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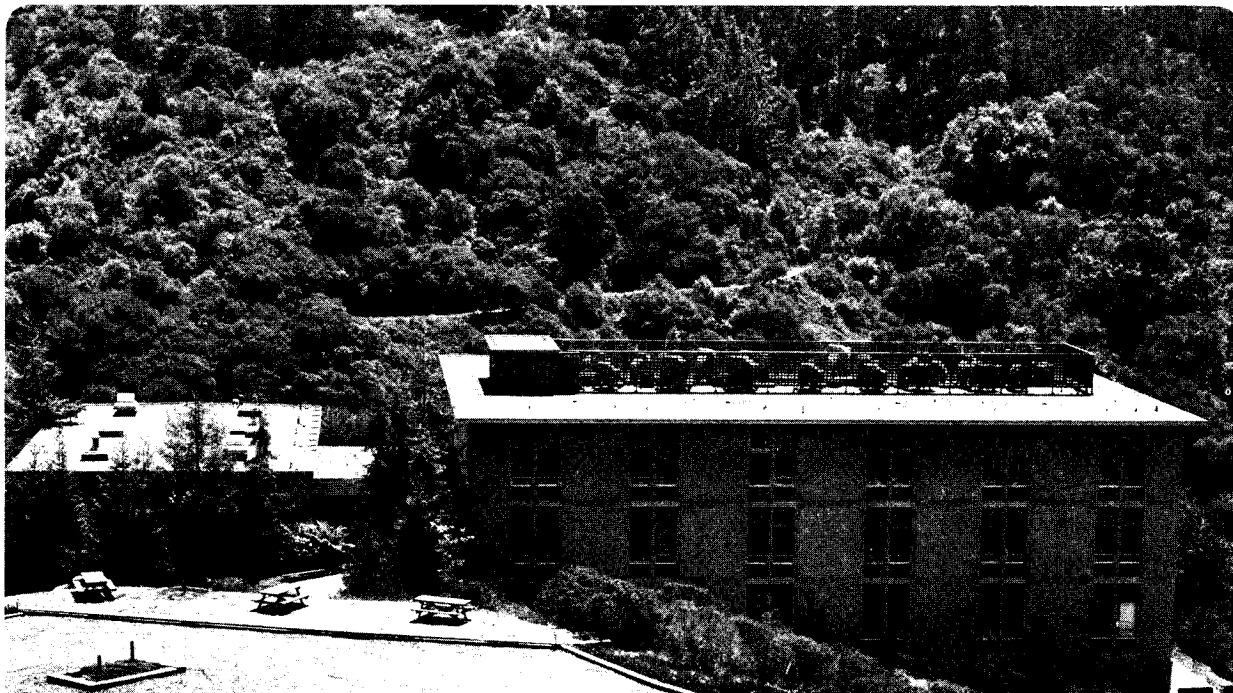
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R.E. Continetti, B.A. Balko, and Y.T. Lee

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MOLECULAR BEAM STUDIES OF HOT ATOM CHEMICAL REACTIONS:  
REACTIVE SCATTERING OF ENERGETIC DEUTERIUM ATOMS

R. E. Continetti, B. A. Balko and Y. T. Lee,  
Department of Chemistry, University of California,  
Berkeley, California 94720 USA  
and  
Materials and Chemical Sciences Division,  
Lawrence Berkeley Laboratory  
1 Cyclotron Road, Berkeley, California 94720 USA

### I. ABSTRACT

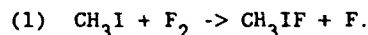
A brief review of the application of the crossed molecular beams technique to the study of hot atom chemical reactions in the last twenty years is given. Specific emphasis is placed on recent advances in the use of photolytically produced energetic deuterium atoms in the study of the fundamental elementary reaction  $D + H_2 \rightarrow DH + H$  and the substitution reaction  $D + C_2H_2 \rightarrow C_2HD + H$ . Recent advances in UV laser and pulsed molecular beam techniques have made the detailed study of hydrogen atom reactions under single collision conditions possible.

