**REPORT DOCUMENTATION PAGE**

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- **AUTHOR(S)**: Curt Wittig, Hanna Reisler, Robert Beaudet, and Gerald Segal
- **PERIOD COVERED**: From 10/87 to 12/88
- **DATE OF REPORT**: December 28, 1988
- **DATE OF PAGE**: December 28, 1988

**ABSTRACT**:
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.

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I. Research

High-energy, collision-induced reactions at surfaces

This work is presently devoted to the study of high-energy collisions between polyatomic molecules and surfaces. A significant advance was made with this experiment during the past year. A year ago, we were at the stage of studying inelastic scattering of small molecules from surfaces under UHV conditions, with state-specific detection of scattered species. We are now able to study collision-induced chemical reactions at several eV (usually < 10) incident kinetic energy. Under these conditions, the molecule-surface interaction is impulsive (i.e. as near as we can determine, there is little or no 'sticking') and capable of distorting the molecule enough to induce unimolecular decomposition following collision with the surface. This has allowed us to move to larger molecular systems, leaving behind experiments involving vibrational and rotational energy transfer in small species such as NO. Our first experiments on collision-induced dissociation were with n-C₃F₇NO. The NO fragment was detected state-selectively using 2-photon 2-frequency laser ionization, and it proved possible to obtain high S/N with dissociation probabilities as low as 1%. This work has been submitted for publication and was presented at our ARO Energetic Materials Symposium (August, 1988) and an ACS Meeting (September, 1988). A parallel set of photofragmentation studies with C₃F₇NO was initiated and showed that many features of the surface-molecule results could be reproduced with photodissociation of the isolated gaseous molecule. This suggests that the energized precursors are similar in the two experiments, and suggests further that the excited molecules may well dissociate via a unimolecular decomposition mechanism. The emphasis with these experiments is to firmly establish the reaction mechanism. If it turns out that the surface is simply vehicular to converting incident kinetic energy into molecular internal energy, then it will be possible to apply the method to a large number of cases in which molecules are excited using this technique in order to bring about reaction.

We were also able to start experiments with 2-methyl-5-vinyl tetrazole (MVT). In its polymeric form, this material is a binder with several desirable properties (e.g. desensitization, somewhat energetic), and in monomeric form it has adequate stability and vapor pressure for molecular beam experiments. This was done in collaboration with Dr. Indu Mishra (BRL) who provided the samples and participated in the experiments.
Molecular beams of MVT monomer were prepared by expanding MVT/H₂ mixtures into vacuum, and collisions with MgO(100) surfaces were shown to result in significant internal excitation and possibly dissociation. The point here is to examine the different excitation/reaction pathways under conditions of impulsive excitation. The method is applicable to species such as RDX, and, as stated above, provides a clear upper bound to the energy available to the system (i.e. the incident kinetic energy). A short internal write-up is available (E. Kolodney, P.S. Powers, H. Reisler, C. Wittig and I.B. Mishra) but these preliminary results are not yet ready for publication. These results were presented at the Energetic Materials Symposium (August, 1988) and an abstract has been submitted and accepted for presentation at the 1989 Detonation Symposium. The work is ongoing and we are optimistic about future prospects. In a recent visit by Dr. Mishra, it was learned that nitrosyl groups can be placed selectively in the tetrazoles, thus providing the needed 'chromophore' for establishing dissociation.

**Reactions in clusters**

During the past year, our studies of bimolecular reactions in clusters changed from systems involving CO₂ (e.g. CO₂-HBr) to those involving nitrogen oxides. Our last paper on the CO₂-HBr system was written up and will appear soon in Chemical Physics Letters. The first of the nitrogen oxide systems examined was H+N₂O using N₂O-HBr complexes, which can react via both NH+NO and OH+N₂ channels. The H+N₂O reaction is important in combustion, and has been studied both experimentally and theoretically. The low energy channels have been computed ab initio and suggest a mechanism (1,3 hydrogen shift to form OH+N₂) that has far-reaching implications. We have determined several channels under bulk (i.e. single-collision, arrested-relaxation) conditions and in complexes, and have measured the [NH]/[OH] ratio. This has been written-up (G. Hoffmann, D. Oh, H. Iams and C. Wittig, Chem. Phys. Lett., (1988) accepted pending minor changes) and a larger paper has been prepared in connection with the Faraday Discussion being held in Bad Honnef, West Germany (12-14 December, 1988). It will be possible to pursue the very fundamental aspects of this work with NSF support and we plan to push the complexes to species such as NO₂, RNO₂, etc.

