface Penning electrons. Mounted on a commercial motorized translation stage, the detector could be scanned  $\pm 12$  mm from beam center. For  $\text{Ne}^*$  through  $\text{Xe}^*$ , fine structure population ratios  $^3\text{P}_2/^3\text{P}_0$  using three independent means of evaluating the deflection data were obtained as a function of electron energy. At 400 eV electron energy, the ratios are:  $\text{Ne}^* - 3.35 \pm 0.2$ ;  $\text{Ar}^* - 2.97 \pm 0.2$ ;  $\text{Kr}^* - 6.05 \pm 0.8$ ; and  $\text{Xe}^* - 2.75 \pm 0.2$ . For all the metastables, the ratio declines by 20-40% as the electron energy is increased from 100 to 400 eV. The results are useful for analysis of non-state-selected scattering experiments and estimation of absolute laser-state-selection efficiencies, and the method shows promise for both state-selection and aligned-angular-momentum studies of metastable quenching collisions.

---

1. R. R. Herm and D. R. Herschbach, UCRL Report 10526 (1962). We are grateful to Prof. Herschbach for the loan of magnet "B".

INELASTIC AND REACTIVE SCATTERING OF EXCITED ALKALI ATOMS WITH O<sub>2</sub>.

J.M. MESTDAGH, D. PAILLARD, J. CUVELLIER, P. de PUJO and J. BERLANDE  
 SERVICE DE PHYSIQUE DES ATOMES ET DES SURFACES. CEN SACLAY.  
 91191 GIF-SUR-YVETTE CEDEX, FRANCE

Collisions of excited alkali atoms with O<sub>2</sub> have been studied both experimentally and theoretically.

On the experimental side, the cross section of the Na(4D+5S) collisional transfer has been measured in absolute values as a function of the collision energy using a crossed beam apparatus. Experimental results are also available on reactions of Na(4D) with O<sub>2</sub> giving NaO as product [1].

On the theoretical side, both inelastic and reactive channels have been included into a single model based on multiple crossings between curves describing the Na(n,l)-O<sub>2</sub>, Na<sup>+</sup>-O<sub>2</sub><sup>-</sup>(X<sup>2</sup>Πg) and Na<sup>+</sup>-O<sub>2</sub><sup>-</sup>(A<sup>2</sup>Πu) system. Additionally, estimation of the excited ion pair surface Na<sup>+</sup>-O<sub>2</sub><sup>-</sup>(A<sup>2</sup>Πu) is provided.

Regarding the inelastic process, quantitative agreement is observed between the calculations and the experimental results for both the absolute value of the cross-section and its energy dependence. Similar agreement is found for another colliding system (Rb(7S+→5D)/O<sub>2</sub>). This suggests that in spite of its approximations, the calculation model gives fairly reliable predictions for inelastic processes involving 4 eV electronic excited states [2].

The reactive cross section has been calculated as a function of several parameters: collision energy, impact parameters and approach geometry of the Na-O<sub>2</sub> system. The results have been sorted according to the reactive intermediate Na<sup>+</sup>-O<sub>2</sub><sup>-</sup>(X<sup>2</sup>Πg) and Na<sup>+</sup>-O<sub>2</sub><sup>-</sup>(A<sup>2</sup>Πu). Reaction via Na<sup>+</sup>-O<sub>2</sub><sup>-</sup>(X<sup>2</sup>Πg) has a very small cross-section and do not contribute efficiently to the reaction. The competition of the inelastic processes Na(4D)→n,l with the reaction via Na<sup>+</sup>-O<sub>2</sub><sup>-</sup>(X<sup>2</sup>Πg) is the essential reason for this channel to make such a small contribution to the reaction. Reaction via Na<sup>+</sup>-O<sub>2</sub><sup>-</sup>(A<sup>2</sup>Πu) seems to account for the experimental observations. This includes a high threshold energy for the reaction, and backward scattering of the NaO product with respect to the incoming Na atoms.

- [1] H. Schmidt, P.S. Weiss, J.M. Mestdagh, M.H. Covinsky and Y.T. Lee  
 Chem. Phys. Lett. 118, 539 (1985).  
 [2] D. Paillard, J.M. Mestdagh, J. Cuvellier, P. de Pujo, and J. Berlande  
 To appear in J. Chem. Phys.

QUANTUM-MECHANICAL STUDY OF FINE-STRUCTURE TRANSITIONS  
IN COLLISIONS OF Rb( $5^2P_j$ ) WITH H<sub>2</sub> AND D<sub>2</sub>

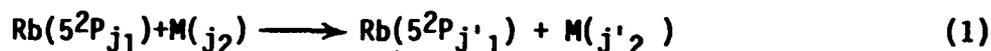
J. Pascale, F. Rossi and W.E. Baylis\*

Institut de Recherche Fondamentale

Service de Physique des Atomes et des Surfaces, CEN/SACLAY

91191 Gif-sur-Yvette Cedex, France

Three-dimensional close-coupling quantum-mechanical calculations have been carried out for the processes



in which M is H<sub>2</sub> or D<sub>2</sub> in the  $^1\Sigma_g^+$  ( $v=0$ ) ground state and in a rotational level  $j_2$ . The method treats M as a rigid-rotator /1/ and is a generalization of that developed for processes (1) when M is a structureless rare gas atom /2/. In this method, the three-body interaction describing the Rb-M system is expanded in a limited number of spherical harmonics if only the  $5^2P$  configuration of Rb and a few rotational levels  $j_2$  are considered. The expansion coefficients are determined from pseudopotential molecular-structure calculations /3/, leading to realistic adiabatic potential surfaces and the evaluation of the main nonadiabatic coupling terms involved during the collision. A space-fixed formulation of the scattering theory is used and the close-coupling calculations include the rotational levels  $j_2=0, 2, 4$  and  $j_2=1, 3$ . The total cross sections for the level-to-level transitions (1) are determined in the energy range from thresholds up to about 0.3 eV. Good agreement between experiment /4/ and theory has been obtained /5/ for the  $5^2P_{1/2} \rightarrow 5^2P_{3/2}$  transition in Rb.

\* On leave August to December 1985 from Department of Physics, University of Windsor, Windsor, Ontario N9B 3P4.

References:

- /1/ A.M. Arthurs and A. Dalgarno, Proc. Roy. Soc. A256, 540 (1960).
- /2/ R.H.G. Reid; J. Phys. B6, 2018 (1973).
- /3/ F. Rossi and J. Pascale; Phys. Rev. A32, 2657 (1985).
- /4/ J. Cuvellier, J.M. Mestdagh, M. Ferray and P. de Pujo; J. Chem. Phys. 79, 2848 (1983).
- /5/ J. Pascale, F. Rossi and W.E. Baylis; Europhysics Letters 3, 183 (1987).

$T_1$  Barrier Height,  $S_1 - T_1$  Intersystem Crossing Rate, and the  
 $S_0$  Radical Channel Threshold of Formaldehyde

Mei-Chen Chuang, Mary F. Foltz, and C. Bradley Moore

Department of Chemistry, University of California at Berkeley  
Berkeley, California 94720

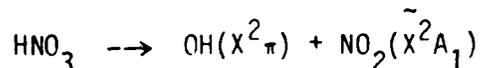
Vacuum UV Laser-induced fluorescence has been used to detect the atomic products in the photofragmentations of  $H_2CO$ ,  $D_2CO$ , and  $HDCO$ . For the first time, the  $T_1$  exit barrier height and the  $S_1 - T_1$  intersystem crossing rate near the  $T_1$  barrier top have been determined from sharp increases in the H/D branching ratio as well as the Doppler widths of the atomic transitions. The exit barrier height lies between 3.0 - 6.0 kcal/mol, and the intersystem crossing rate equals  $4 \times 10^7 \text{ s}^{-1}$ .

From the energy where the atomic fragment disappears, the threshold for the radical dissociation channel on the  $S_0$  surface has also been measured with an unprecedented accuracy. For  $H_2CO$  the threshold energy is  $86.42 \pm 0.14$  kcal/mol. The best values for the heat of formation and the C-H bond enthalpy of HCO radical derived from the threshold energies are  $9.84 \pm 0.18$  kcal/mol and  $15.84 \pm 0.15$  kcal/mol, respectively.

The highest level of ab initio calculation so far could not match the measured threshold energy within the uncertainties of either the experiment or the calculation.

M.H. Covinsky, H.F. Davis, B.A. Balko, and Y.T. Lee  
Materials and Chemical Sciences Division Lawrence Berkeley Laboratory and  
Department of Chemistry, University of California, Berkeley, California 94720

The photodissociation of nitric acid has been extensively studied. the quantum yield for the process



has been measured to be close to one.<sup>1</sup>

Laser induced fluorescence measurements show that the OH(X<sup>2</sup><sub>π</sub>) is formed in the ground vibrational state with a peak in the rotational distribution around K=6.<sup>2</sup> Although the formation of OH(A<sup>2</sup><sub>Σ</sub><sup>+</sup>) is thermodynamically allowed at this wavelength the threshold for this channel was found to be 147.5nm.<sup>3</sup>

Emission from electronically excited NO<sub>2</sub> was measured and found to extend down to 398nm, its dissociation limit. However this channel is believed to have a quantum yield of less than 0.5%<sup>4</sup> The same authors observed the formation of electronically excited OH(A<sup>2</sup><sub>Σ</sub><sup>+</sup>) via a two photon process in which the second step is postulated to be the secondary photodissociation of a low-lying triplet state of HONO.<sup>5</sup>

The crossed laser-molecular beam technique has been applied to the photodissociation of HNO<sub>3</sub> at 193 nm. The time-of-flight spectra of masses 17 (OH<sup>+</sup>) and 30 (NO<sup>+</sup>) reveal at least three different primary photodissociation channels. In addition the anisotropy parameter β will be determined.

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under contract No. DE-AC-0376SF00098

<sup>1</sup>H.S. Johnston, S.G. Chang, and G. Whitten J. Phys. Chem. 78, 1 (1974)

<sup>2</sup>Axel Jacobs, Karl Kleinermans, Helmut Kuge, and Jurgen Wolfrum  
J. Chem. Phys. 79, 3162 (1983)

<sup>3</sup>H. Okabe J. Chem. Phys. 72,(12), 6642 (1980)

<sup>4</sup>Th. Papenbrock, H.K. Haak, and F. Stuhl Ber. Bunsenges. Physik Chem  
88 (1984) 675

<sup>5</sup>R.D. Kenner, F. Rohrer, and F. Stuhl, Chem. Phys. Lett. 116, (1985) 374.

### A TIME-RESOLVED FTIR EMISSION STUDY OF THE LASER PHOTOLYSIS OF $\text{CH}_2\text{CFCl}$ at 193nm.

T. Rick Fletcher and Stephen R. Leone. Joint Institute for Laboratory Astrophysics, University of Colorado and National Bureau of Standards, and Dept. of Chemistry and Biochemistry, University of Colorado, Boulder, Colorado, 80309-0440.

The technique of time-resolved FTIR photofragment emission spectroscopy has been used to study the photodissociation of 1,1 chlorofluoroethylene at 193nm. Time-resolved interferograms are obtained by slaving a high repetition rate excimer laser to the moving mirror of the interferometer. This allows each point of the interferogram to be collected at the same fixed delay time relative to the pulsing of the laser. The time resolution is limited by the risetime of the infrared detector in use, typically between 3 - 20 microseconds. The sensitivity of the technique is sufficient to allow use of precursor pressures low enough to observe product rovibrational state distributions under collisionless conditions.

We have examined in detail the HF elimination pathway of the title photodecomposition. Nascent HF rotational and vibrational energy distributions have been obtained. The vibrational energy distribution in the first four excited levels of product HF are  $V = 1/2/3/4 = 0.36/0.31/0.23/0.11$ . The observed HF rotational distributions exhibit marked dynamical effects, with HF observed up to  $J = 14$  and rotational temperatures in the range of 3000 K. A comparison of the rotational distributions in different vibrational levels indicates that a larger fraction of the remaining energy is partitioned into HF rotation in the higher vibrational levels. This result suggests that the rotational energy in the HF product is determined by the relative motions of the hydrogen and fluorine atoms at the time of HF bond formation.

Future experiments will consider the HCl elimination product and the branching fractions into other energetically allowed fragmentation pathways.

## Product State Distribution and Spectroscopy of Half Collision Processes Studied by Vector Correlations.

Dr. K. H. Gericke, Institute für Physikalische Chemie, Universität Frankfurt  
D-6000 Frankfurt am Main, FED. REP. GERMANY

---

Vector correlations open a new area to study the dynamics of half collisions. Furthermore, the excited transition state just before the dissociation process can be characterized (e.g., geometry, symmetry), as well as the contribution of different dissociative states to the product state distribution.

Hydrogen peroxide has been optically excited at different wavelengths and the OH photofragment completely characterized by Doppler and polarization spectroscopy. The entire internal state distribution, translational energy, angular distribution, rotational alignment, and vector correlations between rotational ( $\vec{J}$ ) and translational ( $\vec{v}$ ) motions of OH products are measured. The  $(\vec{v}, \vec{J})$  correlation was determined quantitatively from experimental data. In addition, the expectation values  $\langle J_x^2 \rangle$ ,  $\langle J_y^2 \rangle$ , and  $\langle J_z^2 \rangle$  were obtained, giving information about the origin of the product rotation.

The symmetry, geometry and lifetime of the excited  $H_2O_2$  parent were determined. When hydrogen peroxide is excited at 193 nm the two electronic excited states,  $\tilde{A}^1A$  and  $\tilde{B}^1B$ , are involved in the dissociation process with a contribution of 60% and 40%, respectively. Information about microscopic reaction probabilities of coincident pairs is also obtained. This correlation between the rotational angular momentum of the two molecular fragments is obtained by high resolved Doppler profiles.

# CN-fragment orientation produced in the photodissociation of ICN with circularly polarized light\*

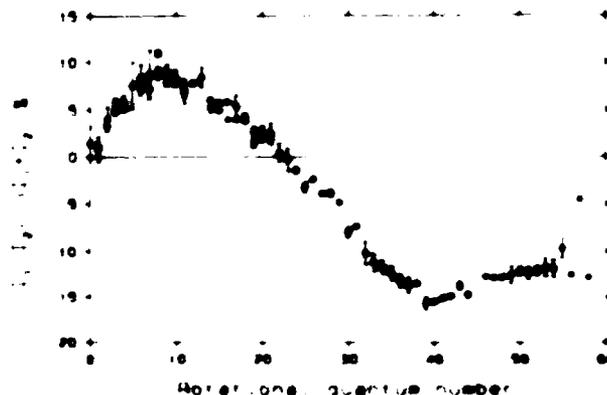
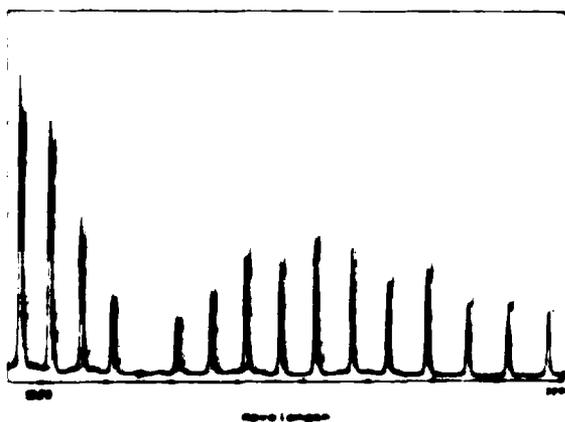
P5

E. Hasselbrink, J. R. Waldeck and R. N. Zare  
Department of Chemistry, Stanford University, CA 94305

Using polarized light, detailed insights into the nature of photodissociation processes are achievable. In many studies linearly polarized light has been used to deduce the alignment of the photofragments and thereby the nature of the electronic states involved.