### II. Introduction

During the last forty years, "Hot Atom Chemists" have accumulated a vast amount of important information about the chemical behavior of numerous atomic and radical species. A great deal of our early understanding of the chemical behavior of energetic atoms was derived from research carried out in the area of "Hot Atom Chemistry" using reactants generated by nuclear decay. The hyperthermal recoil energy which accompanies nuclear decay and the ease of detection of the radioisotopes produced are the two most important features which have been exploited by "Hot Atom Chemists" for the investigation of endothermic reactions or reactions with high activation energies. Photochemical methods using the photodissociation of a suitable precursor through electronic excitation to a repulsive state to produce energetic atoms for the study of hot atom chemical reactions in the bulk have also long been recognized<sup>1</sup>. The extensive application of this technique was rather limited, however, until the arrival of various intense UV lasers. The multicollision environment of bulk hot atom studies using either nuclear decay or photodissociation processes

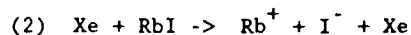
has limited the quantitative microscopic information such as excitation functions and the detailed dynamics of chemical reactions which may be obtained. Only during the last 20 years, with the advent of the seeded supersonic beam technique and the "universal" crossed molecular beams apparatus,<sup>2</sup> have systematic investigations of chemical reactions at elevated translational energies under well defined conditions become possible. The crossed molecular beams technique has provided many interesting results on the dynamics of endothermic abstraction and substitution reactions, as well as molecule-molecule reactions, for the first time. The examples discussed below will provide the reader with an idea of the wide range of chemical phenomena that have been probed to date.

In the collision between  $CH_3I$  and  $F_2$ , surprisingly, the  $CH_3IF$  radical was produced at collision energies exceeding 0.48 eV through a reaction



The threshold energy for the formation of  $CH_3IF$  indicates that the I-F bond energy in  $CH_3IF$  is as strong as 1.13 eV.<sup>3a</sup> Similar reactions also lead to the formation and elucidation of the stabilities of intriguing triatomic radicals<sup>3b</sup> such as I-I-F, Cl-I-F, H-I-F,<sup>3b</sup> and  $C_6H_6F$ .

In collision induced dissociation studies of alkali<sub>4</sub> halides impinged by energetic rare gas atoms<sup>4</sup>, for example,



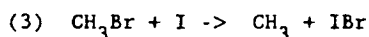
the angular distributions of dissociation products,  $Rb^+$  and  $I^-$  measured in the laboratory clearly indicate that near the dissociation threshold collisions which induce dissociation are nearly collinear, and Rb-I bond compression

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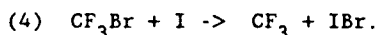
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accounts for most of the initial energy transfer. This dissociation is found to be more efficient when Xe collides with the lighter Rb atom rather than the I atom. The dynamics of the energy transfer processes which eventually lead to bond rupture can be described accurately by the amount of momentum transfer between Xe and one of the atoms in RbI in the limit of the impulse approximation.

The Walden inversion was not found to occur in the endothermic reactions between methyl halides and halogen atoms. Halogen abstractions are found to be the major channels in the reactions

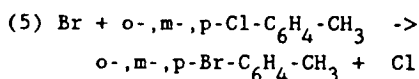


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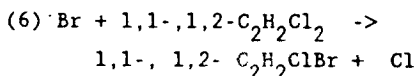


The IBr products peak sharply backward with respect to the motion of the I atoms and carry away a large fraction of the excess energy available. Apparently, the chemical reaction occurs only when the I atom approaches the molecule from the Br side along the C-Br bond axis. The reaction cross sections were found to be strong functions of collision energy, but using a pulsed CO<sub>2</sub> laser to prepare highly vibrationally excited CF<sub>3</sub>I by multiphoton absorption did not enhance the reactivity substantially. This result is a clear indication of the presence of a potential energy barrier in the entrance channel.

