

# Lawrence Berkeley National Laboratory

## LBL Publications

### **Title**

Molecular Beam Studies of Reaction Dynamics

### **Permalink**

<https://escholarship.org/uc/item/479336gx>

### **Author**

Lee, Y T

### **Publication Date**

1989-03-01



# Lawrence Berkeley Laboratory

UNIVERSITY OF CALIFORNIA

## Materials & Chemical Sciences Division

To be presented at the 1989 Combustion Research  
Contractor's Meeting, Hempstead, NY,  
June 7-9, 1989

### Molecular Beam Studies of Reaction Dynamics

Y.T. Lee

March 1989



! LOAN COPY !  
! Circulates !  
! for 2 weeks !

Bldg. 50 Library.

LBL-26905

## **DISCLAIMER**

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

1989 Combustion Research Contractor's Meeting  
 Hofstra University, Long Island, New York  
 June 7-9, 1989

LBL-26905 ABS

### Molecular Beam Studies of Reaction Dynamics

Yuan T. Lee  
 Materials and Chemical Sciences Division  
 Lawrence Berkeley Laboratory  
 Berkeley, California 94720

#### Scope of Project

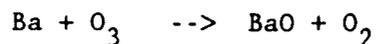
The major thrust of our project is to elucidate the detailed dynamics of simple elementary chemical reactions and primary photochemical processes which are theoretically important and to unravel mechanisms of complex chemical reactions which play important roles in many macroscopic processes. Various advanced molecular beam and laser techniques are used for this research. A new spectroscopic method was also developed recently for obtaining IR absorption spectra of important carbonium ions and various solvated ions.

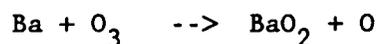
#### Current Research and Recent Results

##### A) Reaction Dynamics

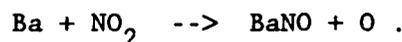
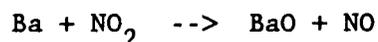
1) Reaction of D Atoms with Acetylene. A preliminary study of the  $D + C_2H_2 \rightarrow C_2HD + H$  reaction, which is interesting because of its role in combustion chemistry and possible theoretical applications, is being carried out. The dynamics of this system are being investigated by measuring the time-of-flight of the  $C_2HD$  product at various laboratory angles, giving an idea of both the product energy and angular distribution at a given collision energy. The experiment probes the  $D + C_2H_2$  reaction at various collision energies to determine the effect of reagent translational energy. A photodissociation source is used to produce D atoms thus allowing the D atom velocity and thus the reaction collision energy to be controlled by changing the D atom precursor (using DI or DBr) and/or by changing the laser frequency and polarization. Work has been done at 21, 40, and 55 kcal/mol, but other energies are possible. Some variation in the angular distribution of the  $C_2HD$  product with collision energy has been observed, but more work will be required to confirm these initial observations and determine what changes in reaction mechanism account for the experimental results. It would also be interesting to see what happens to the abstraction channel ( $D + C_2H_2 \rightarrow HD + C_2H$ ). Finally, with a few modifications of the experimental apparatus, it will be possible to use the photodissociation of  $CH_3I$  as a source of  $CH_3$  radicals. This will allow the investigation of  $CH_3$  reaction systems such as  $CH_3 + C_2H_2$  and  $CH_3 + C_2H_4$ .

2) Reaction Dynamics of Ground State Barium Atoms With  $O_3$  and  $NO_2$ . The reactions of barium with  $O_3$  and  $NO_2$  were studied at several collision energies in the range from 9.1 to 57. kcal/mol. In both cases, two reaction channels were observed:





and



Neither  $\text{BaO}_2$  nor  $\text{BaNO}$  has previously been observed in the gas phase. From the translational energy distributions of the products we calculate lower bounds for the  $\text{Ba--O}_2$  and  $\text{Ba--NO}$  bond dissociation energies of 144 and 67 kcal/mol, respectively. The depth of the  $\text{Ba--O}_2$  potential well explains the dynamics of the  $\text{Ba} + \text{O}_2$  reaction, which is thought to occur through the formation of a long-lived collision complex. The center of mass angular distributions for the first three reactions (above) peaked along the relative velocity vector and showed significant contributions in the backward hemisphere relative to the barium beam. Since the formation of ground state products is highly exothermic in these reactions (3-5 eV), it is unlikely that the observed distribution is due to a long-lived collision complex. Alternatively, the distribution may result from an insertion mechanism wherein the divalent barium atom inserts into the O--O or N--O bond, and the symmetry of the reaction configuration is responsible for the observed distributions. The  $\text{BaNO}$  channel showed an angular distribution entirely forward scattered relative to the barium beam, which peaked well away from the relative velocity vector, suggesting a direct reaction mechanism resulting from collisions with a narrow range of impact parameters.

