Held 12-13 May 1987 in Rosslyn VA

September 1987

Editors:
W. J. Lauderdale
W. A. Sowell

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FOREWORD

This is the conference proceedings of the High Energy Density Matter (HEDM) Contractor's Conference held 12-13 May 1987 in Rosslyn, VA. AFAL editors were 1Lt Walt Lauderdale and Capt Bill Sowell.

This conference proceedings has been reviewed and is approved for distribution in accordance with the the distribution statement on the cover and on the DD Form 1473.

WALTER J. LAUDERDALE, 1Lt, USAF
Project Manager

FOR THE COMMANDER

ROBERT C. CORLEY
Chief, ARIES Office
The High Energy Density Matter (HEDM) Contractor's Conference was held 12-13 May 1987 in Rosslyn, VA. It provided HEDM researchers an opportunity to become acquainted with the work of their colleagues in this area. The speakers were researchers who had been under contract by October 1986. In addition, presentations on Air Force in-house research were made by the Air Force Astronautics Laboratory (AFAL) and the Air Force Aeropropulsion Laboratory (AFAPL).
18. $H_2$, hydrogen, $He_2$, spin-orbit, spin-spin, multi-configuration self-consistent field, MCSCF, condensed phase, metastability, quantum Monte Carlo, trial function, polyatomic hydrogen, ions, charge transfer, $D_3^+$, $SiH_4$, fluorine azide, $FN_3$, laser initiated decomposition, IR, UV-Vis, ultraviolet, visible, spectroscopy, $H_3O$, $N_2O_2$, dinitrogen dioxide, CO, carbon monoxide, CH, high spin states, spin forbidden, radiative transition, electronic structure, molecular geometry, rare gas fluorides, $NF_5$, nitrogen pentafluoride, high oxidation state, rhombic structure, tetramers, $Si_2C_2$, disilicon dicarbide, zintl, photoexcitation, metastable metals, atomic metals, metal dimers, matrix isolation, matrix, rare gas matrix, theoretical, $H_3$, trihydrogen.
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Aron Kuppermann (California Institute of Technology)

"Theoretical Studies of the Lifetime of Metastable Trihydrogen
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O. Jensen (Ballistic Research Laboratory), David R. Yarkony
(Johns Hopkins Univ)

"The Influence of Condensed Phase on Metastability"
P. K. Svaminathan, C. S. Murphy, B. C. Garrett, M. J. Redmon
(Chemical Dynamics Corporation)

"Optimized Trial Functions for Quantum Monte Carlo Study of
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Distribution/ Availability Codes
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"Metastable Molecular Fuels: Theoretical Study of Ion-Pair States -- Low Lying Surfaces of H$_3^0$"
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Involving Unusual Bonding Situations
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The Prevalence of Rhombic Structures in $A_2B_2$ Tetraatomics
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Photoexcitation of Triatomic Hydrogen
H. Helm, L. J. Lembo (SRI International)

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EXECUTIVE SUMMARY

The need for propellants capable of delivering Isp's of 600 seconds or better has led to an investigation into high energy density molecules. Such species may derive their energy from electronic excitation and metastability, unusual bonding situations, or from high energy ground states. The Air Force is currently sponsoring research in this area through the AF Astronautics Laboratory, the AF Office of Scientific Research, and the AF Aero Propulsion Laboratory. A Technical Panel*, funded by AFOSR, administered by Dr Joseph Early of Georgetown University and chaired by Dr William Stwalley from the University of Iowa provided guidance in proposal selection and insight in the form of peer review to the Air Force Steering Group. The work involves both theoretical and experimental investigations and some of the nations leading research teams. In order to derive synergistic benefits from the two types of research, the first annual High Energy Density Matter Contractors Conference was held in May 1987.

Technical issues facing the researchers include formation mechanisms, the amount of energy stored vs the molecular weight of the reaction products, duration of the energy storage (lifetime), methods of stabilization and storage, novel bonding structures, and decay mechanisms. The work can be loosely grouped under the following categories: screening; bonding and reaction studies; theory verification and specie characterization; and feasibility/stability demonstration. Theorists are performing quantum mechanical calculations to determine energy states and predict possible decomposition pathways. Experiments are underway to verify theory, characterize species, and investigate stability. Several of the important conclusions presented at this meeting are reported here.

An energetic stable state of H₄ had been predicted by Nicolaides in his maximum ionicity excited states (MIES) theory. Initial studies showed that an energy minimum existed in the ground state and first excited state of the proposed molecule. After extensive investigation, the ground state of tetrahydrogen (H₄) was found to be an unbound saddle point. This was confirmed independently by the groups from UC Berkeley (Lester), United Technologies Research Center (Michels), and the US Army Ballistic Research Laboratory (Lengsfeld). Two other MIES candidates, HLi₃ and the excited state of H₄, still show promise of stability and high energy content.

Several groups reported on powerful new computational methods developed to investigate energy configurations. Their almost simultaneous independent findings on H₄ lend great credence to the concept of "theoretical experiments" being done on supercomputers. The new computational tools allow investigators to quickly and
accurately predict the potential stability of a candidate system before it is prepared in the laboratory. Once a stable state is identified, formation and decomposition pathways can also be calculated. This greatly reduces the time and risk involved with laboratory experiments on the species.

Michels reported calculations on a new energetic oxidizer predicted to be stable in the ground state. This compound, asymmetric dinitrogen dioxide (α-N2O2), is an analogue of fluorine azide (FN3) and is predicted to be a cryogenic solid.

Benard reported that FN3 can be viewed as a loosely bound complex of N2 and the metastable excited singlet NF. He found that by using FN3 as a starting material, one can generate high concentrations of the excited singlet NF, a short wavelength laser species.

Yarkony presented a recently developed algorithm for treating spin interactions in the computation of radiative lifetimes. This method enables previously untenable calculations to be performed which help predict the lifetimes of candidate species.

Helm reported on a newly developed technique for experimentally observing high Rydberg states. This rather elegant method is used to precisely characterize the energy surfaces of candidate molecules.

These items represent some of the positive results gained in the first year of work by the initial HEDM investigators. There are now over twice as many efforts underway, expanding our view into new theoretical and experimental approaches. While our main objective is to identify and develop new high energy density molecules, it is important to note that we are also advancing the state of the art in chemistry and chemical physics.

*The Steering Group has established a Technical Panel to consult on the scientific merit of proposals and to provide peer group review of technical progress as research investigations proceed. Dr William Stwalley, University of Iowa, a noted specialist in both chemistry and physics chairs the Panel. Other Panel members are:

Dr Charles F. Bender Advanced Computational Methods Center, Athens, GA
Dr William Happer Princeton University
Dr M. Frederick Hawthorne UCLA
Dr Ron R. Herm Aerospace Corporation, Los Angeles, CA
Dr Marilyn Jacox National Bureau of Standards
Dr Lewis H. Nosanow National Science Foundation
Dr Isaac Silvera Harvard University
May 12, 1987

1300 Welcome
   Dr John O. Dimmock (AF Office of Scientific Research)

1310 "HEDM Research at the Air Force Astronautics Laboratory"
   Stephen Rodgers (AF Astronautics Laboratory) and Nathan Presser
   (Aerospace Corporation)

1325 "Towards Understanding the Stability of the H₄*(C₃ᵥ) Cluster"
   A. Metropoulos and C. Nicolaides (Theoretical and Physical
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Concluding remarks

Dr Steve Rodgers (AF Astronautics Laboratory)
High Energy Density Matter

Research at the

Air Force Astronautics Laboratory
HEDM IN-HOUSE RESEARCH TEAM

* Theoretical
  - Two AFAL researchers
  - Two on-site contract researchers
  - One NRC Post-Doc

* Experimental
  - One on-site contract researcher
  - Two collaborative efforts with Aerospace
  - Two summer professors
HEDM Experimental Research

Facilities
- Temporary lab space
- New labs completed by Sep 87
- Equipping laboratory
  Spectroscopy
  Cryogenics
  Flowing Afterglow

Areas of Interest
- HEDM materials in cryogenic matrices
- Rare gas compounds
- Spectroscopy
HEDM Theoretical Research

Computational Facilities

- Cray XMP
- Cray 2 (Sep 87)
- VAX 8650, 785, 750
- FPS 164/MAX
- CDC 840

Programs Implemented

- GAMESS
- Gaussian 82
- MOPAC
- MM2

Areas of Interest

- Metastable Metals
- Na, Li, B monomers, dimers, clusters
- Other HEDM candidates
High Energy Density Materials in Cryogenic Matrices

- Metal atoms, dimers, clusters
- Other candidate species
- Cryogenic liquids
HIGH ENERGY DENSITY MATERIALS
IN
CRYOGENIC MATRICES

N. PRESSER and A. T. PRITT, JR.

CHEMISTRY AND PHYSICS LABORATORY
THE AEROSPACE CORPORATION
Combustion Energies of the Elements

$X + O_2 \rightarrow$ PRODUCTS

He Li Be B C N O F Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Na Vo
Specific Impulse

- \( I_{sp} = \frac{\text{THRUST}}{\text{MASS FLOW}} \)
- \( I_{sp} = \frac{V_e}{g} \) (sec)
  - \( V_e = \text{MASS VELOCITY AT NOZZLE EXIT} \)
  - \( g = \text{GRAVITATIONAL ACCELERATION AT EARTH'S SURFACE} \)
- \( I_{sp} \propto (\text{enthalpy of reaction/product mass})^{1/2} \)
Properties of Atoms in Cryogenic Matrices

- **ENTHALPY OF ATOM IN MATRIX** = **ENTHALPY OF ATOM IN GAS**

- **EVIDENCE:**
  - *Spectra of small molecules in cryogenic matrices are weakly perturbed*
  - *Vibrational frequencies are only very slightly shifted from gas phase values*
  - *Vibrational relaxation measurements indicate that matrices may be treated as gases of comparable density*
  - *Matrices are held together by relatively weak dispersion forces*
Specific Impulse

- \( i_{sp} = \text{THRUST/MASS FLOW} \)

- \( i_{sp} = \frac{V_e}{g} \) (sec)

  \( V_e = \text{MASS VELOCITY AT NOZZLE EXIT} \)

  \( g = \text{GRAVITATIONAL ACCELERATION AT EARTH'S SURFACE} \)

- \( i_{sp} \propto (\text{enthalpy of reaction/product mass})^{1/2} \)
Comparison With LO_x + H_2 System

- FIGURE OF MERIT = ENTHALPY OF REACTION/PRODUCT MASS
- FIGURE OF MERIT FOR THE O_2 + H_2 REACTION IS 3.21
- BORON
  - 2 B(matrix) + 3/2 O_2 → B_2O_3(s) (=8.14)
- ΔH/M = 567 * X_a/(Mm + (69.6 - Mm) * X_a)
  - X_a = MOLE FRACTION OF B IN THE MATRIX
  - M_m = MOLECULAR WEIGHT OF MATRIX MOLECULE
  - 69.6 = MOLECULAR WEIGHT OF B_2O_3
- MATRIX MATERIAL = H_2

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<tr>
<td>Si</td>
<td>107</td>
</tr>
<tr>
<td>Si₂</td>
<td>140</td>
</tr>
</tbody>
</table>
Key Scientific Issues
TO BE INVESTIGATED

- WHAT ARE THE ENTHALPIES OF ATOMS IN MATRICES?
- WHAT ARE THE ACTIVATION ENERGIES OF CLUSTERING?
  - WHAT IS THEIR SIZE DEPENDENCE
  - WHAT IS THEIR TEMPERATURE DEPENDENCE?
  - WHAT IS THEIR MAGNITUDE
- WHAT ARE THE DIMERIZATION RATES?
- WHAT PART IF ANY DOES THE SPECIFIC MATRIX PLAY IN THESE PROCESSES?
- CAN THE ATOMIC SPECIES BE STABILIZED AT THE MONOMER OR DIMER LEVEL?
  - WHAT ARE THE CHARACTERISTICS OF SUCH WEAKLY BOUND COMPOUNDS
Towards Understanding the Stability of the $H_4^*(C_{3v})$ Cluster

A. Metropoulos and C.A. Nicolaides

Theoretical and Physical Chemistry Institute, National Hellenic Research Foundation, Athens, Greece

As a first attempt to study the stability of the $H_4^*(C_{3v})$ cluster we have used the MRD-CI methods and a medium size basis set to calculate various sections of the potential energy surfaces of its ground and first excited states. We show that these correlate to the $(X^1\Sigma^+_g,X^1\Sigma^+_u)$ and $(X^1\Sigma^+_g,B^1\Gamma^+_u)$ states of the two $H_2$ constituents respectively. Finally, we report on the calculation of the diabatic matrix elements of the vibronic interaction in the region of the avoided crossing which is crucial to the stability of $H_4^*$. 

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HISTORICAL PERSPECTIVE

In our institute there has been a long standing emphasis on the study of atomic and molecular excited states. Within the course of these studies, it was decided in 1982 to compute the low lying excited states of the $\text{He-H}_2$ system with the objective of doing dynamics on these surfaces. The idea was to do more accurate calculations than those reported in the literature /1/ and to map a wider portion of the hypersurface including the $\text{H-H}$ stretch and a 45° section. What was expected was the construction of accurate ground and excited states van der Waals surfaces for energy transfer calculations. In the course of the investigation it became evident that for a long enough $\text{H-H}$ distance (4.0 bohr) and a 45° angle there was a non-van der Waals minimum of about 1.52 eV with respect to $\text{He} + \text{H}_2$. The corresponding $\text{He-H}_2$ distance was about 1.5 bohr, or, else, the closest $\text{He-H}$ distance was 1.41 bohr. In this stable geometry there is an avoided crossing between the $\text{He+H}_2 (\Sigma^+)$ excited and the $\text{He+H}_2 (\Sigma^-)$ ground states as the $\text{H-H}$ distance varies /2/ (not
present in colinear or $C_{\infty v}$ geometries). Figure 1 shows the potentials of the ground and the first excited states near the minimum. The existence of such an avoided crossing has explained for the first time the observed fluorescence quenching of HD/3/
very satisfactorily. The discovery of a geometry for HeH$_2$ with a chemical minimum gave rise to the so-called maximum ionicity excited state (MIES) theory as a means of explaining the existence of such a minimum in terms of general chemical features. The impetus for such a theory was the fact that the H$_2$(B' $\Sigma^+_u$) state is ionic at intermediate H-H distances with the maximum ionicity occurring at 4.0 bohr/1/1. Thus, as He approaches HeH$_2$, the H-H bond stretches close to the maximum ionicity limit which favors energy reduction through small overlap between H$_2^+$ and He and a large Coulomb interaction between H$_2^+$ and He. Support for this model comes from the fact that the equilibrium distance of the HeH$^+$ molecular ion is 1.44 bohr/15/ which is very close to the closest He-H distance at the equilibrium geometry.

Extending this model of bonding to larger systems of interacting singlet, closed shell moieties, one can make very useful predictions of approximate "stable" geometries of excited surfaces. Taking H$_4$ as an example, this scheme can be described as follows. An excited state of clusters, say (ABCD)$^*$, correlating with the fragments (AB)+(CD)$^*$, is thought of as occurring by an interaction of the type (ABC)$^*$+(CD)$^*$. The geometry of the bound (ABCD)$^*$ complex is obtained from the geometry of (ABC)$^*$, and by placing D a distance from C at which
ionic VB structures have a maximum contribution to the wave function of the (CD)\(^+\) fragment. For H\(_4^+\), the geometry of the positive ion, H\(_4^+\), is an equilateral triangle with side of 1.65 bohr /5/. The fourth H atom is then placed above the centre of the triangle at a distance of about 4.0 Bohr, which is the maximum ioncity distance of the B \(^1\Sigma_u^+\) state of H\(_2^+\)/4/. Figure 2 shows the relevant geometry and the coordinate system used. The MIES prediction on H\(_4^+\) was supported by the results of MRD-CI calculations, which gave a minimum at the triangle side of 1.70 bohr and a distance of 3.8 bohr from the centre of the triangle for the fourth H /6/. The calculations were done in C\(_5\) symmetry and figure 3 shows the potentials of the two lowest A' states for various lengths of the side of the equilateral triangular base. Notice that while work on the H\(_4\) excimer has been done by other workers for various geometries /7/, the application of the MIES scheme has lead directly to a pyramidal geometry as the minimum energy geometry for the H\(_4\) excimer. All previous considered geometries lead only to saddle points of the H\(_4^+\) hypersurface /8/.

FURTHER INVESTIGATION OF THE H\(_4\) EXCIMER

After the MIES theory had been succesfully tested /6/, it was decided to investigate more accurately the H\(_4\) excimer state because we needed its character and its accurate wavefunctions and surfaces. As previously, the MRD-CI method /9/ was employed and the calculations were done in C\(_5\) symmetry, due to program
limitations, but now a larger basis set was used /10/. Our attention was focused on the following: a) Obtain more accurate surfaces and wavefunctions while maintaining the C3v geometry. b) Use these wavefunctions to obtain the non-adiabatic matrix elements of the vibronic interaction in the vicinity of the avoided crossing, assuming all motions frozen except the one along R (see fig. 2). c) Verify that the first two 1A' states of H4 correlate to the (X 4Σ+g X 4Σ+g) and (X 1Σ+g B 1Σ+u) states of two hydrogen molecules.

At this point, the approximate nature of the MIES basis prediction of the geometry of the excited state minimum became evident. As it was pointed out to us /11/ and as it can be deduced from the calculations in ref. 8, if the true C3v symmetry is considered, there is no avoided crossing between the first two totally symmetric states but a true crossing between an 1A1 and an 1E state (E = A' + A''). The geometry of this crossing was later calculated in C1 symmetry /12/ and it was found to be R = 1.8 bohr and R = 4.225 bohr at an energy of -2.3617 a.u. Figure 4 shows the extrapolated curves of the 1A1 and 1E states the intersection of which has been taken as the crossing point. Obviously then, the stable geometry must be of a true C5 symmetry. From the optimization calculations with respect to motions of Hα in C3v geometry, represented in figure 5, it was inferred that the C5 symmetry has to be arrived at by a deformation of the triangular base rather than by displacing Hα. We thus started searching for the optimum geometry of the triangular base.
Here, we consider only the deformation of the equilateral triangular base into an isosceles (but not into a scalene) triangle /12/. After a sequence of optimizations, we arrived at a geometry having a true avoided crossing between the X $^1A'$ and the A $^1A'$ states which is about 154 meV lower than the ($^1A_2$, $^1E$) crossing point (-2.0674 a.u. for the A $^1A'$ and -2.0707 a.u. for the X $^1A'$ (state) and which is a minimum of the A $^1A'$ state. At this geometry, the equal sides of the isosceles triangle are 1.78 bohr each, the third side is 1.62 bohr and $\text{H}_a$ is situated on the z axis, 3.90 bohr above the plane of the triangle. The origin of the coordinate system is taken at a point 2/3 from the vertex of the perpendicular bisector of the isosceles triangular base. Figure 6 shows the variation of the potential with R for the optimized triangular base.

Regarding the correlations previously mentioned, table 1 shows that they are correct as stated. Although the final H$_4$ symmetry in this table is C$_3v$, the correlations are valid for the optimized C$_s$ symmetry as well. This is so because in this case, the $A_1$ irrep of C$_3v$ correlates uniquely to the $A'$ irrep of C$_s$ ($\sigma^e = \sigma_v$) /10/.

Finally, the non-adiabatic matrix elements for the radial coupling were computed in the neighborhood of the avoided crossing for the optimized H$_4^+$ (C$_s$) geometry. The finite differences method of Lorquet and coworkers as it has been modified for the MRD-CI programs /11/ was used. All degrees of freedom were frozen.
except for the \( R \) internal coordinate. Table 2 gives the result of this calculation. Notice that while the strength of the interaction is small, it persists for a rather large interval. The usefulness of this result is that one can make an order of magnitude estimate of the transition rate to the ground dissociative state by using methods already developed for diatoms /13/.

**LIFETIME OF THE \( \text{H}_4 \) EXCIMER**

A computation of the lifetime of \( \text{H}_4^* \) is very desirable. There appear to be three mechanisms by which \( \text{H}_4^* \) may dissociate: a) By a radiative transition to the ground dissociative state. The probability of this transition should be rather small due to the proximity of the levels at the avoided crossing and due to the smallness of the Frank-Condon factors away from it. b) By exciting the system to the level of the \((1\_a, 1\Sigma)\) crossing point. Thus, the system can be "stable" only at low vibrational states and the highest such state must be found. c) By a diabatic crossing to the ground state. The probability of this transition may very well be the factor controlling the stability of \( \text{H}_4^* \). Calculations for the elucidation of the first two mechanisms are now in progress. Order of magnitude calculations regarding the third mechanism (for the \( R \) internal coordinate only) are contemplated for the near future.
REFERENCES


15. K. P. Huber and G. Herzberg, "Constants of Diatomic Molecules" (van Nostrand Reinhold, New York, 1979)
Table 1. Comparison between 1) the sums of the potential energies of two hydrogen molecules at infinite separation and a T shaped $C\overset{\circ}{2V}$ $H_2-H_2$ complex at large intermolecular separations (1st three columns) and 2) the potential energies of $H_4^*$ computed with reference configurations initially corresponding to $H_2-H_2(C\overset{\circ}{2V})$ and $H_4^*(C_3\overset{\circ}{V}/Cs)$ (last three columns). The MRDCI potential energies of the $H_2$ molecules are also given. For the Cs symmetries, $^1A_1$ should be replaced with $^1A'$; $\Theta$ is the angle between $H_2$ and the $z$ axis. $\rho$ is the bond length of an $H_2$ diatom.

<table>
<thead>
<tr>
<th>Geometry</th>
<th>$\rho$ (a.u.)</th>
<th>$H_4^*(r=1.8, R=4.2$ a.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1.4</td>
<td>1.5</td>
</tr>
<tr>
<td>$X \sum_g + X \sum_g$</td>
<td>-2.3400</td>
<td>-2.3375</td>
</tr>
<tr>
<td>$X \sum_g + X \sum_g$</td>
<td>-2.3393</td>
<td>-2.3369</td>
</tr>
<tr>
<td>$X \sum_g + X \sum_u$</td>
<td>-1.8735</td>
<td>-1.8867</td>
</tr>
<tr>
<td>$X \sum_g + X \sum_u$</td>
<td>-1.8730</td>
<td>-1.8863</td>
</tr>
<tr>
<td>$H_2$ ($X \sum_g$)</td>
<td>-1.16999</td>
<td>-1.16874</td>
</tr>
<tr>
<td>$H_2$ ($B \sum_u$)</td>
<td>-0.70350</td>
<td>-0.71799</td>
</tr>
</tbody>
</table>

$^\alpha$ $\Theta = 45$ deg (Cs) $^\beta$ $\Theta = 0$ deg (C$\overset{\circ}{3V}$)
Table 2. Non-adiabatic matrix elements (in a.u.) of the vibronic coupling along the $R$ coordinate ($R$ in bohr).