**Spectroscopy**

A parallel effort in which high-resolution spectroscopy is used to measure structures of complexes progressed rapidly during the past year. Data acquisition is now quite rapid, and the recording of spectra is routine, except for the fact that the suppliers of
diode lasers (Laser Analytics) is unreliable and it is quite miserable trying to set suitable diodes for our experiments. The analyses of these data are also progressing nicely - the average time to go from a spectrum to a structure is now ~ 1 month. During the past year, we finished an 'initiation rites' project (CO$_2$-Ar) and have now recorded spectra of CO$_2$-HF, CO$_2$-HCl and CO$_2$-HBr. These are being analyzed and the results will be written-up shortly. Spectra have also been recorded for N$_2$O-Ar and N$_2$O-N$_2$. We will do N$_2$O-HF, N$_2$O-HCl, and N$_2$O-HBr next. The last species have been instrumental in our studies of the H+N$_2$O reaction. We anticipate continued improvements in the data acquisition and reduction rates. In the near future, we hope to produce complexes consisting of a free radical and a stable molecule.

**Theory**

The theory effort in support of these and similar experiments did well last year. About a half dozen projects were completed. These ranged from not-so-relevant starter projects (e.g. H+ClCN, NCNO, NOCl) to recent studies of H+N$_2$O and HNO$_3$. 
II. Equipment

During the past year, several experiments were built/completed for our ARO-sponsored research: (i) A second chamber for the work with complexes was finished this past summer and is now in full operation. (ii) A tunable diode laser spectrometer was built and is in operation except for an insidious RF-pickup problem that we have just recently solved with a screen room. This apparatus was not mentioned in the last section because it did not produce publishable data during the past year. It will be used to study the decomposition of materials such as dimethyl nitramine (i.e. the diode laser can find fragments such as NO, NO2, OD, etc.). (iii) Our molecule-surface scattering apparatus (also AFOSR sponsored) was modified slightly to accommodate species such as MVT, RDX, and tetranitromethane. (iv) The high-resolution spectroscopy machine has been producing publishable results during the past year and was modified so that spectra can be recorded very quickly (i.e. a 2 cm⁻¹ tuning range at 0.0003 cm⁻¹ resolution can be covered in less than 5 min.). (v) Our photodissociation spectrometer (also NSF sponsored) was moved into new Center space associated with Professor Reisler’s tenured appointment. This has provided a data base on the photophysics and photodissociation of nitroso molecules that is used in the surface-molecule collision induced dissociation studies.
III. Students and postdocs

Student recruiting has been, and remains, a very central part of the Center’s activities. More than anything else, it is the enlistment and participation of first-rate graduate students during their formative years that will impact future research in energetic materials. During the past year, a new departmental brochure was developed that explicitly presented the Center as a major entity in Physical Chemistry at USC. In addition, a separate 23 page brochure, exclusive to the Center, was developed this past summer, and following examination at the ARO review (Aug. 8) has now been printed. Along with posters having tear-off postcards, they were sent to approximately 250 colleges and universities. Highly-qualified applicants are brought to USC for interviews.