3) Dynamics of  $\text{D} + \text{H}_2 \rightarrow \text{DH} + \text{H}$  Reactions. In the last year complete differential cross sections have been measured for the reaction  $\text{D} + \text{H}_2 \rightarrow \text{DH} + \text{H}$  at two collision energies: 0.51 and 0.98 eV. The 0.98 eV data yield vibrational state resolved product angular distributions, with a peak product recoil angle of  $130^\circ$  in the center of mass frame. At 0.51 eV collision energy the  $\text{DH}$  product is strongly backscattered (c.m. angle =  $180^\circ$ ). These results provide the highest resolution, most complete data available on this fundamental chemical reaction. A full analysis of the data is currently underway to provide an important test of the recent fully converged 3-dimensional quantum mechanical dynamics calculations of Zhang and Miller.

## B) Photochemical and Unimolecular Processes

1) Production and Photodissociation of  $\text{CCl}_3$  Radicals. Although a systematic and predictive understanding of the primary chemistry and translational energy release of unimolecular reactions of stable molecules is starting to develop, little is known about such processes in radicals. For the purpose of exploring their reaction dynamics, a pulsed molecular beam source of radicals with sufficient number density for use in photodissociation experiments has been built. A teflon nozzle with a transverse slot cut through it is attached to the end of a pulsed valve. A laser beam passes through the slot and intersects the gas pulse, producing radicals by photolysis of a suitable precursor molecule. The radicals are thermalized in the high pressure region of the nozzle, then cooled in the supersonic expansion out the end of the nozzle.  $\text{CCl}_3$  radicals were produced by photolysis of  $\text{CCl}_4$  at 193 nm in the source. After passing through a collimating skimmer, cold  $\text{CCl}_3$  is photodissociated at 308 nm to give  $\text{Cl}$  and  $\text{CCl}_2$ .

some of which undergoes secondary photodissociation producing Cl + CCl. There is no evidence for the reaction producing Cl<sub>2</sub> and CCl from CCl<sub>3</sub>. From the time-of-flight spectra of the fragments, detected with a rotatable mass spectrometer, the product translational energy distributions for each reaction channel can be obtained. The primary reaction, producing Cl and CCl<sub>2</sub>, releases an average of 12-13 kcal/mol into translation, or about a third of the available energy. Analysis of the data to extract the translational energy release from secondary photodissociation is now underway. It is expected that this source will be useful in further studies of polyatomic radicals.

2) Molecular Beam Studies of the Photodissociation of Benzene at 193 and 248 nm. The photodissociation processes of benzene following excitation at 193 and 248 nm have been studied by molecular beam photofragmentation translational spectroscopy. When benzene was excited to the B<sub>1u</sub> state by absorption at 193 nm, dissociation occurred through three primary channels, C<sub>6</sub>H<sub>5</sub> + H, C<sub>6</sub>H<sub>4</sub> + H<sub>2</sub>, and C<sub>5</sub>H<sub>3</sub> + CH<sub>3</sub>, following internal conversion to the vibrationally excited ground state. When benzene was excited to the B<sub>2u</sub> state at 248 nm, two primary dissociation channels, C<sub>6</sub>H<sub>4</sub> + H<sub>2</sub>, and C<sub>5</sub>H<sub>3</sub> + CH<sub>3</sub>, were observed. Photodissociation to produce two C<sub>3</sub>H<sub>3</sub> was induced by two-photon absorption of benzene at both 193 and 248 nm. Numerous secondary photodissociation processes of the primary photoproducts were also observed at both 193 and 248 nm.