<table>
<thead>
<tr>
<th>$R$</th>
<th>$\langle X^1A' \rvert \frac{d}{dR} \lvert A^1A' \rangle$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.6</td>
<td>0.65</td>
</tr>
<tr>
<td>3.7</td>
<td>1.1</td>
</tr>
<tr>
<td>3.8</td>
<td>2.1</td>
</tr>
<tr>
<td>3.9</td>
<td>3.0</td>
</tr>
<tr>
<td>4.0</td>
<td>2.4</td>
</tr>
<tr>
<td>4.1</td>
<td>1.5</td>
</tr>
<tr>
<td>4.2</td>
<td>0.83</td>
</tr>
<tr>
<td>4.3</td>
<td>0.50</td>
</tr>
</tbody>
</table>
Figure 1. The potentials of the ground and the first excited state as functions of the H-H distance. —— R = 2.0 bohr; —— R = 1.5 bohr.
Figure 2. The coordinate system employed. The basis of the pyramid is an equilateral triangle of side $r$ while $R$ is the distance of the $H_a$ atom at the apex of the pyramid from the center of the triangle. An auxiliary angle $\theta$ (not shown) may be defined on the $XY$ plane between the vector $\mathbf{R}$ and the $Z$ axis so that it is positive if $H_a$ is in the first quadrant, negative if it is in the fourth quadrant and zero if it is on the $Z$ axis ($-90^\circ \leq \theta \leq 90^\circ$).
Figure 3. Potential energy surfaces (in a.u.) for the two lowest states of $^1A'$ symmetry of $H_4$ at the trigonal pyramidal geometry shown in fig. 2.
Figure 4. The crossing of the $^1A_1$ and $^1E$ states of $H_4 (C_{3v})$ appearing as an avoided crossing (done in $C_1$ symmetry).
Figure 3. A section of the \textsuperscript{2}A' and \textsuperscript{4}A' potential energy surfaces of H\textsubscript{2} corresponding to a motion of H\textsubscript{2} in the CE plane from $\Theta = -90^\circ$ to $\Theta = 90^\circ$; a) Dotted line: A circular motion with $r=3$ and $r=6$ b) Chain dashed line: A circular motion with $r=1.5$ and $r=3$ from the results of ref. 6. c) Solid line: A surrilinear motion so that the energy of the \textsuperscript{2}A' state is minimized with respect to $\Theta$. d) Solid circles and connecting dashed line: A surrilinear motion so that \textsuperscript{4}A' is minimized with respect to both $\Theta$ and $R$.  

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Figure 6. The variation of the potential with $R$ for the $X^1A_1$ and the $A^1A_1$ states of $H_4$ ($C_3$); ---- eigenvalues; -- extrapolated energies. The horizontal lines show the corresponding levels of the $(^1A_1, ^1E)$ crossing point.
EXPERIMENTAL STUDIES OF THE PROPERTIES OF TRIHYDROGEN AND TETRAHYDROGEN

Aron Kuppermann

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ABSTRACT

These studies consist in attempting to detect the existence of a metastable 1A' state of the H₄ molecule and in determining its lifetime. The H₄ preparation methodology consists in crossing an intense beam of metastable H₃ molecules in the 2p₂ 2A'₂ Rydberg state with a beam of ground state X 1Σ⁺ HI molecules. The calculated geometry of H₄ (1A') is a pyramid whose base has a nuclear configuration close to that of the 2p₂ 2A'₂ H₃ molecules. Furthermore, the height of that pyramid is approximately the same as the effective length of the 2p₂ Rydberg orbital. The reaction H₃ (2p₂ 2A'₂) + HI (X 1Σ⁺) → H₄ (1A') + I (2P₃/₂) is endothermic by about 1 eV and the H₃ (2p₂ 2A'₂) beam has an average translational energy of about 8 eV.

The crossed beam apparatus has been assembled and put into operation. The primary H₃ (2p₂ 2A'₂) beam is generated in a high temperature arc discharge source through which H₂ flows. The discharge plasma emerges from a cathode nozzle orifice, and the beam passes through a skimmer, then through a differentially pumped chamber and into the main scattering chamber. The secondary beam of Ar (in control experiments) or HI (or DI) is generated by expansion of the corresponding gas through a capillary array. The scattered species are detected by a rotatable quadrupole mass spectrometer. A report will be given on the progress achieved in these experiments so far.
I. EXPERIMENTAL STUDIES OF THE PROPERTIES OF TRIHYDROGEN AND TETRAHYDROGEN

II. THEORETICAL STUDIES OF THE LIFETIME OF METASTABLE TRIHYDROGEN AND TETRAHYDROGEN

Aron Kuppermann, Caltech

1. The spectroscopic properties of the Rydberg states of H₃.

2. An intense beam of metastable H₃.

3. Dynamic properties of metastable H₃: total scattering, photoionization and surface ionization.

4. A proposed scheme for producing and detecting metastable H₄ from metastable H₃.

5. Experiments with the crossed molecular-beam apparatus.

7. Hyperspherical coordinate calculations of the ground (continuum) state of H₃.

8. Properties of the potential energy surface of the first excited state of H₃ (conical intersection).

9. Next steps in the experimental and theoretical efforts.

Collaborators

Experimental work: Mary Rodgers, Q. Jin and Z. Peng.

Theoretical work: Paul Hipes, Steve Cuccaro, Mark Wu and Z. Peng.
$H_2(X^1\Sigma_g^+) + H^+ + e^-$

$H_2(X^1\Sigma_g^+) + H(n=3)$

$H_2(X^1\Sigma_g^+) + H(n=2)$

$H_2(b^3\Sigma_u^-) + H(n=1)$

$H_3^+ + e^-$

$H_3$

$H_2(X^1\Sigma_g^+) + H(n=1)$

Potential Energy (eV)
[Image of a graph showing ion current as a function of pressure (p/torr) with markers for H, H₂ (x5), and H₃. The graph illustrates the variation of ion current with pressure for different gas species.]

**Graph Details:**
- **Y-axis:** Ion Current / 10⁻¹⁰ A
- **X-axis:** p / torr
- **Markers:**
  - ○ H
  - □ H₂ (x5)
  - △ H₃

**Graph Interpretation:**
- The graph shows a peak in ion current for H between 60 to 70 torr, followed by a decrease.
- H₂ shows a similar trend but with a peak at higher pressure (70 to 80 torr) and increased by a factor of 5.
- H₃ shows a lower ion current compared to H and H₂.

**Note:** The graph is a visual representation of the data, showing how the ion current changes with pressure for different gas species.
Energy levels for the H₃ + HI system.

\[ \text{H}_3^+ + \text{H}(1s) + e^- + I(2P_{3/2}) \]

\[ \text{H}_4^+ + e^- + I(2P_{3/2}) \]

\[ \text{H}_3^+ + e^- + \text{HI}(X^1 \Sigma^+) \]

\[ \text{H}_3(2p^2A'^2_2) + \text{H}(1s) + I(2P_{3/2}) \]

\[ \text{H}_3(2p^2A''_2) + \text{HI}(X^1 \Sigma^+) \]

\[ \text{H}_4(^1A') + I(2P_{3/2}) \]
Possible reactions:

\[ H_3 \left( ^2P_1, ^2A'' \right) + \begin{cases} 
  \text{HI} \left( X'\Sigma^+ \right) \rightarrow H_A \left( A' A' \right) + I \left( ^2P_{3/2} \right) \\
  \text{DI} \left( X'\Sigma^+ \right) \rightarrow H_3 D + I \left( ^2P_{3/2} \right)
\end{cases} \]
Vertical cut view of the crossed molecular beam apparatus, drawn approximately to scale. DP - diffusion pumps, PB - primary beam source (with the beam axis in the plane of the drawing), Nz - nozzle, SK - skimmer, VS - velocity selector, SB = secondary beam source (with the beam perpendicular to the plane of the drawing), CC = correlation chopper blade, MS = mass spectrometer detector, TMB_b = 50 l/s turbomolecular pump for buffer chamber, I = ionizer and ion-focus lenses, CEM = channeltron electron multiplier, CP = 350 l/s liquid He cryopump, TMP = 360 l/s turbomolecular pump, IG = ionization gauge.
Side view of hybrid apparatus with the metastable H₃ arc discharge primary beam source connected to the crossed molecular beam apparatus. VCI, vacuum chamber; S, water-cooled copper skimmer; GV, pneumatic gate valve; F, flexible flange; B5, 50-inch bell jar. Dashed lines indicate box within the bell jar which contains the magnetic velocity selector.
5. Experiments with the crossed molecular beam apparatus.

Since the last HEDM meeting (March 87), we have:

- Performed 150 runs with the H3 beam
- Each run lasted an average of 5 hours, for a total running time of 750 hours.
- Made 3 major changes in the apparatus:
  a. Rebuilt the arc source to eliminate the bellows and shorten the length of the cathode rode.
  b. Built a simple beam steering mechanism.
  c. Rebuilt the arc source electromagnet.

The objective of these changes was to overcome the following experimental difficulties:

- Interference due to the intense light emitted by the arc.
- Stringent alignment requirements (±0.05).
- Beam position shifts during runs due to deformation of cathode
These difficulties have been overcome one by one. We are currently running the beam 4 times a week, each run lasting about 8 hours. Each anode and cathode last for an average of 6 runs.

Crossed beam experiments $H_3(2p^3, ^3A_2) + A^-$ have now been started. These are preparatory experiments (of a background nature) for the $H_3(2p^3, ^3A_2) + HI, DI$ runs.
$H_5$

FWHM $\sim 0.6^\circ$

Intensity (arbitrary units)

$\Theta_h$ (degrees)
THEORETICAL STUDIES OF THE LIFETIME OF METASTABLE TRIHYDROGEN AND TETRAHYDROGEN

Aron Kuppermann

Division of Chemistry and Chemical Engineering, A.A. Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, CA 91125

ABSTRACT

The $2p_z 2A^1_2$ Rydberg excited state of $H_3$ is known experimentally to be metastable, but its predissociative lifetime has neither been measured nor calculated, although a lower bound of 40 μsec has been experimentally estimated for it. Furthermore, the potential energy surface of the $1A'$ state of $H_4$ has been calculated to have a well whose depth is 1.86 eV. The objective of our theoretical studies is to perform calculations of the predissociative lifetimes of both of these molecules.

The initial calculations are being performed for the $H_3$ system. We are using initially a double many-body expansion (DMBE) of the two lowest potential energy surfaces of $H_3$. The computation involves three steps: a) Scattering calculations on the lowest state. We have performed these accurately for energies up to 1.6 eV using hyperspherical coordinates and are investigating approximate methods for extending them to the higher energies required. b) Bound state calculations on the upper surface. The structure of that surface is being analyzed and a selection is being made of the basis functions to be used. c) Interaction matrix calculations. These have not yet been initiated. The results obtained so far will be presented and discussed.
Radiative and predissociative selection rules for the Rydberg states of H$_3$.

1. Radiative selection rules

<table>
<thead>
<tr>
<th>Transition</th>
<th>$\Delta$ dipole</th>
<th>$\Delta$ quad.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$2p_\parallel^2A''<em>2 \rightarrow 2p</em>\parallel^2E'$</td>
<td>forbidden</td>
<td>allowed</td>
</tr>
<tr>
<td>$2p_\parallel^2A''_2 \rightarrow 2s^2A'_1$</td>
<td>allowed</td>
<td>forbidden</td>
</tr>
<tr>
<td>$2s^2A'<em>1 \rightarrow 2p</em>\parallel^2E'$</td>
<td>allowed</td>
<td>forbidden</td>
</tr>
</tbody>
</table>

2. Predissociative selection rules

<table>
<thead>
<tr>
<th>Transition</th>
<th>Electronic</th>
<th>Vibronic</th>
<th>Rotovibronic</th>
</tr>
</thead>
<tbody>
<tr>
<td>$2p_\parallel^2A''_2 \rightarrow 2p^2E'$</td>
<td>forbidden</td>
<td>forbidden</td>
<td>allowed for $J\neq C$</td>
</tr>
<tr>
<td>$2s^2A'_1 \rightarrow 2p^2E'$</td>
<td>forbidden</td>
<td>allowed</td>
<td></td>
</tr>
</tbody>
</table>

To calculate transition lifetimes, the following quantities are needed:

a. The rovibrational wave function of the upper state
b. The scattering (continuum) wave function of the lower state
c. The coupling operator (electromagnetic or electronically non-radiative predissociative) between these states
\[ R' = \left( \frac{\text{mass}}{\mu} \right)^{1/2} R' \]
\[ \lambda = \left( \frac{\text{mass}}{\mu} \right)^{1/2} \lambda' \]
\[ \mu = \left( \frac{\text{mass} \times \text{mass} \times \text{mass}}{\text{mass} + \text{mass} + \text{mass}} \right)^{1/2} \]
\[ \rho = \left( R_x^2 + \lambda^2 \right)^{1/2} \]
\[ \omega = 2 \tan^{-1} \frac{\lambda}{R_x} \]

\[ R_x, \lambda \Rightarrow \rho, \omega \]
\[ R_x, \theta, \phi, \lambda, \gamma, \psi \Rightarrow \rho, \omega, \theta, \phi, \gamma, \psi \]

\[ V = V(\rho, \omega, \gamma) \]

\[ X = \rho \sin \omega \cos \gamma \]
\[ Y = \rho \sin \omega \sin \gamma \]
\[ Z = \rho \cos \omega \]

"Big Bang" picture
FORMULAS FOR CALCULATING DISTINGUISHABLE
ATOM TRANSITION PROBABILITIES

\[
\begin{align*}
\text{even} \to \text{even} & \quad 1 \frac{1}{\sqrt{3}} S_{A_1} - \sqrt{\frac{2}{3}} S_{E} \quad |^2 \\
\text{even} \to \text{odd} & \quad 1 \frac{1}{\sqrt{3}} S_{E} \quad |^2 \\
\text{odd} \to \text{even} & \quad 1 \frac{1}{\sqrt{3}} S_{E} \quad |^2 \\
\text{odd} \to \text{odd} & \quad 1 \frac{1}{\sqrt{3}} S_{A_2} - \sqrt{\frac{2}{3}} S_{E} \quad |^2 
\end{align*}
\]

COLLISION LIFE-TIME MATRIX

\[
Q = i \hbar \frac{dS^+}{dE}
\]
PK2
\[ J = 0, R \]
\[ \underline{000 \rightarrow 000} \]
Hips resuTs PK17 E8 results A, J=0 50ωα/50γ, mesh

Row No. 3 Column No. 3 Premultiplication by: 1.0

E04/EV

Probability

E/EV
Coxson's results PMII H States $H_j = 0.0 \pm 0.5$ cusp - premines (error in overlap matrix between internal - asymptotic regions)
WITH X=0.0 Bohr AND Z=0.0 Bohr
WITH \( x = 0.0 \) Bohr AND \( z = 0.0 \) Bohr

\[ \text{POTENTIAL / eV} \]

\[ \text{Y AXIS / Bohr} \]
CONICAL INTERSECTION WITH $Y = Y_{min}$ AND $X = 0.0$ Bohr
CONICAL INTERSECTION WITH Y=Ymin AND Z=0.0 Bohr
CHARACTERIZATION OF TETRAHYDROGEN VIA STATE-SELECTED EXCITATION OF $H_2$

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Physical Sciences Inc.
Research Park, P.O. Box 3100
Andover, MA 01810

The four-center $H_4$ system has been the subject of theoretical studies since the late sixties, primarily due to interest in the relationship of the ground state hypersurface to the $H_2 + D_2 \rightarrow 2HD$ exchange reaction.\(^1\),\(^2\),\(^3\) Investigations into the nature of the excited state(s) of such system have been limited in number even though SCF-MO-CI calculations in 1976 by Goddard and Csizmadia indicated the existence of a bound "excimer state."\(^4\) Recently, however, Nicolaides et al., using an extension of their modeling work on rare gas hydrides\(^5\) have predicted the existence of a bound singlet excited state of $H_4$ and have extended this analogy to the ($H_2)_3$ and ($H_2)_5$ clusters.\(^6\),\(^7\)

The theoretical studies of Refs. 6 and 7 predict that the bound state of $H_4$ arises from the reaction of molecular hydrogen in its ground state with $H_2$ that has been excited to the $B(^1\Sigma_u^+)$ state.

$$H_2(B^1\Sigma_u^+) + H_2(X^1\Sigma_g^+) + M + H_4^* + M$$  \((1)\)

Further, the stable excited state is predicted to be produced only when the $B^1\Sigma_u^+$ state precursor has sufficient "ionic" character for reaction with $H_2(X)$. This is predicted to occur for $v > 3$ in the upper state.\(^6\),\(^7\)

Quenching studies of HD(B,v) performed by Atkins, Moore, and coworkers\(^8\)-\(^10\) show an unusually large quenching cross section (79Å\(^2\)) for $H_2$. This has led to further speculation that formation of a complex is involved. The $H_2(B)$ state in $v' = 3$ has sufficient energy to dissociate itself as well as an $H_2$ collision partner:

$$H_2(B) + H_2 + 4H \quad \Delta E = -2.70 \text{ eV}$$

Hence, quenching of $H_2(B)$ by $H_2$ may be highly reactive with $H$-atoms as the products.

The goal of our experimental program is to produce $H_2(B,v)$ in a supersonic jet by several techniques, provide a sufficient number of collisions with $H_2$ to produce $H_4^*$, stabilize the $H_4^*$, and probe for its existence and molecular properties. Four different methods have been chosen to produce $H_2(B,v)$ in the jet: 1) energy transfer from Ar\(^*$ resonance states (1048Å, 1066Å lines) in Ar/$H_2$ mixtures via discharge production of Ar\(^*$ in the nozzle expansion region; 2) energy transfer from Ar\(^*$ resonance states in Ar/$H_2$ mixtures via resonant excitation of Ar\(^*$ with a VUV discharge lamp; 3) direct three photon laser excitation of $H_2(B,v)$ at the nozzle throat; and 4) direct single photon laser excitation of $H_2(B)$ via generation of tunable VUV radiation from third harmonic generation in rare gases.
The primary reason for using a supersonic molecular beam to produce \( \text{H}_4^* \) is to provide a locally high density but optically thin source of \( \text{H}_2 \) for direct VUV excitation of the \( \text{H}_2(\text{B}) \) state as well as collisional production and stabilization of \( \text{H}_4^* \). Three primary criteria must be met by the source:

1. There must be sufficient collisions in the expansion beyond the nozzle throat for collisional quenching of \( \text{H}_2(\text{B}) \) to occur at a rate at least comparable to that for spontaneous radiation.

2. When energy transfer from \( \text{Ar}^* \) to \( \text{H}_2 \) is employed there must be sufficient collisions beyond the nozzle throat for \( \text{Ar}^* \) to be quenched by \( \text{H}_2 \).

3. Formation of stabilized \( \text{H}_4^* \) is a three-body process. Hence, sufficient collisions must occur in the excitation region between the colliding \( \text{H}_2(\text{B}) - \text{H}_2 \) complex and a third body (\( \text{H}_2 \) or \( \text{Ar} \)).

An analysis of the nozzle flow characteristics (Figure 1) show that \( \text{H}_2(\text{B}) \) must be excited within 0.9 mm of the nozzle throat in order for conditions 1 to 3 to be satisfied.

The calculations of Nicolaides and coworkers\(^5-7\) show that \( \text{H}_4^* \) is bound by 3.1 eV with respect to dissociation to form \( \text{H}_2(\text{B}) \) and \( \text{H}_2 \). However, they also have shown that the complex is bound by 1.86 eV with respect to dissociation along the \( H^- + H_3^+ \) coordinate. Hence, photolysis of \( \text{H}_4^* \) may produce \( H_3^+ + H^- \), \( H_3 + H \), or \( \text{H}_2(\text{B}) + \text{H}_2 \). A careful selection of photolysis wavelengths may result in selective excitation into any of these channels. In our experimental effort we will be using a range of photolysis wavelengths in order to excite the channel leading to \( \text{H}_2(\text{B}) + \text{H}_2 \). We are also considering detection schemes to observe ionic dissociation pathways and \( \text{H}_2(\text{B}) \) quenching collisions which produce atomic hydrogen. Observation of \( \text{H}_4^* \) may also be accomplished via detection of passive emission from the radiating excimer, if such radiation does indeed exist.

Photolysis of \( \text{H}_4^* \) will initially be attempted using a broadband flash-lamp source (\( \lambda = 190 \) to 3000 nm). A solar blind PMT will be used to detect \( \text{H}_2(\text{B}) \) emission.
resulting from the photolysis. Use of this broadband source is desirable in order to minimize the time required for a long search for appropriate photolysis wavelengths. As \( \text{H}_2(B) \) emission is observed the flashlamps will be filtered to narrow the effective photolysis bandwidths until a spectral range is defined over which more selective laser-based photolysis studies can be conducted.


CHARACTERIZATION OF TETRAHYDROGEN VIA
STATE-SELECTED EXCITATION OF H₂

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TO

HIGH ENERGY DENSITY MATTER CONFERENCE
ROSSLYN, VIRGINIA

12-13 MAY 1987
PROGRAM OBJECTIVES

- PRODUCE AND CHARACTERIZE H₄⁺
- EXPERIMENTAL APPROACH TO H₄ STUDIES
  - PRODUCTION OF H₂(B)
  - STABILIZATION OF H₂(B) - H₂ COMPLEX AND RELAXATION OF H₄⁺
  - DETECTION OF H₄
- EXPERIMENTAL OBSERVATIONS
  - THREE PHOTON EXCITATION OF H₂(B)
  - ENERGY TRANSFER FROM Ar⁺ (106.6 nm) to H₂(B)
TETRAHYDROGEN: NICOLAIDES et al.