More recently, in a series of studies on the endothermic Br for Cl substitution reactions involving chloro-toluene and dichloroethylene



and



it was found that the extent of intramolecular energy transfer in the reaction intermediates seems to be rather restricted before the completion of the chemical reaction and surprisingly no reaction was seen to occur for m-Cl-C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>, although reactions for o-Cl-C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub> and p-Cl-C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub> can be observed easily at collision energies above 0.6 eV. The pronounced effect of the location of the CH<sub>3</sub> group on the substitution reaction is not likely to be due to the relative stability of the reaction intermediate, since the collision energy is considerably in excess of the endothermicity. This effect must be due to the slope of the potential energy surface along the

reaction coordinate which determines how effectively the translational energy can be used to overcome the potential energy barrier to product formation.

In carrying out successful crossed molecular beams experiments with energetic atoms and molecules, in addition to having a sensitive detector to identify the products formed and to obtain their angular and velocity distribution, the most important requirement is to have a beam of intense and monoenergetic reactants. There are many methods available for this purpose. For example, one can use a resonant charge exchange process to convert a beam of well defined ions into a beam of neutral atoms or molecules. An alternating gradient dipole accelerator was constructed for the purpose of accelerating diatomic molecules with large dipole moments. One can also use surface sputtering techniques with a high energy ion beam or high power lasers to generate energetic atoms. For heavier atoms or molecules, the seeded supersonic expansion through a high temperature nozzle is a convenient way to accomplish aerodynamic acceleration. With the arrival of various high power pulsed UV lasers, the recoil from the photodissociation process has become an increasingly important way to generate atoms and radicals with higher kinetic energies.

All these methods have some advantages, but also suffer from some limitations. In terms of the intensity of the beam one can generate and the ease of operation, the seeded supersonic beam source is by far the best. For example, by seeding 1% I atoms, (from thermal dissociation of 0.5% I<sub>2</sub>) in He carrier gas and expanding the gaseous mixture at 3000K from a very high stagnation pressure, both I and He atoms will reach the same terminal velocity  $\bar{v}$ , characterized by the average atomic weight of the gaseous mixture  $\bar{m}$ , the stagnation temperature T and the equation

$$(I) \quad 1/2\bar{m}\bar{v}^2 = 5/2kT \approx 0.65 \text{ eV}.$$

The kinetic energy of the I atom will then have a value of

$$(II) \quad 1/2m_I v_I^2 = 1/2\bar{m}\bar{v}^2 (m_I/\bar{m}) \\ \approx 0.65 (127/5.23) \text{ eV} \approx 15.8 \text{ eV},$$

with a beam intensity easily reaching a range as high as 10<sup>18</sup> - 10<sup>19</sup> atoms·sr<sup>-1</sup>·sec<sup>-1</sup>. This is certainly a very impressive I atom beam source to carry out many interesting crossed molecular beams experiments. But when one tries to produce an F atom beam using the same method, not only does the mass ratio  $m_F/\bar{m}$  become unfavorable, the highest temperature one can use to operate the beam source will be limited to 1000K due to the reactivity of F<sub>2</sub>. Consequently, by seeding 1% F atoms in He, the

maximum kinetic energy one can attain will only be

$$(III) \frac{1}{2} m_F v_F^2 = \frac{1}{2} m v^2 \left( \frac{m_F}{m} \right) \\ = \frac{5}{2} kT \left( \frac{m_F}{m} \right) \approx 1 \text{ eV.}$$

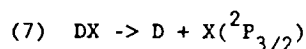
Of course, the aerodynamic acceleration of H atoms is not possible, since there is no other atomic species which has a smaller mass number than the hydrogen atom.