Using *circularly* polarized light even more information about the dynamics of the photodissociation process might be obtainable. We have performed an experiment whereby excimer laser light is circularly polarized and used to photodissociate ICN at 249 nm. The resulting  $CN(X^2\Sigma^+)$ -fragment is detected using a pulsed dye laser which is also circularly polarized. The lasers are counterpropagating and define thereby a common quantization axis. A photomultiplier in a direction perpendicular to this axis observes the fluorescence. By changing the probe laser polarization from left- to right-hand circularity we obtain a pair of signals whose difference measures the orientation of the rotational angular momentum of the CN-fragment.

We see strong effects and remarkable variation with the rotational state. Particularly, low rotational states show an orientation in the opposite direction to that of the high states. This difference may well be related to the finding that low rotational quantum numbers are formed with excited  $k(2P_{1/2})$ , whereas high rotational states correlate with  $l(2P_{3/2})$ . For the fine-structure states in  $v=2$  we find opposite orientation of these states. We conclude that our method promises new insights into the angular momentum recoupling which controls the branching between these exit channels.



**Left Fig.**  $CN(X^2\Sigma^+, v=0)$ -spectrum around the band origin, showing the obtained signal for both circular probe polarizations. P- versus R-lines are showing opposite effects

**Right Fig.** Normalized signal differences for probing with left- or right-hand circular polarized light as function of the rotational quantum number. Diamonds: R-lines, open circles: P-lines (sign inverted).

\* We wish to thank the National Science Foundation for support of this work under NSF-PHY 85-06668. E. H. thanks the Deutsche Forschungsgemeinschaft for support.

## Rotationally and Vibrationally Resolved Final State Distributions in CO<sub>2</sub> Photofragments formed in the UV Photolysis of Pyruvic Acid

Thomas G. Kreutz, James A. O'Neill, and George W. Flynn  
Department of Chemistry and Columbia Radiation Laboratory,  
Columbia University, New York, N.Y. 10027

Time domain absorption spectroscopy using a tunable infrared diode laser has been used to measure rotational and vibrational product state distributions in the 193 nm photofragmentation of pyruvic acid. Nascent vibrational population distributions have been obtained for ten vibrational levels in CO<sub>2</sub> (00<sup>0</sup>0), (01<sup>1</sup>0), (02<sup>2</sup>0), (03<sup>3</sup>0), (04<sup>4</sup>0), (00<sup>0</sup>1), (00<sup>0</sup>2), (00<sup>0</sup>3), (01<sup>1</sup>1), and (02<sup>2</sup>1). Approximately 97% of the CO<sub>2</sub> photofragments are formed directly in the vibrational ground state. The remaining CO<sub>2</sub> molecules are found to have with a significant degree of vibrational excitation, having mode temperatures of  $T(v_2)=1800\pm 150$  K,  $T(v_3)=3700\pm 1000$  K, and  $T(v_2+v_3)=2000\pm 400$  K. These results suggest that the 193 nm photolysis proceeds through more than one dissociation channel and involves a number of different photofragments. Preliminary results at 248 nm show a similar partitioning of vibrational energy between the excited bending ( $v_2$ ) and antisymmetric stretching ( $v_3$ ) modes. We have also obtained rotationally resolved state distributions of the CO<sub>2</sub> photoproduct in the (00<sup>0</sup>0), (01<sup>1</sup>0), and (02<sup>2</sup>0) vibrational levels. These results indicate substantial rotational excitation of CO<sub>2</sub>, with broad distributions having peaks near  $J=30$  (as compared with  $J=17$  for CO<sub>2</sub> at 298 K) and significant rotational excitation beyond  $J=60$ . Preliminary results also indicate that rovibrationally excited CO photofragments are formed immediately following the 193 nm laser pulse.

**Vibrationally Mediated Photodissociation of Hydrogen Peroxide**

T.M. Ticich, H.-R. Dubal, M.D. Likar, L.J. Butler,  
and F.F. Crim

Department of Chemistry, University of Wisconsin,  
Madison, Wisconsin 53706

Vibrationally mediated photodissociation is a means of studying the spectroscopy of bound vibrational overtone states and of probing the photodissociation dynamics of highly vibrationally excited molecules.<sup>1</sup> Highly vibrationally excited hydrogen peroxide molecules are prepared by initial excitation in the region of the third ( $4\nu_{OH}$ ) or fourth ( $5\nu_{OH}$ ) overtone of the OH stretching vibration. A second photon dissociates the initially prepared molecule and yields vibrational overtone excitation spectra of bound states. The rotational-vibrational states of the OH fragments are probed with laser induced fluorescence. The excitation spectra and product state distributions obtained provide information on the nature of the bound intermediate state and on the influence of the vibrational excitation on the dissociation dynamics. The coarse vibrational structure of the excitation spectra agree with a spectroscopic model that includes the torsional vibration.<sup>2</sup> For dissociation through the  $4\nu_{OH}$  transition, 10% of the OH fragments are vibrationally excited, in contrast to direct ultraviolet photodissociation experiments that find no vibrationally excited OH. While only states having significant OO stretching character are efficiently dissociated by the second photon, the dissociation preserves some of the initial OH stretching vibration.

Vibrationally mediated photodissociation of hydrogen peroxide molecules cooled in a supersonic expansion<sup>3</sup> allows study of vibrational states below the dissociation barrier without complications from thermal congestion.

<sup>1</sup>T.M. Ticich, H.-R. Dubal, M.D. Likar, L.J. Butler, and F.F. Crim, *J. Chem. Phys.* (1987), submitted for publication

<sup>2</sup>H.-R. Dubal and F.F. Crim, *J. Chem. Phys.* **83** 3863 (1985)

<sup>3</sup>L.J. Butler, T.M. Ticich, M.D. Likar, and F.F. Crim, *J. Chem. Phys.* **85** 2331 (1986); 6251 (1986)

**METASTABLE DECAY OF PHOTOIONIZED NIOBIUM CLUSTERS\***

S. K. Cole and K. Liu  
Chemistry Division  
Argonne National Laboratory  
Argonne, Illinois 60439

The metastable decay of photoionized niobium clusters ( $Nb_n^+$ ) has been observed in a newly constructed cluster beam machine. The decay manifests itself in the time-of-flight (TOF) mass spectrum as an asymmetric broadening of daughter ion peaks at the photoionizing laser photon energy from 3.5 to 5.6 eV. At 6.4 eV photon energy the asymmetric broadening is diminishingly small. Furthermore, the broadening is specific in the daughter ion cluster size in that it is very pronounced for some clusters but not as much for others. Several new experimental techniques have been developed to unravel the decay mechanism and its kinetics. The electron TOF spectrum consists of a single narrow peak (FWHM  $< 30$  ns), eliminating the possibility of any delayed ionization process. The pulse ion extraction method has been developed to measure the decay rate constants and to establish the mechanisms of the fragmentation, evaporation and/or fission of the photoionized clusters. For example, at 5 eV photon energy it is found that within the experimental time window evaporation dominates for the smaller clusters ( $n < 15$ ), whereas fission fragmentation becomes facile for  $15 < n < 30$ . The decay constants obtained all fall within  $0.5 - 2.0 \times 10^6 \text{ sec}^{-1}$ . By using the two-color, multiphoton technique the existence of long-lived intermediate states in the metal clusters ( $n > 4$ ) has been clearly demonstrated for the first time. This result is in sharp contrast with general conjectures based upon the "vibronic soup" picture in describing the metal clusters. The details of the experimental results and their implications will be presented.

\*Work supported by the U. S. Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences, under Contract W-31-109-Eng-38.

ENERGY-SELECTIVE ELECTRON-IMPACT IONIZATION IN A  
MOLECULAR BEAM: APPLICATIONS TO VIBRATIONAL OVERTONE  
SPECTROSCOPY AND UV PHOTODISSOCIATION STUDIES

S.M. Penn, C.C. Hayden, K.J. Carlson, and F.F. Crim  
Department of Chemistry  
University of Wisconsin, Madison, WI., 53706

We have developed new techniques to study vibrational overtone spectroscopy and ultraviolet photodissociation processes in molecular beams using energy-selective electron-impact ionization. We will describe our versatile molecular beam apparatus which incorporates a pulsed, low-energy electron gun and a time-of-flight mass spectrometer.

Using this apparatus we have observed the (301)-(000) transition in water by energy-selective electron-impact ionization of the overtone-excited molecules. This demonstrates a new technique that may be generally applicable for detecting vibrationally excited molecules in molecular beams.

Energy-selective electron-impact ionization is also useful for detecting photodissociation products in the presence of large quantities of parent molecules. Our time-of-flight mass spectrometer allows us to identify primary photofragmentation pathways and measure translational energy distributions of the neutral photofragments. Results from the ultraviolet photodissociation of ethyl iodide illustrate this technique.

TWO COLOR VIBRATIONALLY MEDIATED PHOTODISSOCIATION  
OF NITRIC ACID

P10

A. Sinha, R. Vander Wal, L.J. Butler\*, and F.F. Crim  
Department of Chemistry, University of Wisconsin  
Madison, Wisconsin 53706

The study of molecular photodissociation has recently attracted considerable interest from both experimentalists and theorists<sup>1</sup>. Because photodissociation is a process in which the initial conditions are defined accurately, a thorough study of these "half" collisions offers excellent insight into more complicated collisional processes.

One important aspect of the photodissociation process that needs to be explored further is the effect of vibrational excitation. We present the first results on the photodissociation of highly vibrationally excited molecules using photons of two different wavelengths. In these two-color experiments, one photon excites a vibrational overtone transition and a second photon, of a different wavelength, promotes the vibrationally energized molecules to a dissociative electronic state. We have applied this two-color vibrationally mediated photodissociation scheme to nitric acid ( $\text{HONO}_2$ ) by using the third overtone of the OH stretching vibration ( $4\nu_{\text{OH}}$ ) to deposit the initial energy and a second photon (355 nm) to dissociate the energized molecule. A third laser monitors the dissociation process by laser induced fluorescence on the A-X transition of the OH photofragment. The present results on nitric acid<sup>2</sup> in conjunction with our earlier work on hydrogen peroxide<sup>2</sup> illustrate the potential generality of using vibrational overtone excitation as a preparative first step for investigating photodissociation of vibrationally excited molecules.

1) S.R. Leone, Adv. Chem. Phys. 50, 255(1982); J.P. Simons, J. Phys. Chem. 88, 1287(1984); R. Bersohn, J. Phys. Chem. 88, 5195(1984).

2) L.J. Butler, T.M. Ticich, M.D. Likaar and F.F. Crim, J. Chem. Phys. 85, 2331(1986) 6251(1986).

\* Present address Department of Chemistry, University of Chicago, Chicago, Illinois 60637

## Theory of Electronically Inelastic Infrared Multiphoton Processes

P. K. Swaminathan and B. C. Garrett  
Chemical Dynamics Corporation  
9560 Pennsylvania Avenue  
Upper Marlboro, MD 20772

We have implemented a generalization of an eikonal treatment of photodissociation<sup>1</sup> of polyatomics to treat polyatomic Infrared Multiphoton Excitation and Dissociation (IRMPE and IRMPD) processes. In the Self-Consistent Eikonal Method (SCEM)<sup>2</sup>, a common eikonal wavefunction ansatz is employed leading to selfconsistent "electronic plus nuclear" dynamics in terms of Hamilton's equations in electronic amplitude as well as nuclear position and momentum variables.

The treatment of few photon IRMPE processes is best done by employing the electron-field representation, where the SCEM amplitude equations will directly yield time-dependent populations of specified IR frequency-dressed states, representing dynamical evolution of selective multiphoton absorption. Dissociative levels of excitation (IRMPD) involving several dozens of photons and incoherent absorption are readily modelled by employing a driving-field semiclassical representation of the radiation field that forces the SCEM electronically inelastic Hamiltonian dynamics. Trajectories of an electronically nonadiabatic driven field model system show dramatic effects when contrasted with the equivalent electronically adiabatic limiting case trajectories compiled earlier by Martin and Wyatt.<sup>3</sup>

This work was supported by NSF under grant number ISI-8560163

<sup>1</sup> (a) P. K. Swaminathan and D. A. Micha, *Int. J. Quantum Chem.* **S16**, 377 (1982). (b) D. A. Micha and P. K. Swaminathan, *Photodissociation of Polyatomics by Visible and UV Radiation: The Self-Consistent Eikonal Approximation*, *J. Chem. Phys.* to be published. (c) P. K. Swaminathan, C. L. Stodden, and D. A. Micha, *Fragment Vibrational Distributions from Photodissociation of Methyl Iodide: Results from a Selfconsistent Eikonal Approximation*, to be published.

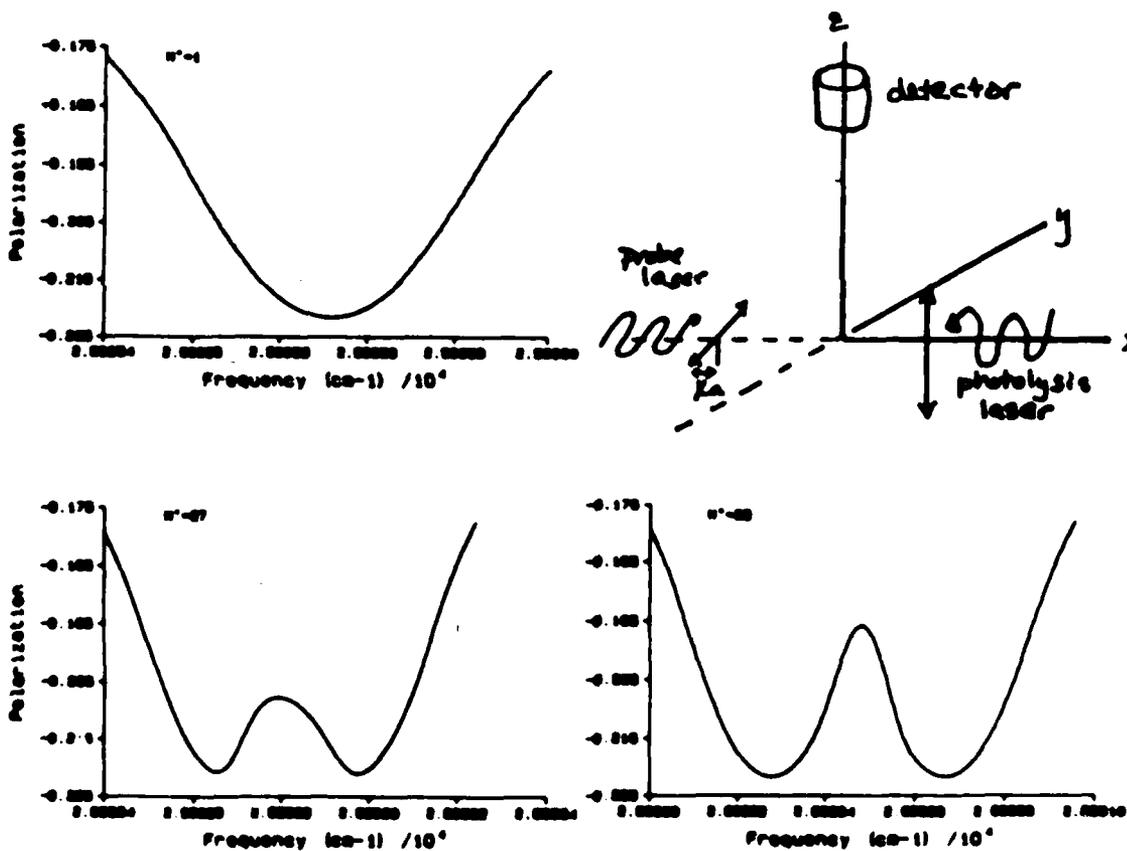
<sup>2</sup> D. A. Micha, *J. Chem. Phys.* **78**, 7138 (1983).