- **STABLE EXCIMER OF** \( \text{H}_2(\text{B}) + \text{H}_2 \)
  - **FORMED WHEN** \( \text{H}_2(\text{B}) \) **IN STATE OF** "**MAXIMUM IONICITY**"
    **CORRESPONDING TO** \( v' = 3 \) **OF** B-STATE
  - **STABILITY OF** \( \text{H}_4 \)
    \[
    \begin{align*}
    \text{H}_4 + \text{H}_2(\text{B}) + \text{H}_2 & \quad \Delta E = -2.48 \text{ eV} \\
    \text{H}_4 + \text{H}_3^+ + \text{H}^- & \quad \Delta E = -1.86 \text{ eV}
    \end{align*}
    \]
  - **VIBRATIONAL FREQUENCIES PROBABLY SIMILAR TO** \( \text{H}_3^+ \)
    **SYMmetric STRETCH:** \( v = 3185 \text{ cm}^{-1} \)
    **BEND:** \( v = 2516 \text{ cm}^{-1} \)

- **GEOMETRY**

![Tetrahydrogen Structure](image)

\( 0.95 \text{A} \)

\( 2.22 \text{A} \)
EXPERIMENTAL APPROACH

- COLLISIONALLY QUENCH H₂(B,v) WITH H₂ CLOSE TO THROAT OF SUPersonic JET
  - H₂ OPTICALLY THIN HENCE DIRECT EXCITATION POSSIBLE
  - COLLISION RATE NEAR THROAT SUFFICIENT FOR QUENCHING OF H₂(B) TO EFFICIENTLY COMPETE WITH RADIATION
  - EXPANSION "COOLS" COMPLEX AND PROVIDES COLLISION-FREE REGION FOR CHARACTERIZATION

- PROVIDE DIFFERENT EXCITATION SOURCES FOR H₂(B) TO MINIMIZE H₄ DESTRUCTION
  - DISCHARGE EXCITATION OF H₂/Ar MIXTURE
  - RESONANT EXCITATION OF H₂/Ar MIXTURE WITH Ar 1048Å AND 1066Å LINES
  - DIRECT VUV EXCITATION OF H₂(B)
  - THREE PHOTON EXCITATION OF H₂(B)
QUENCHING IN $H_2$ AND $H_2/Ar$

- $H_2$(B) QUENCHING BY $H_2$
  - MOORE et al. $\sigma_{H_2} = 79\AA^2$
    
    $$k_Q = \tilde{c}_e \bar{c} = (\frac{8kT}{\pi\hbar^2})^{1/2}$$

    $$k_Q = 1.1 \times 10^{-9} \left(\frac{T}{300}\right)^{1/2} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

  - QUENCHING CONDITION. $k_Q[H_2] = k_{rad}$
    
    $k_{rad} = 1.5 \times 10^9 \text{ s}^{-1}$

    $[H_2] = 1.4 \times 10^{18} \text{ molecule cm}^{-3} \text{ AT 300 K}$

- $Ar^*$ QUENCHING BY $H_2$
  - BOXALL et al. $\sigma = 48\AA^2$
    
    $$k_Q = 1.9 \times 10^{-10} \left(\frac{T}{300}\right)^{1/2} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

  - QUENCH $Ar^*$ 1066Å LINE: $k_{rad} = 1.2 \times 10^8 \text{ s}^{-1}$
    
    $[H_2] = 6.3 \times 10^{17} \text{ molecule cm}^{-3} \text{ AT 300 K}$

- IN $Ar/H_2$ MIXTURES $[H_2] = 1 \times 10^{18} \text{ molecule cm}^{-3}$ WILL QUENCH BOTH $Ar^*$ AND $H_2$(B)
MOLECULAR BEAM NOZZLE EQUATIONS

\[
\frac{N}{N_0} = \left[ 1 + (\gamma + 1) \frac{M^2}{2} \right]^{1/(1-\gamma)}
\]

\[
\frac{T}{T_0} = \left[ 1 + (\gamma + 1) \frac{M^2}{2} \right]^{-1}
\]

\[
\bar{v} = \left( \frac{\gamma kT}{M} \right)^{1/2}
\]

WHERE \( M \) IS THE EXPANSION MACH NUMBER AND A FUNCTION OF \((L/D)\)

L = DISTANCE DOWNSTREAM

D = THROAT DIAMETER

- ANALYTICAL EXPRESSIONS FOR \( M \) VERSUS \((L/D)\) FROM ANDERSON
$H_2(B)$ COLLISION FREQUENCY AS A FUNCTION OF DISTANCE FROM THE NOZZLE THROAT

250 $\mu$m DIAMETER NOZZLE, $P_{H_2} = 5$ ATM

Diagram showing the collision frequency as a function of expansion distance (mm) with a logarithmic scale on the y-axis from $10^7$ to $10^{11}$ and a linear scale on the x-axis from 0.0 to 1.8 mm.
STABILIZATION OF $H_4^*$

- LIFETIME OF $H_2(B) - H_2$ COMPLEX $10^{-10} - 10^{-12}\text{s}$

\[ H_2(X) + hv + H_2(B,v) \quad j_1 = \sigma I \]

\[ H_2(B) + H_2 + H_4^* \quad \phi k_2 \]

\[ H_4^* + M + 2H_2 + M \quad k_{-3} \]

\[ H_4^* + M + H_4 + M \quad k_3 \]

\[ H_4^* + H_2(B) + H_2 \quad k_4 \]

\[ H_2(B) + H_2 + hv \quad A_5 \]

- $H_4^*$ LIFETIME SHORT - STEADY-STATE SOLUTION APPROPRIATE

\[
\frac{d[H_4]}{dt} = j_1[H_2] \left( \frac{\phi k_2[H_2]}{k_2[H_2] + A_5} \right) \left( \frac{k_3[H_2]}{2k_3[H_2] + k_4} \right)
\]

- ESTIMATED $H_4$ FORMATION EFFICIENCIES/$H_2(B)$

$[H_2] = 10^{18}$ molecule cm$^{-3}$

<table>
<thead>
<tr>
<th>$k_4$ (s$^{-1}$)</th>
<th>$H_4$ EFFICIENCY</th>
</tr>
</thead>
<tbody>
<tr>
<td>$10^{10}$</td>
<td>$10^{-2}$</td>
</tr>
<tr>
<td>$10^{11}$</td>
<td>$10^{-3}$</td>
</tr>
<tr>
<td>$10^{12}$</td>
<td>$10^{-4}$</td>
</tr>
</tbody>
</table>
RELAXATION OF $H_4^*$

- DYNAMICAL SIMULATIONS OF OTHER SYSTEMS (Ar-0$_3$) SHOW APPROXIMATELY 100 COLLISIONS SUFFICIENT TO RELAX COMPLEX SIGNIFICANTLY

- OTHER REACTIVE CHANNELS FOR $H_2(B)$

  \[
  H_2(B) + H_2 + 4H \quad \Delta E = -2.7 \text{ eV} \\
  H_2(B) + H_2 + H_2 + H_2^+ + e^- \quad \Delta E = +4.2 \text{ eV} \\
  H_2(B) + H_2 + H + H^+ + e^- \quad \Delta E = +6.9 \text{ eV} \\
  - H-ATOM FORMATION POSSIBLE CHANNEL
DETECTION OF H₄

**PHOTODISSOCIATION TO FORM H₂(B)**
- \( \lambda < 500 \text{ nm} \)
- DETECT \( \text{H₂}(B) \) EMISSION WITH PMT
- FLASHLAMP PHOTOLYSIS, \( \lambda = 200 \text{ TO } 800 \text{ nm} \)
- LASER PHOTOLYSIS, \( \lambda = 337 \text{ nm}, 266 \text{ nm} \)
- CROSS SECTION UNCERTAIN: \( 10^{-18} \text{ TO } 10^{-20} \text{ cm}^2 \)
- AT \( 10^{-20} \text{ cm}^2 \) CAN DISSOCIATE 5 TO 10 PERCENT WITH 337 nm

**PHOTODISSOCIATION TO FORM H₃⁺ + H⁻**
- \( \lambda < 670 \text{ nm} \)
- COLLECT TOTAL IONS FORMED WITH ELECTRODES
- POSSIBLE CONSTRUCTION OF TIME-OF-FLIGHT MASS SPECTROMETER
- IMPROVED COLLECTION EFFICIENCY FOR IONS INCREASES EXPECTED SIGNAL BY \( 10^4 \)

**PASSIVE EMISSION**
- QUASI-CONTINUOUS, \( \lambda > 153 \text{ nm} \)
- LOOK WITH PMT/VUV MONOCHROMATOR
EXPERIMENTAL CHAMBER

- Possible TOF mass spectrometer
- H₂ nozzle
- Rare gas nozzle
- Laser access ports
- Solar blind PMT
- Monochromator or laser photolysis ports
- Flashlamps
- To diffusion pump
- Baffles
THREE PHOTON $H_2$ EXCITATION SPECTRUM

$P_{Ar} = 20$ Torr  $P_{H_2} = 80$ Torr

RELATIVE INTENSITY (mv)

DYE LASER WAVELENGTH (nm)
THREE PHOTON H₂ EXCITATION SPECTRUM

H₂(B, v' = 3) - H₂(X, v' = 0)  80 Torr H₂
Ar EXCITATION SPECTRUM

$P_{Ar} = 20$ Torr

RELATIVE INTENSITY (mV)

DYE LASER WAVELENGTH (nm)
SUMMARY

- H_4 TO BE PRODUCED VIA QUENCHING OF H_2(B) BY H_2
  - H_2(B) EXCITED VIA DIRECT EXCITATION AND Ar* ENERGY TRANSFER
  - SUPersonic jet employed to enhance formation and characterization

- ACTIVE AND PASSIVE DETECTION OF H_4 TO BE EXPLORED
  - PhOTOLYSIS TO PRODUCE H_2(B) OR IONIC PRODUCTS
  - DETECTION OF PASSIVE EMISSION FROM DECOMPOSING EXCIMER

- DEMONSTRATED H_2(B) PRODUCTION VIA THREE-PHOTON EXCITATION AT 319 nm
  - OTHER FEATURES OBSERVED WHICH SCALE NON-LINEARLY WITH H_2 DENSITY
  - COLLISIONAL ENERGY TRANSFER FROM Ar* TO H_2 OBSERVED VIA THREE-PHOTON EXCITATION OF Ar
ABSTRACT

Theoretical Studies of Metastable States of \( \text{He}_2 \) and \( \text{H}_4 \)

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SLCBR-IB-I
Aberdeen, MD 21005-5066

David R. Yarkony
Department of Chemistry
Johns Hopkins University
Baltimore, MD 21218

We have recently developed a series of theoretical methods which are capable of calculating the quenching rates of metastable molecular states due to nuclear and relativistic non-adiabaticity. We currently have the ability to analytically compute the first and second order nuclear non-adiabatic coupling matrix elements, \( \langle \psi | \frac{\partial \Psi}{\partial r_i} | \psi \rangle \) and \( \langle \psi | \frac{\partial^2 \Psi}{\partial r_i^2} | \psi \rangle \), as well as to compute quenching rates arising from spin-orbit interactions. The ability to include the effect of spin-spin interactions is being incorporated in our program package and we will report the progress attained in that effort.

These methods have been applied to the studies of \( \text{H}_4 \) and \( \text{He}_2 \), and we will report the results of that work. For \( \text{H}_4 \) we have optimized the structures of the low-lying states at the multi-reference CI level. The lowest state in the pyramidal (\( C_3v \)) configuration was found to be unstable with respect symmetry breaking nuclear displacements. The first excited state was of \( E \) symmetry in \( C_3v \) and was found to distort to a \( C_1 \) minimum with full geometry optimization. Dipole transition moments and non-adiabatic coupling matrix elements were calculated at the minimum of the excited state.

For \( \text{He}_2 \) we have considered the spin-forbidden radiative transition between the lowest triplet state and the ground state, \( \text{a}^3\Sigma^+ \rightarrow \text{x}^1\Sigma^+ \). We have also calculated the spin-orbit coupling matrix elements which are needed to compute the quenching of the lowest triplet atomic state.
Theoretical Studies of Metastable States of He$_2$ and H$_4$

Byron Lengsfield, James Jensen, George Adams and Cary Chabalowski
US ARMY Ballistic Research Laboratory

David Yarkony
Johns Hopkins University

Speaker's comments are enclosed in brackets.
Develop Theoretical Methods

- Characterize Potential Energy Surfaces
  - locate stable points on ground and excited state surfaces
  - compute vibrational frequencies and intensities

- Compute Spin-Forbidden Lifetimes
  - spin-orbit coupling
  - spin-spin coupling

- Compute Nonadiabatic Coupling Terms
  - d/dR terms
  - Rotational couplings

Goal is to develop the needed theoretical tools and to apply them to promising molecular systems.
Theoretical Methods Used to Characterize Potential Energy Surfaces

Perturbation Theory
Coupled-Cluster Wavefunction
Multi-Reference CI  1,000,000 CSFs

MCSCF  10,000 CSFs
SCF  1 CSFs
[Multi-Configuration description is needed for excited states and for systems where resonance is important]

TABLE III. COMPARISON OF EXPERIMENTAL AND THEORETICAL FREQUENCIES, TOTAL ENERGIES, AND GEOMETRIES FOR H₂CO
(Frequencies in cm⁻¹)

<table>
<thead>
<tr>
<th>NODE</th>
<th>EXP. SCF</th>
<th>UZP SCF</th>
<th>BAC DMC</th>
<th>BAC SDMC</th>
<th>DZP DMC</th>
<th>DZP C1 DMC</th>
<th>dDZP DMC</th>
<th>dDZP+dSPD DMC</th>
</tr>
</thead>
<tbody>
<tr>
<td>v₆(B₁)</td>
<td>1190</td>
<td>1335</td>
<td>1287</td>
<td>1170</td>
<td>1221</td>
<td>1222</td>
<td>1223</td>
<td>1272</td>
</tr>
<tr>
<td>v₅(B₂)</td>
<td>1282</td>
<td>1367</td>
<td>1319</td>
<td>1244</td>
<td>1291</td>
<td>1292</td>
<td>1291</td>
<td>1305</td>
</tr>
<tr>
<td>v₃(A₁)</td>
<td>1561</td>
<td>1636</td>
<td>1604</td>
<td>1506</td>
<td>1560</td>
<td>1560</td>
<td>1560</td>
<td>1596</td>
</tr>
<tr>
<td>v₂(A₁)</td>
<td>1767</td>
<td>2007</td>
<td>1861</td>
<td>1712</td>
<td>1849</td>
<td>1850</td>
<td>1870</td>
<td>1868</td>
</tr>
<tr>
<td>v₁(A₁)</td>
<td>2940</td>
<td>3148</td>
<td>3081</td>
<td>2897</td>
<td>2940</td>
<td>2944</td>
<td>2957</td>
<td>3074</td>
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<tr>
<td>v₄(B₂)</td>
<td>3016</td>
<td>3226</td>
<td>3178</td>
<td>2979</td>
<td>3002</td>
<td>3007</td>
<td>3023</td>
<td>3173</td>
</tr>
</tbody>
</table>

| Total * Energy (Hartrees) | --- | -.895328 | -1.031216 | -1.063136 | -1.195568 | -1.070912 |
| Bond Angle (degrees)      | --- | -.852032 | -1.063553 | -1.133902 | -1.074239 |          |
| Bond Length CO (Å)        | 1.203 | 1.189    | 1.209    | 1.236    | 1.213    | 1.210      |
| (Å) CH                    | 1.099 | 1.094    | 1.091    | 1.110    | 1.115    | 1.114      |

*Energies needed to be added to -113.0.

*Finite-Difference Results (step length of .001 bohr)

Example of Recent Work Employing Derivative Techniques
<table>
<thead>
<tr>
<th>MODE</th>
<th>EXP</th>
<th>BAC/EXP</th>
<th>BAC/DZP</th>
<th>BAC/dTZP$^\Delta$</th>
<th>BAC/DZP</th>
<th>dTZP+d$^f$/dTZP</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>SCF</td>
<td>DMC</td>
<td>CI</td>
<td>DMC</td>
<td></td>
</tr>
<tr>
<td>v_6</td>
<td>6.5</td>
<td>6.2</td>
<td>5.5</td>
<td>5.3</td>
<td>8.2</td>
<td>4.1</td>
</tr>
<tr>
<td>v_5</td>
<td>9.9</td>
<td>18.9</td>
<td>12.4</td>
<td>12.9</td>
<td>11.0</td>
<td>14.4</td>
</tr>
<tr>
<td>v_3</td>
<td>11.</td>
<td>33.2</td>
<td>10.9</td>
<td>7.4</td>
<td>13.8</td>
<td>11.6</td>
</tr>
<tr>
<td>v_2</td>
<td>74.</td>
<td>107.9</td>
<td>81.2</td>
<td>85.7</td>
<td>72.</td>
<td>107.8</td>
</tr>
<tr>
<td>v_1</td>
<td>75.</td>
<td>72.7</td>
<td>59.4</td>
<td>62.8</td>
<td>53.7</td>
<td>68.1</td>
</tr>
<tr>
<td>v_4</td>
<td>87.</td>
<td>112.1</td>
<td>87.1</td>
<td>83.3</td>
<td>80.5</td>
<td>96.6</td>
</tr>
</tbody>
</table>

$^+$ The notation XXX/YYY indicates that the dipole derivatives were computed with basis XXX at the geometry obtained with basis YYY and using the YYY normal modes.

$\Delta$ dTZP = Bacskey sp basis + tight set of polarization functions.

$^f$ dTZP basis + diffuse polarization functions.
Spin-Orbit interactions

(Sum over states is avoided by solving a large set of linear equations (eqn 2.5a of reference). This means large, direct-CI wavefunctions can be employed and the slow convergence of a sum over states perturbation expansion is avoided. See Yarkony, J Chem Phys, 85, 7261(1986))

(Same approach is being developed for spin-spin interaction)

-------------------------------- NEXT SLIDE--------------------------------

(We can exploit work on derivatives of CI wavefunctions to compute non-adiabatic matrix elements)


-------------------------------- NEXT SLIDE--------------------------------

See equation 2.8 of J Chem Phys, 81(10), 4549(1984)

(Two terms need to be evaluated)


(Trace of a one-particle density matrix with a half-derivative overlap integral)
Non-Adiabatic Coupling
Born-Oppenheimer Approximation

Matrix Elements

\[ \langle 4_i : 1 \frac{d}{dR} 14_j \rangle \]
\[ \langle 4_i : 1 \frac{d^2}{dR^2} 14_j \rangle \]

Derivative Methods

CI gradient

Rotational Coupling

(CI gradient evaluated with a transition density matrix)

See Figure 1 of Ginter, H.L. and Battino, R., 4470.

[A large number of curve crossings must be considered. Relativistic interactions can result in avoided crossings.]
Theoretical Studies of $H_4^+$

- Characterize both stable points optimized structures
- Compute Vibrational Frequencies Multi-Reference CI Level
- Estimate the Radiative Lifetime of the Excited State
- Compute Nonadiabatic Coupling Terms
Figure 4

Potential Energy Curve for a Metastable Molecular State

Excited state (B) can radiate in H₄ via a dipole-allowed mechanism.

Region A is of interest for energy storage in H₄. A fourth isomer found to be unstable in region A at SCF and MO-SCF levels in preliminary calculations.
Theoretical Studies of He$_2$

Input Parameters to Liquid Simulation

- Stability of the $^3S$ _STATE_ of He
- Spin-Orbit Lifetime $^3\Sigma^+_u$ state of He$_2$
- Spin-Spin Coupling
- Nonadiabatic Terms
- Characterize states of He$_2$, He$_3$, He$_4$, etc
Lifetime of the $^3{\Sigma}^+_u$ State of He$_2$

spin-orbit operator

$$\frac{1}{2c^2} \frac{Z^2 \kappa}{r_{ik}} \frac{2(K)}{Y_{ik}^3} \mathbf{P}_i \cdot \mathbf{S}_j + h^{300}$$

dipole allowed transition

$$\langle \pi, 1, 1, {\Sigma}^+ \rangle$$

$$\langle ^3{\Sigma}^+_u, 1, 1, \pi \rangle$$

think in terms of relativistic states

$$\langle 4^0, \pi_2^+, 4^0, \pi_1, 4^0, \pi_2^+, 4^0, \pi_1 \rangle$$
Abstract for
The First Annual High Energy Density Matter (HEDM) Conference
May 12-13, 1987
Crystal City, VA

The Influence of Condensed Phase on Metastability

by

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Condensed phase influence on HEDM candidates plays a critical role in determining the lifetimes and storage conditions, thereby ultimately influencing their practical usefulness. We have developed a comprehensive theoretical methodology involving quantum chemistry input, modern computer simulation techniques (such as Monte Carlo, Molecular Dynamics, and Generalized Langevin Dynamics), and semiclassical eikonal description of electronic inelasticity to investigate various aspects of the underlying microscopic energy transfer mechanisms.

We will show illustrative results obtained with the new methodology for the well known examples of liquid Helium metastables, so far employed in this research as convenient prototypes. The experience gained in modeling metastability in these cases has laid the foundation for future studies on other potential HEDM candidates.
Program Plan

HEDM Candidate

Applications Feasibility

Effect of Condensed Phase on Metastability

Our Role:

Develop Methods for Elucidation of Quenching Mechanisms in Gas and Condensed Phases
HEDM's involve energetic species, usually in an ELECTRONICALLY EXCITED state

Therefore, the chemistry and quenching mechanisms involve ELECTRONICALLY NONADIABATIC Collision Dynamics

Condensed Phase materials low molecular weight inert species

Temporary Prototypes:
Helium Metastables $\text{He}^*(^3\Sigma)$ and $\text{He}_2^*$ (a - state) in Helium Liquid
Technical Approaches

Gas-Phase

Self-Consistent Eikonal Method (SCEM)
Electronic amplitudes coupled to
Nuclear Trajectories via an Ehrenfest
Effective Potential
A Self-Consistent Semiclassical
Description practical for polyatomics

Condensed Phase

Computer Experiments: Monte Carlo,
Molecular Dynamics

Few- body Models:
SCEM + Generalized Langevin Equation (GLE)
based STOCHASTIC MODELS

System + Heatbath Decomposition with
one-time heatbath parameterization via
computer experiments
He–He Effective Pair Potentials

\[ \frac{U(r^*)}{k} \text{ (K)} \]

- Aziz Model
- LJ Model

\[ r^* = r / \sigma \]
He–He Short–Range Interactions

$U(r')/k (K)$ vs $r' (r' = r/\sigma)$

- Aziz Model
- LJ Model
Liquid Structures of Model Helium

Aziz Model

LJ Model

$g(r^*)$

$r^*(r^* = r/\sigma)$
Liquid Dynamics of Model Helium

\[
\frac{\langle \dot{\ddot{x}}(0) \ddot{x}(0) \rangle}{\langle \dot{x}(0) \dot{x}(0) \rangle^2}
\]

- Aziz Model
- LJ Model

Time (pS)
Fluid Structures of Model Helium

$r^*(r^*=r/\sigma)$

$g(r^*)$

- - - - - 14.3 GPa
- - - - - 12.7 GPa
- - - - - 10.4 GPa

○ 1.4 GPa
x 0.5 GPa
□ 0.3 GPa
Fluid Dynamics of Model Helium

![Graph of fluid dynamics for model helium](image)
GLE parameters

\[ \omega (\text{THz}) \]

\[ P (\text{GPa}) \]

\[ \omega_{c1} \]

\[ \omega_{e0} \]
He$^+$-He RDF for a-state

1.4 GPa
10 GPa
14 GPa

1.4 and 10 GPa (2M moves) 14 GPa (200K moves)
He\textsuperscript{2} Interaction Potentials

![Graph showing interaction potentials for different states (1P, 3P, 1S, 3S) as functions of r/bohr. The graph plots U(r)/hartree against r/bohr.]