The 1988 Department of Chemistry class of incoming graduate students is the best in its history. This is overwhelmingly true in Physical Chemistry, where 2 NSF predoctoral fellows and one University merit fellow also add to the ARO program. One can never prove cause/effect in such a situation. However, Curt Wittig wrote the brochures and is heavily involved in graduate student recruitment, and it is our reasoned opinion that the Center’s activities and recruitment drive are responsible for a major change in the Department of Chemistry’s graduate program. There are other side benefits as well. Morale is high, new faculty positions have been made available by the administration, and the increased level of research activity has been instrumental in obtaining new laboratory space (a $30,000,000 building is envisioned for the early 90's).
Graduate students and postdoctoral fellows working on ARO-funded projects

<table>
<thead>
<tr>
<th>Name</th>
<th>Status</th>
<th>Advisor</th>
<th>Project</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eli Kolodney(b)</td>
<td>postdoctoral</td>
<td>Reisler/Wittig</td>
<td>surfaces</td>
</tr>
<tr>
<td>Scott Powers</td>
<td>graduate student</td>
<td>Wittig</td>
<td>surfaces</td>
</tr>
<tr>
<td>Delroy Baugh</td>
<td>graduate student</td>
<td>Wittig</td>
<td>surfaces</td>
</tr>
<tr>
<td>Lori Iwata(c)</td>
<td>graduate student</td>
<td>Reisler/Wittig</td>
<td>surfaces</td>
</tr>
<tr>
<td>Günter Hoffmann(a)</td>
<td>postdoctoral</td>
<td>Wittig</td>
<td>complexes</td>
</tr>
<tr>
<td>Daniel Oh</td>
<td>postdoctoral</td>
<td>Wittig</td>
<td>complexes</td>
</tr>
<tr>
<td>Yongqin Chen(a)</td>
<td>postdoctoral</td>
<td>Wittig</td>
<td>complexes</td>
</tr>
<tr>
<td>Helen Iams</td>
<td>graduate student</td>
<td>Wittig</td>
<td>complexes</td>
</tr>
<tr>
<td>Steven Sharpe</td>
<td>postdoctoral</td>
<td>Beaudet</td>
<td>spectroscopy</td>
</tr>
<tr>
<td>Yongpin Zeng(d)</td>
<td>graduate student</td>
<td>Beaudet</td>
<td>spectroscopy</td>
</tr>
<tr>
<td>Diane Reifschneider</td>
<td>graduate student</td>
<td>Beaudet</td>
<td>spectroscopy</td>
</tr>
<tr>
<td>Raphael Lavi</td>
<td>postdoctoral</td>
<td>Wittig</td>
<td>photodissociation/kinetics</td>
</tr>
<tr>
<td>Scott Nickolaisen(e)</td>
<td>graduate student</td>
<td>Wittig</td>
<td>kinetics</td>
</tr>
<tr>
<td>Amy Ogai(c)</td>
<td>graduate student</td>
<td>Reisler</td>
<td>photodissociation</td>
</tr>
<tr>
<td>Charles Qian(a)</td>
<td>postdoctoral</td>
<td>Reisler</td>
<td>photodissociation</td>
</tr>
<tr>
<td>Yi-Yan Bai</td>
<td>postdoctoral</td>
<td>Segal</td>
<td>theory</td>
</tr>
</tbody>
</table>

(a) also supported by NSF
(b) Chaim Weizmann Postdoctoral Fellow, also supported by AFOSR
(c) NSF Predoctoral Fellowship
(d) Teaching Assistant
(e) University Merit Fellowship
IV. Communication

During 1988, we had several visitors from Army and other DOD labs and organizations. Some visits were of the information-exchange type and lasted for a day or less [e.g. Dr. Richard Paur (ARO) and Dr. Michael Schroeder (BRL)], while others that involved experiments lasted for days or weeks [e.g. Dr. Indu Mishra (BRL)]. In the case of the latter, Dr. Mishra made 3 major visits in 1988 in connection with a collaborative experiment involving a material used for binding explosives (2-methyl,5-vinyl tetrazole, MVT). We had developed an 'impact machine' in which molecules are accelerated to high kinetic energies and then collide with a stationary surface; the impact thus generated can initiate different kinds of chemical reactions. These reactions can range from simple bond fission to complex internal rearrangements that involve molecular elimination. The motivation behind the MVT experiments was to (i) see if high-energy impact can lead to dissociation, (ii) see if such dissociation follows the low energy (thermal) channels, (iii) incorporate the binder with energetic materials such as RDX in the gas/surface high energy collision environment. The results, while not yet conclusive, were written as an internal report and have recently been accepted for presentation at the 1989 Detonation Symposium. In the near future, we will examine the collision-induced dissociation of nitroso-substituted tetrazoles, and binder-RDX interactions at the surface, and compare the results to those obtained using thermal decomposition methods.