3) Time and State Resolved H<sub>2</sub> Elimination from 1,3 and 1,4-Cyclohexadiene. In the photolysis of 1,4-cyclohexadiene (CHDN) at 193nm, it has been shown that the concerted H<sub>2</sub> elimination and C-H bond rupture are two primary reaction channels following internal conversion. 1,3-CHDN, on the other hand, isomerizes to 1,4-CHDN before H<sub>2</sub> elimination occurs. Preliminary studies have been carried out on the photodissociation dynamics of both 1,4-CHDN and 1,3-CHDN at 212nm by probing the vibrational, rotational as well as translational energy distributions in the H<sub>2</sub> product through a VUV-UV two photon REMPI process. The population of H<sub>2</sub> in each rovibrational state was determined by measuring the transition intensities of the Lyman and Werner bands using a recently developed transform-limited VUV-XUV laser system. Since the transitions to the B<sup>+</sup>Σ<sub>g</sub><sup>+</sup> or C<sup>u</sup>Π states are direct absorption processes, the state population of H<sub>2</sub> can be calibrated rather accurately based on the theoretical oscillator strengths and known experimental parameters.

Some of the H<sub>2</sub> formed in this reaction is found to be highly vibrationally excited with products up to the v<sup>+</sup>=6 observed. On the contrary, the rotation is somewhat less excited with J<sub>max</sub> = 2 or 3 for most of the vibrational states. The H<sub>2</sub> product state distributions are virtually the same for 1,4-CHDN and 1,3-CHDN within the experimental uncertainty. However, the time evolution of the H<sub>2</sub> product is significantly different for the two isomers which indicates that 1,3-CHDN undergoes an isomerization to 1,4-CHDN before ejecting H<sub>2</sub>.

### C) Infrared Spectroscopy of Ionic Clusters

Infrared spectra of the hydrated hydronium, ammoniated ammonium and water substituted (hydrated) ammoniated ammonium ions were obtained between 2600 and 4000 cm<sup>-1</sup> at 0.7 cm<sup>-1</sup> resolution for a wide range of mass-selected cluster sizes. Spectra were generated by trapping the mass selected parent ions in a radio frequency ion trap, for a variable delay while the ions interacted with a

tunable, pulsed infrared laser beam. If the cluster ions absorb sufficient energy from the laser, vibrational predissociation can take place, resulting in the loss of one or more solvent molecules. Spectra are obtained by using a second mass analyzer to monitor the number of daughter ions produced as a function of laser wavelength.

1) Infrared Spectroscopy of the Hydrated Hydronium Cluster Ions.

$\text{H}_3\text{O}^+(\text{H}_2\text{O})_m$ . In an extension of previous work, spectra have been obtained for the  $\text{H}_3\text{O}^+(\text{H}_2\text{O})_m$  ions for  $m=3$  to 8. These spectra show features assignable to motions involving the  $\text{H}_3\text{O}^+$  core and  $\text{H}_2\text{O}$  solvent molecules. Preliminary analysis suggests that the first shell (I) is indeed completed by three  $\text{H}_2\text{O}$  subunits and that the favored geometry while the second shell (II) is being filled involves each II  $\text{H}_2\text{O}$  hydrogen bonded to a I  $\text{H}_2\text{O}$ . One important issue which we hope to resolve is whether the spectra indicate the presence of geometric isomers. Absorptions due to second shell subunits are observed.

2) Infrared Spectroscopy of the Ammoniated Ammonium Cluster Ions.

$\text{NH}_4^+(\text{NH}_3)_n$ . Spectra have also been obtained for the  $\text{NH}_4^+(\text{NH}_3)_n$  cluster ion series for  $n=1$  to 10. Features have been observed that have been assigned to both  $\text{NH}_4^+$  and  $\text{NH}_3$  type vibrational motions. Of the latter, vibrations of species in both the primary and secondary solvation shells have been distinguished in the larger clusters. Spectral data support the generally accepted notion that there are 4 ammonias in the first solvation shell of the cluster. The data also suggest in conflict with ab initio predictions, that the structure of the dimer  $\text{NH}_4^+\text{NH}_3$  is symmetric, or nearly so. Spectral features broaden and their frequencies converge with large  $n$  to values similar to those observed in concentrated solutions of ammonium salts in liquid ammonia, suggesting a liquid-like environment around the ammonium ion core.