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STOCHASTIC TREATMENT
OF
HELIUM BUBBLE

He

He*

He

\begin{align*}
\omega_{\epsilon_0}^2 & \quad X_0 \\
\omega_{\epsilon_1}^2 & \quad X_1 \\
\omega_{\epsilon_{N-1}}^2 & \quad X_{N-1} \\
\omega_C^2 & \quad X_N
\end{align*}

\begin{align*}
\omega_{\epsilon_0}^2 & \quad X'_0 \\
\omega_{\epsilon_1}^2 & \quad X'_1 \\
\omega_{\epsilon_{N-1}}^2 & \quad X'_{N-1} \\
\omega_C^2 & \quad X'_N
\end{align*}

HEAT BATH
Helium bubble with a-state and X-state He* using arbitrary coupling. Figures show effect of increasing the coupling by a factor of two.
The plot shows the behavior of different variables over time (t in psec). The variables are labeled as follows:

- \( P_i \)
- \( X_0 (a_0) \)
- \( R (a_0) \)
- \( X_0' (a_0) \)

Each variable is plotted against time, with the time axis ranging from 0 to 5 psec.
OPTIMIZED TRIAL FUNCTIONS FOR QUANTUM MONTE CARLO STUDY OF $\text{H}_4^*$

Sheng-yu Huang, Zhiwei Sun, and William A. Lester, Jr.

Materials and Chemical Sciences Research Division
Lawrence Berkeley Laboratory
University of California
Berkeley, CA 94720

In recent years the fixed-node quantum Monte Carlo method (FNQMC) has been successfully applied to the calculation of electronic energies of small molecules. The attractive feature of this method is that with a modest basis set and often a single-Slater determinant one typically recovers over 90% of the correlation energy.

Because the simulation is dominated by a trial function that fixes the nodal positions, a good trial function is essential in order to obtain an accurate result. It is often chosen to be an ab initio approximate Hartree-Fock wavefunction in which case the many-electron nodes are established without consideration of electron correlation. Introduction of an explicit correlation factor in the Jastrow form (exponential) improves the variational energy, but this nodeless function does not improve the nodes of the system. Ideally, the Slater determinant needs be re-optimized in the presence of the correlation factor.

We have developed an algorithm to optimize trial function parameters (linear coefficients, non-linear exponential factors, and parameters of the correlation function) based on a random walk procedure. In order to obtain accurate energies for excited states, we introduce a projection operator method based on group theory to constrain the optimization process. It effectively distinguishes all the states of a given symmetry. We also apply the Young tableaux of permutation group theory to facilitate the treatment of fermion properties and multiplets.

Using an optimized trial function, we are studying pyramidal $\text{H}_4$ at the maximum ionicity excited state (MIES) and other geometries relevant to understanding decomposition pathways in this system. The calculated potential energies show 0.6-0.8 eV lowering compared to a previous study\(^1\). In a separate multi-configuration ab initio study we have determined that there is a pathway without a barrier for $\text{H}_2(\text{B})$ approach to ground state $\text{H}_2(\text{X})$. Work is in progress to fully characterize the first-excited state of the $\text{H}_4$ system and its coupling to the ground state, and will be discussed.

\(^1\) This work was supported by the U.S. Air Force Rocket Propulsion Laboratory (AFRPL) through agreement with the Department of Energy under Contract No. DE-AC03-76SF00098.
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\(^\ddagger\) Permanent address: Institute of Mechanics, Academia Sinica, People’s Republic of China
QMC AND MCSCF STUDY OF TETRAHYDROGEN

Sheng-Yu Huang, Zhiwei Sun, and William A. Lester, Jr.
Materials and Chemical Sciences Division
Lawrence Berkeley Laboratory
University of California, Berkeley
Berkeley, California 94720

1. MCSCF Pilot Study of Trigonal Pyramidal Ground- and Excited-State H₄.

We have demonstrated that MCSCF (multiconfiguration self-consistent field) wave functions as trial functions for FNQMC (fixed-node quantum Monte Carlo) calculations can recover ~100% of the correlation energy of ground states and ~95% of the correlation energy of excited states. Using an extended (triple zeta-plus-polarization (TZP)) basis set, MCSCF calculations were carried out for the H₄ MIES (maximum ionicity excited state), see Fig. 1. They confirmed the characteristics depicted in Fig. 2 for the C₃ᵥ pyramidal structure including the minimum energy geometry, the doubly degenerate E ground state as H separates from H₃ for R > 3.8 a.u., and the nondegenerate A ground state for R < 3.8 a.u., consistent with an E- to A-state crossing at R = 3.8 a.u. For C₅ᵥ symmetry the avoided crossing was obtained. Figure 3 displays the results of the MCSCF pilot computations. These curves lie above those of Nicolaides, Theodorakopoulos, and Petsalakis (NTP) and reflect the better capability of the ab initio MRD-CI wave functions compared to the compact MCSCF trial functions needed here as FNQMC trial functions. The key comparison, however, will be with the FNQMC results obtained with the MCSCF functions. We discuss this point in Sec. III.

II. MCSCF Pilot Study of the H₂(X) + H₂(B) → H₄ MIES Pathway.

Calculations were carried out for H₂(B) approach to H₂(X) in which these molecules are contained initially in perpendicular planes that bisect
each other. Figure 4 displays this arrangement and summarizes, in the accompanying table a sequence of geometry changes, labeled I-VII, that carry the system from the asymptotic region to the neighborhood of the $H_4$ MIES configuration. The table also contains the energy lowering associated with the steps that are plotted in Fig. 5. It is noteworthy that no energy barrier is encountered along this path. Further, Fig. 6 shows that when $H(B)$ is displaced from bisecting $H_2(X)$ in step II, charge transfer immediately occurs. (Similar behavior has been found for the related $H_2(B) +$ He system in an independent study by WAL.)

III. FNQMC Study of the Ground-State Pyramidal Structure for $C_{3v}$ Symmetry

FNQMC calculations using the MCSCF trial functions discussed in Sec. I yield $-0.6-1.0$ eV energy lowering compared to the results of NTP and are presented in Fig. 7. Such a large change was not anticipated and so it was important to test the validity of this finding. To this end a configuration interaction calculation including all single and double excitations (SDCI) using the MCSCF pilot study basis set was carried out at $R = 3.4$ a.u. The energy was 0.32 eV lower than NTP's value and is consistent with the improvement expected based on studies of other systems. The FNQMC results of Fig. 7 obtained using a new trial function optimization algorithm, see Sec. IV, are generally an improvement over those of Fig. 7 obtained using MCSCF trial functions.

IV. FNQMC Study of the Excited State

These calculations provide the severest test of the FNQMC approach because
of the lack of knowledge of the accuracy of the excited state trial function needed to provide a nodal description that assures orthogonality to the ground state of the same (A') symmetry (C₅). MCSCF calculations close to the avoided crossing suffered from root flipping. Despite the use of familiar MCSCF strategies to address the problem, it could not be resolved.

The MCSCF convergence problem had been encountered earlier for He + H₂(B) but resolved by the use of an ab initio CI method. Interest here in using the FNQMC method led us to develop a method for trial function construction that avoids the MCSCF procedure. The approach amounts to the introduction of parameter optimization in the random walk process. Using group theory a projection operator is constructed and used to constrain the wave function to have the symmetry properties of the state of interest. This method has been employed in the present effort to generate the A-state FNQMC results, denoted A(FNQMC), of Fig. 7. Calculations using this method are in progress to complete the E-state curve, labeled E(FNQMC), in Fig. 7 for 3.8 < R < 6.0 a.u.

V. SA-MCSCF Study of Distorted Geometries

Calculations have been carried out using the state averaged (SA)-MCSCF method to develop trial functions for a QMC study of the topography of the ground- and excited-state potential energy surface (pes) in the region of the symmetric geometry of the MIES determined by NTP. Figure 8 presents the coordinate system, Fig. 9 provides perspective views, and Fig. 10 (R = 4.0 a.u.) and Fig. 11 (R = 3.8 a.u.) show contour maps of the pes in the MIES region. Figures 10 and 11 show that the ground state has a saddle point at smaller R than the minimum of the excited state and that both features
correspond to an isosceles triangle base for the MIES system. Further
geometry optimization is explored in Fig. 12 which plots potential energy as a
function of \( d \), the displacement of \( H_a \) towards the base of the \( H_3 \) isosceles
arrangement. The minimum for the excited state is found for \( d = 0.1 \) a.u.

VI. Nonadiabatic Coupling

The stability of the MIES system is dependent on nonadiabatic coupling
\((NAC)\) to the ground state. Although the focus of this study is characteriza-
tion of the region of pes of the MIES, the need to ascertain first the
stability of the excited system is a high priority here because of the effort
associated with the trial function optimization method and the expense of QMC
calculations with small statistical variances. To calculate the NAC matrix
elements we took advantage of the simplifications made possible by the use of
normal mode distortions (Fig. 13) from the highly symmetric \( C_{3v} \) symmetry.
Our calculations show that nuclear displacements associated with modes \( Q_1 \)
and \( Q_2 \) lead to strong coupling between the A and E states. Relatively
weaker coupling is found in \( Q_4 \) and \( Q_5 \). The two totally symmetric modes
\((Q_3 \) and \( Q_6 \)) give no contribution.

The size of the NAC matrix elements connecting the A' state to the E-state
components \((C_{3v} \) notation is used here to indicate parentage) are tabulated
in Fig. 14 for the minimum energy geometry of the A state. These results
establish that there is strong coupling between these states. Further
computational study is needed to confirm these predictions and estimate
reliably, the excited state lifetime.
References and Footnotes

†Also, Department of Chemistry, University of California, Berkeley 94720.


3S.-Y. Huang, Z. Sun, and W. A. Lester, Jr., "Algorithm for Optimizing Parameters in a Quantum Monte Carlo Trial Function," to be published.
Figure Captions

Figure 1. MIES coordinate system (assuming $C_3^v$ symmetry): $R$ is the distance from $H_a$ to plane of $H_bH_cH_d$ equilateral triangle of side $r$.

Figure 2. Ground- and excited-state $H_4$ potential energy curves for trigonal pyramidal geometry: upper panel ($C_3^v$ symmetry), lower panel ($C_s$ symmetry).

Figure 3. Potential energy curves from MCSCF trial functions for trigonal pyramidal geometry and $C_3^v$ symmetry ($r = 1.70$ a.u.). State designations for $C_s$ symmetry are indicated in parentheses. The lack of coincidence of the degenerate $E$ curves reflects their calculation in lower symmetry and provides an indication of MCSCF convergence.

Figure 4. Geometries used to calculate an approach of $H_2(B)$ to $H_2(X)$.

Figure 5. Plot of total energies corresponding to the pathway presented in Figure 4.

Figure 6. Change of charge distribution between $H_a$ and $H_b$ as a function of $d$, the displacement of the midpoint of $H_2(B)$ above the plane of $H_2(X)$.

Figure 7. Potential energy of trigonal pyramidal $H_4$ versus $R$. The $A$ (variational) results were determined using a new optimization method for QMC trial functions.

Figure 8. MIES coordinate system used for geometry variation. $d$ is the magnitude of the displacement of $H_a$ along the bisector of the $H_cH_d$ side of length $b$.

Figure 9. Potential energy surfaces for the ground- and excited-state separately for easy visualization and in computed relative positioning. Note the minimum of the excited state and saddle point of the ground state.
Figure 10. Potential energy contour map for $R = 4.0$ a.u. as a function of $a$ and $b$; see Fig. 8.

Figure 11. Same as Fig. 10 for $R = 3.8$ a.u.

Figure 12. Potential energy curves for selected $R$ (in a.u.) vs $d$; see Fig. 8.

Figure 13. Normal mode displacements of $H_4$ in $C_{3v}$ symmetry.

Figure 14. CI contribution to coupling matrix elements for normal mode displacement, see Fig. 13.
Fig. 2
Fig. 3
Geometries and energies for the approach of H₂(B) to H₂(X)

<table>
<thead>
<tr>
<th>step</th>
<th>R'</th>
<th>L₁</th>
<th>L₂</th>
<th>L₂(+)</th>
<th>L₂(-)</th>
<th>D</th>
<th>energy lowering</th>
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<tbody>
<tr>
<td>I</td>
<td>5-2.2</td>
<td>1.40</td>
<td>2.43</td>
<td>1.215</td>
<td>1.215</td>
<td>0.0</td>
<td>-0.91</td>
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<tr>
<td>II</td>
<td>2.2</td>
<td>1.40</td>
<td>2.43</td>
<td>1.215-1.93</td>
<td>1.215-0.5</td>
<td>0.715</td>
<td>-0.20</td>
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<tr>
<td>III</td>
<td>2.2</td>
<td>1.60</td>
<td>2.63</td>
<td>1.93-2.13</td>
<td>0.5</td>
<td>0.865</td>
<td>-0.20</td>
</tr>
<tr>
<td>IV</td>
<td>2.2-1.75</td>
<td>1.60</td>
<td>2.63</td>
<td>2.14</td>
<td>0.5</td>
<td>0.865</td>
<td>-0.20</td>
</tr>
<tr>
<td>V</td>
<td>1.75-1.55</td>
<td>1.60</td>
<td>2.73</td>
<td>2.23</td>
<td>0.5</td>
<td>0.915</td>
<td>-0.48</td>
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<td>VI</td>
<td>1.55</td>
<td>1.60</td>
<td>3.13</td>
<td>2.23-2.63</td>
<td>0.5</td>
<td>1.115</td>
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<tr>
<td>VII</td>
<td>1.50</td>
<td>1.70</td>
<td>3.23</td>
<td>2.63-2.73</td>
<td>0.5</td>
<td>1.165</td>
<td>-0.11</td>
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TOTAL ENERGY LOWERING FOR THE SEVEN STEPS IS 3.75 ev.

* Distances in a.u.; energies in ev.

R' - distance between the midpoint of H₂(X) and the point where H₂(B) meets the H₂(X) plane.
L₁ - length of H₂(X).
L₂ - length of H₂(B).
L₂(+) - length of H₂(B) above H₂(X) plane.
L₂(-) - length of H₂(B) below H₂(X) plane.
D - magnitude of shift of H₂(B) midpoint (above (+)/below(-)) plane of H₂(X).

![Diagram](image-url)
Fig. 5
Fig. 6

CHARGE POPULATION vs. SHIFT OF H₂(B)

H (or H₂(B))

H (or H₂(B))

SHIFT OF MIDPOINT OF H₂(B) FROM BISECTOR PLANE

CHARGE POPULATION

0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0
POTENTIAL ENERGY OF PYRAMIDAL H₄

DISTANCE BETWEEN H AND H₃ (a.u.)
CONTOUR MAP (R=3.8 a.u.)

Fig. 11
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POTENTIAL ENERGY vs d

Fig. 12

-2.004
-2.002
-2.000
-1.998
-1.996
-1.994

○ R = 3.7
□ R = 3.8
◆ R = 3.9

d (a.u.)
Fig. 13
Coupling matrix elements $D^{CI}$ by a finite difference method (extrapolated from $\delta Q = 0.002, 0.001, \text{ and } 0.0005$).

| $Q_1$   | $<E_2 | A' >$ | $<E_1 | A' >$ |
|---------|--------------|--------------|
|         | -2.0112(64) | 0.0015(0)    |
| $Q_2$   | 0.0017(0)   | 2.0127(98)   |
| $Q_3$   | 0.0000      | 0.0000       |
| $Q_4$   | -0.3904(389)| -0.0010(3)   |
| $Q_5$   | -0.0039(13) | -0.3113(196) |
| $Q_6$   | 0.0000      | 0.0000       |

1. $E_1$ and $E_2$ are doubly degenerate states where $E_1$ is symmetric and $E_2$ is antisymmetric.
Abstract for HEDM Conference  
Spectroscopy of Polyatomic Hydrogen Ions  
Takeshi Oka  

Infrared laser spectroscopy of the $v_2$-fundamental band of $\text{H}_3^+$ and the extension of work towards higher energy state and isotopic species will be reported. The chemical and physical dynamics of this ion in gaseous discharge will be discussed. Our plan to observe spectra of $\text{H}_3^+$ and its cluster ions in condensed phase plasma will be discussed.

References

\[ H_3^+ \]

\[ \text{H}_2 + \text{P} \leftrightarrow \text{H}_3^+ + 4.5 \text{eV} \]

\[ \text{H} + \text{H} \rightarrow \text{H}_2 + 4.5 \text{eV} \]

\[ \text{H}_2 + \text{H}_2^+ \rightarrow \text{H}_3^+ + \text{H} + 1.8 \text{eV} \]

\[ \sigma \sim 100 \text{Å}^2 \]
Hydrogen Discharge

\[ \text{D.C. } 50 \text{ kV } 0.5 \text{A} \]

\[ \overset{f}{\text{H}_2 + \text{H}_2^+ \rightarrow \text{H}_3^+ + \text{H}} \]

Energy \( \approx 0.1 \text{ eV} \)

**Discharge Tube**

- 2m, 2cm\( \phi \)
- \( \eta (\text{H}_3^+) \approx 3 \times 10^{10} / \text{cm}^3 \)
- \( \frac{[\text{H}_3^+]}{[\text{H}_2]} \approx 10^{-6} \)
- **Column Density** \( \approx 10^{14} / \text{cm}^2 \)
- **Temperature** \( \approx 200 \text{K} \)
$NH_3$

$\times 20$

$\times 30$

$\times 600$

$\times 30$

Doppler-Ltd Diode Laser

$\frac{\Delta \nu}{\nu} \sim \frac{n}{c} \sim 10^{-6}$

Sub-Doppler

Chen, Frye,
Soc. Am. (1986)
<table>
<thead>
<tr>
<th>Species</th>
<th>Band</th>
<th>References</th>
<th>Year</th>
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<td>$\text{H}_3^+$</td>
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<td>IR Emission</td>
<td>Mjewsky, Watson, Johns</td>
<td>1985</td>
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<td>Bogey, Remynck, Denis, Destombes</td>
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<td>Saito, Kawaguchi, Hirota</td>
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<td>Foster, McKellar, Petenkin, Watson. Pan, Crofton, Altman</td>
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<tr>
<td></td>
<td>Foster, McKellar, Watson</td>
<td>1985</td>
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$H_3^+$ vibrational States

$2\nu_1$

$\nu_1 + \nu_2$

$2\nu_2$

2383 cm$^{-1}$

2484 cm$^{-1}$

669 cm$^{-1}$

2521 cm$^{-1}$

3185 cm$^{-1}$

Carny + Porter (1976)
Fig. 5. Predicted optimum geometries of some cationic hydrogen clusters

a) Ahlrich predicts the relative stability $D_{2d} > D_{2h} > C_{2v}(I) > C_{2v}(II)$ whereas Yamaguchi et al. predict $C_{2v}(I) \sim C_{2v}(II) > D_{2d} > D_{2h}$

Ahlrich 1975

Schaefter 1983, 1986
Fig. 1

Okumura, Yeh, and Lee (1985)
Fig. 1. Block diagram of the experimental set-up.
Fig. 2. Helium Dewar with the sample cell
Fig. 4. Optical path in the sample cell
\[ \begin{align*}
H_2 + p^* & \rightarrow H_2^+ + e + p^* \\
H_2^+ + H_2 & \rightarrow H_3^+ + H \\
H_3^+ + H_2 & \rightarrow H_5^+ \rightarrow H_7^+ \rightarrow H_9^+ \\
H_2 + p & \rightarrow H_3^+
\end{align*} \]
ADVANCED RESEARCH

IN ENERGY STORAGE

MAJ LARRY P. DAVIS

DR FRANCIS J. WODARCZYK

AFOSR/NC

MAY 1987
OBJECTIVE

SEARCH FOR HIGH ENERGY DENSITY PROPELLANTS OR ENERGY CARRIERS

• LONG-LIVED ELECTRONIC EXCITED STATES
• CHEMICALLY METASTABLE SPECIES
• SPIN-POLARIZED SPECIES
HIGH ENERGY DENSITY MATERIALS

PROGRAM PLAN

HIGH ENERGY GROUND STATES

- $H_4$ STUDIES
- REVOLUTIONARY HIGH ENERGY GROUND STATES
- EVOLUTIONARY SYSTEMS

ELECTRONIC EXCITED STATES

SPIN-ALIGNED SYSTEMS

SURFACE AND MATRIX STORAGE
THE LIMITS OF METASTABILITY

CURRENT PROPELLANTS

PROGRAM GOAL

CONVENTIONAL CHEMICAL SYSTEMS

LASERS

ENERGY

LIFETIME

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TECHNICAL ISSUES

- Formation Mechanisms
- Amount of Energy Stored
- Duration of Energy Storage (Lifetime)
- Methods of Stabilization and Storage
- Novel Bonding Structures
- Decay Mechanisms
TECHNICAL SPIN-OFFS

- Fuels
- Explosives
- Chemical Lasers
- Energy Conversion
HIGH ENERGY DENSITY MATERIALS

AFOSR CONTRACTORS

AIR FORCE ASTRONAUTICS LAB - IN-HOUSE PROGRAM

AIR FORCE AERONAUTICS PROPULSION LAB - IN-HOUSE PROGRAM

JOHNS HOPKINS UNIVERSITY - PROFESSOR DAVID YARKONY

SRI - DR HANSPETER HELM

CORNELL - PROFESSORS JOHN WIESENFELD AND BARRY CARPENTER

NBS - DRS MICHAEL CASASSA, JOHN STEPHENSON, AND DAVID KING

NATIONAL HELLENIC INSTITUTE - PROFESSOR C A NICOLAIDES
FUNDAMENTAL STUDIES OF CARBON, NH, AND OXYGEN RINGS
AND OTHER HIGH ENERGY DENSITY MOLECULAR SYSTEMS

PROFESSOR HENRY F SCHAEFER III

UNIVERSITY OF CALIFORNIA, BERKELEY

OBJECTIVE - THEORETICAL INVESTIGATIONS OF STABILITY AND ENERGETICS OF
O_N(NH)_N, AND C_N RINGS

APPROACH - USE HIGH-LEVEL MULTI-REFERENCE CONFIGURATION INTERACTION
AB INITIO MOLECULAR ORBITAL METHODS

1 APRIL 1987 - 30 MARCH 1990 (3 YEARS)
ENERGY FLOW AND DECOMPOSITION OF ENERGETIC
MOLECULES FROM METASTABLE VIBRATIONAL STATES

DRS MICHAEL CASASSA, JOHN STEPHENSON, AND DAVID KING
NATIONAL BUREAU OF STANDARDS
GAITHERSBURG, MD

OBJECTIVE: TO DETERMINE LIFETIMES AND FINAL STATE DISTRIBUTIONS RESULTING
FROM GROUND ELECTRONIC STATE VIBRATIONAL EXCITATION AND DECOMPOSITION OF
ENERGETIC, THERMALLY UNSTABLE MOLECULES

APPROACH: USE TIME-RESOLVED SHORT-PULSE LASER TECHNIQUES TO STUDY E, V, R, T, STATE
DISTRIBUTIONS AND STATE-TO-STATE DECOMPOSITION RATES FOLLOWING DIRECT OVERTONE
EXCITATION OF SMALL ENERGETIC MOLECULES.