While it is commonplace for us to have visitors spend a day touring the labs, it is far less common to engage in fruitful collaborative work of the type carried out with Dr. Mishra. Members of the Center also visited Army facilities on several occasions. These visits involved a seminar and informal discussions, usually centered around a specific topic.

C. Wittig visited BRL (February, 1988)
I.B. Mishra (BRL) visited USC (February, 1988)
R.A. Beaudet visited BRL (August, 1988)
H. Reisler visited BRL (July, 1988)
R.A. Beaudet visited BRL (September, 1988)
I.B. Mishra (BRL) visited USC (July, 1988)
R. Paur (ARO) visited USC (September, 1988)
M. Schroeder (BRL) visited USC (September, 1988)
I.B. Mishra (BRL) visited USC (December, 1988)
As in 1987, a 2-day research symposium was held following the annual review. This year the conference concentrated on decomposition mechanisms of materials such as RDX, and there were 20 speakers from government, industrial and university laboratories. The conference agenda is given below. The decision to keep the meetings quite topical seems to have paid off. A small group (~ 65) and active audience participation keeps things lively, and there is no sense of competition with the larger meetings.

The Center's newsletter is now distributed to several hundred people every two months at no cost to subscribers. This service provides lists of future conferences and meetings, job opportunities (including postdocs), current mailing addresses (including electronic-mail), and abstracts of publications submitted and/or in press.

CHARACTERIZATION AND DIAGNOSTICS
OF ENERGETIC MATERIALS

8-10 August, 1988
University of Southern California

Monday, August 8

5:00 - 6:00 Dinner
7:00 pm Mixer and social hour

Tuesday, August 9

7:00 - 8:00 Breakfast
8:00 - 8:10 Introductory Comments
8:10 - 8:45 Carl Melius (Sandia) Reaction Mechanisms in the Ignition and Combustion of Nitramines.
8:45 - 9:20 Tom Brill (Delaware) Fast Thermolysis Studies in which Temperature, Mass and Species are Simultaneously Monitored.
9:20 - 9:55 Rich Behrens (Sandia) Thermal Decomposition of HMX and RDX.
9:55 - 10:15 Break
<table>
<thead>
<tr>
<th>Time</th>
<th>Speaker (Affiliation)</th>
<th>Topic</th>
</tr>
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<tbody>
<tr>
<td>12:00 - 1:00</td>
<td>Lunch</td>
<td></td>
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<tr>
<td>1:00 - 1:35</td>
<td>Dave Golden (SRI)</td>
<td>Laser Pyrolysis Studies of the Unimolecular Decomposition of Nitramines and Nitroaromatics.</td>
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<tr>
<td>1:35 - 2:10</td>
<td>George Adams (BRL)</td>
<td>Thermochemistry of Boranes and Related Compounds.</td>
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<td></td>
<td>Michael Koszykowski</td>
<td></td>
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<tr>
<td></td>
<td>(Sandia)</td>
<td></td>
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<tr>
<td>3:10 - 3:30</td>
<td>Break</td>
<td></td>
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<tr>
<td>3:30 - 4:05</td>
<td>Basil Swanson (LANL)</td>
<td>Static-Type Pressure and Shock Studies of Nitrogen Oxides.</td>
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<tr>
<td>5:00 - 6:30</td>
<td>Dinner (Mexican-style buffet)</td>
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Wednesday, 10 August