A significant discovery is the observation of rotational structure imposed on the  $\nu_3$  band of the solvent ammonia molecules for  $n=2$  to 7. The wide spacing of these features ( $\sim 12.6\text{cm}^{-1}$ ) precludes assigning them to a rotation of the cluster as a whole. Rather, they have been assigned to the internal rotation of the solvent ammonias in the first solvation shell about their  $C_3$  axes with the nitrogens pointing towards the hydrogens of the ammonium ion. Fitting these data with a theoretical model for internal rotation gives a low ( $<10$  kcal/mole) barrier to internal rotation and essentially no vibrational coupling with other ammonias.

3) Infrared Spectroscopy of Hydrated Ammoniated Ammonium Ions.

$\text{NH}_4^+(\text{NH}_3)_n(\text{H}_2\text{O})_m$ . A large quantity of spectral data have been obtained from the clusters  $\text{NH}_4^+(\text{NH}_3)_n(\text{H}_2\text{O})_m$  ( $m+n=3$  to 5). The analysis of these data is in progress and already reveals the same nearly free internal rotation of  $\text{NH}_3$  subunits as in the  $\text{NH}_4^+(\text{NH}_3)_n$  case. The presence of  $\text{H}_2\text{O}$  in these complexes, however, can produce an inequivalence of otherwise identical  $\text{NH}_3$  subunits which results in a lifting of degeneracy and more complex spectra. The internal rotation of  $\text{H}_2\text{O}$  subunits is also evident in many of these complexes. This is particularly interesting in view of the fact that the spectra of  $\text{H}_3\text{O}^+(\text{H}_2\text{O})_m$  complexes have no comparable structure obviously attributable to internal rotation. The preliminary analysis also strongly suggests that more than one geometric isomer is frequently observed. This is not unexpected if the isomers differ in energy by only 1 or 2 kcal/mole.

## Future Plans

### A. Reaction Dynamics

1) Reaction of Sodium Dimer With O<sub>2</sub>. The reaction of ground state sodium atoms with oxygen to form NaO and O atom is not possible due to its endothermicity. The reaction is energetically possible for sodium excited to the 4D or 5S electronic states, yet reaction is only seen in the case of Na(4D). However, two reaction channels are thermodynamically possible for the dimer:



These two channels are likely to result from very different mechanisms. The center-of-mass angular distributions and translational energy distributions should provide insight into these reactions, and into the monomer reaction as well.

2) Reactions of Electronically Excited Barium Atoms. A broad understanding of the reactions of ground state barium with a variety of small molecules provides the foundation for an examination of the consequences of exciting one of the two barium valence electrons to a higher electronic state. The dependence of chemical reactivity on barium electronic state and on the alignment of the excited state orbitals relative to the reactants' relative velocity vector will provide a detailed understanding of the nature of the initial bond formation process.

3) Crossed Beam Chemistry of Transition Metals. The recent development of an apparatus capable of generating seeded supersonic beams of transition metals will open the door to the study of a broad spectrum of reactions of importance in combustion, catalysis, and corrosion. An exciting prospect, for example, is the reaction of transition metals with hydrocarbons. Owing to the involvement of d-orbitals in bond formation, insertion of the metal atom into the carbon-carbon bond is likely to occur, with subsequent H<sub>2</sub> elimination. By studying the actual molecular events under precisely defined conditions, a microscopic understanding of these important catalytic reactions may be obtained.

### B. Photochemical and Unimolecular Processes

1) Secondary Dissociation of Phenoxy Radicals from the Primary Photo-dissociation of Anisole and Phenol. Phenoxy radical is one of the most important intermediates in the combustion of benzene. The decomposition of phenoxy through formation of carbon monoxide and cyclopentadienyl radical is the major route of destruction of the six-membered ring system. In order to study the dynamics of formation and unimolecular decomposition of phenoxy radical, the infrared multiphoton dissociation of phenol and anisole were studied in a molecular beam experiment. The lowest energy dissociation pathway for both molecules leads to formation of phenoxy radical which was detected mass spectrometrically. In the case of anisole, there is evidence for secondary dissociation of the phenoxy radical to carbon monoxide and cyclopentadienyl radical.

Ultraviolet excitation at 193 and 248 nm was also used to study the photo-dissociation of anisole. In contrast to the infrared multiphoton dissociation experiment, several reaction channels were observed. The primary dissociation routes tentatively identified for the case of excitation at 193 nm are the formation of phenoxy radical and methyl radical accompanied by the release of large amounts of translational energy, the elimination of methanol forming benzyne, and the formation of toluene and  $O(^1D)$ . Secondary decomposition of the phenoxy radical forming cyclopentadienyl radical and possibly the absorption of a second photon by toluene and subsequent decomposition to phenyl and methyl radicals were also observed. Analysis of the results at 248 nm is in progress.