1 JANUARY 1987 - 31 DECEMBER 1989 (3 YEARS)
DYNAMIC CONSTRAINTS ON STOCHASTIC BEHAVIOR
IN THE CHEMISTRY OF HIGHLY EXCITED MOLECULES

PROFESSORS BARRY K CARPENTER AND JOHN R WIESENFELD
CORNELL UNIVERSITY
ITHACA, NY

OBJECTIVE: TO DEVELOP A QUANTITATIVE PICTURE OF HIGHLY ENERGETIC CHEMICAL PROCESSES IN ORDER TO CREATE CRITERIA FOR THE EVALUATION OF NEW PROPELLANT SYSTEMS AND THEIR EFFICIENCIES.

APPROACH: DESIGN AND SYNTHESIZE MOLECULES FOR WHICH NON-STOCHASTIC BEHAVIOR IS PREDICTED. COMPARE THE EFFECT OF REGIONAL EXCITATION IN MOLECULES BY LASER OR STORED CHEMICAL ENERGY. DETERMINE IF PREDICTED NON-STOCHASTIC BEHAVIOR IS OBSERVED AND ITS CONSEQUENCES.

15 APRIL 1987 - 14 APRIL 1990 (3 YEARS)
SRI International
Y.K. Bae, P.C. Cosby

Ionic Solid Hydrogen Fuel: Production and Properties
of Hydrogen Ion and Energetic Neutral Clusters

Storage of Hn+ Hm- ions in hydrogen matrix

- Production and characterization of Hn+ Hm- ions
- Formation and capture of energetic MIES species
  - Electron capture in hydrogen cluster beam
  - Co-deposition of ionic clusters in H2 matrix
University of Pennsylvania
W.P. Dailey
Nitrocarbene and Diazirinone Synthesis

Experimental investigation of highly strained nitro compounds
- Lone pair substituted nitrocarbenes
- Organometallic routes to nitrocarbenes
- Synthesis and analysis of diazirinone
- Spectroscopic studies
University of Utah
C.A. Wight
Photoinitiated Chain Reactions in Low Temperature Solids

Experimental Investigation of Cryogenic Solids
- Examine hydrocarbon oxidation reactions
- Examine ignition rates and processes
- Correlate reaction rate to stress fracture propagation

Species
- Cl2 with hydrocarbons (propane, butane, cyclopropane, ...)
- Seeded hydrocarbons for oxidation reactions
- Diazomethane, hydrozoic acid, or nitromethane for unimolecular reactions
McMaster University
G.J. Schrobilgen
Synthesis and Structural Characterization of New High-Valent Inorganic Fluorine Compounds and their Oxidizing Properties

Synthesis and Preliminary Characterization
- Perfluoro xenon and interhalogen precursors for synthesis
- Substitution reactions to make new xenon, krypton compounds
- Characterize by NMR, IR, mass spec, x-ray crystallography

Species
- O-IF$_4$O$^-$ derivatives
- F$_5$TeO$^-$ derivatives
- Bromine (VII) oxyfluorides
- Compounds containing a Xe-N bond
- New compound containing first known Xe-C bond
Chemical Physics Institute, Univ of Oregon
P.C. Engelking
Investigations of Hypervalent Compounds as High Energy Materials

Synthesis and Spectroscopy
- Flowing afterglow and cold molecular expansion
- SiH5-, CH5-, NH4-
- Photoelectron and IR spectroscopy
- Photodetachment and photodissociation

Properties.
- Thermodynamically or kinetically stable
- Number of equivalent bonds
- Dissociation pathways and barriers
- Geometry and bond constants
- Rigidity of geometry
Louisiana State University
N.E. Brener
Theoretical Studies of Highly Energetic CBES Materials and Spin Aligned Systems

Theoretical Exploration
- Configuration Interaction (CI) method
- Local density cluster program
- Determine potential energy surfaces and geometries

Species
- Fluorine azide (FN3) monomer and clusters
  - Other CBES materials
University of California, Irvine
V.A. Apkarian
Energy Storage in Condensed Media via Charge Separation and Trapping

- Energy storage by charge separation and ion-hole trapping
- Energy stored until released by thermal shock
- Charge transfer dynamics in RGS of F, Cl, C2
- Other solid matrices include CO, N2, and O2
University of California
C.B. Moore, Y.T. Lee, A.H. Kung
Photochemical Preparation and Spectroscopic
Characterization of H4 and Its Decay Products

- Prepare lowest metastable state of H4 and to determine
  its stability against radiative decay

- Two approaches:
  1) prepare on potential surface by single photon excitation
  2) prepare on a more highly excited surface by excitation
     at shorter wavelengths: stimulated emission drops the
     molecule into the H4 potential well

- Probe decomposition products by laser photoionization
  and laser induced fluorescence
University of California
W.A. Lester
Quantum Monte Carlo Study of Decomposition Pathways of Tetrahydrogen

- Fixed-node quantum Monte Carlo method to characterize formation and decomposition pathways of tetrahydrogen

- Examine both H3 + H and H2* + H2 pathways
University of Arizona
P.F. Bernath
Laser and Fourier Transform Spectroscopy of Novel Propellant Molecules

N3: Fourier transform absorption spectroscopy
Metal Azides: IR laser spectroscopy of LiNNN
Metal Nitrides: Near IR spectra of LiN and LiNH
Rydberg Molecules: Fourier transform detection of IR electronic transitions of XeH, NeH, and H4
Metal Acetylides and Carbides: Visible and IR laser spectroscopy of LiC2, MgC2, and LiCCH
HIGH ENERGY DENSITY SYSTEMS IN CRYOGENIC MEDIA
PROF ERIC WEITZ, NORTHWESTERN UNIVERSITY

OBJECTIVE:  
- DETERMINE DIFFUSION RATES OF SELECTED RADICALS IN SOLID AND LIQUID MEDIA
- DIFFUSION IS THE MAJOR PROCESS CONTROLLING LOSS OF CRYOGENICALLY STORED RADICALS

APPROACH:  
- GENERATE ATOMS AND RADICALS (H, O, F, Cl, C_2O, NH_x, N_3) PHOTOLYTICALLY
- DETERMINE REACTION PATHWAYS, RATES AND BRANCHING RATIOS FOR BOTH GENERATION AND LOSS
- COMPARE REACTIONS IN SOLID VERSUS LIQUID MEDIA
- USE OPTICAL DIAGNOSTICS, INCLUDING TIME RESOLVED INFRARED ABSORPTION, LIF, FTIR
Studies of dissociative charge transfer in silane collisions with SiH$_2^+$ and SiH$_3^+$ ions have indicated that H$^+$ is transferred. In silane deposition reactor plasmas, H$^+$ and H$_2^+$ also are formed and are expected to rapidly form H$_3^+$. The reaction of H$_3^+$ on silane is therefore of interest. In order to resolve ambiguities in the reaction, the measurements were made using D$_3^+$. The experiment utilized a modified Nicolet Fourier Transform Mass Spectrometer. A mixture of deuterium and silane was ionized by an electron beam. The silane ions were then ejected from the trap. The deuterium molecular ions react rapidly with background deuterium to form D$_3^+$. The D$_3^+$ reacts with the background silane to give SiH$_3^+$ and neutral products. This rate constant is estimated as approximately $2 \times 10^{-9}$cm$^3$s$^{-1}$. 
MEASUREMENT OF THE CHARGE TRANSFER RATE CONSTANT FOR $D_3^+ + SiH_4$

CAPT PETE HAALAND
ALAN GARSCADDEN

WRIGHT-PATTERSON AFB, OHIO

ABLY ASSISTED BY MR. JIM BARNHART
H⁻ transfer observed in double resonance experiments

\[ \text{H}^+ + \text{H}_2 \rightarrow \text{H}_3^+ + \text{H}_2 \]

\[ k = 1.35 \times 10^{-9} \text{ cm}^3 \text{ sec}^{-1} \]

\[ \text{SiH}_2^+ + \text{SiH}_4 \rightarrow \text{SiH}_3^+ + (\text{SiH}_3) \]

\[ k = 1.07 \times 10^{-9} \text{ cm}^3 \text{ sec}^{-1} \]

$\text{He}^+ / \text{D}_2^+$ MASS SPECTRUM

$\Delta m$

$608.4856 \text{ Hz} \quad 604.6168 \text{ Hz}$

$\Delta E = \Delta m c^2$

$^4\text{He}^+ \quad ^2\text{D}_2^+$

\[+\quad -\]

\[+ \quad +\quad + \quad +\]

\[+ \quad +\quad +\quad +\]

\[+ \quad +\quad +\quad +\]

\[+\quad +\quad +\quad +\]

\[+\]
FOURIER TRANSFORM MASS SPECTROMETRY: UNIQUE FEATURES

1. IONS ARE FORMED AND OBSERVED ON TIME SCALES SHORT COMPARED TO THOSE OF PERTURBING REACTIONS

2. IONS ARE FORMED AND DETECTED IN SAME SPATIAL REGION
   NO EXTRACTION AMBIGUITIES

3. DETECTED SIGNAL IS LINEAR IN ION NUMBER NO MASS/ENERGY DEPENDENT FACTORS

4. EXCELLENT SENSITIVITY ($N_j \geq 100$ IONS)

5. VERY HIGH MASS RESOLUTION ($M/\Delta M > 10^8$)

6. EXPERIMENTAL CONFIGURATION ADAPTABLE TO ION SOURCES, LASER PLASMAS, ELECTRON IONIZATION
FTMS EXPERIMENT

*IONIZE MIXTURE OF DEUTERIUM AND SILANE
*Sweep out all ions except $D_2^+$
*Allow $D_2^+$ to react with $D_2$
*Sweep out all ions except $D_3^+$
*Allow $D_3^+$ to react with silane
DEUTERIUM TRIMER ION PLUS SILANE

D_3^+ + SiH_4

NO DELAY
DEUTERIUM TRIMER ION
PLUS SILANE

$D_3^+ + SiH_4$

83.5 MSECS DELAY

RELATIVE INTENSITY

MASS IN A.M.U.
DEUTERIUM TRIMER ION
PLUS SILANE

$D_3^+ + SiH_4$

410 MSEC DELAY
CONCLUSIONS

* Although He⁺, electrons and D₂⁺ react with silane to give Si⁺, SiH⁺, SiH₂⁺ and SiH₃⁺ the reaction of D₃⁺ gives only SiH₃⁺.

* The results of Allen, Cheng and Lampe are correct: no SiH₂D⁺ is observed.

Hence, D₃⁺ + SiH₄ → SiH₃⁺ + D₂ + HD: direct H⁻ transfer.

* Rate constant for (2V trapping bias) thermal ions ≤ 2.5 × 10⁻⁹ cm³ sec⁻¹.
EXPLOSIVE DECOMPOSITION OF FLUORINE AZIDE FILMS

D.J. Benard

Rockwell Science Center
1049 Camino dos Rios
Thousand Oaks, CA 91360

ABSTRACT

The molecule FN₃, known as fluorine azide, can be viewed as the metastable species NF(a¹Δ) bound with N₂. The nature of the binding will be discussed in terms of the potential surfaces and their correlations to the various excited electronic states of N₂ and NF. Experimental data will also be presented in the form of emission spectra obtained from the laser initiated detonation of thin FN₃ films. These data are expected to shed some new light on methods to stabilize high concentrations of metastable molecules which may be useful as high impulse rocket propellants. The use of FN₃ as a starting material for the generation of high concentrations of NF(a¹Δ), to power short wavelength laser systems, will also be discussed.
EVERYTHING YOU EVER WANTED
TO KNOW ABOUT FLUORINE AZIDE *

D.J. BENARD

* BUT WERE AFRAID TO ASK

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$v' = 8$

$\text{ArF} \rightarrow \text{FN}_3$

$\text{N}_2(A) + \text{NF}(b)$

$\text{N}_2(A) + \text{NF}(a)$

$\text{N}_2(B) + \text{NF}(X)$

$\text{N}_2(A) + \text{NF}(X)$

$\text{N}_2(X) + \text{NF}(b)$

$\text{N}_2(X) + \text{NF}(a)$

$\text{N}_2(X) + \text{NF}(X)$

\text{Rockwell International Science Center}
POTENTIAL CURVES OF FLUORINE AZIDE

- NF + N₂⁺
- NF⁺ + N₂
- NF + N₂

Potential energy

FN-N₂ distance

SINGLET
TRIPLET
FN$_3$ GROUND STATE CALCULATION

- H. MICHELS, UTRC
  - AB INITIO (SELF CONSISTENT FIELD)
  - HARTREE FOCK SOLUTION, ACCURACY 10 - 20%

- VIBRATIONAL FREQUENCIES (CM$^{-1}$)

<table>
<thead>
<tr>
<th>Mode</th>
<th>Calculated</th>
<th>Measured</th>
</tr>
</thead>
<tbody>
<tr>
<td>BENDING</td>
<td>V$_1$</td>
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</tr>
<tr>
<td>BENDING</td>
<td>V$_2$</td>
<td>606</td>
</tr>
<tr>
<td>SYM. N$_3$</td>
<td>V$_3$</td>
<td>757</td>
</tr>
<tr>
<td>NF STRETCH</td>
<td>V$_4$</td>
<td>1045</td>
</tr>
<tr>
<td>ASYM. N$_3$</td>
<td>V$_5$</td>
<td>1225</td>
</tr>
<tr>
<td>N$_2$ STRETCH</td>
<td>V$_6$</td>
<td>2386</td>
</tr>
</tbody>
</table>

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DISTORTED MOLECULE CALCULATION

- FN-N₂ BOND SPECIFIED (GROUND STATE)
- F-N₃, FN₂-N BONDS OPTIMIZED (3-D)
- LOWEST CHANNEL (CONSERVED SPIN)

![Graph showing FN-N₂ distance vs. energy with equilibrium state and lowest channel with 0.472 eV energy difference.]
FN₃ RESEARCH FACILITY
AFRPL CONTRACT

• RATIONALE: FN₃ MODELS H₄

• APPROACH:
  PRODUCE FN₃ IN GAS STREAM
  CONDENSE ONTO COLDFINGER
  DETONATE
  ANALYZE EMISSION / ABSORPTION DATA
  SPECTROSCOPY
  KINETICS

• OBJECT: STABILIZATION METHODS
KEY ELEMENTS OF SWCL

CHEMICAL FUELS → METASTABLE GENERATOR → LASING MECHANISM

MOST CRITICAL ELEMENT

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FLOWTUBE EXPERIMENT

MICROWAVE DISCHARGE

F₂

FN₃

N₂H₄/D₂

FIBER OPTIC CABLE

OMA

VACUUM

Rockwell International
Science Center
KEY REACTION STEPS

• \[
\begin{align*}
F + H_2 & \rightarrow HF (v) + H \\
F + D_2 & \rightarrow DF (v) + D
\end{align*}
\] (known)

• \[
\begin{align*}
HF (v) + FN_3 & \rightarrow HF + N_2 + NF^* \\
DF (v) + FN_3 & \rightarrow DF + N_2 + NF^*
\end{align*}
\] (new)

• \[
\begin{align*}
H + NF^* & \rightarrow HF + N^* \\
D + NF^* & \rightarrow DF + N^*
\end{align*}
\] (known)

• \[
\begin{align*}
N^* + NF^* & \rightarrow N_2^* + F \\
N_2^* + N_2^* & \rightarrow N_2^{**} + N_2 \\
N_2^{**} & \rightarrow N_2^* + \text{hv (red-orange)}
\end{align*}
\]
VISIBLE F + D₂ + FN₃ CHEMILUMINESCENCE

N₂ (B - A)

WAVELENGTH (nm)
NEAR IR FLOWTUBE CHEMILUMINESCENCE

F + HN₃

F + D₂ + HN₃

F + D₂ + FN₃

WAVELENGTH (nm)

NF (a → X)

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CHEMILUMINESCENCE COMPARISON

- $F + N_2H_4 + FN_3$ —
  (SCALABLE)

NF (b $\rightarrow$ X)

- $F + HN_3$ —
  (NOT SCALABLE)

NF (a $\rightarrow$ X)

528 nm

874 nm
SLOW DECAY OF NF (a^1Δ)

\[ \lambda_d \sim 220/s \]

\[ F + D_2 + FN_3 \]

\[ \lambda_{wall} = 250 \pm 30/s (F + HN_3 \text{rxn}) \]

Coombe, AFWL-29601-79-C-0016

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CONCLUSIONS

- FN3 IS A LOOSELY BOUND COMPLEX OF EXCITED SINGLET NF AND N2.

- BARRIER HEIGHT TO DISSOCIATION IS APPROXIMATELY 0.5 eV.

- ENERGY TRANSFER FROM HF/DF(ν) TO FN3 IS AN EFFICIENT SOURCE OF EXCITED NF.
ELECTRONIC STRUCTURE AND STABILITY OF ENERGETIC CHEMICAL SPECIES

H.H. Michels
J.A. Montgomery, Jr.

Presented at
AFRPL/HEDM Conference
Rosslyn, Va
May 12 - 13, 1987
Electronic Structure and Stability of Energetic Chemical Species

H. H. Michels and J. A. Montgomery, Jr.
United Technologies Research Center
East Hartford, CT 06108

ABSTRACT

Theoretical quantum mechanical calculations have been carried out for several potentially high energy chemical species. Our research objectives are to identify those light element molecular species that have sufficient internal energy to be useful in advanced chemical propulsion systems. A parametric study of the deliverable specific impulse as a function of available reaction energy and propellant weight indicates that primary consideration should be given to molecular structures that can be formed from hydrogen through boron and that have a molecular weight of 40 or less.

Calculations to date have been performed on three classes of light element compounds: C\textsubscript{3v} structures such as H\textsubscript{4} and Li\textsubscript{3}H, azide structures such as N\textsubscript{3}F and \(\alpha\text{N}_2\text{O}_2\) and cyclic boron structures such as B\textsubscript{3}H\textsubscript{3} and B\textsubscript{2}H\textsubscript{2}NH. We find that the ground state potential energy minimum found for H\textsubscript{4} in C\textsubscript{3v} symmetry corresponds to a saddle region rather than a stable bound state and that distortion via vibrational or rotational modes leads monotonically to dissociation into two H\textsubscript{2} molecules. In contrast, Li\textsubscript{3}H appears to be chemically stable in C\textsubscript{3v} symmetry. Our studies of asymmetric dinitrogen dioxide (\(\alpha\text{N}_2\text{O}_2\)) indicate a stable azide-like structure in C\textsubscript{s} symmetry for the ground \(^1\text{A}'\) state, with an indicated heat of formation of +430 kilojoule/mol. This molecule is a very attractive candidate as an advanced oxidizer. Our preliminary calculations for boron compounds indicate that B\textsubscript{3}H\textsubscript{3} is unstable in D\textsubscript{3h} symmetry but that iminodiborane (B\textsubscript{2}H\textsubscript{2}NH) is stable in C\textsubscript{2v} symmetry. The electronic structure, vibrational analysis and thermodynamic stability of these compounds will be described.
SPECIFIC IMPULSE OBTAINABLE FROM FUEL/OXIDANT ENERGY RELEASE WITH HYDROGEN AS A WORKING FLUID

HYDROGEN CONTENT VARIED TO OPTIMIZE IMPULSE (1000 - 14'000 lbs.)

IDENTIFICATION OF MOLECULAR FUEL SPECIES
NUMBERS INDICATE POSITION ON DIAGRAM OF CORRESPONDING MOLECULAR SPECIES

<table>
<thead>
<tr>
<th>CONVENTIONAL FUELS</th>
<th>HIGH ENERGY FUELS</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 H_2</td>
<td>11 H_4*</td>
</tr>
<tr>
<td>2 LiH</td>
<td>12 HeH_3</td>
</tr>
<tr>
<td>3 COMPOSITE</td>
<td>13 H_2O</td>
</tr>
<tr>
<td>4 RPI</td>
<td>14 BeH_2</td>
</tr>
<tr>
<td>5 BeH_3</td>
<td>15 FeH_2</td>
</tr>
<tr>
<td></td>
<td>16 Ne_2</td>
</tr>
<tr>
<td></td>
<td>17 LiH_3</td>
</tr>
</tbody>
</table>

SPECIFIC IMPULSE, \( I_p \) (sec)

ENERGY CONTENT (\( \mu \)joule)

MOLECULAR WEIGHT OF ENERGETIC SPECIES
CATEGORIES OF ENERGETIC SPECIES

1) Ordered (or metallic) forms of matter which at conventional temperatures and pressures are molecular solids. Metallic hydrogen and ammonium are examples.