<sup>3</sup> D. L. Martin and R. F. Wyatt, *Chem. Phys.* **64**, 203 (1982).



Photodissociation of ICN at 249 nm : Correlation between  $\underline{v}$  and  $\underline{J}$  in the CN photofragment, \*J.R.Waldeck, E.Hasselbrink and R.N.Zare, Stanford University--When dissociating a triatomic molecule, one expects the rotational angular momentum,  $\underline{N}$ , to be opposed to the orbital angular momentum (therefore perpendicular to  $\underline{v}$ ) as the primary dissociative force (impulse between I and CN) is in the plane of the molecule. However, it seems that out-of-plane forces, are necessary to explain the fine-structure populations which are observed for the CN photofragment.<sup>1</sup> We investigate the correlation between  $\underline{v}$  and  $\underline{J}$  by measuring variation in polarization  $\{P = (I_{\parallel} - I_{\perp}) / (I_{\parallel} + I_{\perp})\}$  across Doppler-broadened CN rotational lines. Examining correlations such as those between  $\underline{v}$  and  $\underline{J}$  may help to elucidate the nature of angular momentum recoupling or the role or nonadiabatic effects during dissociation.

Shown below is the expected variation of polarization across the CN ( $X^2I^+$ ) rotational line profile. The simulation is done assuming a parallel transition,  $\underline{v}$  perpendicular to  $\underline{J}$ , and the experimental geometry shown :



\* We wish to thank the National Science Foundation for support of this work under NSF PHY 85-06668.

1. H.Joswig, M.A.O'Halloran, R.N.Zare and M.S.Child, Faraday Discuss.Chem.Soc., 1986 (in press).

PHOTOFRAGMENT SPECTROSCOPY OF IRON CARBONYL AT SEVERAL  
PHOTOLYSIS WAVELENGTHS

I.M. Waller and J.W. Hepburn  
Centre for Molecular Beams and Laser Chemistry  
University of Waterloo  
Waterloo, Ont., N2L 3G1, CANADA

The photofragmentation dynamics of  $\text{Fe}(\text{CO})_5$  has been studied under molecular beam conditions, using vacuum ultraviolet laser-induced fluorescence to detect the CO photofragments. Using this technique we have determined the detailed energy release (vibrational, rotational, and translational) for 193, 249, 266, and 351 nm photolysis wavelengths.

At all photolysis wavelengths, the product energy distributions are Boltzmann-like, with all degrees of freedom showing the same behaviour. These results can be described by a fully statistical model for the photofragmentation, in which the photolysis photon energy is completely randomized in the parent  $\text{Fe}(\text{CO})_5$  molecule before any dissociation occurs. Fragmentation then occurs by sequential CO loss, with the energy release in each step being fully statistical. This mechanism is independent of photolysis wavelength.

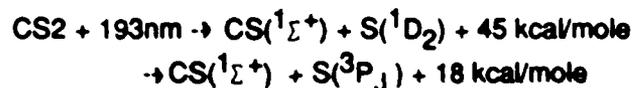
We have carried out calculations using a microcanonical statistical model based on the postulated mechanism. In these calculations literature values for bond energies and vibrational frequencies were used, without adjustment, and all modes were included. The agreement between the calculated and measured  $\text{CO}(v,J,T)$  distributions was excellent at all wavelengths, which we interpret as being conclusive proof that our statistical model is correct.

In this poster, both experimental and theoretical results will be presented. A preliminary report of these results (for 193 nm only) has already been published [J Phys Chem **91**, 506 (1987)]

PHOTOFRAGMENT SPECTROSCOPY OF CS<sub>2</sub>: DIRECT RESOLUTION OF SINGLET AND  
TRIPLET DYNAMICS

Irene M. Waller and John W. Hepburn  
Centre for Molecular Beams and Laser Chemistry  
University of Waterloo  
Waterloo, Ontario, Canada N2L 3G1

The photofragmentation dynamics of CS<sub>2</sub> at 193nm has been studied under supersonic molecular beam conditions, using vacuum ultraviolet laser-induced fluorescence spectroscopy (VUV LIF) to detect the atomic S photoproducts. We have used the VUV LIF method to study the photofragmentation of metal carbonyls<sup>1</sup>, and it has been described previously<sup>1,2</sup>. The 193nm photolysis of CS<sub>2</sub> yields the following:



where the first reaction is the singlet channel, and the second reaction is the triplet channel. By directly detecting the S atom products under collision free conditions, the branching between these two channels has been determined to be triplet/singlet = 2.8, thus resolving a long-standing controversy in the literature.

The high resolution of our VUV detection system enables us to measure the translational energy distribution and recoil velocity angular distribution by Doppler spectroscopy. As the S(<sup>3</sup>P<sub>J</sub>) and S(<sup>1</sup>D<sub>2</sub>) products are detected separately, this method also unambiguously resolves the singlet and triplet dissociation dynamics. These results will be discussed in terms of the detailed photofragmentation mechanism for CS<sub>2</sub>.

- (1) I.M. Waller, H.F. Davis and J.W. Hepburn, *J. Phys. Chem.* **91**, 506 (1987).
- (2) I.M. Waller, H.F. Davis and J.W. Hepburn, "Short Wavelength Coherent Radiation: Generation and Applications", D.T. Atwood and J. Bokor eds. (AIP, 1986), pp.430-441.

PHOTOFRAGMENTATION DYNAMICS OF H<sub>2</sub>S AT 193, 222 AND 248 nm: DIRECT  
PROBING OF ROTATIONAL EXCITATION IN SH( $\nu=0,1$ )

Brad R. Weiner<sup>†</sup> and A. P. Baronavski, Chemistry Division, Naval Research  
Laboratory, Washington, D.C. 20375

The nascent rotational distribution of the SH( $X^2\Pi_{3/2,1/2}, \nu=0$ ) fragment following photodissociation of H<sub>2</sub>S at 193, 222 and 248 nm has been measured by laser induced fluorescence (LIF). Additionally, the SH( $X^2\Pi_{3/2,1/2}, \nu=1$ ) fragment has been directly probed for the first time by LIF following photodissociation of H<sub>2</sub>S at 193 and 222 nm. In all cases, the rotational distributions can be characterized as Boltzmann, with only a small percentage of the the total available energy appearing as rotation in the SH photofragment. Previous experiments suggest that approximately 90% of the total exoergicity is partitioned into the translational degrees of freedom of the photofragments.<sup>1,2</sup> In our experiments, the rotational lines arising from SH( $X^2\Pi_{3/2,1/2}, \nu=0$ ) show Doppler broadening consistent with that observation. However, the rotational lines originating from SH( $X^2\Pi_{3/2,1/2}, \nu=1$ ) are considerably narrower. The possibility of two distinct dissociation channels is discussed.

<sup>†</sup> NRC/NRL Postdoctoral Research Associate

W. G. Hawkins and P. L. Houston, *J. Chem. Phys.* **73**, 2481 (1980); **76**, 2487 (1982);  
J. N. A. van Veen, K. A. M. Brion, G. J. Brode and J. A. F. Bolger, *J. Chem. Phys.* **74**, 1011 (1981).

PHOTOPHYSICS AND PHOTOCHEMISTRY OF H<sub>2</sub>S AT 157 nm

Brad R. Weiner<sup>†</sup> and A. P. Baronavski, Chemistry Division, Naval Research Laboratory, Washington, D.C. 20375

Irradiation of H<sub>2</sub>S at 157 nm leads to three experimentally observed photophysical and photochemical processes. First, prompt emission in the wavelength region 320-360 nm is attributed to the direct photochemical production of SH(A<sup>2</sup>Σ). Second, structured vacuum ultraviolet (VUV) emission in the wavelength region 155-190 nm is most likely due to fluorescence from the lowest lying Rydberg state of H<sub>2</sub>S, which is accessed by absorption of a 157 nm photon. The spacing between bands in the VUV emission is consistent with vibrational spacing of the bending mode ( $\nu_2$ ) of ground state H<sub>2</sub>S, suggesting a quasi-linear geometry for the Rydberg state. Finally, SH(X<sup>2</sup>Π<sub>3/2,1/2</sub>) produced by 157 nm photodissociation is probed by laser induced fluorescence (LIF). No SH(X<sup>2</sup>Π<sub>3/2,1/2</sub>, v=0) is produced promptly, but is detected within 200 ns. The origin of this photoproduct is discussed.

<sup>†</sup> NRC/NRL Postdoctoral Research Associate

## MULTIPHOTON DISSOCIATION OF ORGANOMETALLIC NITROSYLS

Savas Georgiou and Charles A. Wight

Chemistry Department  
University of Utah

## Abstract

The mechanism of dissociation of organometallic nitrosyls is assessed by studying the state distributions of the NO photofragments. The nascent NO population is probed both in the 450-520 nm region by [2+2] MPI and in the 220-225 nm by [1+1] MPI. The fragment distributions are found to depend on the competition between multiphoton excitation and metal-ligand dissociation. In the visible, the first factor dominates resulting in a highly nonstatistical rotational distribution, which is very similar for all compounds studied. In the U.V., the experimentals can be performed at low laser power densities. In this case, intramolecular energy transfer is favored, and the fragment is characterized approximately by statistical state distribution. In all cases, high rotational excitation is observed, indicative of dissociation from a bent metal-nitrosyl potential surface.

# THEORY OF DIATOMIC PHOTODISSOCIATION TO OPEN SHELL ATOMS IN THE PRESENCE OF AN EXTERNAL MAGNETIC FIELD

*Carl J. Williams and Karl F. Freed*

The James Franck Institute and the Department of Chemistry  
The University of Chicago, Chicago, Illinois 60637

*Yehuda B. Band*

Department of Chemistry  
Ben Gurion University of the Negev, Beer-Sheva, Israel

The theory of diatomic photodissociation in the presence of a magnetic field is developed from the generalized theory of diatomic photodissociation of Singer et al.<sup>1,2</sup> by incorporating the magnetic interactions and by decoupling the asymptotic Hund's case e states. The external magnetic field is predicted to produce several novel effects on the photodissociation of a heteronuclear diatomic molecule dissociating to open shell fragments, in part, because the magnetic field makes the total angular momentum  $J$  no longer a good quantum number and also because it lifts the asymptotic degeneracies of the fragment magnetic sublevels. Thus, the magnetic field may couple nearby resonances of different total  $J$  that are noninteracting in the absence of the field, while other resonances may be broadened by coupling to states of different total  $J$  in the continuum. The lifting of the fragment magnetic sublevel degeneracies imparts an orientation to the photofragments, which can be determined by kinematics and knowledge of the initial bound state. When only a single fragment magnetic channel is open asymptotically, it is shown that the near threshold photodissociation provides a means of producing polarized atomic beams. The effects of magnetic fields on resonances in the near threshold dissociation of  $\text{CH}^+$  are studied to illustrate the theory and to show changes in the relative orientation of fragments in passing through resonances.

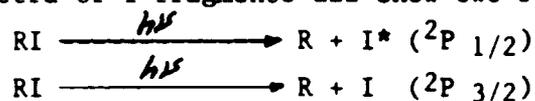
1. S.J. Singer, K.F. Freed, and Y.B. Band, *J. Chem. Phys.* **79**, 6060 (1983).
2. S.J. Singer, K.F. Freed, and Y.B. Band, *Adv. Chem. Phys.* **61**, 1 (1985).

PHOTOFRAGMENTATION OF ALKYL IODIDES — Photofragmentation  
Channels and Energy Partitioning of the Fragments

Qihe Zhu, Shouling Huang, J.R. Cao, Ye Wen, Jianming Zhang,  
Xian Zhong, Yuhui Huang, Wanquan Fang and Xiaojun Wu

Institute of Chemistry, Academia Sinica,  
Beijing, China

Studies on the photofragmentation of  $\text{CH}_3\text{I}$ ,  $\text{C}_2\text{H}_5\text{I}$ ,  $n\text{-C}_3\text{H}_7\text{I}$ ,  $\text{iso-C}_3\text{H}_7\text{I}$  and  $t\text{-C}_4\text{H}_9\text{I}$  have been carried out using our newly-built photofragment spectrometer with rotatable molecular beam source. The pulsed molecular beam is crossed with KrF (248nm) laser beam. TOF spectra of I fragments all show two reaction channels,



The obtained channel ratios  $\text{I}^*/\text{I}$  are 3.0, 2.4, 1.6, 1.0 and 1.3, respectively.

The bond dissociation energy  $D_{\text{C-I}}$  for  $\text{CH}_3\text{I}$  and  $\text{C}_2\text{H}_5\text{I}$  are determined to be  $55.0 \pm 0.5$  and  $55.3 \pm 1.0$  Kcal/mol, respectively, according to the highest translational energy release in  $\text{I}^*$  channels.

The internal excitation  $E_{\text{int}}$  of alkyl fragments R has been determined by energy balance. The fraction of available energy  $E_{\text{avl}}$  going into  $E_{\text{int}}$  of R,  $E_{\text{int}}/E_{\text{avl}}$ , are

Channel	$\text{CH}_3\text{I}$	$\text{C}_2\text{H}_5\text{I}$	$n\text{-C}_3\text{H}_7\text{I}$	$\text{iso-C}_3\text{H}_7\text{I}$	$t\text{-C}_4\text{H}_9\text{I}$
$\text{I}^*$	0.12	0.32	0.49	0.63	0.71
<u>I</u>	<u>0.17</u>	0.39	0.57	0.64	0.73

These values agree to direct impulsive model of unimolecular decomposition and most of them are close to the "soft" radical limit.

The underlined results are quite different from those given by other laboratories.

Discussions of the results have been also given.

THE PHOTODISSOCIATION OF HO<sub>2</sub>  
AN INSIGHT BASED ON AB-INITIO ELECTRONIC STRUCTURE CALCULATIONS

Vázquez, G.J., Instituto de Física, UNAM, AP-139B, Cuernavaca, México

Buenker, R.J., Theoretische Chemie, Bergische Universität, Wuppertal, W-Germany

Peyerimhoff, S.D., Theoretische Chemie, Universität Bonn, West Germany

The photodissociation of the hydroperoxyl radical is discussed based on MRD-CI electronic structure calculations. A previous study<sup>(1)</sup> based on a cut of the potential energy surfaces along the O-OH coordinate is broadened by also considering cuts along OO-H and  $\Theta$  which permit a wider and deeper insight into process.