In the future, this work will be extended to study the ultraviolet photo-dissociation of phenol in order to improve the understanding of the dynamics of reactions involving molecules and radical species of major importance in combustion systems, as well as to extend our knowledge of aromatic photochemistry.

2) Mode Specific Decomposition of  $NH_4^+(H_2O)(NH_3)_2$ . The IR absorption spectrum of  $NH_4^+(H_2O)(NH_3)_2$  obtained in our laboratory clearly indicates that  $H_2O$  and two  $NH_3$  molecules are hydrogen bonded to three of the four H atoms in  $NH_4^+$ , leaving one free N-H bond unoccupied. The vibrational frequencies of stretching modes of  $H_2O$ ,  $NH_3$  and N-H in  $NH_4^+$  are well separated and they all lie in the range between  $3200\text{ cm}^{-1}$  and  $3800\text{ cm}^{-1}$ .

When the vibrational degrees of freedom of this molecules are excited beyond 30 kcal/mol, the elimination of either  $H_2O$  or  $NH_3$  will become energetically possible. An interesting investigation can be carried out by using a pulsed tunable IR laser to excite various stretching frequencies in these solvated ions to study how the competition between  $H_2O$  elimination and the  $NH_3$  elimination depends on the mode through which IR photons are deposited.

For many stable molecules, intramolecular energy transfers are shown to be faster than the unimolecular dissociation processes, but for weakly bound van der Waals molecules, the bond rupture often occurs before the vibrational energy is completely randomized. The solvated ions represent an intermediate case and should provide very interesting information on the mode specific dissociation processes. If the intramolecular energy transfer is again shown to be faster than the dissociation processes, no matter whether one excites N-H in  $NH_4^+$ , or stretching frequencies of  $H_2O$  or  $NH_3$ , the slightly weaker binding  $H_2O$  will be preferentially eliminated.

### C) Dynamic Spectroscopy

IR absorption, overtone excitation of polyatomic radicals, vibrational spectroscopy of carbonium ions and solvated ions, and the high resolution photoionization spectroscopy of polyatomic radicals are some of our future projects.

### Acknowledgment

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

Publications

1. Yuan T. Lee, Chemical Dynamics: Introduction. Chemical Reviews, **87**, 7A, February 1987.
2. Haruo Shiromaru, Yohoji Achiba, Katsumi Kimura, and Yuan T. Lee, Determination of the C-H Bond Dissociation Energies of Ethylene and Acetylene by Observation of the Threshold Energies of H<sup>+</sup> Formation by Synchrotron Radiation. J. Phys. Chem. **91**, 17-19 (1987).
3. S. W. Bustamente, M. Okumura, D. Gerlich, H. S. Kwok, L. R. Carlson, and Y. T. Lee, Spin-Forbidden Radiative Decay of the a  $^4\Pi_u$  State of O<sub>2</sub><sup>+</sup>. J. Chem. Phys. **86**, 508-515 (1987). LBL-22097
4. Timothy K. Minton, Gilbert N. Nathanson, and Yuan T. Lee, Photodissociation of CF<sub>2</sub>BrCH<sub>2</sub>I at 248, 266, and 308 nm. J. Chem. Phys. **86**, 1991-2006 (1987). LBL-22098
5. L. J. Butler, E. J. Hints, S. F. Shane, and Y. T. Lee, The Electronic State-Selective Photodissociation of CH<sub>2</sub>BrI at 248, 210, and 193 nm. J. Chem. Phys. **86**, 2051-2074 (1987). LBL-21896
6. Laisheng Wang, J. E. Pollard, Y. T. Lee, and D. A. Shirley, Molecular Beam Photoelectron Spectroscopy: The C<sub>2</sub>D<sub>4</sub><sup>+</sup> ( $\bar{X}^2B_3$ ) Ground State. J. Chem. Phys. **86**, 3216-3218 (1987). LBL-21997
7. M. Okumura, L. I. Yeh, D. Normand, J. J. H. van den Biesen, S. W. Bustamente, Y. T. Lee, Timothy J. Lee, Nicholas C. Handy, and Henry F. Schaefer III, Radiative Decay Lifetimes of CH<sub>2</sub><sup>-</sup>. J. Chem. Phys. **86**, 3807-3815 (1987). LBL-22428
8. Yuan T. Lee, Molecular Beam Studies of Elementary Chemical Processes. Nobel Lecture, Les Prix Nobel en 1986, Nobel Foundation (1987) pp.168-206; Chem Scripta **27**, 2489-2497 (1987); Science **236**, 793-798 (1987); Angew Chem. **99**, 967-980 (1987).
9. Timothy K. Minton, Gilbert N. Nathanson, and Yuan T. Lee, Photodissociation of CH<sub>2</sub>ClCH<sub>2</sub>I at 308 nm. Laser Chem. **7**, 297-304 (1987). LBL-22099
10. Laisheng Wang, Y. T. Lee, and D.A. Shirley, Molecular Beam Photoelectron Spectroscopy of SO<sub>2</sub>: Geometry, Spectroscopy, and Dynamics of SO<sub>2</sub><sup>+</sup>. J. Chem. Phys. **87**, 2489-2497 (1987). LBL-22413
11. Ralph H. Page, Robert J. Larkin, A. H. Kung, Y. R. Shen, and Y. T. Lee, Frequency Tripling into the 720-1025 Å Region with Pulsed Free Jets. Rev. Sci. Instrum. **58**, 1616-1620 (1987); **59**, 673 (1988); **60**, 243 (1988). LBL-23306
12. Ralph H. Page, Y. R. Shen, and Y. T. Lee, Highly-Resolved Spectra of Local Modes of Benzene. Phys. Rev. Lett. **59**, 1293-1296 (1987). LBL-23768