2) Free radicals, either atomic or molecular in nature, that are stabilized against recombination by condensation and immobilization on noble gas matrices held at very low (4 K) temperatures. Atomic hydrogen, beryllium monohydride (BeH) and the hydroxyl (OH) radical are examples in this category.

3) Electronically excited metastable atoms or molecules that are stabilized against radiative decay by externally applied electric, magnetic or radiation fields, or by an intrinsic field within a condensed phase of such material which acts as a barrier to their decay. Metastable atoms, such as He* (3S) or N* (2D), and metastable molecules, such as He2* (a3Σ_u^+ or 5Σ_g^+) and H2* (BΣ_u^+), are examples in this category that would constitute significant energy sources (> 1000 kJoule/mol). Other energetic metastable species such as O2 (a1Δg), NF (a1Δ) and Mg* (3P), with long radiative lifetimes, may also be useful as temporary energy storage media.

4) Strained molecules with high positive heats of formation. This is an important class of molecules which are really isomeric forms of conventional chemical species but are structurally prevented from relaxation to their lowest energy state by significant activation barriers on their potential energy surface. Examples in this category include cycloproplyne (C3H4), aziridine (C2H2NH), azetidine (C3H3NH), hydrogen azide (HN3) and fluorine azide (FN3).
HIGH ENERGY MOLECULAR CONFORMATION

Potential energy $V(\xi)$

$\xi$, nuclear coordinate

$\xi_1$, $\xi_2$
TYPES OF COMPOUNDS STUDIED TO DATE

A. Light element $C_{3v}$ structures
   $H_4, LiH_3, Li_3H, Li_4$

B. Azide structures
   $FN_3, FNCO, a-N_2O_2, FNBF$

C. Cyclic boron structures
   $B_3H_3$ cyclotriborane
   $B_2H_2NH$ iminodiborane
A. HIGH-ENERGY LIGHT ELEMENT MOLECULAR STRUCTURES

b) LiH₃ (C₃ᵥ)

c) Li₃H (C₃ᵥ)

d) Li₄ (C₃ᵥ)
### $H_4(C_{3v})$ Calculations

<table>
<thead>
<tr>
<th>Theory</th>
<th>Energy (hartrees)</th>
<th>Frequencies (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>SCF / small</td>
<td>1.8784</td>
<td>0.8433</td>
</tr>
<tr>
<td></td>
<td>1.8094</td>
<td>0.8477</td>
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<tr>
<td>MP2 / small</td>
<td>1.8048</td>
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<tr>
<td></td>
<td>1.8634</td>
<td>0.8421</td>
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<tr>
<td>CISD / small</td>
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<td>0.8451</td>
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<tr>
<td>SCF / large</td>
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<td>0.8421</td>
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<tr>
<td></td>
<td>1.8634</td>
<td>0.8421</td>
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<tr>
<td>MP2 / large</td>
<td>1.8170</td>
<td>0.8451</td>
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</table>

Energies (hartrees), distances (Å), frequencies (cm\(^{-1}\)).
# Li₃H CALCULATIONS

<table>
<thead>
<tr>
<th>Theory</th>
<th>h</th>
<th>r</th>
<th>Energy</th>
<th>Frequencies</th>
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<tr>
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<td>2.5993</td>
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<td>291 421</td>
</tr>
</tbody>
</table>

Energies (hartrees), distances (Å), frequencies (cm⁻¹)
## LiH₃ AND Li₄ CALCULATIONS

<table>
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<th>Theory</th>
<th>h</th>
<th>r</th>
<th>Energy</th>
<th>Frequencies</th>
</tr>
</thead>
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<tr>
<td>Li₄</td>
<td></td>
<td></td>
<td></td>
<td>e  a₁ e  a₁</td>
</tr>
<tr>
<td>SCF / 3-21G</td>
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<td>SCF / 3-21+G</td>
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<td>SCF / 6-31G*</td>
<td>3.1439</td>
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<td>SCF / 6-31+G*</td>
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<tr>
<td>LiH₃</td>
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<td></td>
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<td>SCF / 3-21G**</td>
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<td>1.5954</td>
<td>1.2294</td>
<td>-8.887511</td>
<td>Unstable (2)</td>
</tr>
</tbody>
</table>

Energies (hartrees), distances (Å), frequencies (cm⁻¹)
B. AZIDE-TYPE STRUCTURES

Hydrogen azide
\[ H \text{\ N} \text{\ N} \]

Fluorine azide
\[ F \text{\ N} \text{\ N} \]

Fluorine isocyanate
\[ \text{F} \text{\ C} \text{\ O} \text{\ N} \text{\ N} \]

Difluoroaminoborane
\[ \text{F} \text{\ N} \text{\ B} \text{\ F} \]

Asymmetric dinitrogen dioxide
\[ \text{O} \text{\ N} \text{\ N} \]

RF 1130TX.008
ENERGETICS OF THE CHEMICAL SYNTHESIS OF FLUORINE AZIDE (FN₃)

\[
F \quad \rightarrow \quad FN \quad \rightarrow \quad FN_3 \quad \rightarrow \quad FN - - NN
\]

\[
\text{ΔE} = 3809 \text{ cm}^{-1}
\]

\[
\text{ΔE}_{c_{orr}}^{2p} = 2707 \text{ cm}^{-1}
\]

Available energy, kjoule/mol

\[
\text{[uncertain]}
\]
FN₃ DISSOCIATION PATHWAY

Potential energy, cm⁻¹

E_{act} = 3809 \text{ cm}^{-1}

E_{act} (corrected for zero-point energy)

= 2707 \text{ cm}^{-1}

R_{max} = 1.597

R_e = 1.254

FN-N₂ reaction coordinate (Å)

RB1788TX.001
## FLUORINE AZIDE (FN₃) FREQUENCY ANALYSIS

<table>
<thead>
<tr>
<th>Normal mode</th>
<th>Calculated</th>
<th>Experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>HF</td>
<td>MP2</td>
</tr>
<tr>
<td>a' (N-N-N bend)</td>
<td>281</td>
<td>247</td>
</tr>
<tr>
<td>a'' (out-of-plane bend)</td>
<td>606</td>
<td>494</td>
</tr>
<tr>
<td>a' (F-N-N bend)</td>
<td>757</td>
<td>690</td>
</tr>
<tr>
<td>a' (N-F stretch)</td>
<td>1045</td>
<td>948</td>
</tr>
<tr>
<td>a' (N₁-N₂ asymmetric stretch)</td>
<td>1225</td>
<td>1153</td>
</tr>
<tr>
<td>a' (N₂-N₃ asymmetric stretch)</td>
<td>2386</td>
<td>2406</td>
</tr>
</tbody>
</table>

THEORETICAL VIBRATIONAL ANALYSIS OF FLUORINE AZIDE (FN3)

Standard orientation

a' (247 cm\(^{-1}\)) N-N-N bend

a'' (494) out-of-plane bend

a' (690) F-N-N bend

a' (948) NF stretch

a' (1153) \(N_1 - N_2\) asymmetric stretch

a' (2406) \(N_2 - N_3\) asymmetric stretch
ENERGETICS OF THE CHEMICAL SYNTHESIS OF ASYMMETRIC DINITROGEN DIOXIDE (a-N₂O₂)

\[
\begin{align*}
\text{Available energy, kJ/mol} & \\
\hline
\Delta H^\circ & +521.1 \\
N_2O_2[1\Sigma^+] & \text{OO} \cdots \text{NN} (\sim 470) \\
\hline
O[3\Pi] + N_2O[1\Sigma^+] & +331.2 \\
\hline
O_2[3\Sigma^+] + N_2[1\Sigma^+] & +157.0 \\
O_2[1\Delta_g] + N_2[1\Sigma^+] & +94.1 \\
O_2[3\Sigma^-] + N_2[1\Sigma^+] & 0.0
\end{align*}
\]
# ASYMMETRIC DINITROGEN DIOXIDE (a-N\textsubscript{2}O\textsubscript{2}) FREQUENCY ANALYSIS

<table>
<thead>
<tr>
<th>Normal mode</th>
<th>Frequency (cm(^{-1}))</th>
<th>HF</th>
<th>MP2</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a') (O-O-N bend)</td>
<td></td>
<td>188</td>
<td>210</td>
</tr>
<tr>
<td>(a'') (Out-of-plane bend)</td>
<td></td>
<td>648</td>
<td>498</td>
</tr>
<tr>
<td>(a') (O-N-N bend)</td>
<td></td>
<td>291</td>
<td>568</td>
</tr>
<tr>
<td>(a') (O-O stretch)</td>
<td></td>
<td>697</td>
<td>656</td>
</tr>
<tr>
<td>(a') (O-N asymmetric stretch)</td>
<td></td>
<td>1262</td>
<td>1200</td>
</tr>
<tr>
<td>(a') (N-N asymmetric stretch)</td>
<td></td>
<td>2677</td>
<td>2150</td>
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</table>

RD16421X.004
## OPTIMIZED GEOMETRIES OF AZIDES

![Diagram of azide molecule with bond angles and distances](image)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Theory</th>
<th>$R_1$ (Å)</th>
<th>$R_2$ (Å)</th>
<th>$R_3$ (Å)</th>
<th>$\alpha$ (deg)</th>
<th>$\beta$ (deg)</th>
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<tbody>
<tr>
<td>HN$_3$</td>
<td>SCF</td>
<td>1.0055</td>
<td>1.2381</td>
<td>1.0987</td>
<td>108.181</td>
<td>173.815</td>
</tr>
<tr>
<td></td>
<td>MP2</td>
<td>1.4309</td>
<td>1.2799</td>
<td>1.1521</td>
<td>103.765</td>
<td>171.803</td>
</tr>
<tr>
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<td>1.2799</td>
<td>1.1521</td>
<td>103.765</td>
<td>171.803</td>
</tr>
<tr>
<td>FN$_3$</td>
<td>SCF</td>
<td>1.3820</td>
<td>1.2536</td>
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<td>MP2</td>
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<td>1.2622</td>
<td>1.1765</td>
<td>110.717</td>
<td>168.914</td>
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<tr>
<td>FNCO</td>
<td>SCF</td>
<td>1.3737</td>
<td>1.2387</td>
<td>1.1354</td>
<td>109.846</td>
<td>173.235</td>
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<tr>
<td></td>
<td>MP2</td>
<td>1.4185</td>
<td>1.2622</td>
<td>1.1765</td>
<td>110.717</td>
<td>168.914</td>
</tr>
<tr>
<td></td>
<td>CISD</td>
<td>1.5815</td>
<td>1.2238</td>
<td>1.1072</td>
<td>102.840</td>
<td>179.360</td>
</tr>
<tr>
<td>a-N$_2$O$_2$</td>
<td>SCF</td>
<td>1.7574</td>
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<td>103.966</td>
<td>179.506</td>
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<td>MP2</td>
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<td>1.2272</td>
<td>1.1548</td>
<td>103.591</td>
<td>179.488</td>
</tr>
<tr>
<td></td>
<td>CISD</td>
<td>1.5815</td>
<td>1.2238</td>
<td>1.1072</td>
<td>102.840</td>
<td>179.360</td>
</tr>
<tr>
<td>FNBF</td>
<td>SCF</td>
<td>1.2993</td>
<td>1.2068</td>
<td>1.2871</td>
<td>180.000</td>
<td>180.000</td>
</tr>
<tr>
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<td>1.2491</td>
<td>1.3069</td>
<td>154.650</td>
<td>169.291</td>
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### Experimental bond length (Å)

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<th>Length (Å)</th>
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<tbody>
<tr>
<td>N-N</td>
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<tr>
<td>C-O</td>
<td>1.128</td>
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<tr>
<td>H-N</td>
<td>1.041</td>
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<tr>
<td>O-O</td>
<td>1.216</td>
</tr>
<tr>
<td>F-N</td>
<td>1.308</td>
</tr>
<tr>
<td>N-O</td>
<td>1.151</td>
</tr>
<tr>
<td>B-N</td>
<td>1.281</td>
</tr>
<tr>
<td>B-F</td>
<td>1.262</td>
</tr>
</tbody>
</table>
C. HIGH ENERGY BORON STRUCTURES

a) $B_3H_3$ ($D_{3h}$)  
cyclotriborane

b) $B_2H_2O$ ($C_{2v}$)  
1, 2 epoxydiborane/diborylene oxide  
c: ethylene oxide

c) $B_2H_2NH$ ($C_{2v}$)  
iminodiborane  
c: aziridine/ethyleneimine

d) $B_3H_3NH$ ($C_{2v}$)  
triboryleneimine  
c: azetidine/trimethyleneimine
CYCLIC BORON COMPOUNDS

Cyclotriborane \((B_3H_3)\)

\[
\begin{array}{c}
\text{H} \\
\text{B} \\
\text{B} \\
\text{B} \\
\text{H}
\end{array}
\]

\[
\begin{array}{c}
\text{H} \\
\text{B} \\
\text{B} \\
\text{B} \\
\text{H}
\end{array}
\]

- \(R_{BB} = 1.626 \text{ Å}\)
- \(R_{BH} = 1.232 \text{ Å}\)
- \(E = -75.038853\), stable

\[
\begin{array}{c}
\text{H} \\
\text{B} \\
\text{B} \\
\text{B} \\
\text{H}
\end{array}
\]

\[
\begin{array}{c}
\text{H} \\
\text{B} \\
\text{B} \\
\text{B} \\
\text{H}
\end{array}
\]

- \(R_{BB} = 1.734 \text{ Å}\)
- \(R_{BH} = 1.178 \text{ Å}\)
- \(E = -75.174458\), unstable (2)

Iminodiborane \((B_2H_2NH)\)

\[
\begin{array}{c}
\text{H} \\
\text{N} \\
\text{B} \\
\text{B} \\
\text{H}
\end{array}
\]

\[
\begin{array}{c}
\text{H} \\
\text{B} \\
\text{B} \\
\text{B} \\
\text{H}
\end{array}
\]

- \(R_{BB} = 1.621 \text{ Å}\)
- \(R_{BH} = 1.174 \text{ Å}\)
- \(\angle \text{HBN} = 136.2^\circ\)
- \(\angle \text{BNH} = 145.3^\circ\)
- \(R_{NH} = 0.989 \text{ Å}\)
- \(R_{BN} = 1.423 \text{ Å}\)
- \(E = -104.981636\)

Frequencies (cm\(^{-1}\))

|  |  |  |  |  |  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|---|---|---|---|
|  |  |  |  |  |  |  |  |  |  |  |
| 700 | 818 | 921 | 923 | 989 | 1000 | 1110 | 1268 | 1423 | 2878 | 2916 | 3965 |
CONCLUSIONS

1. Tetrahydrogen (H₄), LiH₃ and Li₄ are not stable molecules in their ground state in C₃ᵥ symmetry.

2. Li₃H is stable in its ground state in C₃ᵥ symmetry. Additional calculations of the energetics of Li₃H are in progress.

3. All of the azide-like structures: FN₃, FNCO, a-N₂O₂, and FNBF, are vibrationally stable in the lowest ¹A' state with predicted high positive heats of formation. FN₃ also has a stable low-lying ³A'' state.

4. B₃H₃ has no stability as a D₃h structure. The anion, B₃H₃⁻, is stable as predicted by Lipscomb's rules. B₂H₂NH is stable as a C₂ᵥ structure with symmetry ¹A₁. Preliminary thermodynamics indicate, however, that B₂H₂NH is not very energetic.

5. Best systems studied to date: a-N₂O₂ and FNBF

6. Areas for further study: Hₙ, LiₘHₙ structures, azides and further simple boron compounds
METASTABLE MOLECULAR FUELS:
THEORETICAL STUDY OF ION-PAIR STATES
LOW-LYING SURFACES OF H₃O

Roberta P. Saxon
Dahbia Talbi

SRI International
OBJECTIVE

Predict new energetic metastable molecular species that do not decay by radiation, tunneling, or other means when isolated in vacuum.

PROPOSAL

Ion-pair bonding between stable negative ions may lead to high-energy (locally) bound states that have not been studied previously.

Example: $\text{H}_4$
Metastable Molecular Fuels: Theoretical Study of Ion-Pair States - Low-Lying Surfaces of H$_3$O$^+$

Robert P. Saxon and Dahbia Talbi
SRI International
Menlo Park, California 94025

Metastable molecular fuels, long-lived molecular species that do not decay by radiation, tunneling, or other means, when isolated in vacuum, have been proposed as the basis for possible new propulsion schemes. The recent prediction of an energetic excimer state of H$_4$ suggests the possibility of a whole series of molecules bound by the Coulomb attraction between a stable positive ion and a stable negative ion. The fate of an ion-pair species, once formed, will depend sensitively on the details of the potential surfaces that govern decay processes such as optical transitions, predissociation, and internal conversion. This theoretical program is devoted to examining ion-pair species composed of first-row atoms that could serve as candidate fuels. In this paper, CASSCF-FOCI calculations on the low-lying doublet and quartet potential surfaces of the H$_3$O system are reported.

Consistent with our model of an ion-pair state as an H$_3$ equilateral triangle with an O$^-$ located above the center of the triangle, our calculations to date have concentrated on C$_3v$ geometries. A D2P basis set augmented by diffuse s and p functions on O was used. The correlation diagram linking the H$_3$O states studied here to states of the separated fragments has been established. The connection between this work and the portions of the ground state (doublet) potential surface considered by previous workers$^1,2$ i.e. the H$_3$O local minimum and the H$_2$ + OH $\rightarrow$ H$_2$O + H transition state has also been explored. While portions of the lowest potential surface corresponding to the ion-pair H$_3$O$^-$ can be identified, at the minimum energy, the lowest state may be described as H$_3$O$^+$ with an electron in an oxygen Rydberg orbital, in agreement with the previous report$^2$.

This conformation is known to dissociate to H$_2$O + H. There is no barrier inhibiting conversion of the ion-pair geometry to the Rydberg geometry. Within the restricted C$_3v$ geometry, however, a stable ion-pair state with H-H distance very similar to that in the H$_3$ ion is observed on the first excited doublet potential surface. Investigation of this surface in unrestricted geometries is underway.

$^1$Work supported by Air Force Flight Test Center under contract F04611-86-C-0070
ION-PAIR STATES IN O₂

R.P. Saxon and B. Liu
J. Chem. Phys. 73 (676) 1980

RA m 2531 15
SELECTION OF SPECIES

Maximum specific impulse

\[ I_{sp} \propto \sqrt{\frac{\text{heat of reaction}}{\text{mass of products}}} \]

- low molecular weight
  \( H_3^+ \) positive ion - 1st row negative ion

- optimal electron affinity - a tradeoff
  large EA \( \Rightarrow \) stable negative ion
  small EA \( \Rightarrow \) high-energy minimum

\[ V = -\frac{1}{R} \]

A + B

\( A^+ + B^- \)
**ELECTRON AFFINITIES**

<table>
<thead>
<tr>
<th>Neutral</th>
<th>EA (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>0.75</td>
</tr>
<tr>
<td>O</td>
<td>1.46</td>
</tr>
<tr>
<td>F</td>
<td>3.40</td>
</tr>
<tr>
<td>O₂</td>
<td>0.43</td>
</tr>
<tr>
<td>O₃</td>
<td>2.10</td>
</tr>
<tr>
<td>Li</td>
<td>0.62</td>
</tr>
</tbody>
</table>
CALCULATIONS ON H₃O

BASIS SETS:

- 4-31G (preliminary survey)
- DZP + diffuse s and p on O

CASSCF (Complete Active Space)

- 9 active electrons (include O (2s) )
- 250 configurations Cₛ symmetry
- converge on 1 ²A' state
  solution totally symmetric

FOCI (First Order CI)

- Single excitations with respect to CAS
- DZP: 14902 configurations ²A'

SOCI (Second Order CI)

- DZP: 370330 configurations

Calculations to date:

- molecule in C₃ᵥ symmetry
- calculations in Cₛ symmetry

RA-m-2531-5
$H_3O$

$^2A'$

$H_2O$ 4-31G FCNI Results at Fixed H-H Distance = 1.65$\alpha_0$
INDICATIONS FROM PRELIMINARY 4-31G RESULTS

1) Can locate attractive region of potential surface due to ion-pair bonding

2) Asymptotes can be interpreted
   ( FOCl - $a = 1.65 \ a_0$, $d = 10.0 \ a_0$ )

\[
\begin{align*}
H_3^+ + O^- (^2P) \\
H_3 + O (^1D) &\quad 2.25 \text{ eV} \quad \text{(spec 1.97)} \\
H_3 + O (^3P)
\end{align*}
\]
DZP/FOCI RESULTS AT FIXED H-H DISTANCE
AS A FUNCTION OF VERTICAL DISTANCE

H$_3$O ($1^2$A')

(C$_{3v}$ symmetry)
DZP/FOCI RESULTS AT FIXED H-H DISTANCE
AS FUNCTION OF VERTICAL DISTANCE

$H_3O (2^{2}A')$

Total Energy (hartrees)

$\begin{align*}
-76.35 & \quad a = 1.9 \\
-76.40 & \quad a = 2.2 \\
-76.45 & \quad a = 2.50 \\
-76.50 & \quad a = 2.75 \\
\end{align*}$

$d (a_0)$
DZP/FOCI RESULTS AT FIXED H-H DISTANCE AS FUNCTION OF VERTICAL DISTANCE

![Graph showing the total energy (hartrees) as a function of vertical distance (d) for H3O. The graph includes curves for different states: \(2^2A'\) with \(a = 3.05\) and \(a = 1.65\), and \(1^2A'\) with \(a = 3.05\). The x-axis represents the distance (a₀), and the y-axis represents the total energy (hartrees).]
H$_3$O CORRELATION DIAGRAM
(2A' Symmetry)

[Diagram showing energy levels and transitions involving OH, H$_2$, H$_3$O, H$_2$O, H, and O species]
Notes on Correlation Diagram