<table>
<thead>
<tr>
<th>Time</th>
<th>Speaker (Affiliation)</th>
<th>Topic</th>
</tr>
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<tbody>
<tr>
<td>8:00 - 8:35</td>
<td>Lee Harris (ARDEC)</td>
<td>The Low Pressure Combustion of Nitramine Propellant and the Ignition of Low Vulnerability Tank and Artillery Ammunition.</td>
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<tr>
<td>9:00 - 9:35</td>
<td>Tim Edwards (AFAL)</td>
<td>Spectroscopic Measurements of High Pressure Propellant Flames.</td>
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<tr>
<td>10:15 - 10:30</td>
<td>Break</td>
<td></td>
</tr>
<tr>
<td>10:30 - 11:05</td>
<td>Herb Nelson (NRL)</td>
<td>Production and Reactions of Boron Hydrides.</td>
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<tr>
<td>11:05 - 11:40</td>
<td>Dave Chandler (Sandia)</td>
<td>Deuterated Methyl Iodide Photochemistry.</td>
</tr>
<tr>
<td>11:40 - 12:10</td>
<td>Curt Wittig (USC)</td>
<td>Photon and Collision-Induced Excitation.</td>
</tr>
<tr>
<td>12:00 - 1:00</td>
<td>Lunch</td>
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</tr>
<tr>
<td>1:00 - 5:00</td>
<td>Laboratory tours at USC</td>
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</tr>
</tbody>
</table>
V. List of personnel affiliated with the Center

Faculty
CURT WITTI
HANNA REISLER
ROBERT BEAUDET
GERALD SEGAL
SIDNEY BENSON

Postdoctoral Fellows
Jeffrey Segall(d)
Julian de Juan(c)
Günter Hoffmann(b)
Eliezer Kolodney(e)
Steven Sharpe
Brent Koplitz(c)
Diana Schwartz-Lavi(d)
Raphael Lavi
Daniel Oh
Yongqin Chen
Charles Qian(b)
Yi Yan Bai

Administrative
Sarah Novak
Shirin Mistry(a)
Yuki Yabuta(a)

Graduate Students
Martin Hunter(h)
Helen Iams
Lori Iwata(g)
David Scott
Scott Nickolaisen(f)
Amy Ogai(g)
Scott Powers
Diane Reifschneider
Carrie Jacques(h)
Yongping Zeng(h)
Wen Ye(h)
Delroy Baugh

(a) Departmental Secretaries
(b) Supported by NSF
(c) Left Summer 1988
(d) Supported by DOE
(e) Supported by AFOSR
(f) University Merit Fellowship
(g) National Science Foundation Predoctoral Fellowship
(h) Teaching Assistant
VI. Publications (1988)

1. H + ClCN \rightarrow HCl + CN: Product excitations and reaction mechanism at \( E(\text{c.m.}) = 21.6 \ \text{kcal mol}^{-1} \)

2. Photoinitiated H + CO\(_2\) \rightarrow OH + CO: OH distributions and 3-body interactions in CO\(_2\)-H\(_2\)S complexes

3. Photoinitiated reactions in weakly-bonded complexes

4. Infrared absorption spectroscopy of the CO\(_2\)-Ar van der Waals complex

5. The rotational spectrum, structure, and dipole moment of ethynylphosphine, H\(_2\)PC=CH

6. The molecular structure of boron hydrides and carboranes

7. Microwave spectrum, structure, and dipole moment of methylaminodiborane, B\(_2\)H\(_5\)NHCH\(_3\)

8. Microwave spectrum, boron skeletal structure, and dipole moment of 5-fluoro, 2,4-dicarbaheptaborane (7), C\(_2\)B\(_5\)H\(_6\)F

9. Molecule-surface dissociative scattering of n-C\(_3\)F\(_7\)NO from MgO(100) at hyperthermal energies: nascent NO(X\(^2\Pi\))

10. Singlet and triplet potential energy surfaces of NCNO

11. Reactions of hot H atoms with N\(_2\)O under single-collision, gas-phase conditions and in photoexcited N\(_2\)-HBr complexes: OH(X\(^2\Pi\))+N\(_2\), and NH(X\(^3\Sigma\))+NO(X\(^2\Pi\)) channels

12. Thermochemistry of methylene phosphine: initial determination of the carbon-phosphorus double bond strength

13. State-selective photodissociation dynamics of NOCl: The influence of excited state bending and stretching vibrations

14. The electronic spectrum of NOCl: photofragment spectroscopy, vector correlations and ab initio calculations

15. Photoinitiated H + N₂O reactions: N₂O-HBr complexes and gas-phase, single-collision, arrested-relaxation conditions