The absorption of light is analyzed based on the calculated vertical excitation spectrum and oscillator strengths for transitions from the ground to the lowest excited states. This permits to pinpoint the photoexcited species. Its subsequent evolution is examined in light of the data provided by the curves, i.e., shape, interactions and correlations of the electronic states along the fragmentation pathways. This information enables one to visualize diverse fragmentation mechanisms. Further theoretical arguments together with experimental data are then used to establish feasibility criteria for the various possibilities.

The photodissociation of HO<sub>2</sub> in the range of excitation energies  $5 < \Delta E < 6.4$  eV appears to proceed as follows: upon light absorption the system is promoted, via a Franck-Condon transition, to the <sup>2</sup>A"(1a<sup>-</sup>2a<sup>+</sup>) excited state, the only species with a sizeable oscillator strength. Once on the excited state surface, HO<sub>2</sub><sup>\*</sup> (<sup>2</sup>A") may dissociate either into O + OH or O<sub>2</sub> + H, both instances being permitted from the energetical viewpoint; yet, <sup>2</sup>A" is repulsive along O-O and bound along O-H, so the former is the viable dissociation channel. There remain two fragmentation possibilities OH(X<sup>2</sup>Π) + O(<sup>3</sup>P) and OH(X<sup>2</sup>Π) + O(<sup>1</sup>D); according to the curves O(<sup>3</sup>P) is produced in the adiabatic process, whereas the non-adiabatic one yields O(<sup>1</sup>D). Arguments are presented which indicate the dissociation proceeds diabatically on the surface of the initially populated <sup>2</sup>A" state yielding O(<sup>1</sup>D), so providing an explanation of the experimental findings.

(1) Vázquez, G.J., Peyerimhoff, S.D., Buenker, R.J., Chem. Phys., 99, 239 (1985)

THE p-DIFLUOROBENZENE-Ar VAN DER WAALS COMPLEX. VIBRATIONAL PREDISSOCIATION AND IVR.

K.W. Butz, H.-K. O, M.L.-C.L. Su, and C.S. Parmenter,  
Department of Chemistry, Indiana University, Bloomington, IN 47405

The  $S_1$  p-difluorobenzene-Ar (pDFB-Ar) complex has been characterized by fluorescence excitation spectra and by fluorescence spectra after pumping each of twelve  $S_1$  vibrational levels ranging up to  $\nu_{16} = 1250 \text{ cm}^{-1}$ . The fluorescence spectra variously contain structure from the initially pumped complex level, other complex levels, and the pDFB monomer. In some cases, additional fluorescence spectra were obtained from pumping the Ar-ring stretch. Vibrational predissociation (VP) was probed by exciting the complex to the vibrational levels higher than the complex dissociation energy and observing the final states of pDFB monomer after dissociation. VP characterizes seven of the excited levels consisting of six different vibrational modes. In every case, VP is highly selective with respect to the "product" states in  $S_1$  pDFB monomer. It appears that VP time scales are generally in the nsec range but vary modestly for different initial modes. IVR within the  $S_1$  complex occurs from a few of the initial levels and is highly sensitive to the initial level identity.

Time- and State-Resolved Studies of Vibrational Predissociation  
of Weakly Bound Molecular Clusters

Michael P. Casassa, John C. Stephenson, and David S. King  
National Bureau of Standards, Molecular Spectroscopy Division  
Gaithersburg, MD 20899

ABSTRACT

Experimental measurements of the complete product state distributions and predissociation lifetimes of vibrationally excited nitric oxide dimer are described. Single-quantum excitations of the symmetric ( $\nu_1$ ,  $1870\text{ cm}^{-1}$ ) and antisymmetric ( $\nu_4$ ,  $1789\text{ cm}^{-1}$ ) NO stretching fundamentals produce fragments which carry away most ( $\sim 80\%$ ) of the available energy as kinetic energy. Interestingly, there is a significant difference in the fragment spin-orbit state distributions observed following excitation of these two modes. Picosecond laser pump-probe experiments reveal a dramatic mode-specific effect: excitation of the  $\nu_4$  mode leads to a 39ps predissociative lifetime, while excitation of the higher energy  $\nu_1$  mode initiates a much less efficient predissociation, with a lifetime of 880ps.

**Predissociation dynamics of methyl iodide clusters**

D. J. Donaldson, V. Vaida

Dept. of Chemistry, University of Colorado

Boulder, CO 80309-0215

and R. Naaman

Dept. of Isotopes Research, Weizmann Institute of Science

Rehovot, 76100 ISRAEL

We have measured the u.v. direct absorption spectra of jet-cooled methyl iodide in its valence (A) and Rydberg (B,C) states. The formation of methyl iodide dimers results in several changes to the observed spectra. A significant blue shift ( 500  $\text{cm}^{-1}$ ) is seen in the purely dissociative valence state upon when methyl iodide dimers are present in the jet. The Rydberg states are not significantly shifted with respect to the ground state upon dimer formation. However, we observe splittings in the origin bands, very different relative intensities in the main progression and "new" modes, not seen in the monomer spectrum. These observations are all explained by a solvent-induced shift in the position of the predissociative surface crossing of the A-state with B and C. This shift slows the predissociation, allowing vibronic states which are rapidly dissociating in the monomer to become visible in the dimer. Similar effects are observed in clusters of acetone.

Methyl iodide clusters higher than the dimer exhibit a strong continuum beneath the B-state and interferences between this continuum and the main progression. This effect is observed for methyl iodide clustered with itself and with rare gases (Ar, Kr, Xe). It may be due to an excitation of exciton-type states in the higher clusters.

State-to-State Measurements of the Vibrational  
Predissociation Dynamics of  $\text{HeCl}_2$

Joseph I. Cline, N. Sivakumar, Dwight D. Evard, and  
Kenneth C. Janda

Department of Chemistry  
University of Pittsburgh  
Pittsburgh, PA 15260

**Abstract**

Well resolved state-to-state data are reported for the vibrational predissociation of specific rotational levels of  $\text{HeCl}_2(\text{B})$  with 8 vibrational quanta in the Cl-Cl stretching mode. The state resolution is sufficient to clearly reveal the symmetry constraints on the dynamics. The product rotational state distribution has two distinct maxima separated by a node which implies the existence of either a rotational rainbow or quantum interference in the product channels. "Parity-selected" excitation spectra are obtained which reduce spectral congestion and aid in the assignment of individual rovibronic transitions.

Direct Measurement of the Vibrational Predissociation  
Lifetime of  $\text{NeBr}_2$  in the Ground Electronic State

N. Sivakumar, Dwight D. Evard, Joseph I. Cline,  
and Kenneth C. Janda

Department of Chemistry  
University of Pittsburgh  
Pittsburgh, PA 15260

**Abstract**

The vibrational predissociation lifetime of  $\text{NeBr}_2$  in the ground electronic state with one vibrational quantum in the halogen stretch was measured directly in a free jet expansion.  $\text{NeBr}_2(X, v=1)$  was detected by optical-optical double resonance to monitor the population as a function of distance from the nozzle to the laser interaction region. The vibrational predissociation lifetime for  $\text{NeBr}_2(X, v=1)$  was determined to be  $8 \pm 3 \mu\text{s}$ . The results are compared to previous studies of  $\text{Br}_2(B)$  using the energy gap model.

STATE SELECTIVE PHOTOFRAGMENTATION OF ICl-Ne VAN DER WAALS  
COMPLEXES

Janet C. Drobits and Marsha I. Lester, Department of Chemistry,  
University of Pennsylvania, Philadelphia, Pennsylvania 19104-6323

The vibrational predissociation dynamics of ICl-Ne van der Waals complexes has been investigated for a series of vibrational levels in the  $A(^3\Pi_1)$  state manifold. Visible laser excitation prepares the complexes in selected rovibrational levels in the A state. Coupling of the vibrational excitation, initially localized in the ICl bond, to the weak van der Waals bond results in predissociation of the complex. Fragmentation proceeds with the loss of one or two quanta of ICl vibrational energy. The nascent rotational/vibrational distribution is probed by excitation of the ICl A state photofragments to an ion pair state. The product state distribution reflects the dominant features of the reaction pathway and provides an important key to understanding the reaction mechanism.

By initially populating different vibrational levels in the complex, the energetics and lifetime of the predissociation can be selectively altered. Detailed product state distributions will be presented for dissociation of ICl-Ne from A state vibrational levels with predissociation lifetimes ranging from nanoseconds<sup>1</sup> to a few picoseconds. Analysis of results will be discussed in the context of statistical theories of photodissociation and inelastic scattering theories.

---

<sup>1</sup>J.C. Drobits, J.M. Skene and M.I. Lester, *J. Chem. Phys.* **84**, 2896 (1986).

RESONANT PHOTOIONIZATION SPECTROSCOPY OF REFRACTORY METAL-  
RARE GAS COMPLEXES

John M. Gardner and Marsha I. Lester, Department of Chemistry and  
Laboratory for Research on the Structure of Matter, University of  
Pennsylvania, Philadelphia, Pennsylvania 19104-6323.

The weakly attractive interatomic potential between a refractory metal and a rare gas atom is explored by direct spectroscopic access of rovibronic levels in the AlAr van der Waals complex. Mass-resolved resonance-enhanced multiphoton ionization is used to probe the spectral region about the Al  $^2S_{1/2} - ^2P_{1/2}$  transition. A vibrational progression in the AlAr  $^2\Sigma^+$  state is identified on the AlAr $^+$  mass channel. Lower limits for binding energies in the X  $^2\Pi_{1/2}$  and B  $^2\Sigma^+$  states are found to be 133 and 373  $\text{cm}^{-1}$ , respectively. Results are compared to earlier work on NaAr.

**PHOTODISSOCIATION DYNAMICS OF ICl-RARE GAS COMPLEXES IN THE B<sup>3</sup>Π<sub>0+</sub> STATE**

John M. Skene and Marsha I. Lester, Department of Chemistry,  
University of Pennsylvania, Philadelphia, Pennsylvania 19104-6323

The unimolecular dissociation dynamics of ICl-He and ICl-Ne van der Waals (vdW) complexes in the B <sup>3</sup>Π<sub>0+</sub> state is examined at the state-to-state level of detail through optical-optical double resonance methods. The vdW complex is prepared in the B state with 2 or 3 quanta of vibrational excitation in the ICl stretching mode. Vibrational predissociation is monitored by subsequent excitation of ICl photofragments on B(vg)-B(vg=1,2) transitions. The predissociation dynamics, evolve on a nanosecond timescale, yet result in highly peaked, nonstatistical ICl rotational product state distributions. The nascent rotational distributions are compared with statistical theories and models of inelastic scattering.

Production of  $C_2H_4Cl^+$  by Photoionization of the  
Weak Complex  $C_2H_4:HCl$

J. R. Grover<sup>a</sup>, E. A. Walters<sup>b</sup>, D. L. Arneberg<sup>b</sup>, G. Santandrea<sup>a</sup>  
and M. G. White<sup>a</sup>

<sup>a</sup> Chem. Dept., Brookhaven Natl. Lab., Upton, NY 11973

<sup>b</sup> Chem. Dept., U. of New Mexico, Albuquerque, NM 87131

The photoionization efficiency (PIE) spectrum from 1200 Å for production of the ion  $C_2H_4Cl^+$  from the products of room-temperature jet expansions of a 1:4 mixture of  $C_2H_4$  and HCl was measured at several nozzle pressures. Careful analysis of the jet expansion products was then used to resolve the PIE spectrum for the process



from the spectra for the production of  $C_2H_4Cl^+$  from trimers and larger clusters. The spectrum for rxn 1 is dominated by two peaks; at 15.2 eV, sharply cut off on the high-energy side and skewed to lower energies, and at 17.4 eV, broad. Facts significant to understanding the lower-energy peak are: (1) in free HCl there are two overlapping progressions of strong, autoionizing Rydberg lines in the region; (2) the abrupt drop-off that forms the high-energy side occurs very near the energy at which the Cl atom becomes unbound from product  $C_2H_4Cl^+$  (15.1 eV). The first onset of  $C_2H_4Cl^+$  occurs at  $12.40 \pm 0.15$  eV, while the true threshold is at 11.17 eV. This substantial difference, 28 kcal mol<sup>-1</sup>, is caused by the large change in geometry between the complex and the product. The complex has a perpendicular structure in which the chlorine atom is distant from the  $C_2H_4$  plane with the H atom intervening, while the product has the Cl atom sigma-bonded to a carbon atom. The energy of the first onset is only a little lower than the ionization potential of free HCl (12.75 eV), and nearly the same as the photoionization threshold of the  $1^2B_{2g}$  state of  $C_2H_4^+$  from free  $C_2H_4$ . On the other hand, the next higher obvious onset, at 14.2 eV, does not correspond to any state of  $HCl^+$ , but is very close to the photoionization threshold of the  $1^2A_g$  state of  $C_2H_4^+$ . Therefore, which moiety serves as chromophore depends sensitively on photon energy. Reaction 1 cannot be statistical as observed because the energies needed to dissociate  $C_2H_4:HCl$  into  $C_2H_4 + HCl$  and  $C_2H_5Cl^+$  into  $C_2H_4^+ + HCl$ ,  $\sim 3$  and 5 kcal mol<sup>-1</sup> respectively, are very much smaller than the 4 eV needed to break a C-H or Cl-H bond. Consequently the latter process cannot compete detectably with the former in a statistical mechanism. The partitioning of energy between translation and excitation is not known, except that the excitation of product  $C_2H_4Cl^+$  stable enough to be detected is unlikely to exceed 3.9 eV.

Work done at Brookhaven National Laboratory under contract DE-AC02-76CH00016 with the U. S. Dept. of Energy and supported by its Division of Chemical Sciences, Office of Basic Energy Sciences.

Vibrational and rotational wave functions for He...Cl<sub>2</sub>, Ne...Cl<sub>2</sub> and Ar...Cl<sub>2</sub>  
and

A three dimensional quantum mechanical study  
of Ne...Cl<sub>2</sub> vibrational predissociation

by

Brian P. Reid and Kenneth C. Janda

*Department of Chemistry, University of Pittsburgh, Pittsburgh PA 15260, USA,*  
Nadine Halberstadt

*Laboratoire de Photophysique Moléculaire, Université de Paris Sud, 91405 Orsay, France,*  
and J. Alberto Beswick

*LURE, Laboratoire CNRS, CEA et MEN, Université de Paris Sud, 91405 Orsay, France*

**Abstract**

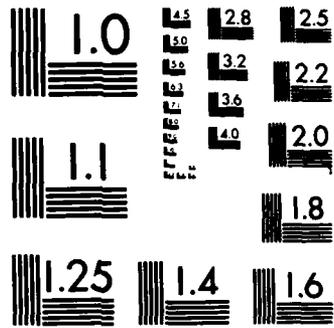
We present calculations that form a basis for understanding the structure, spectroscopy and dynamics of the van der Waals molecules He...Cl<sub>2</sub>, Ne...Cl<sub>2</sub> and Ar...Cl<sub>2</sub>. Using realistic model intermolecular potentials, we have calculated vibrational wave functions for the modes associated with the van der Waals degrees of freedom. Pictorial representations of these wave functions show the excitations of the bending and the stretching motions of the weak bond. The energy levels obtained are used to check the validity of one dimensional model potentials for the stretching coordinate, while calculations for different total angular momentum allow comparison with rigid rotor models.