1. H$_3$O, H$_3$, and H$_3^+$ calculated at C$_3v$ geometries
2. Energies determined at equilibrium geometries
3. Ground state surface of H$_3$ is repulsive; energy independent of H-H distance, $a$, for $a > 1.65a_0$
4. Energies from DZP/FOCI calculations except:
   a. OH($A^2\Sigma^+$) and H$_2$O($A^1B_1$) spectroscopic excitation energy
   b. H$_2$ experimental binding energy used to place H$_2$ + H + 0 with respect to H$_3$ + 0
H$_3$O LOWEST POTENTIAL SURFACE RELATIONSHIP TO OTHER STUDIES

(WD) S. P. Walch and T. H. Dunning
POL-Cl

E. Kraka and T. H. Dunning, unpublished

(NRS) K. S. E. Niblaeus, B. O. Roos, and P. E. M. Siegbahn
Chem. Phys. 25, 207 (1977)
UHF-SDCI

H$_3$O present work

<table>
<thead>
<tr>
<th>Energies (kcal m)</th>
</tr>
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<tbody>
<tr>
<td>OH+H$_2$ 6.1</td>
</tr>
<tr>
<td>OHH$_2$† (WD) 16.0</td>
</tr>
<tr>
<td>OH+H$_2$ 3.4</td>
</tr>
<tr>
<td>H$_2$O+H 26.9</td>
</tr>
</tbody>
</table>

GEOMETRY DETERMINATION

UHF

a = 3.05a$_o$ at a = 3.05a$_o$
d = 0.62a$_o$ d = 0.92a$_o$

H$_3$O wave function qualitatively same
H$_3$O$^+$ + diffuse s on O

RA m 253: 12
H$_3$O CONCLUSIONS TO DATE

$C_{3v}$ Restricted Geometries

DZP/FOCI

$1^2A'$

Large portions of potential surface may be characterized as ion-pair

Lowest energy (in $C_{3v}$ geometry) corresponds to 0(3s) Rydberg and dissociates to H$_2$O + H with small barrier

$2^2A'$

Ion-pair minimum (in $C_{3v}$ geometry) at $a \approx 3.05$ a$_o$, $d = 1.0$ a$_o$ 106.5 kcal/m above H$_2$O + H

No adiabatic correlation with ground state OH + H$_2$ or H$_2$O + H

Bound with respect to OH($A^2\Sigma^+$) + H$_2$
and H$_2$O($A^1B_1$) + H

Second ion-pair local minimum at $a = 1.65$ a$_o$, $d = 3.5$ a$_o$ 143.9 kcal/m above H$_2$O + H

Higher in energy than OH($A^2\Sigma^+$) + H$_2$

Barrier to $2^2A'$ lower minimum
H$_3$O WORK IN PROGRESS

$^{2}A'$
SOCI for better determination of absolute energies

$^{2}A''$
Characterization of surfaces

At most C$_{3v}$ geometries, $^{1}2A''$
equivalent to $^{2}2A'$

$^{1}2A''$ correlates to ground state OH + H$_2$,

QUARTETS

Characterization of surfaces

Much higher in energy - small binding, if
any, with respect to H$_3$ + O ($^{3}P$)

No correlations with lowest OH + H$_2$O + H
asymptotes
ARIES Contractor's Meeting
Rosalyn, VA, 12-13 May 1987

High Spin States of CO and CH
by
Daniel D. Konowalow and Marcy E. Rosenkrantz
State University of New York at Binghamton
Binghamton, N.Y. 13901
Ab Initio Calculations On High Spin States of CO and CH

by

DANIEL D. KONOWALOW
Department of Chemistry
SUNY-Binghamton, Binghamton, NY 13901

ABSTRACT

As part of our current interest in potential novel energy storage devices we have investigated several high spin states of CO and CH. The results of our calculations on the $^5\Sigma^+$ and $^5\Pi$ states of CO and the $^4\Sigma^-$ state of CH will be discussed. The possibilities for spin-orbit interactions involving these high-spin states will also be considered.
The basic idea behind this phase of our research is to investigate the properties of pairs or aggregates of high spin atoms which may combine to form a deeply bound low spin molecule. The binding energy of the ground state molecule may in principle be stored as suitably protected atoms or else as high-spin van der Waals molecules. Examples of the latter are the $^3\Sigma_u^+$ state of $H_2$ which could release about 4.5 eV on a spin flip and formation of the $^1\Sigma_g^+$ state or the $^7\Sigma_u^+$ state of $N_2$ which could undergo a series of spin flips to form the ground $^1\Sigma_g^+$ state with the release of about 9.7 eV. Figure 1 compares our $^1\Sigma_g^+$ van der Waals curve of CO together with the ground $^1\Sigma_g^+$ state potential curve to emphasize the tremendous energy storage potential of such a high-spin van der Waals molecule.

The $^7\Sigma_u^+$ state of $N_2$ has been examined from this point of view by Ferrante and Stwalley [J. Chem. Phys. 78, 3107 (1983)] who estimated its potential curve by adding an estimate of the dispersion attractive energy to their calculated repulsive self consistent field (SCF) energy. Their SCF plus dispersion potential had a $D_e$ of just over 40 cm$^{-1}$. Later, Partridge, Langhoff, and Bauschlicher [J. Chem. Phys. 84, 6901 (1986)] found from an exhaustive set of configuration interaction (CI) computations in terms of a substantial basis set and careful estimates of basis set superposition errors that the $D_e$ value was in fact only about 21 cm$^{-1}$.

In view of these new results Ferrante and Stwalley [J. Chem. Phys. 85, 1201 (1986)] showed that their earlier values of critical temperature and triple point temperature, for example, had to be revised downward by about a factor of two. The point of this recitation is to note that extreme care must be taken to assure the highest possible accuracy in the calculation of such weakly bound van der Waals potential curves if they are to provide useful estimates of thermal properties, for example.

We are currently investigating high spin states of CO which promise to give greater specific impulse than high spin $N_2$. The bulk of the experimental and theoretical information available on CO treats mainly spin singlets and to a much lesser extent spin triplets. The only published information on quintets we found is the pioneering work of O'Neil and Schaefer (ONS) [J.
<table>
<thead>
<tr>
<th>$\alpha_d$</th>
<th>$m_l$</th>
<th>C</th>
<th>O</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
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<td>0</td>
<td>10.10</td>
<td>5.005</td>
<td>7.353</td>
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<tr>
<td></td>
<td></td>
<td>(10.10)</td>
<td>(5.14)</td>
<td>(7.36)</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>12.99</td>
<td>4.54</td>
<td>25.673</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(13.05)</td>
<td>(4.58)</td>
<td>(25.66)</td>
</tr>
<tr>
<td>$\alpha_q$</td>
<td>0</td>
<td>41.60</td>
<td>20.32</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(41.73)</td>
<td>(20.61)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>61.80</td>
<td>14.74</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(61.28)</td>
<td>(15.05)</td>
<td></td>
</tr>
<tr>
<td>$\alpha_o$</td>
<td>0</td>
<td>449.6</td>
<td>141.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>697.7</td>
<td>98.4</td>
<td></td>
</tr>
</tbody>
</table>
Figure 2 displays all their calculated bound states corresponding to the C(3P) + O(3P) interaction except for the ground state. Their minimal basis set, full valence configuration interaction calculation is subject to very substantial basis set superposition error (we estimate an error of about 2500 cm\(^{-1}\) at \(R=4\) a\(_0\) for the \(1^5\Pi\) state) and, thus, can provide only a qualitative guide to our own work. We show in Fig. 3 that the ONS curves for the lowest \(5\Sigma^+\) and \(5\Pi\) states are substantially deeper than our own (primarily due to their BSSE).

Let us describe our own calculations. It is performed with the apparatus shown schematically in Fig. 4, which ably is operated by Marcy Rosenkrantz and Jim Francis-Bohr, among others. We augmented the basis set of Liu and McLean [unpublished] with two s-, two p-, and one each of d-, f- and g- functions needed to optimize the dipole, quadrupole and octupole polarizabilities of the ground state atoms C and O. Our polarizability results are given in Fig. 5 and are compared with available literature values (in parentheses) [H.J. Werner and W. Meyer Phys. Rev. A13, 13 (1976); E.A. Reinsch and W. Meyer Phys. Rev. A18, 1973 (1978)]. The atomic polarization basis is needed in order to insure an adequate description of the long-range interaction energies commonly approximated by the familiar multipole series:

\[ E_{\text{Disp}} = -C_6R^{-6} - C_8R^{-8} - C_{10}R^{-10} - \ldots \]

Note that we do not use perturbation theory to calculate the long-range interactions, we merely use its familiar language in this discussion.

We have found that there is a substantial amount of configuration mixing between the two lowest \(5\Sigma^+\) states of CO, especially in the region of 5-8 \(\nu_6\). Unless we were extremely careful with our choice of reference state(s) and input vectors on which to base the multireference second order CI (SOCI) calculation, we obtained potential curves that appeared to be nonsense. We shall not regale you with the details of our early computations, but rather describe the approach we have taken to obtain our current best results.

First we performed SOCI calculations on the 1,2 \(5\Sigma^+\) states where the excitations were performed from the seven configurations that arise from allowing the six p electrons to occupy any of two \(\sigma\) and two \(\pi\) orbitals consistent with \(5\Sigma^+\) symmetry. These calculations employed the molecular
orbitals obtained from an SCF computation on the $^5\Sigma^+$ state with the configuration $[5\sigma^66\sigma^1\pi^32\pi]$ we then analyzed the natural orbitals as shown in Figs 6 and 7 which suggested that a good multireference SOCI base would obtain from a CASMCSCF in which the six "p" electrons were allowed to occupy any of the three $\sigma$ and two $\pi$ orbitals consistent with $^5\Sigma^+$ symmetry. The corresponding SOCI comprised about 119,000 configuration state functions (CSF).

The resulting binding energies for the 1,2 $^5\Sigma^+$ and $^5\Pi$ states are shown in Fig. 8. As shown in Fig. 8, we obtain slightly different results depending on whether our input vectors for the multireference (119,000 CSF) 6/3 +2 computation came from the SCF computation for $^3\Pi^+$ $[5\sigma^66\sigma^1\pi^32\pi]$ or from a state averaged (1 and 2 $^5\Sigma^+$) 6/3$\sigma$+2$\pi$ MCSCF calculation. We presume that the latter computation is the more reliable.

Figure 9 shows that the 1 $^5\Pi$ state has nine or more bound, J=0 vibrational levels and that it is expected to be relatively stable thermally at or below room temperature. Even the 2 $^5\Sigma^+$ and 1 $^5\Pi$ states are seen to be at least weakly bound (the former has at least two bound vibrational levels), so they too could be potential energy storage states at sufficiently low temperatures. However, it remains to be seen what the radiative lifetimes of these states are.

We have started on calculations of other high spin quintet and triplet states of CO which correspond to the $C(^3P) + O(^3P)$ asymptote. When those calculations are complete we shall be able to consider various decay mechanisms of the potential energy storage states.
Applications of a recently developed methodology\(^\text{1}\) for treating spin-
forbidden radiative processes within the Breit-Pauli approximation will be
reported. Briefly the electronic wavefunctions \(\psi_1\) are determined through
first order in perturbation theory, \(\psi_1 = \psi_0^I + \psi_1^I\), with \(\psi_0^I\) and \(\psi_1^I\) expanded in a
configuration state function (CSF) basis

\[
\psi_0^I = \sum_k c_k^I \phi_k \tag{1a}
\]

and

\[
\psi_1^I = \sum_k v_k^I \phi_k \tag{1b}
\]

\(\phi^I\) satisfies the secular equation

\[
(H^0 - E_0^I) \phi^I = 0 \tag{2}
\]

while \(\psi^I\) satisfies

\[
(H^0 - E_0^I) \psi^I = -\frac{\hbar^2}{2m} \phi^I \tag{3}
\]
where $h^{SO}$ is the full microscopic spin-orbit hamiltonian. The CSF basis, \( \varphi \), is developed from orthonormal molecular orbitals determined within the state average MCSCF approximation.

The determination of \( \psi_1^1 \) using \( \epsilon \) and \( \gamma \) is preferred computationally over the traditional eigenfunction expansion method which gives \( \psi_1^1 \) as

\[
\psi_1^1 = \sum_{\gamma} \frac{C^1_{\gamma}}{E_{\gamma}^0 - \epsilon_{\gamma}} \varphi_{\gamma}^K.
\]

In particular, use of eq. 3 permits treatment of spin-forbidden radiative processes originating in coupling to bound states in the continuum ('resonances'). The use of eq. 4 in this instance would be difficult if not impossible.

The situation is illustrated with the determination of the radiative lifetime for the \( a^1\Delta \rightarrow X^3\Sigma^- \) transition in CH\(^+\). Okamura et al.\(^2\) have reported the lifetime for this transition as 5.9 ± 0.8 ms. This transition acquires oscillator strength by coupling of the \( 1\Delta \) and \( 3\Sigma^- \) states respectively to \( 3\Pi \) and \( 1\Pi \) states embedded in the CH + e\(^-\) continuum. The solution of eq. 5 will be obtained in a large CSF basis (~10\(^5\) terms) and analyzed using a natural orbital procedure. The possibility of optimizing molecular orbitals to describe the \( 3\Pi, 1\Pi \) 'resonances' using an iterative natural orbital procedure will be discussed.

Recently, the radiative lifetime \( \tau \) of the \( a^1\Delta \) state in NCl has been measured by two different experimental techniques with significantly different results, \( \tau = 1440\) ms and \( \tau = 740\) ms. To address this discrepancy, calculations of the radiative lifetimes for the \( (b^1 \Pi, a^1\Delta) \rightarrow X^3\Sigma^- \) transitions in NCl have been
Our results support the longer lifetime measurement.

If time permits we will discuss the application of recently developed computational techniques for the evaluation of first derivative nonadiabatic coupling matrix elements

\[ g(J,I,R_\alpha,R) = \langle \psi_J(r;R) \bigg| \frac{\partial}{\partial R_\alpha} \psi_I(r;R) \rangle \]

using analytic gradient methods to discuss nonadiabatic chemical reactions. In particular we will consider the charge exchange reaction

\[ \text{H}^+ + \text{NO} \rightarrow \text{H} + \text{NO}^+. \]

References:

Spin Forbidden Radiative Processes

1. Change total spin angular momentum
   Breit-Pauli Approximation

2. $H^{SO}$ spin orbit hamiltonian

\[ H^{SO} = h^{SO} + h^{SOO} \]

$h^{SO}$ 1e$^-$ spin orbit interaction

$h^{SOO}$ 2e$^-$ spin other orbit interaction
TODAY:

ELECTRONIC STATES ORIGINATING FROM

ELECTRON OCCUPATION

\[ \sigma^2 \pi^2 \]

\[ 2S+1 \Lambda \Omega \]

'b'est' quantum number

point group: \( C_{\text{v}} \)

\[ b \, ^1\Sigma^+_0 \quad a \, ^1\Lambda_2 \quad x \, ^3\Sigma^{-}_{1,0+} \]
See "Spectra, lifetimes, and kinetics of matrix-isolated NI $b^1\Sigma^+$ and $a^1\Delta$", J Chem Phys, 84, 2907(1986).

See "The lifetimes for spontaneous emission from the $X^3\Sigma^-(v=1)$ and $a^1\Delta$ states of CH\(^-\)", J Chem Phys, 85, 1971(1986)
3. Mechanism

\[ \mu_1, \mu_1 \]

\[ b^1\Sigma^+ \]

\[ a^1\Delta \]

\[ \chi^3\Sigma^- \]

\[ \nu \]

\[ A^{3\sigma} \]

\[ \psi(3\Sigma^-) = \psi(3\Sigma^-) + \psi(1\Pi^1, 3\Sigma^-) \]

\[ \psi(4\Delta_2) = \psi(4\Delta_2) + \psi(3\Pi_2, 4\Delta_2) \]

\[ \psi(1\Sigma_0^+) = \psi(1\Sigma_0^+) + \psi(3\Pi_0^1, 2\Sigma_0^+) \]

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Approach

Two Unique Features

1. SPACES: approach to treating Perturbation theory

2. Symbolic Matrix Method for treating $H^{\text{o}}$
States [Spectral Representation - Conventional]

\[
\psi_I = \sum_K \frac{\langle \psi | H | \psi \rangle}{(E_I - E_K)} \psi_K
\]

ADVANTAGES

1. Facilitates incorporation of experimental data
2. Mixed representations


\[
(H^0 - E^0_I) \psi^1_I = -H^{SO} \psi^0_I
\]

Advantages

1. AVOIDS (IMPOSSIBLE) TASK OF OBTAINING ALL ZEROTH ORDER EIGENSTATES
2. PERMITS TREATMENT OF PROCESSES ORIGINATING IN COUPLING TO STATES EMBEDDED IN A CONTINUUM
3. ORBITAL OPTIMIZATION!
IN GENERAL

1. TRANSITION MOMENTS ARE SENSITIVE to the QUALITY OF THE WAVEFUNCTION

2. SPACE approach permits use of a large CSF space

To exploit (2) with an eye to (1) we have implemented

SYMBOLIC MATRIX METHOD for $\mathbf{R}^\infty \psi^0$

CONCEPT:

Representative MATRIX Elements

DIRECT PRODUCT SPACES
Benefits

1. AVOIDS SIZE LIMITATION OF CONVENTIONAL CI
   \(10^5 - 10^6\) CSF's 'routine'

2. PERMITS MAXIMAL EXPLOITATION of SPACE METHOD
\[
NCl
\]

\[
b^3\Sigma^+ \rightarrow X^3\Sigma^-, \quad a^3\Delta \rightarrow X^3\Sigma^-
\]

\[X^3\Sigma^- \]

\[X^3\Sigma^+ \]

\[3^1\Pi \text{ spaces } \sigma \pi^3 \text{ valence orbitals} \]

Method: 1. Orbitals: SA-MCSCF
\[3\Sigma^-, \, \Delta, \, \Sigma, \, 3^1\Pi \]

2. \[\psi^3(3\Pi, a^3\Delta) \psi^5(3\Sigma, b^3\Sigma^+) \psi(3\Pi, X^3\Sigma) \psi(3\Sigma, X^3\Sigma) \psi(\Sigma, b^3\Sigma)\]


CABLE I. Spin-forbidden transition moments* for \(b \rightarrow X\) and \(a \rightarrow X\) transition in NCl.

<table>
<thead>
<tr>
<th>Reference</th>
<th>[\mu; (a \Sigma^+, X \Sigma^-)]</th>
<th>[\mu; (b \Sigma^+, X \Sigma^-)]</th>
<th>[\mu; (b \Sigma^+, X \Sigma^-)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>CVB [Ref. 4(a)]</td>
<td>EXP</td>
<td>0.174(−1)</td>
<td>0.153(−1)</td>
</tr>
<tr>
<td>Becker et al. (Ref. 5)</td>
<td></td>
<td>0.659(−3)</td>
<td></td>
</tr>
<tr>
<td>Wayne-Coibourn (Ref. 6)</td>
<td>SCF</td>
<td></td>
<td></td>
</tr>
<tr>
<td>This work FO 5000 CSF</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SO 80000 CSF</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Only total radiative rate measured
\[ \text{CH}^- \quad 1_{\Delta_2} \quad [\nu_1] \quad \rightarrow \quad 3_{\Sigma^-} \]

Lengsfield Jensen Yarkony

\[ 3_{\Sigma^-} \quad 1\sigma^22\sigma^23\sigma^2 \quad 1\pi^2 \quad \text{VALENCE States} \]

\[ 1_{\Delta} \quad \text{n}_{\sigma} + \pi \quad 1\sigma^22\sigma^23\sigma1\pi^3 \quad \text{VALENCE} \]

\[ 3_{\Pi} \quad \pi + \sigma^* \quad 1\sigma^22\sigma^23\sigma^24\sigma1\pi \]

\[ \text{n}_{\sigma} = 3\sigma \quad \sigma^* = 4\sigma \quad ? \]

GOAL: Construct \( 3,1_{\Pi} \) space appropriate for \( \psi^1 \)

STEP 1: VARIATIONAL PRINCIPLE

\[ 3_{\Sigma^-}, 1_{\Delta}, 3,1_{\Pi} \quad \text{into State averaged MCSCF} \]

RESULT: 4\( \sigma \) is very diffuse

\[ \text{CH}(2_{\Pi}) + e \quad \text{as expected} \]
Step 2: (a) Construct $\psi^1(3\pi, a^1\Delta)$

$\psi^1(1\pi, \chi^3\Sigma^-)$

in flexible "2nd order space"
80,000 & 130,000 terms

(b) Analyze the solutions using
NATURAL ORBITALS

QUALITATIVELY:

$1\sigma^2 2\sigma^2 3\sigma 1\pi^3$ is correct

but

$1\sigma^2 2\sigma^2 3\sigma 2\delta 1\pi$

should be valence orbital

Step 3: Using 4$\sigma$ NATURAL ORBITAL redo Step 2.

Conclusion: Now possible to optimize the space used to describe the perturbation in a manner analogous to that used to optimize space for the zeroth order wavefunction!
Unclassified


H. J. Landerdale et al.

Unlabeled
<table>
<thead>
<tr>
<th>$R = 2.00$</th>
<th>Orbital Space</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MCSCF</td>
</tr>
<tr>
<td>$E(3\Sigma^-)$</td>
<td>$\text{au}$</td>
</tr>
<tr>
<td>$E(1\Delta)$</td>
<td>$\text{au}$</td>
</tr>
<tr>
<td>$\Delta E(3\Sigma^- - 1\Delta)$</td>
<td>$\text{cm}^{-1}$</td>
</tr>
<tr>
<td>$E(2)(3\Sigma^-, 1\Pi)$</td>
<td>$\text{cm}^{-1}$</td>
</tr>
<tr>
<td>$E(2)(1\Delta, 3\Pi)$</td>
<td>$\text{cm}^{-1}$</td>
</tr>
<tr>
<td>$\nu(1\Delta, 3\Sigma^-)$</td>
<td>$\text{au}$</td>
</tr>
<tr>
<td>$\tau$</td>
<td>$\bar{g}$</td>
</tr>
</tbody>
</table>

$\tau^{-1} = 2.0261 \times 10^{-6} \cdot \sigma^3 \cdot \nu^2$
The primary objective of this program is to demonstrate the feasibility of synthesizing hypervalent, high oxidation state fluorides of nitrogen, oxygen and noble gases. Typical target compounds are \( \text{NF}_4, \text{OF}_4 \) and \( \text{ArF}_2 \).