13. Ralph H. Page, Matthew F. Vernon, Y. R. Shen, and Y. T. Lee, Infrared Vibrational Predissociation Spectra of Large Water Clusters. *Chem. Phys. Lett.* **141**, 1-6 (1987); **144**, 104 (1988). LBL-24006
14. Alec M. Wodkte and Yuan T. Lee, High-Resolution Photofragmentation-Translational Spectroscopy. In *Advances in Gas-Phase Photochemistry and Kinetics, Molecular Photodissociation Dynamics*, edited by M.N.R. Ashfold & J.E. Baggott, Royal Society of Chemistry (1987) pp.31-59. LBL-22264
15. Gary N. Robinson, Robert E. Continetti, and Yuan T. Lee, Dynamics of Endoergic Aromatic Substitution Reactions. *Faraday Discuss. Chem. Soc.*, **84**, 25-37 (1987). LBL-23701
16. J. M. Mestdagh, B. A. Balko, M. H. Covinsky, P. S. Weiss, M. F. Vernon, H. Schmidt, and Y. T. Lee, Reactive Scattering of Electronically Excited Alkali Atoms with Molecules. *Faraday Discuss. Chem. Soc.*, **84**, 145-157 (1987). LBL-23588
17. M. Okumura, L. I. Yeh, and Y. T. Lee, Infrared Spectroscopy of the Cluster Ions  $H_3^+(H_2)_n$ . *J. Chem. Phys.* **88**, 79-91 (1988). LBL-23995
18. Ralph H. Page, Robert J. Larkin, Y. R. Shen, and Y. T. Lee, High-Resolution Photoionization Spectrum of Water Molecules in a Supersonic Beam. *J. Chem. Phys.* **88**, 2249-2263 (1988). LBL-24158
19. A.H. Kung, T. Trickl, N.A. Gershenfeld, and Y.T. Lee, State-Selective Detection of  $H_2$  by 1+1 REMPI via the  $C^1\Pi_u$  ( $\nu'=0, J'$ ) States. *Chem. Phys. Lett.* **144**, 427-430 (1988).
20. E. Cromwell, A.H. Kung, T. Trickl, and Y.T. Lee, XUV Source for Ultra-High Resolution Spectroscopy. *Proc. SPIE-Int. Soc. Opt. Eng.* **912**, 145-149 (1988). LBL-24636
21. L. I. Yeh, M. Okumura, J. D. Myers, and Y. T. Lee, Vibrational Spectroscopy of Cluster Ions: Two Novel Methods. *Workshop on Molecular and Cluster Beam Science, National Research Council*, 57-66, 1988. LBL-23842
22. R. H. Page, Y. R. Shen, and Y. T. Lee, Local Modes of Benzene and Benzene Dimer; Studied by Infrared-Ultraviolet Double Resonance in a Supersonic Beam. *J. Chem. Phys.* **88**, 4621-4636 (1988). LBL-24007
23. R. H. Page, Y. R. Shen, and Y. T. Lee, Infrared-Ultraviolet Double Resonance Studies of Benzene Molecules in a Supersonic Beam. *J. Chem. Phys.* **88**, 5362-5376 (1988). LBL-23769
24. J.R. Grover, Y. Wen, Y.T. Lee, and K. Shobatake, Crossed-beam Reactive Scattering of  $F_2 + C_6H_6$ : Heat of Formation of Ipso-fluorocyclohexadienyl Radical. *J. Chem. Phys.* **89**, 938-946 (1988).