As for the dynamics, we present detailed three dimensional quantum mechanical calculations for vibrational predissociation of the Ne...Cl<sub>2</sub> van der Waals complex and compare the results with experiments. Two processes have been studied:

- i) Ne...Cl<sub>2</sub>(X,  $v = 1$ ) → Ne + Cl<sub>2</sub>(X,  $v = 0$ ), and
- ii) Ne...Cl<sub>2</sub>(B,  $v = 11$ ) → Ne + Cl<sub>2</sub>(B,  $v = 10, 9$ ),

where  $v$  denotes the vibrational quantum number of Cl<sub>2</sub> while X and B specify electronic states of Ne...Cl<sub>2</sub> which correlate with the X<sup>1</sup>Σ<sub>0<sup>+</sup></sub> and B<sup>3</sup>Π<sub>0<sup>+</sup></sub> states of the free Cl<sub>2</sub> molecule respectively. The calculations provide lifetimes and final rotational state distributions of the Cl<sub>2</sub> fragments. The effects of exciting the van der Waals bending mode and the overall rotation of the complex have also been studied.





MICROCOPY RESOLUTION TEST CHART  
NATIONAL BUREAU OF STANDARDS-1963-A

## NEAR INFRARED LASER SPECTROSCOPY OF NITROUS OXIDE DIMER

Z.S. Huang and R.E. Miller  
Department of Chemistry  
University of North Carolina  
Chapel Hill, NC 27514

The optothermal detection method has been used to obtain a sub-Doppler resolution infrared spectrum of  $(\text{N}_2\text{O})_2$ . This spectrum has been assigned and fit to obtain an accurate set of rotational constants. Spin statistics associated with the centro-symmetric structure are easily discerned in the spectrum. Comparisons between the experimental structure and those predicted from an empirical potential surface for  $(\text{N}_2\text{O})_2$  are given.

Poster Session

High Resolution 193nm Laser Photofragmentation Time of  
Flight Mass Spectrometric Study of CS<sub>2</sub> and CS<sub>2</sub> Clusters

W.B.Tzeng, H.M.Yin, W.Y.Leung, J.Y.Luo, S.Nourbakhsh, and C.Y.Ng

Ames Laboratory, USDOE, and Department of Chemistry,  
Iowa State University, Ames, Iowa 50011

Abstract:

High resolution time-of-flight (TOF) spectra for CS and S produced by the process  $CS_2 + h\nu(193 \text{ nm}) \rightarrow CS(X,v) + S(^3P \text{ or } ^1D)$  have been measured using a rotating beam source laser photofragmentation TOF mass spectrometer. Structures corresponding to the formation of  $CS(X,v=0-5) + S(^1D)$  are resolved. The production of  $S^+$  from CS fragments by electron impact at electron energies  $<50\text{eV}$  is found to be insignificant. The product kinetic energy distribution derived from the TOF spectra of CS and S are in agreement, indicating that the further dissociation of the CS fragment due to the absorption of a second photon within the laser pulse is not important. The product kinetic energy distribution is consistent with the conclusion of previous laser induced fluorescence experiments <sup>1,2</sup> (that the  $^3P:^1D$  branching ratio is 2 and that the vibrational population of CS is peaked at  $v=3$ ).

Time-of-flight spectra for photofragments originating from CS<sub>2</sub> clusters reveal that  $(CS_2)_n$ ,  $n>1$ , formed in the process  $(CS_2)_{n+1} + h\nu(193\text{nm}) \rightarrow CS + S + (CS_2)_n$ , acquire only a small amount of kinetic energy.

References

- 1) I.M.Waller, H.F.Davis, and J.W.Hepburn, in D.T.Attwood and J.Boker, eds. (AIP Conference Proceedings, 1986).
- 2) J.E.Butler, W.S.Drozdoski, and J.R.McDonald, Chem.Phys. 50, 413 (1980).

## Dynamics of Collisional Energy Flow in Weakly Bound Complexes

H. K. Shin, Department of Chemistry, University of Nevada, Reno, Nevada 89557

## ABSTRACT

Collisional energy transfer dynamics in weakly bound complexes is studied at collision energies above and below the fragmentation threshold in classical mechanics. The collinear collision of a linear complex  $C \cdots B-A$ , where  $C$  is an atom or a diatomic molecule, with an incident atom is considered. For the collision energy range 0.01 - 10 eV, energy transfer to the complex is efficient, and essentially all of the energy transferred to the complex is localized in the bond. The energy initially stored in the molecular bond remains in it when the collision is over, and the bond gains essentially no energy from translation. The collision model is formulated such that the incident atom hits the outer atom  $A$  of the molecular unit  $B-A$ , so the efficient energy build-up in the weak bond indicates an easy flow of energy across the stiff molecular bond from the initial impact region. Energy flows from the molecular bond to the weak bond through a sequence of energy gain-loss steps on a subpicosecond time scale.

VIBRATIONAL PREDISSOCIATION OF THE He-I<sub>2</sub>-Ne COMPLEX.  
APPROXIMATE QUASICLASSICAL AND QUANTAL CALCULATIONS.

Nieves Martin, Andres Varade, Pedro Femau,  
Pablo Villarreal and Gerardo Delgado-Barrico  
Instituto de Estructura de la Materia, C.S.I.C.,  
Serrano 123, 28006-Madrid, SPAIN.

We study the dynamics of vibrational predissociation of the He-I<sub>2</sub> (B, v=28)-Ne cluster. As it is well known, a full quantal treatment of the four-body system becomes prohibitively difficult. Hence, we simplify the problem by assuming a configuration in which the iodine molecule remains perpendicular to a plane containing the rare gas atoms, accounting for the iodine stretching, the He and Ne vibrations, and also the oscillation in the angle formed by both weak bonds. This is a realistic configuration since, for each isolated X-I<sub>2</sub> complex (X=He, Ne) the perpendicular situation is the more stable. Moreover, there is a large difference between the rotational constants of I<sub>2</sub>, Ne-I<sub>2</sub> and He-I<sub>2</sub>, 0.04, 0.05 and 0.30 cm<sup>-2</sup>, respectively, on one hand, and the stretching frequency of He-Ne, 10 cm<sup>-1</sup>, on the other hand.

Now, we apply a quasiclassical trajectory method (QCT) close to that previously used<sup>1</sup>. According to a total energy equal to the iodine vibrational energy plus the quantal ground energies corresponding to He-Ne and perpendicular He-I<sub>2</sub> and Ne-I<sub>2</sub>, the necessary initial conditions are randomly selected. The relevant Hamilton equations are then numerically integrated and the distribution of non-dissociated trajectories is fitted to an exponential law of decay providing us the total rate of dissociation of the complex.

Also, after using a diabatic approximation to describe the iodine vibrations, we solve the resulting effective tri-atomic problem within an adiabatic angular framework<sup>3</sup>, obtaining angular-dependent ground energies of the complex and associated rates<sup>4</sup> that are finally averaged on the angular motion.

We present in Table I a comparison between quasiclassical and quantal results, showing the good agreement of these approximate treatments. Also, from the quantal partial rates, the lower stability of the stronger van der Waals bond in the complex may be noted.

Table I	ETOT	$\theta$ -range	$\Gamma_{He}$	$\Gamma_{Ne}$	$\Gamma_{TOT}$
=====	(cm <sup>-1</sup> )	(degrees)	(cm <sup>-1</sup> )	(cm <sup>-1</sup> )	(cm <sup>-1</sup> )
QCT	[-93.5, -94.7]	[40, 70]			0.55
Quant.	-93.97	[41, 65]	0.23	0.46	0.69

1 G.C.Schatz, V.Buch, M.A.Ratner, and R.B.Gerber, J.Chem.Phys., 79(1983)1808.

2 G.Delgado-Barrico, P.Villarreal, P.Mareca, and G.Albelda, J.Chem.Phys., 78(1983)280.

3 G.A.Natanson, G.S.Ezra, G.Delgado-Barrico, and R.S.Berry, J.Chem.Phys., 84(1986)2035.

4 G.Delgado-Barrico, P.Villarreal, A.Varade, N.Martin, and A.Garcia, NATO Advanced Study Institutes "Structure and Dynamics of Weakly Bound Molecular Complexes", Series B (in press).

VIBRATIONAL PREDISSOCIATION OF Ne-Cl<sub>2</sub>: A CLOSE-  
COUPLING INFINITE ORDER SUDDEN APPROXIMATION

P. Villarreal, A.M. Cortina, O. Roncero  
and G. Delgado-Barrio  
Instituto de Estructura de la Materia, CSIC.  
Serrano 123, 28006-Madrid, SPAIN

We apply a model closely related to the "infinite order sudden approximation" (IOSA) to study the vibrational predissociation of the Ne-Cl<sub>2</sub>(v=11) van der Waals molecule. The stretching motions within the complex are exactly solved in the close-coupling formalism at each atom-diatomic molecule orientation, providing us angular-dependent energies and rates. The bending motion is then considered in an approximate way and three-dimensional energies together with averaged predissociation rates are obtained. The potential energy surface was that previously used by N. Halberstadt<sup>1</sup>. Since the experiment<sup>2</sup> and also very recent full-quantal calculations<sup>3</sup> show a strong dominance of the  $\Delta v = -1$  predissociation channel, only the vibrational channels v=11 (closed) and v=10 (open) were taken into account.

A total angular momentum J=0 has been assumed along all the calculations, that have been carried out for twenty-five values of the orientation angle  $\theta$  equally spaced over the range  $[0, \pi/2]$ .

In Table I we present a few energies and linewidths, in cm<sup>-1</sup>, calculated at collinear,  $\pi/3$  and perpendicular configurations, together with averaged 3D values

	coll.	$\pi/3$	$\pi/2$	3D
E	-16.39	-30.40	-53.18	-46.90
$\Gamma$	0.0015	0.00011	0.0105	0.0081

Table I

The 3D energy and lifetime ( $\tau = h/2\Gamma \approx 330$  ps) are in agreement with full quantal results<sup>3</sup>. However, the last quantity becomes three times bigger than the experimental value<sup>2</sup>. This fact may be attributed to the potential energy surface employed.

References

- 1 N. Halberstadt, PhD. Thesis, Paris (1987)
- 2 J.L. Cline, N. Sivakumar, D.D. Evard, and K.C. Janda, J. Chem. Phys. **86**, 1636 (1987)
- 3 N. Halberstadt and J.A. Beswick, private communication.

## INDEX TO AUTHORS OF CONTRIBUTED PAPERS

Aker, P. M.....	RE1
Alexander, M. H.....	ET1,ET11,ET18
Ali, A.....	EE1
Alvarifo, J. M.....	RT18
Anderson, J. B.....	RT1
Anderson, S. L.....	RE11,RE19
Aquilanti, V.....	EE5
Archer, B. J.....	RT22
Archirel, P.....	ET9
Arneberg, D. L.....	V9
Arqui, H.....	EE20
Atabek, O.....	RT5
Baer, M.....	RT2
Balko, B. A.....	P2
Band, Y. B.....	ET15,P19
Baronovski, A. P.....	P16,P17
Baylis, W. E.....	EE28
Becker, M.....	EE13
BelBruno, J. J.....	RE22
Beneventi, L.....	EE4
Bergmann, K.....	EE13
Berlande, J.....	RE17,EE27
Bernasek, S. L.....	SE1
Berry, R. S.....	ET5
Beswick, J. A.....	V10
Billing, G. D.....	RT20,EE20
Billy, N.....	RE29
Binkley, J. S.....	RT23
Blanchard, Y.....	EE20
Blauer, J.....	RE31
Boeglin, A.....	ST7
Bourgignon, B.....	RE21
Bower, R.....	RE31
Bowman, J. M.....	RT9
Boyle, E. J.....	RE32
Brenner, D. W.....	ST1
Brooks, P. R.....	RE28
Broquier, M.....	EE20
Budenholler, F. E.....	ET2,ET3
Buenker, R. J.....	P21
Buntin, S. A.....	RE2
Butler, L. J.....	P7,P10
Butz, K. W.....	EE2,V1
Campbell, M. L.....	RE3
Campos-Martinez, J.....	ET6
Candori, R.....	EE5
Cao, J. R.....	P20
Carlson, K. J.....	P9
Carrasquillo, E. M.....	EE3
Casassa, M. P.....	V2
Casavecchia, P.....	EE4
Catlett, D. L.....	EE23
Chandler, D. W.....	EE6
Chawla, G. K.....	EE7
Chiu, L.-Y. C.....	RT3
Chiu, Y.-N.....	ET4

Chu, P.	RE24
Chuang, M.-C.	P1
Cline, J. I.	V4,V5
Cole, S. K.	P8
Coltrin, M. E.	ST2,SE2,SE3
Copeland, R. A.	EE8,EE9
Continetti, R. E.	RE4,RE23
Corey, G. C.	ET11
Cortina, A. M.	V15
Covinsky, M. H.	P2
Creasy, W. R.	RE7
Crim, F. F.	EE3,EE18,P7,P9,P10
Crosley, D. R.	EE8,EE9
Cullen, D. W.	SE5
Cunha, S. L.	EE10
Curl, R. F.	RE28
Cuvellier, J.	RE17,EE27
Dagdikian, P. J.	RE3,EE1
Davis, H. F.	P2
Delgado-Barrio, G.	ET5,ET6,V14,V15
Dentamaro, A. V.	ET7
DePristo, A. E.	RT17
de Pujo, P.	EE27
Derouard, J.	ET11
Diestler, D. J.	ST2
Dolson, D. A.	RE5,RE6
Donaldson, D. J.	V3
Drobits, J. C.	V6
Du, H.	EE2
Dübal, H.-R.	P7
Duchovic, R. J.	RT4
Durocher, S.	RT5
Eaker, C. W.	ET8
Elofson, P. A.	RT12
Eno, L.	RT6,RT7
Evard, D. D.	V4,V5
Fang, C. C.	RE20
Fang, W.	P20
Farrar, J. M.	RE7
Farrow, R. L.	EE6
Fleming, D. G.	RT4
Fletcher, T. R.	P3
Flynn, G. W.	EE11,EE12,EE15,P6
Foltz, M. F.	P1
Freed, K. F.	P19
Frost, R. J.	RT25
Fujimura, Y.	RE12
Gadzuk, J. W.	ST3
Gardner, J. M.	V7
Garner, D. R.	RT1
Garner, D. M.	RT4
Garrett, B. C.	RT8,ST9,P11
Garrison, B. J.	ST1
Gaubatz, U.	EE13
Gazdy, B.	RT9
Gentry, W. R.	RE2,EE23
George, T. F.	ET10
Georgiou, S.	P18