Our initial efforts are concentrated on the synthesis of \( \text{NF}_5 \). A sapphire reactor was set up for uv-photolysis in liquid \( \text{F}_2 \) at -196°C. The efficiency of the apparatus was demonstrated by preparing \( \text{NF}_4^+\text{BF}_4^- \) from \( \text{NF}_3 + \text{F}_2 + \text{BF}_3 \), but photolysis of \( \text{NF}_3 + \text{F}_2 \) alone did not produce detectable amounts of \( \text{NF}_5 \) or \( \text{NF}_4^+\text{F}^- \). A matrix isolation apparatus was built and the \( \text{NF}_3 - \text{F}_2 - \text{BF}_3 \) system was studied in Ar matrix at 5°K using uv-photolysis. Since no evidence for the formation of either any new species or \( \text{NF}_4^+\text{BF}_4^- \) was obtainable under these conditions, the apparatus was modified to use microwave discharge instead of uv-photolysis for the generation of F atoms. This method has the advantages of producing much higher F atom concentrations without photolytically destroying the desired products. The efficiency of the system was demonstrated for the \( \text{O}_2 - \text{F}_2 \) system producing the known \( \text{O}_2\text{F} \) radical in good yields. The reactions of microwave discharged generated F atoms with either \( \text{NF}_3 \) or \( \text{BF}_3 \) alone in Ar matrix so far have not generated detectable amounts of any new species.

Preliminary experiments using \( ^{18}\text{F} \) radio tracer studies were carried out to determine whether nitrogen can exhibit a coordination number of five with fluorine. Unfortunately, the facilities available (at the University of Glasgow) did not permit the generation of sufficiently large amounts of the \( ^{18}\text{F}_2 \) required for our experiments.
EXPERIMENTAL STUDIES ON THE SYNTHESIS OF NEW NOBLE GAS FLUORIDES AND HIGH OXIDATION STATE ENERGETIC FLUORINE COMPOUNDS INVOLVING UNUSUAL BONDING SITUATIONS

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ROCKETDYNE DIVISION OF ROCKWELL INTERNATIONAL, CANOGA PARK, CA

OBJECTIVES

- ACHIEVE ENERGY INCREASE BY UNUSUAL BONDING SITUATIONS SUCH AS HYPERVALENCE
- PREPARE AND CHARACTERIZE NEW HYPERVALENT FLUORIDES OF NITROGEN, OXYGEN AND THE LIGHTER NOBLE GASES
HYPervalency

- Definition

In hypervalent compounds the number of valence electrons on central atom exceeds 8.

- Typical Example

\[ \text{Kr-F} \]

Free valence electron pairs (VEP) on Kr want as much s-character as possible. This can be achieved by formation of semi-ionic 3-center 4-electron bonds for the two Kr-F bonds:

\[ \text{FKr}^+ \rightarrow F^- \rightarrow F^- \rightarrow \text{Krf}^+ \]
RESULT

HYPERVALENT SEMI-IONIC 3c-4e BONDS POSSESS ABOUT HALF THE BOND STRENGTH OF A NORMAL COVALENT BOND

\[
\begin{align*}
\ce{Kr &< F} & & \ce{[Kr - F]^+} \\
2.46 & & 3.55 \\
\ce{\left[ F \quad Cl \quad F \right]^-} & & \ce{[Cl - F]} \\
2.3 & & 4.4
\end{align*}
\]

WEAKENING OF THE BONDS WILL INCREASE THE ENERGY CONTENT OF A MOLECULE

- TYPICAL HYPERVALENT TARGET COMPOUNDS

\[
\text{NF}_5, \text{OF}_4, \text{ArF}_2
\]
NF₅ CHEMISTRY

- NF₅ COULD EXIST IN COVALENT OR IONIC FORM

\[
\begin{align*}
\text{Covalent Form:} & \quad \text{NF}_5 \\
\text{Ionic Form:} & \quad \left[ \begin{array}{c} F \\ N \\ F \end{array} \right]^+ \left[ \begin{array}{c} F \\ F \end{array} \right]^- \\
\end{align*}
\]

ENERGY DIFFERENCE ~ 102 KCAL/MOL

- CALCULATED ΔHᶠ OF NF₅ = 71 KCAL/MOL

- THEORETICAL PERFORMANCE CALCULATIONS

\[ I_{\text{VAC}} (50 \text{ PSI}, \varepsilon = 100) \text{ FOR NF}_5-\text{H}_2 \text{ SYSTEM} = 505 \text{ SEC} \]

\[ F_2-\text{H}_2 \text{ SYSTEM} = 487 \text{ SEC} \]
NF₅ CHEMISTRY, EXPERIMENTAL STUDIES

- UV-PHOTOLYSIS AT -196°C IN LIQUID F₂ IN SAPPHIRE REACTOR USING
  1 KW FOCUSED HIGH-PRESSURE H₂ ARC WITH H₂O-PYREX FILTER

  MODEL REACTION SUCCESSFUL

  \[ \text{NF}_3 + \text{F}_2 + \text{BF}_3 \rightarrow \text{NF}_4\text{BF}_4 \]

  BUT ATTEMPTED NF₅ SYNTHESIS

  \[ \text{NF}_3 + \text{F}_2 \rightarrow \text{NF}_5 \text{ OR } \text{NF}_4^+\text{F}^- \]

  DID NOT PRODUCE ANY NEW PRODUCT STABLE AT -186°C

  RESIDUE AFTER NF₃ AND F₂ REMOVAL AT -186°C

  WAS TRACE OF O₂F₂ (O₂ + F₂ \rightarrow \text{hv} \rightarrow O₂F₂)

  PURIFICATION OF F₂

  \[ 2 \text{O}_2 + \text{F}_2 + 2\text{BIF}_5 \rightarrow 250°C \rightarrow 2 \text{O}_2^+\text{BIF}_6^- \]
NF₅ CHEMISTRY, EXPERIMENTAL STUDIES

- UV-PHOTOLYSIS IN N₂ MATRIX (MR = 300) AT 10⁰K

SYSTEMS STUDIED

\[
\begin{align*}
\text{NF}_3, & \quad F_2, BF_3 \\
\text{NF}_3-F_2, & \quad BF_3-F_2 \\
\text{NF}_3-F_2-BF_3 & \quad \text{NO NEW SPECIES OBSERVED}
\end{align*}
\]

POSSIBLE PROBLEMS

\[ F \text{ CONCENTRATION TOO LOW} \]

DESIRED PRODUCTS DESTROYED BY PHOTOLYSIS
NF₅ CHEMISTRY, EXPERIMENTAL STUDIES

- GENERATION OF F' ATOMS BY MICROWAVE DISCHARGE TECHNIQUE AND APPARATUS SIMILAR TO THAT OF DR. JACOX

APPARATUS TESTED FOR O₂ + F' REACTION IN Ar (~JACOX)
O₂F' FORMED IN GOOD YIELD

SYSTEMS STUDIED SO FAR

\[
\begin{align*}
\text{NF}_3 + &F' \rightarrow \text{NF}_4 + F' \rightarrow \text{NF}_5 \text{ OR NF}_4^+F^- \\
\text{BF}_3 + &F' \rightarrow BF_4
\end{align*}
\]
NF$_5$ CHEMISTRY, EXPERIMENTAL STUDIES

- CONCLUSION

NO EXPERIMENTAL EVIDENCE FOR FORMATION OF EITHER
COVALENT NF$_5$ OR IONIC NF$_4^+$:F$^-$ FROM NF$_3$ AND F
AT TEMPERATURES AS LOW AS 10$^\circ$K

- TWO FUNDAMENTAL QUESTIONS
  - NF$_5$: CAN NITROGEN COORDINATE 5 FLUORINES?
  - NF$_4^+$:F$^-$: HOW EASILY WILL F$^-$ ABSTRACT AN F$^+$ FROM NF$_4^+$
    TO GIVE NF$_3$ + F$_2$?
  - POSSIBLE ANSWER FROM $^{18}$F RADIO TRACER STUDIES
**NF₅ CHEMISTRY. ¹⁸F RADIO TRACER STUDY**

- **DISPLACEMENT REACTION**
  \[
  NF₄⁺BF₄⁻ + FNO \rightarrow NO⁺BF₄⁻ + \left[ \begin{array}{c}
  F \\
  N⁺ \\
  F
  \end{array} \right]
  \]

  IF \( CN_{\text{MAX}} = 4 \)

  - \( NF_3 + F_2 \)
    - 0% * 100% *

  - \( [NF_5] \)
    - 60% * 40% *

- **DISTRIBUTION OF \(^{18}F\) IN PRODUCTS SHOULD CONCLUSIVELY SHOW WHETHER COVALENT NF₅ CAN EXIST OR NOT**
NF$_5$ CHEMISTRY. $^{18}$F RADIO TRACER STUDY

- DISPLACEMENT REACTION BETWEEN NF$_4$BF$_4$ AND FNO WAS DEMONSTRATED FOR $^{19}$FNO
- RADIO TRACER EXPERIMENTS WERE ATTEMPTED BY PROF. WINFIELD (UNIV. OF GLASGOW)
- DIFFICULTIES WITH PRODUCTION OF SUFFICIENT AMOUNTS OF $^{18}$F$_2$ FROM Cs$^{18}$F FOR
  \[(2\text{NO} + ^{18}\text{F}_2 \rightarrow 2^{18}\text{FNO}) \quad (t_{\frac{1}{2}}^{^{18}}\text{F} = 110 \text{ MIN})\]
- HAD BEEN WAITING FOR REPAIR OF ACCELERATOR AT UC IRVINE
  FOR $^{20}$Ne(d,α) $^{18}$F OR $^{19}$F (γ, n) $^{18}$F REACTIONS
- EXPERIMENT WILL BE RESUMED IN COLLABORATION WITH
  DR. SCHROBILGEN AT MCMASTER UNIVERSITY
PLANNED WORK

- COMPLETION OF MATRIX ISOLATION STUDY AND RADIO TRACER STUDY OF NF₅

- SYNTHESIS OF ArF⁺PtF₆⁻ AND ArF₂

- SYNTHESIS OF OF₃⁺PtF₆⁻ AND OF₄
THE PREVALENCE OF RHOMBIC STRUCTURES IN $A_2B_2$ TETRAATOMICS

by KOOP LAMMERTSMA AND OSMAN F. GUNER

Dept. of Chemistry, University of Alabama at Birmingham,
University Station 219 PHS, Birmingham, AL 35294.
A variety of reactive solid state materials contain rhombic building blocks as important structural ingredients. Illustrative are the formul\(\text{Al}_2\text{Si}_2^{2-}\) and \(\text{Li}_2\text{X}_2^-\) (\(\text{X} = \text{N}, \text{P}, \text{As}\)) fragments in the Zintl' complexes \(\text{CaAl}_2\text{Si}_2\) and \(\text{MLi}_2\text{X}_2\) (\(\text{M} = \text{Ce}, \text{Zr}, \text{Pr}\)), respectively, whereas the formul\(\text{Be}_2\text{Ge}_2^{2-}\) part in \(\text{CaBe}_2\text{Ge}_2\) can be viewed as a square network. These building blocks are tetraatomic structures of the \(\text{A}_2\text{B}_2\)-type. We have studied by ab initio MO theory a variety of 10, 12, 14, and 16 valence electron \(\text{A}_2\text{B}_2\) species to determine whether high energy density rhombic structures are preferred at the molecular level.

For the 16 el. species \(\text{C}_4\), \(\text{C}_3\text{HB}\), \(\text{C}_2\text{H}_2\text{B}_2\), and related cations, the rhombic structures are indeed minima on the potential energy surface. This is also the case for the 14 el. \(\text{C}_3\text{Be}\), \(\text{C}_3\text{HBB}\), and related cations. However, for the 12 el. \(\text{C}_2\text{Be}_2\) the linear form (triplet) is more stable than the rhombic isomer, which is a minimum energy structure.

In our full potential energy search on the limiting 12 el. \(\text{C}_2\text{Li}_2^{2-}\) and 10 el. \(\text{B}_2\text{B}_2\) species we focus on the prevalence of the highly energetic rhombic structures and their unique bonding properties. Similarly, preliminary data on the 16 el. disilicondicarbide \(\text{C}_2\text{Si}_2\) will be presented.
No electron density between C\textsubscript{1} and C\textsubscript{3}

The HOMO (I) is a non-bonding $\sigma$-orbital

The short distance between C\textsubscript{1} and C\textsubscript{3} results from two $\sigma$-bridged-\pi-bonding orbitals (II)
INVERTED GEOMETRIES AT CARBON

\[ \text{sp}^2 \quad \text{"inverted" sp}^2 \]
INVERTED $sp^2$

INVERTED $sp^3$

$\sigma$ Deficient bonding
IMPORTANT MO's

LUMO

NON-BONDING

HOMO

BONDING

$4C-2E$ 'AROMATIC'
Table 1. 6-31G* energies (in au), heats of formation (ΔH_f, in kcal/mol), and strain energies (SE, in kcal/mol) for four-membered ring structures.

<table>
<thead>
<tr>
<th>compound</th>
<th>formula</th>
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<th>ΔH_f</th>
<th>SE</th>
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<td>21^29</td>
<td>C_4</td>
<td>-151.14598</td>
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<td>23^29</td>
<td>C_4H_2^2+</td>
<td>-151.53998</td>
<td>726</td>
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<tr>
<td>Cyclobutadiene dication (26)^35</td>
<td>C_4H_4^2+</td>
<td>-152.91650</td>
<td>623</td>
<td></td>
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<tr>
<td>Bicyclo[1.1.0]butene (8)</td>
<td>C_4H_4</td>
<td>-153.58016</td>
<td>142</td>
<td>127</td>
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<tr>
<td>1,3-Cyclobutadiene (15)^23</td>
<td>C_4H_6</td>
<td>-153.6412</td>
<td>103</td>
<td>65</td>
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<tr>
<td>Bicyclo[1.1.0]butane (2)</td>
<td>C_4H_6</td>
<td>-154.87176</td>
<td>51.9</td>
<td>65</td>
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<tr>
<td>Cyclobutene (27)^9g</td>
<td>C_4H_6</td>
<td>-154.89962</td>
<td>37.5</td>
<td>29</td>
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<tr>
<td>Cyclobutane (28)^9g</td>
<td>C_4H_8</td>
<td>-156.09703</td>
<td>6.8</td>
<td>26</td>
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<tr>
<td>Hydrogen^14</td>
<td>H_2</td>
<td>-1.12683</td>
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Enthalpies given to the nearest tenth are experimental data, integer values are based on calculated energies. The strain energy, SE, are derived from Franklin group equivalents: CH_2=-4.93, CH=0.80, cis-CH=CH=18.88, and C=C=24.57 kcal/mol.
Relative (in kcal/mol) Energies of $C_4H_2^{2+}$, $C_4H^+$, and $C_4$ Isomers.

<table>
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<tr>
<th>Structures</th>
<th>$HF/6-31G^*$</th>
<th>$MP2/6-31G^*$</th>
<th>$MP3/6-31G^*$</th>
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<tr>
<td>1 $D_{sh}$</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
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<td>2 $D_{2h}$</td>
<td>48.1</td>
<td>-1.5</td>
<td>13.3</td>
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<tr>
<td>10 $C_{sh}$</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
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<tr>
<td>11 $C_{2v}$</td>
<td>36.3</td>
<td>-13.0</td>
<td>0.2</td>
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<tr>
<td>12 $D_{sh}$</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
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<tr>
<td>13 $D_{2h}$</td>
<td>23.7</td>
<td>-14.6</td>
<td>-2.7</td>
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</table>

*a* $HF/3-21G$ geometry

$$
\begin{align*}
\text{H--C--C--C--C--H} \\
\text{1} \\
\text{H--C--C--C--H} \\
\text{10} \\
\text{C--C--C--C} \\
\text{12}
\end{align*}
$$

$$
\begin{align*}
\text{H} & \text{H} \\
\text{1} & \text{2} \\
\text{C--C--C--C} \\
\text{10} \\
\text{C--C--C--C} \\
\text{12}
\end{align*}
$$
Table 1. 6-31G* Energies, Structural Parameters, and Mulliken Overlap Population Analysis for the Four-Membered Structures 5–15.

<table>
<thead>
<tr>
<th>compound</th>
<th>energy</th>
<th>geometry</th>
<th>overlap population</th>
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<td>r(C₁-C₃)</td>
<td>r(C-X), r(C-Y)</td>
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<td>5, a C₄</td>
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<td>1.352, 1.472</td>
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<tr>
<td>7, a C₄H₂⁺</td>
<td>-151.53998</td>
<td>1.593</td>
<td>1.386</td>
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<tr>
<td>8, C₃BH</td>
<td>-138.65329</td>
<td>1.462</td>
<td>1.479, 1.418</td>
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<td>9, C₃BH₂⁺</td>
<td>-139.01220</td>
<td>1.529</td>
<td>1.526, 1.345</td>
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<tr>
<td>10, C₂B₂H₂</td>
<td>-126.15541</td>
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<td>1.470</td>
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<tr>
<td>11, C₂Be</td>
<td>-127.98366</td>
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<td>12, C₂BeH⁺</td>
<td>-128.39386</td>
<td>1.484</td>
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<td>13, C₂BeH</td>
<td>-115.47831</td>
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<td>1.558, 1.473</td>
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<td>14, C₂Be₂</td>
<td>-104.79129</td>
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<td>1.564</td>
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<td>15, L₄H₂</td>
<td>-99.72164</td>
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a Reference 8. b The respective r(B-B) bonds are given.

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PHOTOEXCITATION OF TRIATOMIC HYDROGEN

H. Helm and L. J. Lembo
Molecular Physics Department
SRI International, Menlo Park, Ca 94025

1. Emission Spectra (Herzberg)

2. Formation of H$_3$ in Charge Transfer

3. Photoionization Spectra

4. Two-Photon Ionization

5. Excited-State Charge Transfer

6. Future Work

Supported by the Air Force Office of Scientific Research
under Contract FQ8671-8700 432
ABSTRACT

Submitted to
The First Annual High Energy Density Matter Conference
(12-13 May) 1987, Rosslyn Virginia

PHOTOEXCITATION OF TRIATOMIC HYDROGEN*

H. Helm, and L. J. Lembo
Molecular Physics Department
SRI International Menlo Park, Ca 94025.

We have used a coaxial laser fast-neutral-beam spectrometer to study photoabsorption of long-lived species of H$_3$. The H$_3$ molecules are formed by electron transfer from cesium to mass-selected H$_3^+$. The neutral molecules are detected by photoionization several microseconds after their formation. Single-photon ionization of H$_3$ has been observed in the near UV (3620 to 3380 Å) via autoionizing Rydberg states. In addition one-photon resonant two-photon ionization has been observed via the 3$d^2_{A_1}$' state at 5781 Å. The photoionization data suggest that the long lived H$_3$ species are molecules in the previously known 2$p^2_{A_2}$" state. We will discuss these results and our current understanding of the structure of this triatomic hydrogen species.

* Work supported by the Air Force Office of Scientific Research.

MP No. 87-085
Three of the Emission bands observed by Herzberg and coworkers are shown by the full arrows. (Ref. 1-5)

The photoionization step from the metastable $H_3$ state is shown by the open arrow. (Ref. 6).
Predissociation of $n=2$ states

$2s \ A_1^1$ vibrational coupling

$H + H_2$

$H_2 + H(2p)$  $H_2 + H$

$2p \ A_2''$
Predissociation of $n=2$ states

$2p \, A_2^+$ Rotational coupling

$2pE'$

$H + H_2$
Metastable triatomic hydrogen

Lifetime of $2p\text{A}_2^+$ state depends on the degree of rotation of the molecule

(Herzberg, Hougen and Watson, Ref.5)

The residual width of the lowest level (N=0, K=0)
is attributed to Doppler Broadening

Radiative lifetime for $2p\text{A}_2^+$ $\rightarrow$ $2s\text{A}_1^+$ transition (1090 cm$^{-1}$)has been calculated to be 87 us (Gellene and Porter, Ref.7)
Formation of $H_3$ by Charge Transfer

$H_3^+$

Cs (6s)

$H_3$

Ionization Potential of Cs: 3.89 eV

Binding Energy of n=2 Electron to $H_3^+ \sim \text{Ry}/4$

References 7-13
Photoionization spectrum at high n-values

PHOTON ENERGY (cm$^{-1}$)

PHOTON ENERGY (cm$^{-1}$)
Assignment of Rydberg Series

The lowest \( n \) member observed in each series is indicated along the series ladders.
Autoionization of $n=7$ states

Autoionization Mechanism:
vibrationally excited core and bound Rydberg electron exchange energy.

The peaks B and D (B' and D') are identified as transitions to the 7d (7s) Rydberg states of vibrationally excited $H_3$. 
Two-Photon Ionization of $H_3$

Ionization limit

3d

3s

5781 Å

5989 Å

2p

Count rate

Wavelength (Å)

0 5700 5780 5860

40
ELECTRON TRANSFER FROM EXCITED TARGET

ground state target

\[ \text{Cs}(6s) + \text{H}_3^+ \rightarrow \text{Cs}^+ + \text{H}_3 (n=2) - 228 \text{ meV} \]

detection

excitation

\[ \text{Cs}(6s) + \text{hv} (3401 \text{ A}) \rightarrow \text{Cs}(11p) \]

detect Rydberg molecule by field ionization

\[ \text{H}_3 (n=26) + E \rightarrow \text{H}_3^+ + \text{e} \]
Timing

to select excitation process in charge exchange cell

![Diagram showing timing for charge transfer and laser arrival.]

- **Charge transfer**
- **Weak field**
- **Strong field**

Laser arrival of ions

- Laser
- Arrival of ions

Time scale:
- 10 ns
- ~100 ns
Excitation Spectrum of Cs

\[ \text{Cs} (1 \, \text{I}^{2} \text{p}^{0}) + \text{H}_3^+ \rightarrow \text{H}_3^{**} + \text{Cs}^+ \]
Future work

- Identify lowest autoionizing levels in the Rydberg series to support assignment of vibrational states of the metastable molecule.

- Measure the linewidth of the transitions to determine the autoionization lifetimes.

- Two-Color Ionization experiments using as intermediate the n=3 levels observed by Herzberg to determine the quantum defects of the np and nf Rydberg series.

- Search for metastable species of the H$_5$ molecule for which a number of metastable states have been predicted theoretically (Ref. 14).

REFERENCES

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