25. Kerry L. Busarow, Geoffrey A. Blak, K.B. Laughlin, R.C. Cohen, Y.T. Lee, and R.J. Saykally, Tunable Far Infrared Laser Spectroscopy of Van der Waals Bonds: Extended Measurements on the Lowest  $\Sigma$  Bend of ArHCl. *J. Chem. Phys.* **89**, 1268-1276 (1988). LBL-24859
26. L. Wang, J. E. Reutt, Y. T. Lee, and D. A. Shirley, High Resolution UV Photoelectron Spectroscopy of  $\text{CO}_2^+$ ,  $\text{COS}^+$ , and  $\text{CS}_2^+$  Using Supersonic Molecular Beams. *J. Electron Spectroscopy* **47**, 167-186 (1988). LBL-23936
27. R.E. Continetti, B.A. Balko, and Y.T. Lee, Symmetric Stretch Excitation of  $\text{CH}_3$  in the 193.3 nm Photolysis of  $\text{CH}_3\text{I}$ . *J. Chem. Phys.* **89**, 3383-3384 (1988). LBL-25355
28. P.S. Weiss, J.M. Mestdagh, M.H. Covinsky, B.A. Balko, and Y.T. Lee, The Reactions of Ground and Excited State Sodium Atoms with Hydrogen Halide Molecules. *Chem. Phys.* **126**, 93-109 (1988). LBL-25529
29. R.C. Cohen, Kerry L. Busarow, K.B. Laughlin, Geoffrey A. Blake, M. Havenith, Y.T. Lee, and R.J. Saykally, Tunable Far Infrared Laser Spectroscopy of van der Waals Bonds: Vibration-Rotation-Tunneling Spectra of Ar- $\text{H}_2\text{O}$ . *J. Chem. Phys.* **89**, 4494-4504 (1988). LBL-25399
30. G.N. Robinson, R.E. Continetti, and Y. T. Lee, Dynamics of Endoergic Substitution Reactions. I. Br + Chlorinated Aromatic Compounds. *J. Chem. Phys.* **89**, 6226-6237 (1988). LBL-25530
31. G.N. Robinson, R.E. Continetti, and Y.T. Lee, Dynamics of Endoergic Substitution Reactions. II. Br +  $(\text{CH}_2\text{CCl}_2) \rightarrow \text{Cl} + (\text{CH}_2\text{CClBr})$ . *J. Chem. Phys.* **89**, 6238-6246 (1988). LBL-25531
32. G. Blake, K.L. Busarow, R. Cohen, K. Laughlin, Y.T. Lee, and R.J. Saykally, Tunable Far Infrared Laser Spectroscopy of van der Waals Bonds: Vibration-Rotation Tunneling Spectra of  $(\text{HCl})_2$ . *J. Chem. Phys.* **89**, 6577- (1988). LBL-25400
33. Gary N. Robinson, Gilbert M. Nathanson, Robert E. Continetti, and Yuan T. Lee, Crossed Molecular Beam Studies of the Reactions of Methyl Radicals with Iodoalkanes. *J. Chem. Phys.* **89**, 6744-6752 (1988). LBL-25553
34. Y. T. Lee, Reactive Scattering: Non-Optical Methods. In "Atomic and Molecular Beams Method," edited by G. Scoles and U. Buck, Oxford University Press, 1988. LBL-20767
35. P.S. Weiss, M.H. Covinsky, H. Schmidt, B.A. Balko, Y.T. Lee, and J.M. Mestdagh, Polarization Effects in Reactive Scattering of Na Atoms in the 4D Level. *Zeitschrift fur Physik D* **10**, 227-232 (1988). LBL-25321