Gericke, K. H.	P4
Germann, G.	RE1
Giese, C. F.	RE2,EE23
Gilbert, R. D.	RT20
Girard, B.	RE29
Gislason, E. A.	ET2,ET9,ET20
Greenblatt, G. D.	RE8
Grover, J. R.	RE9,RE10,V9
Gouedard, G.	RE29
Guan, Y.	RT10
Gundlach, G.	EE22
Halberstadt, N.	V10
Hanley, L.	RE11
Harrison, J. A.	RT19
Hasselbrink, E.	P5,P13
Haug, K.	RT11
Hawley, M.	RE26
Hayden, C. C.	P9
Hepburn, J. W.	P14,P15
Hering, P.	EE10
Herschberger, J. F.	EE11,EE12
Hewitt, S. A.	EE11,EE12
Hoffmeister, M.	RE14
Holland, R. J.	SE1
Holmid, L.	RT12,RT13,ST4,ST5
Honma, K.	RE12
Horn, T. R.	RT7
Houston, P. L.	EE7
Howard, C. J.	RE8
Hsu, D. S. Y.	SE4
Hu, S. C.	ET2,ET3
Huang, S.	P20
Huang, Y.	P20
Huang, Z. S.	V11
Hwang, L. M.	ET3
Inoue, G.	RE12
Irvine, A. M. L.	RE25
Isaacson, A. D.	RT14
Jackson, B. E.	ST6
Jaffe, R. L.	RT15,RT21
Jalink, H.	RE33
Janda, K. C.	V4,V5,V10
Janssen, M.	RE33
Jaquet, R.	RT16
Jaworski, W.	RT30
Jeffries, J. B.	EE14
Jolicard, G.	ET16
Jones, P. L.	SE5,EE13
Kaesdorf, S.	RE28
Kajimoto, O.	RE12
Kanfer, S.	RT20
Katayama, D. H.	ET7
Kay, B. D.	SE2,SE3
Kim, H. L.	EE17
Kim, Y. S.	ET10
King, D. S.	V2
Knight, A. E. W.	EE21
Kompa, K. L.	EE10

Koot, W.....	EE25
Kouri, D. J.....	RT11
Krajnovitch, D. J.....	EE2
Kress, J. D.....	RT17
Kreutz, T. G.....	P6
Kruus, E. J.....	RE13
Kulander, K. C.....	RT28
LaFleur, E. E.....	RT3
Laganà, A.....	RT18
Lee, Y. T.....	RE4,RE10,RE23,RE24,P2
Leitner, D.....	ET5
Lemoine, D.....	ET1,ET11
Lengsfield, B. H.....	RT8
Leone, S. R.....	RE6,RE27,P3
Lester, M. I.....	V6,V7,V8
Leung, W. Y.....	V12
Levkoff, J.....	SE1
Likar, M. D.....	P7
Lin, C. L.....	RE31
Lin, M. C.....	SE4
Lin, S. H.....	ST7
Liu, K.....	P8
Liuti, G.....	EE5
Loesch, H. J.....	RE14
Logan, J.....	RT20
Los, J.....	EE25
Luo, J. Y.....	V12
Luzzatti, E.....	EE5
Lynch, G. C.....	RT10
McAndrew, J. J.....	EE15
McBane, G.....	EE7
McConville, G. T.....	ET12
McDonald, J. D.....	EE17
Macdonald, R. G.....	EE16
McGinley, E. S.....	RE15
McKendrick, K. G.....	RE16
Maguire, T. C.....	RE28
Mansueto, E. S.....	RE30
Martin, N.....	V14
Mascarello, F. G.....	RT15
Mayne, H. R.....	RT19
Mestdagh, J. M.....	RE17,EE27
Mies, F. H.....	ET14,ET15
Miller, R. E.....	V11
Minton, T. K.....	EE17
Möller, K.....	ST4
Moore, C. B.....	P1
Morokuma, K.....	RT31
Moryl, J. E.....	SE5
Muckerman, J. T.....	RT20
Murthy, C. S.....	RT24,ST9,ST10
Muyskens, M. A.....	EE18
Naaman, R.....	V3
Nakamura, H.....	RT2
Natanson, G.....	ET5
Nathanson, G. M.....	RE23
Ng, C. Y.....	V12
Nguyen-Dang, T. T.....	RT5,ET13

Niedner, G.....	EE19
Niefer, B. I.....	RE13
Nieh, J.-C.....	RE18
Noll, M.....	EE19
Nourbakhsh, S.....	V12
Nyman, G.....	RT13,ST5
O, H.-K.....	V1
O'Brien, T. J.....	RE32
O'Neill, J. A.....	P6
Opitz, S.....	RE15
Orlando, T. M.....	RE19
Orr, B. J.....	RE25
Otte, S.....	EE25
Pack, R. T.....	RT22
Paillard, D.....	EE27
Pan, S.-H.....	ET14
Parker, D. H.....	RE33,EE6
Parker, G. A.....	RT22
Parlant, G.....	ET9,ET20
Parmenter, C. S.....	EE2,V1
Parson, J. M.....	RE20
Pascale, J.....	EE28
Pattengill, M. D.....	RT15,RT21
Pemau, P.....	V14
Penn, S. M.....	P9
Peploski, J. C.....	RT6
Perrin, M. Y.....	ET16
Petterson, J. B. C.....	ST5
Peyerimhoff, S. D.....	P21
Picard-Bersellini, A.....	EE20
Pirani, F.....	EE5
Pouilly, B.....	ET18
Preiskorn, A.....	ET17
Preses, J. M.....	EE15
Prisant, M. G.....	RE21
Proch, D.....	RE15
Raff, L. M.....	ST8
Rakestraw, D. J.....	RE16
Raiche, G. A.....	RE22
Rainbird, M. W.....	EE21
Randeniya, A. H. L. K.....	RE26
Raymond, T. D.....	SE3
Redmon, M. J.....	RT23,RT24,ST9
Reid, B. P.....	V10
Rensberger, K. J.....	EE18
Rice, B. M.....	ST8
Riley, M. E.....	ST2
Robbe, J. M.....	ET18
Robertson, A.....	SE1
Robinson, G. N.....	RE4,RE23
Robinson, J. M.....	EE18
Rohlfing, E. A.....	EE6
Roncero, O.....	V15
Rosenkrantz, M. E.....	RT8
Rossi, F.....	EE28
Rostas, J.....	RE21
Rowntree, P.....	SE6
Ruatta, S. A.....	RE11

Rubahn, H.-G. ....	EE22
Ruiz, C. ....	SE6
Rynefors, K. ....	RT12,RT13
Santandrea, C. ....	V9
Schatz, G. C. ....	ET19
Schleysing, R. ....	RE14
Schmoltner, A. M. ....	RE24
Schwenke, D. W. ....	RT11
Scoles, G. ....	SE6
Sedlacek, A. J. ....	RE30
Shafizedeh, N. ....	RE21
Shamarnian, V. A. ....	EE23
Shima, Y. ....	RT11
Shin, H. K. ....	V13
Shobatake, K. ....	RE10
Sinha, A. ....	P10
Siska, P. E. ....	EE24,EE26
Sivakumar, N. ....	V4,V5
Sizun, M. ....	ET20
Skene, J. M. ....	V8
Sloan, J. J. ....	RE13
Smith, G. P. ....	EE9
Smith, I. W. M. ....	RT25,RE25
Smith, M. A. ....	RE26
Snider, N. ....	ET21
Snider, R. F. ....	RT27
Song, M. ....	ET3
Sonnenfroh, D. M. ....	RE27
Sopchyshyn, F. C. ....	EE16
Spence, J. H. ....	RE28
Stephens, R. D. ....	RE5
Stephenson, J. C. ....	V2
Stolte, S. ....	RE33
Su, M.-C. ....	V1
Sun, Y. ....	RT11
Swaminathan, P. K. ....	RT24,ST9,ST10,ST11,P11
Tabor, K. D. ....	RE1
Taieb, G. ....	RE21
Teitelbaum, H. ....	ET22
Thompson, D. L. ....	RT10,ST8,ET17
Ticich, T. M. ....	P7
Tiszauer, D. H. ....	RT28
Toennies, J. P. ....	EE19,EE22
Truhlar, D. G. ....	RT11,RT26
Tucker, S. C. ....	RT26
Tuckett, R. P. ....	RE25
Turner, R. E. ....	RT27
Tzeng, W. B. ....	V12
Ulwick, S. J. ....	RE28
Utz, A. L. ....	EE3
Vaida, V. ....	V3
Valentini, J. J. ....	RE1,RE18
Vander Wal, R. ....	P10
van der Zande, W. J. ....	EE25
van Dishoeck, E. F. ....	P12
Varade, A. ....	V14
Vásquez, G. J. ....	P21
Vigué, J. ....	RE29

Villarreal, P.....	ET5,ET6,V14,V15
Visticot, J. P.....	RE17
Volpi, G. G.....	EE4,EE5
Wagner, A. F.....	RT4,RT29
Waldeck, J. R.....	P5,P13
Walker, R. B.....	RT22
Wall, E. J.....	RE20
Waller, I. M.....	P14,P15
Walters, E. A.....	V9
Wardlaw, D. M.....	RT29,RT30
Webb, B. S.....	EE21
Weiner, B. R.....	P16,P17
Weiser, C.....	EE26
Wen, Y.....	P20
Werner, H.-J.....	ET1
Weston, R. E. Jr.....	EE11,EE12,EE15
White, M. G.....	V9
Wight, C. A.....	RE30,P18
Williams, C. J.....	P19
Wise, M. L.....	EE8
Wu, X.....	P20
Xu, G.-Q.....	SE1
Xu, J.....	SE6
Yamashita, K.....	RT31
Yang, B.....	RE19
Yarkony, D. R.....	RT32
Yin, H. M.....	V12
Young, R. A.....	RE31
Zare, R. N.....	RT15,RT21,RE16,P5,P13
Zhang, J.....	P20
Zhang, J. Z. H.....	RT11
Zhang, Y.....	RT11
Zhang, X.-G.....	RT14,ST7
Zhong, X.....	P20
Zhu, Q.....	P20

REGISTERED ATTENDEES

1987 Conference on the Dynamics of Molecular Collisions  
Wheeling, West Virginia  
July 12-17, 1987

Paul J. Dagdigian, Chairman; William H. Miller, Vice Chairman

Dr. Pamela M. Aker  
Department of Chemistry  
University of California  
Irvine, CA 92717  
(714) 856-5266

Dr. Millard Alexander  
Department of Chemistry  
University of Maryland  
College Park, MD 20742  
(301) 454-2614

Dr. Ashraf Ali  
Department of Chemistry  
The Johns Hopkins University  
Baltimore, MD 21218  
(301) 338-4669

Dr. James B. Anderson  
Department of Chemistry  
Pennsylvania State University  
University Park, PA 16802  
(814) 865-3933

Dr. Scott L. Anderson  
Department of Chemistry  
State University of New York  
Stony Brook, NY 11794-3400  
(516) 632-7915

Mr. Billy J. Archer  
Department of Physics and Astronomy  
University of Oklahoma  
Norman, OK 73019  
(405) 325-3961

Dr. Michael Baer  
Israel Atomic Energy Commission  
Soreq Nuclear Research Institute  
Yavne 70 600, Israel

Dr. G. G. Balint-Kurti  
School of Chemistry  
University of Bristol  
Bristol BS8 ITS, U.K.  
0272-303 681

Dr. K. Bergmann  
Fachbereich Physik  
Universität Kaiserslautern  
Postfach 3049  
D-6750 Kaiserslautern  
Federal Republic of Germany  
(0631) 205-2671

Dr. Steven L. Bernasek  
Department of Chemistry  
Princeton University  
Princeton, NJ 08544  
(609) 452-4986

Dr. Anita Bersellini-Picard  
Laboratoire de Photophysique  
Moléculaire  
Bât. 213 Campus d'Orsay  
91405 Orsay Cedex, France  
(6) 941 78 73

Mr. Craig Bieler  
Department of Chemistry  
University of Pittsburgh  
Pittsburgh, PA 15260  
(412) 624-8681

Dr. Robert Bower  
Rocketdyne Division  
Rockwell International  
6633 Canoga Avenue, FA38  
Canoga Park, CA 91303  
(818) 700-3132

Dr. Frank Budenholzer  
Department of Chemistry  
Fu Jen Catholic University  
Hsinchuang 24205  
Taiwan, ROC  
Taipei (02) 901-4749

Dr. Joel M. Bowman  
Department of Chemistry  
Emory University  
Atlanta, GA 30322  
(404) 727-6592

Dr. Steven H. Buelow  
Los Alamos National Laboratory  
Mail Stop J567 CLS4  
Los Alamos, NM 87545  
(505) 667-1178

Dr. Edward J. Boyle  
U. S. Department of Energy  
Morgantown Energy Technology Center  
P. O. Box 880  
Morgantown, WV 26505  
(304) 291-4000

Mr. Steven A. Buntin  
Department of Chemistry  
University of Minnesota  
Minneapolis, MN 55455  
(612) 625-5092

Dr. Donald W. Brenner  
Department of Chemistry  
152 Davey Lab, Box 9  
University Park, PA 16802  
(814) 863-0289

Mr. Kirk Butz  
Department of Chemistry  
Indiana University  
Bloomington, IN 47405  
(812) 335-6700

Mr. Brian Brewer  
Department of Chemistry  
The Johns Hopkins University  
Baltimore, MD 21218  
(301) 366-1688

Dr. Mark Campbell  
U. S. Naval Academy  
N-3 Phythian Road  
Annapolis, MD 21402  
(301) 267-3403

Dr. Philip R. Brooks  
Chemistry Department  
Rice University  
Houston, TX 77251  
(713) 527-8101 Ext. 3266

Dr. Mark J. Cardillo  
AT&T Bell Laboratories  
Murray Hill, NJ 07974  
(201) 582-2418

Dr. Udo Buck  
Max Planck Institut für  
Strömungsforschung  
Bunsenstrasse 10  
D-3400 Göttingen,  
Federal Republic of Germany  
(0551) 709 2572

Ms. Karen J. Carlson  
Department of Chemistry  
University of Wisconsin  
Madison, WI 53706  
(608) 262-6101

Mr. Simon Cartwright  
Department of P. Chemistry  
Donnan Labs. - Grove St.  
Liverpool, U.K. L69 3BX  
(51) 709-6022 Ext. 2571

Ms. Jing Chen  
Department of Chemistry  
The Johns Hopkins University  
Baltimore, MD 21218  
(301) 338-4669

Dr. Michael P. Casassa  
National Bureau of Standards  
Molecular Spectroscopy Division  
Gaithersburg, MD 20899  
(301) 975-2371

Dr. Lue Yung Chow Chiu  
Department of Chemistry  
Howard University  
Washington, DC 20059  
(202) 636-6882

Dr. Piergiorgio Casavecchia  
Dipartimento di Chimica  
Università di Perugia  
Via Elce di Sotto, 8  
Perugia, Italy 06100  
(075) 44.332 - 41.326

Dr. Ying-Nan Chiu  
Department of Chemistry  
The Catholic Univ. of America  
Washington, DC 20064  
(202) 635-5385

Dr. Sylvia T. Ceyer  
Department of Chemistry  
Massachusetts Institute of Technology  
Cambridge, MA 02139  
(617) 253-4537

Dr. Mei-Chen Chuang  
Department of Chemistry  
University of CA-Berkeley  
Berkeley, CA 94720  
(415) 486-5269

Dr. David W. Chandler  
Sandia National Laboratories  
Division 8353  
Livermore, CA 94550  
(415) 422-3132

Mr. Joe Cline  
Department of Chemistry  
University of Pittsburgh  
Pittsburgh, PA 15260  
(412) 624-8681

Dr. Sally Chapman  
Barnard College  
Columbia University  
New York, NY 10027  
(212) 280-2098

Dr. Ronald B. Cohen  
Aerospace Corporation  
P. O. Box 92957  
Los Angeles, CA 90009-2957  
(213) 336-5946

Dr. Gunjit K. Chawla  
Department of Chemistry  
Cornell University  
Ithaca, NY 14853  
(607) 255-5376

Dr. Michael E. Coltrin  
Sandia National Laboratories  
P. O. Box 5800  
Albuquerque, NM 87185  
(505) 844-7843