## SUBMITTED ONLY

36. T. Trickl, M.J.J. Vrakking, E. Cromwell, Y.T. Lee, and A.H. Kung, Ultrahigh-Resolution (1+1) Photoionization Spectroscopy of  $^5\text{KrI}$ : Hyperfine Structures, Isotope Shifts and Lifetimes for the  $n=5,6,7$   $4p$  ns Rydberg States, Phys. Rev. A (submitted) (1988). LBL-25787
37. E. Cromwell, T. Trick, Y. T. Lee, and A. H. Kung, Ultra-Narrow Bandwidth VUV-XUV Laser System. Rev. Sci. Instrum. (submitted) (1988). LBL-26041
38. Xinsheng Zhao, Robert E. Continetti, Atsushi Yokoyama, Eric J. Hintsa, and Yuan T. Lee, Dissociation of Cyclohexene and 1,4-Cyclohexadiene in a Molecular Beam. J. Chem. Phys. (submitted) (1988). LBL-26333
39. L.I. Yeh, M. Okumura, J.D. Myers, J.M. Price, and Y.T. Lee, Vibrational Spectroscopy of the Hydrated Hydronium Cluster Ions,  $\text{H}_3\text{O}^+ \cdot (\text{H}_2\text{O})_n$  ( $n=1,2,3$ ). J. Chem. Phys. (submitted) (1989). LBL-26708
40. Gilbert M. Nathanson, Timothy K. Minton, Stacey F. Shane, and Yuan T. Lee, UV Photodissociation and Thermochemistry of  $\text{CH}_2\text{BrCH}_2\text{I}$ ,  $\text{CF}_2\text{BrCF}_2\text{I}$ , and  $\text{CF}_2\text{ICF}_2\text{I}$ . J. Chem. Phys. (submitted) (1989). LBL-26709
41. Alec M. Wodtke, Eric J. Hintsa, John Somorjai, and Yuan T. Lee, Photodissociation of Vinyl Bromide and the Heat of Formation of the Vinyl Radical. Israel Journal of Chemistry (submitted) (1989). LBL-26710
42. A.H. Kung, T. Trickl, E. Cromwell, M.J.J. Vrakking, and Y.T. Lee, Ultra-high Resolution VUV-XUV Laser: Application to the Hyperfine Study of Krypton. Optical Society Meeting (1989). LBL-26760
43. R.E. Continetti, B.A. Balko, and Y.T. Lee, Molecular Beam Studies of Hot Atom Chemical Reactions: Reactive Scattering of Energetic Deuterium Atoms. International Symposium on Near-Future Chemistry in Nuclear Energy Field, Japan Atomic Energy Research Institute, Ibaraki-Ken, Japan, February 15-16, 1989. LBL-26762
44. Kerry L. Busarow, R.C. Cohen, G.A. Blake, K.B. Laughlin, Y.T. Lee, and R.J. Saykally, Measurement of the Perpendicular Rotational-Tunneling Spectrum of the Water Dimer by Tunable Far Infrared Laser Spectroscopy in a Planar Supersonic Jet. J. Chem. Phys. (submitted) (1989). LBL-26174
45. M. Okumura, L.I. Yeh, J.D. Myers, and Y.T. Lee, Infrared Spectra of the Solvated Hydronium Ion: Vibrational Predissociation Spectroscopy of Mass-Selected  $\text{H}_3\text{O}^+ \cdot (\text{H}_2\text{O})_n \cdot (\text{H}_2)_m$ . J. Phys. Chem. (submitted) (1989). LBL-26833
46. L.I. Yeh, J.M. Price, and Y.T. Lee, Infrared Spectroscopy of the Penta-coordinated Carbonium Ion  $\text{C}_2\text{H}_7^+$ . J. Am. Chem. Soc. (submitted) (1989). LBL-26767

LAWRENCE BERKELEY LABORATORY  
TECHNICAL INFORMATION DEPARTMENT  
1 CYCLOTRON ROAD  
BERKELEY, CALIFORNIA 94720