Mr. Robert E. Continetti  
Department of Chemistry  
University of California  
Berkeley, CA 94720  
(415) 486-6447

Dr. Anthony V. Dentamaro  
Air Force Geophysics Laboratory  
AFGL/LIU  
Hanscom AFB, MA 01731  
(617) 377-4042

Dr. Richard A. Copeland  
SRI International  
Chemical Physics Laboratory  
333 Ravenswood Ave.  
Menlo Park, CA 94025  
(415) 859-6534

Dr. David A. Dolson  
Department of Chemistry  
Ohio State University  
Columbus, OH 43210  
(614) 292-2949

Mr. Michael Covinsky  
Department of Chemistry  
University of California  
Berkeley, CA 94720  
(415) 486-6447/5241

Dr. James Donaldson  
Department of Chemistry  
University of Colorado  
Boulder, CO 80309-0215  
(303) 492-1422

Dr. F. Fleming Crim  
Department of Chemistry  
University of Wisconsin  
Madison, WI 53706  
(608) 263-7364

Ms. Janet C. Drobits  
Department of Chemistry  
University of Pennsylvania  
Philadelphia, PA 29204-6323  
(215) 898-4762

Dr. Paul J. Dagdigian  
Department of Chemistry  
The Johns Hopkins University  
Baltimore, MD 21218  
(301) 338-7438

Dr. Ronald J. Duchovic  
Argonne National Laboratory  
Chemistry Division, Bldg. 200  
9700 South Cass Avenue  
Argonne, IL 60439  
(312) 972-4803

Mr. David Deaven  
Department of Chemistry  
Pennsylvania State Univ.  
University Park, PA 16802  
(814) 863-2103

Dr. Csilla Duneczky  
Department of Chemistry  
University of Texas  
Austin, TX 78712  
(512) 471-1023

Dr. G. Delgado-Barrio  
Instituto de Estructura de la Materia  
CSIC  
c/Serrano 123  
Madrid, 28006  
Spain  
4112962

Mr. Sylvain Durocher  
Departement de Chimie  
Université de Sherbrooke  
Sherbrooke, Québec J1K 2R1  
Canada  
821-7000 Ext. 3007

Dr. Charles W. Eaker  
Department of Chemistry  
University of Dallas  
Irving, TX 75062-4799  
(214) 721-5391

Dr. George W. Flynn  
Department of Chemistry  
Columbia University  
New York, NY 10027  
(212) 280-4162

Dr. Larry Eno  
Department of Chemistry  
Clarkson University  
Potsdam, NY 13676  
(315) 268-6559

Mr. Donald Frye  
Chemistry Department  
University of Pennsylvania  
Philadelphia, PA 19104  
(215) 898-6462

Mr. Dwight D. Evard  
Chemistry Department  
University of Pittsburgh  
Pittsburgh, PA 15260  
(412) 624-8681

Dr. J. W. Gadzuk  
National Bureau of Standards  
Surface Science Division  
Gaithersburg, MD 20899  
(301) 975-2548

Dr. James M. Farrar  
Department of Chemistry  
University of Rochester  
Rochester, NY 14627  
(716) 275-5834

Mr. John M. Gardner  
Department of Chemistry  
University of Pennsylvania  
Philadelphia, PA 19104-6323  
(215) 898-4762

Dr. John B. Fenn  
Department of Chemical Engineering  
P. O. Box 2159, Yale Station  
New Haven, CT 06520-2159  
(203) 432-4379

Dr. Bruce C. Garrett  
Chemical Dynamics Corporation  
9560 Pennsylvania Ave. Suite 106  
Upper Marlboro, MD 20772  
(301) 588-1050

Dr. George A. Fisk  
Sandia National Laboratories  
Division 8353  
P. O. Box 969  
Livermore, CA 94550  
(415) 422-3376

Dr. Bela Gazdy  
Department of Chemistry  
Emory University  
Atlanta, GA 30322  
(404) 727-6537

Dr. T. Rick Fletcher  
Joint Institute for Laboratory  
Astrophysics  
University of Colorado  
Boulder, CO 80309-0440  
(303) 492-6704

Dr. W. R. Gentry  
Department of Chemistry  
University of Minnesota  
Minneapolis, MN 55455  
(612) 625-3388

Mr. Savas Georgiou  
Department of Chemistry  
University of Utah  
Salt Lake City, UT 84112  
(801) 581-6285

Dr. R. B. Gerber  
Department of Physical Chemistry  
The Hebrew University of Jerusalem  
Jerusalem, Israel 91904

Dr. K.-H. Gericke  
Institut für Physikalische Chemie  
Universität Frankfurt  
Niederurselerhang  
D-6000 Frankfurt am Main 50  
Federal Republic of Germany  
(069) 5800 9405

Dr. Eric A. Gislason  
Chemistry Department  
University of Illinois at Chicago  
Chicago, IL 60680  
(312) 996-5423

Dr. Gary D. Greenblatt  
CIRES/NOAA  
Aeronomy Laboratory, NOAA, R/E/AL2  
325 Broadway  
Boulder, CO 80302  
(303) 497-5825

Dr. J. Robb Grover  
Brookhaven National Laboratory  
Department of Chemistry  
Upton, NY 11973  
(516) 282-4348

Dr. Yuhua Guan  
Department of Chemistry  
Oklahoma State University  
Stillwater, OK 74078-0447  
(405) 624-5940

Dr. Erol E. Gulcicek  
Department of Chemistry  
The Johns Hopkins University  
Baltimore, MD 21218  
(301) 338-4602

Dr. Gerhard E. Hahne  
NASA-Ames Research Center  
Mail Stop 230-3  
Moffett Field, CA 94035  
(415) 694-6140

Ms. Sally Hair  
Department of Chemistry  
University of Pittsburgh  
Pittsburgh, PA 15260  
(412) 624-8681

Dr. Nadine Halberstadt  
Department of Chemistry  
University of Pittsburgh  
Pittsburgh, PA 15260  
(412) 624-8452

Mr. Luke Hanley  
Department of Chemistry  
State University of New York  
Stony Brook, NY 11794-3400  
(516) 632-7913

Dr. Harold H. Harris  
Department of Chemistry  
University of Missouri  
St. Louis, MO 63121  
(314) 553-5344

Dr. William L. Hase  
Wayne State University  
435 Chemistry  
Detroit, MI 48202  
(313) 577-2694

Dr. Eckart Hasselbrink  
Department of Chemistry  
Stanford University  
Stanford, CA 94305  
(415) 723-4398

Mr. Ken Haug  
Department of Chemistry  
University of Minnesota  
Minneapolis, MN 55455  
(612) 624-9843

Dr. Peter Hering  
Max-Planck-Institut für Quantenoptik  
Forschungsgelände  
D-8046 Garching bei München  
Federal Republic of Germany  
(89) 32905 216

Dr. John F. Hershberger  
Columbia University  
Box 214 Havemeyer Hall  
New York, NY 10027  
(212) 280-5026

Mr. Scott Hewitt  
Department of Chemistry  
Columbia University  
New York, NY 10027  
(212) 280-5026

Professor Leif Holmlid  
Department of Physical Chemistry  
University of Göteborg and  
Chalmers University of Technology  
S-41296 Göteborg, Sweden  
(031) 810100 Ext. 1528

Dr. Kenji Honma  
Department of Pure and Applied Science  
University of Tokyo  
3-8-1 Komaba, Meguro-ku  
Tokyo 153, Japan

Dr. David S. Hsu  
Naval Research Laboratory  
Code 6105  
4555 Overlook Ave., SW  
Washington, DC 20375-5000  
(202) 767-2742

Mr. Xiche Hu  
Wayne State University  
435 Chemistry  
Detroit, MI 48202  
(313) 577-2694

Dr. Alan D. Isaacson  
Department of Chemistry  
Miami University  
Oxford, OH 45056  
(513) 529-2832

Dr. Bret E. Jackson  
Department of Chemistry  
University of Massachusetts  
Amherst, MA 01003  
(413) 545-2583

Dr. Richard L. Jaffe  
NASA Ames Research Center  
RTC:230-3  
Moffett Field, CA 94035  
(415) 694-6458

Dr. A. Keith Jameson  
Department of Chemistry  
Loyola University  
Chicago, IL 60626  
(312) 508-3134

Dr. Cynthia J. Jameson  
Department of Chemistry  
University of Illinois at Chicago  
Chicago, IL 60680  
(312) 996-2352

Dr. Kenneth C. Janda  
Department of Chemistry  
University of Pittsburgh  
Pittsburgh, PA 15260  
(412) 624-8680

Mr. M. H. M. Janssen  
Molekuul-en Laserfysika  
Universiteit Nijmegen  
Toernooiveld  
6525 ED Nijmegen  
The Netherlands  
080-613029

Dr. Ralph Jaquet  
FB 8 - Theoretische Chemie  
Adolf-Reichwein-Strasse 2  
D 5900 Siegen 21 (Weidenau)  
Federal Republic of Germany

Dr. Jay B. Jeffries  
SRI International  
Chemical Physics Laboratory  
333 Ravenswood Ave.  
Menlo Park, CA 94025  
(415) 859-6341

Dr. Anne D. Johnston  
Los Alamos Nat'l. Lab.  
P. O. Box 1663 MS J567  
Los Alamos, NM 87545  
(505) 667-1180

Dr. Patrick L. Jones  
Department of Chemistry  
Ohio State University  
Columbus, OH 43210  
(614) 292-9489

Dr. Yonathan Karni  
Atomic Energy Commission  
P. O. B. 9001  
Beer Sheva, Israel

Dr. Daniel H. Katayama  
Air Force Geophysics Lab. (LIU)  
Hanscom Air Force Base, MA 01731  
(617) 377-4042

Dr. Bruce D. Kay  
Sandia National laboratory  
Org. 1841  
P. O. Box 5800  
Albuquerque, NM 87185  
(505) 844-3742

Mr. Ronald Kay  
Department of Chemistry  
Ohio State University  
Columbus, OH 43210  
(614) 292-0089

Mr. Young Sik Kim  
Department of Physics & Astronomy  
239 Fronczak Hall  
SUNY-Buffalo  
Buffalo, NY 14260

Dr. Donald J. Kouri  
Department of Chemistry  
University of Houston  
Houston, TX 77004  
(713) 749-2845

Mr. Joel D. Kress  
Department of Chemistry  
Iowa State University  
Ames, IA 50011  
(515) 294-9926/9927

Mr. Thomas G. Kreutz  
Chemistry Department  
Columbia University  
New York, NY 10027  
(212) 280-5026

Mr. E. J. Kruus  
National Research Council Canada  
Division of Chemistry  
100 Sussex Drive  
Ottawa, K1A 0R6, Canada

Dr. A. Laganá  
Dipartimento di Chimica  
Università di Perugia  
Via Elce di Sotto, 8  
06100 Perugia, Italy  
(075) 44332

Dr. Yuan T. Lee  
Department of Chemistry  
University of California  
Berkeley, CA 94720  
(415) 486-6154

Mr. Didier Lemoine  
Department of Chemistry  
University of Maryland  
College Park, MD 20742  
(301) 454-4709

Dr. Stephen Leone  
JILA  
University of Colorado  
Boulder, CO 80309  
(303) 492-5128

Dr. Marsha I. Lester  
Department of Chemistry  
University of Pennsylvania  
Philadelphia, PA 19104-6323  
(215) 898-4640

Dr. R. D. Levine  
The Hebrew University  
The Fritz Haber Research Center  
for Molecular Dynamics  
Jerusalem, Israel 91904  
(972-2) 585343

Dr. Daniel A. Lichtin  
The Aerospace Corporation  
P. O. Box 92957  
Mail Stop: M5-754  
Los Angeles, CA 90009  
(213) 336-1608

Mr. Michael D. Likar  
Department of Chemistry  
University of Wisconsin  
Madison, WI 53706  
(608) 262-6101

Dr. S. M. Lin  
Institute of Atomic and  
Molecular Sciences  
P.O. Box 23-166  
Taipei, Taiwan  
Republic of China

Dr. James M. Lisy  
Department of Chemistry  
University of Illinois  
Urbana, IL 61801  
(217) 333-2898

Dr. Kopin Liu  
Argonne National Laboratory  
Chemistry Division  
Argonne, IL 60439  
(312) 972-7744

Professor H. J. Loesch  
Universität Bielefeld  
Universitätsstrasse 1  
D-4800 Bielefeld  
Federal Republic of Germany  
106 5418

Dr. R. G. Macdonald  
Argonne National Laboratories  
Chemistry Division  
Argonne, IL 60439  
(312) 972-7742

Dr. James McAndrew  
Department of Chemistry  
Brookhaven National Laboratory  
Upton, NY 11973  
(516) 282-4372

Mr. George C. McBane  
Cornell University  
Box 426 Baker Lab.  
Ithaca, NY 14853  
(607) 255-0573/5152

Dr. G. T. McConville  
Monsanto Research Corp.  
Mound Facility  
P. O. Box 32  
Miamisburg, OH 45342  
(513) 865-3202

Dr. F. R. McCourt  
Department of Chemistry  
University of Waterloo  
Waterloo, Ontario N2L 3G1  
Canada  
(519) 885-1211 Ext. 3024

Dr. Everett McGinley  
Max-Planck-Institut für Quantenoptik  
D8046 Garching  
Federal Republic of Germany  
(89) 32905-217

Dr. J. Manz  
Institut für Physikalische Chemie  
Universität Würzburg  
Marcusstr. 9-11  
Würzburg, 0-8700  
Federal Republic of Germany  
(0937) 31514

Dr. Howard R. Mayne  
Department of Chemistry  
University of New Hampshire  
Durham, NH 03824  
(603) 862-2529

Dr. M. Menzinger  
Department of Chemistry  
University of Toronto  
Toronto, Ontario M5S 1A1  
Canada  
(416) 978-6158

Dr. Jean-Michel Mestdagh  
C. E. N. Saclay  
Service de Physique des Atomes  
et des Surface  
91191 Gif sur Yvette Cedex  
France  
(1) 69 08 65 51

Dr. H. Metiu  
Department of Chemistry  
University of California  
Santa Barbara, CA 93106  
(805) 961-2256

Professor W. Meyer  
Fachbereich Chemie  
Universität Kaiserslautern  
D-6750 Kaiserslautern  
Federal Republic of Germany  
(631) 205-2581

Dr. David A. Micha  
Quantum Theory Project  
University of Florida  
Gainesville, FL 32611  
(904) 392-6977

Dr. Frederick H. Mies  
National Bureau of Standards  
Room B268 Physics Building  
Gaithersburg, MD 20899  
(301) 975-2359

Dr. Roger E. Miller  
Department of Chemistry  
University of North Carolina  
Chapel Hill, NC 77514  
(919) 966-5433

Dr. William H. Miller  
Department of Chemistry  
University of California  
Berkeley, CA 94720  
(415) 642-0653

Dr. Daniel Neumark  
Department of Chemistry  
University of California  
Berkeley, CA 94720  
(415) 642-3502

Dr. Timothy K. Minton  
Department of Chemistry  
University of Illinois  
Urbana, IL 61801  
(217) 333-7606

Professor Cheuk-Yiu Ng  
Department of Chemistry  
Iowa State University  
Ames, IA 50011  
(515) 294-4225

Dr. Louis Monchick  
Applied Physics Laboratory  
The Johns Hopkins University  
Laurel, MD 20707  
(301) 792-6226

Professor T. Tung Nguyen-Dang  
Département de Chimie  
Université de Sherbrooke  
Sherbrooke, Québec  
Canada J1K 2R1  
(819) 821-7086

Dr. Joseph F. Moryl  
Department of Chemistry  
Ohio State University  
Columbus, OH 43210  
(614) 292-0089

Mr. Gereon Niedner  
Max-Planck-Institut für  
Strömungsforschung  
Bunsenstrasse 10  
3400 Göttingen  
Federal Republic of Germany  
(0551) 709 2614

Dr. James T. Muckerman  
Chemistry Department  
Brookhaven National Laboratory  
Upton, NY 11973  
(516) 282-4368

Ms. B. I. Niefer  
National Research Council Canada  
Division of Chemistry  
100 Sussex Drive  
Ottawa K1A 0R6  
Canada

Mr. Mark Muyskens  
Chemistry Department  
University of Wisconsin  
Madison, WI 53706  
(608) 262-6101

Mr. Jong-chen Nieh  
Department of Chemistry  
University of California  
Irvine, CA 92715  
(714) 856-3319

Dr. Gilbert Nathanson  
Department of Chemistry  
University of California  
Berkeley, CA 94720

Mr. Kevin Norwood  
Ames Laboratory  
Iowa State University  
Ames, IA 50011  
(515) 294-9990

Dr. David Nesbitt  
Joint Institute for Laboratory  
Astrophysics  
University of Colorado  
Boulder, CO 80309-0440  
(303) 492-8857

Mr. Sohail Nourbakhsh  
Ames Laboratory  
Iowa State University  
Ames, IA 50011  
(515) 294-9990

Dr. Thomas J. O'Brien  
U. S. Department of Energy  
Morgantown Energy Technology Center  
P. O. Box 880  
Morgantown, WV 26505  
(304) 291-4571

Mr. Thomas M. Orlando  
Department of Chemistry  
State University of New York  
Stony Brook, NY 11794  
(516) 632-7913

Dr. H. Jörg Osten  
Academy of Sciences of the GDR  
Central Inst. of Physical Chemistry  
1199 Berlin, Rudower Chaussee 6  
German Democratic Republic

Dr. Shao-Hua Pan  
National Bureau of Standards  
Room B268 Physics Building  
Gaithersburg, MD 20899  
(301) 975-2364

Dr. Gregory A. Parker  
Department of Physics  
University of Oklahoma  
Norman OK 73019  
(405) 325-3961

Dr. Charles S. Parmenter  
Department of Chemistry  
Indiana University  
Bloomington, IN 47405  
(812) 335-3522

Dr. John M. Parson  
Chemistry Department  
Ohio State University  
Columbus, OH 43210  
(614) 292-3267

Dr. Merle D. Pattengill  
Department of Chemistry  
University of Kentucky  
Lexington, KY 40506  
(606) 257-4741

Mr. Stephen M. Penn  
Department of Chemistry  
University of Wisconsin  
Madison, WI 53706  
(608) 262-9902

Dr. Marie-Yvonne Perrin  
Laboratoire E.M2.C du  
C N R S et de l'ECP  
Ecole Centrale des Arts et  
Manufactures  
92295 Chatenay Malabry Cedex  
France  
(1) 47 02 70 56

Dr. Brigitte Pouilly  
Department of Chemistry  
University of Maryland  
College Park, MD 20742  
(301) 454-4709

Dr. Aleksandra Preiskorn  
Department of Chemistry  
Oklahoma State University  
Stillwater, OK 74078-0447  
(405) 624-5940

Dr. Michael G. Prisant  
Department of Chemistry  
University of California  
Berkeley, CA 94720

Mr. George A. Raiche  
Department of Chemistry  
Dartmouth College  
Hanover, NH 03755  
(603) 646-2115

Mr. Mark W. Rainbird  
School of Science  
Griffith University  
Nathan QLD 4111 Australia  
(07) 275 7587

Mr. David J. Rakestraw  
Department of Chemistry  
Stanford University  
Stanford, CA 94305  
(415) 723-4334

Dr. Michael J. Redmon  
Chemical Dynamics  
9560 Pennsylvania Avenue  
Upper Marlboro, MD 20772  
(301) 599-1050

Mr. Brian Reid  
Chemistry Department  
University of Pittsburgh  
Pittsburgh, PA 15260  
(412) 624-8681

Ms. Betsy M. Rice  
Department of Chemistry  
Oklahoma State University  
Stillwater, OK 74078  
(405) 624-6543

Dr. Thomas R. Rizzo  
Department of Chemistry  
University of Rochester  
Rochester, NY 14627  
(716) 275-2304

Dr. Jean-Michel Robbe  
Université de Lille I.  
UER de Physique Fondamentale  
Bât. P5  
559655 Villeneuve d'Ascq Cedex  
France  
20-43-48-99

Mr. Gary Robinson  
Department of Chemistry  
University of California  
Berkeley, CA 94720  
(415) 486-6447

Mr. Paul A. Rowntree  
Department of Chemistry  
University of Waterloo  
Waterloo, Canada N2L 3G1  
(519) 885-1211 Ext. 3845

Mr. Horst-Günter Rubahn  
Max-Planck Institut für  
Strömungsforschung  
3400 Göttingen  
Federal Republic of Germany  
0551 709 2621

Ms. Deborah G. Sauder  
Department of Chemistry  
The Johns Hopkins University  
Baltimore, MD 21218  
(301) 338-4669

Dr. Ross Sausa  
U.S. Army Ballistic  
Research Laboratory  
SLCIBR-IB-I  
Aberdeen P. G., MD 21005-5066  
(301) 278-7070

Dr. George C. Schatz  
Department of Chemistry  
Northwestern University  
Evanston, IL 60201  
(312) 491-5657

Dr. Reinhard Schinke  
MPI Strömungsforschung  
Bunsenstrasse 10  
D-3400 Göttingen,  
Federal Republic of Germany  
0551-709-2725

Ms. Anne-Marie Schmoltner  
Department of Chemistry  
University of California  
Berkeley, CA 94720

Dr. Tracy Schoolcraft  
Department of Chemistry  
Pennsylvania State University  
University Park, PA 16802  
(814) 863-0219

Mr. Vasgen A. Shamamian  
Department of Chemistry  
University of Minnesota  
Minneapolis, MN 55455  
(612) 625-5092

Dr. Shenghua Shi  
Department of Chemistry  
Princeton University  
Princeton, NJ 08544  
(609) 452-6453

Professor H. K. Shin  
Department of Chemistry  
University of Nevada  
Reno, NV 89557  
(702) 784-6684

Professor S. J. Sibener  
Department of Chemistry  
University of Chicago  
Chicago, IL 60637  
(312) 962-7193

Dr. Amit Sinha  
Department of Chemistry  
University of Wisconsin  
Madison, WI 53706  
(608) 262-6101

Dr. Peter E. Siska  
Department of Chemistry  
University of Pittsburgh  
Pittsburgh, PA 15260  
(412) 624-8640

Dr. M. Sizun  
Laboratoire des Collisions  
Atomiques et Moléculaires  
Université Paris-Sud  
Bâtiment 351  
91405 Orsay Cedex  
France  
(1) 6941 7694

Dr. J. J. Sloan  
Division of Chemistry  
National Research Council Canada  
100 Sussex Drive, Rm. 1081  
Ottawa, K1A 0R6  
Canada  
(613) 990-0980

Professor I. W. M. Smith  
Department of Chemistry  
University of Birmingham  
P. O. Box 363  
Birmingham, B15 2TT  
United Kingdom  
021-472-1301 Ext. 3292

Professor Mark A. Smith  
Department of Chemistry  
University of Arizona  
Tucson, AZ 85721  
(602) 621-2999

Professor Deanne L. Snavely  
Department of Chemistry  
Bowling Green State University  
Bowling Green, OH 43403-0213  
(419) 372-2664

Dr. Neil Snider  
Department of Chemistry  
Queen's University  
Kingston K7L 3N6  
Canada  
(613) 545-2631

Professor Robert F. Snider  
Department of Chemistry  
University of British Columbia  
Vancouver V6T 1Y6  
Canada  
(604) 228-2537

Dr. David M. Sonnenfroh  
Joint Inst. for Laboratory Astrophysics  
University of Colorado  
Boulder, CO 80309  
(303) 492-1265

Mr. James H. Spence  
Department of Chemistry  
Rice University  
Houston, TX 77001  
(713) 527-4844

Dr. John C. Stephenson  
National Bureau of Standards  
Building 221, Room B268  
Gaithersburg, MD 20899  
(301) 975-2372

Professor Thomas A. Stephenson  
Department of Chemistry  
Swarthmore College  
Swarthmore, PA 19081  
(215) 328-8561

Mr. Charles Strauss  
212 Clark Hall  
Cornell University  
Ithaca, NY 14853  
(607) 255-6419

Dr. Ming-Chih Su  
Department of Chemistry  
Indiana University  
Bloomington, IN 47405

Dr. P. K. Swaminathan  
Chemical Dynamics  
9560 Pennsylvania Ave., Suite 106  
Upper Marlboro, MD 20772  
(301) 599-1050

Dr. Guy Taieb  
Laboratoire de Photophysique  
Moléculaire du CNRS  
Bâtiment 213  
Université de Paris-Sud  
91405 Orsay Cedex  
France

Professor Heshel Teitelbaum  
Department of Chemistry  
University of Ottawa  
Ottawa, Ont. K1N 9B4  
Canada  
(613) 564-2930

Professor Donald L. Thompson  
Department of Chemistry  
Oklahoma State University  
Stillwater, OK 74078  
(405) 624-5174

Mr. Detlev H. Tiszauer  
Department of Applied Science  
University of California, Davis  
P. O. Box 808, L794  
Livermore, CA 94550

Dr. Donald G. Truhlar  
Smith Hall  
University of Minnesota  
Minneapolis, MN 55455  
(612) 624-7555

Ms. Susan C. Tucker  
Department of Chemistry  
University of Minnesota  
Minneapolis, MN 55455  
(612) 624-9843

Dr. J. C. Tully  
AT&T Bell Laboratories  
Room 1D-346  
Murray Hill, NJ 07974  
(201) 582-3619

Dr. Arthur Utz  
Department of Chemistry  
University of Wisconsin  
Madison, WI 53706  
(608) 262-6101

Professor T. Uzer  
School of Physics  
Georgia Institute of Technology  
Atlanta, GA 33032  
(404) 894-4986

Mr. W. J. van der Zande  
FOM-Instituut voor Atoom-en  
Molecuulfysica  
Kruislaan 407  
1098 SJ Amsterdam  
The Netherlands  
NL-(0)20-946711

Dr. Ewine F. van Dishoeck  
The Institute for Advanced Study  
School of Natural Sciences, Bldg. E  
Princeton, NJ 08540  
(609) 734-8013

Dr. Gabriel Vasquez  
Instituto de Fisica  
Universidad Nacional Autónoma  
de México  
Apartado Postal 139-B  
Cuernavaca, Mor. 62190  
Mexico

Professor Ram Vasudev  
Department of Chemistry  
Rutgers University  
New Brunswick, NJ 08903  
(201) 932-3667

Dr. Jacques Vigué  
Laboratoire de Spectroscopie  
Hertzienne de l'E.N.S.  
24 Rue Lhomond  
751231 Paris Cedex 05  
France  
43 29 1225 p3379

Professor Pablo Villarreal  
Inst. de Estructura de la Materia  
CSIC  
c/Serrano 123  
Madrid 28006  
Spain  
411 2962

Dr. Jean-Paul Visticot  
C.E.N. Saclay  
Service de Physique des Atomes  
et des Surface  
91191 Gif sur Yvette Cedex  
France  
(1) 6908 6843

Dr. Albert F. Wagner  
Argonne National Laboratory  
200 R-109  
Argonne, IL 60439

Ms. Janet R. Waldeck  
Department of Chemistry  
Stanford University  
Stanford, CA 94305  
(415) 723-4332

Dr. Irene M. Waller  
Centre for Molecular Beam  
and Laser Chemistry  
University of Waterloo  
Waterloo, Ont. N2L 3G1  
Canada  
(519) 885-1211 Ext. 6396

Dr. David M. Wardlaw  
Department of Chemistry  
Queen's University  
Kingston, Ont. K7L 3N6  
Canada  
(613) 545-2632

Dr. Brad R. Weiner  
Chemistry Division, Code 6111  
Naval Research Laboratory  
Washington, DC 20375  
(202) 767-2398

Ms. Cindy Weiser  
Department of Chemistry  
University of Pittsburgh  
Pittsburgh, PA 15260  
(412) 624-8645

Professor Charles A. Wight  
Department of Chemistry  
University of Utah  
Salt Lake City, UT 84112  
(801) 581-8796

Mr. Carl J. Williams  
The James Franck Institute  
University of Chicago  
Chicago, IL 60637  
(312) 702-7223

Dr. Francis J. Wodarczyk  
AFOSR/NC  
Bolling AFB  
Washington, DC 20332  
(202) 767-4963

Mr. Eric Woodbridge  
Joint Institute for Laboratory  
Astrophysics  
University of Colorado  
Boulder, CO 80309-0440  
(303) 492-1528

Mr. Ren Xu  
Department of Chemistry  
Iowa State University  
Ames, IA 50011  
(515) 294-9990

Dr. Koichi Yamashita  
Institute for Molecular Science  
Myodaiji, Okazaki 444  
Japan  
(0564) 54-1111

Professor David R. Yarkony  
Department of Chemistry  
The Johns Hopkins University  
Baltimore, MD 21218  
(301) 338-7462

Professor Richard N. Zare  
Department of Chemistry  
Stanford University  
Stanford, CA 94305  
(415) 723-3062

Dr. Qiyuan Zhang  
Department of Chemistry  
152 Davey Laboratory  
Pennsylvania State University  
University Park, PA 16802  
(814) 863-0289

Professor Qihe Zhu  
Institute of Chemistry  
Academia Sinica  
Beijing  
People's Republic of China

Dr. William R. Creasy  
Naval Research Laboratory  
Chemistry Division/Code 6110  
Washington, DC 20375  
(202) 767-2398

## LAST MINUTE CORRECTIONS

### Additional Registrations

Dr. William A. M. Blumberg  
Air Force Geophysics Laboratory  
AFGL/LSI  
Hanscom AFB, MA 01731  
(617) 377-2810/3688

Prof. Tatsuo Arikawa  
Tokyo University of Agriculture  
& Technology  
Koganei-shi  
Tokyo 184, JAPAN  
0423-81-4221

Prof. Mark Keil  
Department of Chemistry  
Univeristy of Alberta  
Edmonton, Alberta T6G 2G2  
CANADA  
(403) 432-2853

Prof. Joyce Guest  
Department of Chemistry  
University of Cincinnati  
Cincinnati, OH 45221

Dr. Russell Johnson  
National Bureau of Standards  
Room A147, Bldg. 222  
Gaithersburg, MD 20899  
(301) 975-2513

### Cancelled Registrations

R. B. Cohen  
L. Eno  
G. Greenblatt  
T. Tung Nguyen-Dang  
G. Vasquez

### Cancelled Posters

RT6, RT7, RE8, ST7, P21

### Additional Posters

RE24a - D. Neumark and Y. T. Lee  
RT33 - C. Dunczky and R. E. Wyatt  
EE29 - W. A. M. Blumberg

END

10-87

DTIC