For the generation of energetic H atom beams, there are several methods available. Charge exchange of a proton beam has the advantage that the kinetic energy can be varied and the energy resolution controlled via charged particle optics. Space charge blowup of the beam presents a significant problem at relatively low kinetic energies, however, and in the energy range below 5 eV it is not likely that a beam intensity of more than  $10^{10}$  atom·cm<sup>-2</sup>·sec<sup>-1</sup> can be obtained in this manner, which is insufficient for crossed molecular beams studies. Thermal dissociation can only produce beams of ≈0.5 eV translational energy, insufficient for studying many important chemical processes with higher activation energies. One technique that has been used is an arc-heated supersonic expansion. The high temperatures achieved in the arc discharge can produce H atoms with kinetic energies beyond 5 eV; however, the high temperature in the source naturally gives rise to an extremely broad velocity distribution, making detailed dynamics studies under controlled conditions difficult to achieve. In principle, velocity selection techniques could be used to achieve a narrow velocity distribution, although the resulting beam intensity would be quite low. In addition, velocity selectors for such high velocity species pose considerable technical difficulties in terms of materials of construction and operation.

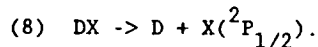
Photodissociation of hydrogen halides provides a unique way of generating high intensity pulsed monoenergetic beams of hydrogen atoms. Prior to the advent of high-power high-repetition rate excimer lasers, complete differential cross section (DCS) measurements by this approach were not feasible, although a limited study of D + H<sub>2</sub> reactive scattering was performed previously by measuring the velocity distribution of DH products at a fixed laboratory angle.<sup>10</sup> The limitations inherent in the photochemical approach to atomic beam generation are those imposed by light source availability and precursor photophysics. The atomic beam energy is given directly by the difference between the photon energy and the dissociation energy of the diatomic precursor. The distribution of beam velocities using a diatomic atom precursor is dictated by the laser bandwidth and any parent rotational and translational velocity distributions. Since

the pulse duration of the laser (~20 nsec) is negligible compared with the transit time of the pulsed H atoms across the photolysis volume (~2 μsec), the temporal resolution of the pulse is inversely proportional to the size of the photolysis volume, whereas the beam intensity is proportional to the size of the photolysis volume, precursor density, and the laser fluence. The use of a diatomic precursor allows one to reach a nice compromise between these factors; since the other fragment is also an atomic species, the laser may be focussed into a small spot, allowing saturation of the photodissociation process, without concern about secondary photon absorption. With a high power excimer laser operating at 248 nm, delivering 150 mJ of polarized light into a 3 x 3 mm spot crossing a high intensity pulsed precursor beam, 10<sup>9</sup> atoms may be delivered to a 0.027 cm<sup>2</sup> cross beam interaction region per laser shot, giving, at 100 Hz repetition rate, 10<sup>12</sup> atoms·cm<sup>-2</sup>·sec<sup>-1</sup>. The temporal resolution of the atom production mechanism is excellent, allowing the direct measurement of product velocities by time-of-flight (TOF) relative to the laser pulse, without any intervening mechanical modulation.

One complication inherent in bulk photodissociation hot atom studies which can be discriminated against in a beam experiment such as this is the fact that the deuterium halides tend to produce both ground and spin orbit excited halogen atoms following UV photolysis at wavelengths where the absorption cross section is large, yielding two velocity distributions of D atoms. In general, it is observed that a perpendicular electronic transition correlates with the ground state halogen atom,



and a parallel transition correlates with the spin-orbit excited halogen atom,



Since the hydrogen halides dissociate on a time scale much shorter than the molecular rotational period, the  $E_{\text{ph}} \cdot \mu_{\text{molec}}$  photofragment anisotropy may then be used to spatially separate the two discrete D atom velocity groups with a linearly polarized UV laser.<sup>11</sup> In practice there are some curve crossing processes occurring in these molecules, so this technique does not provide perfect discrimination; however, due to the large energy difference between the velocity groups this poses little difficulty in the analysis of the scattering data.

### III. Experimental

The details of the experiment described here chiefly pertain to the  $D + H_2$  measurements. A schematic of the experimental setup is shown in Fig.(1). The D atom beam is produced in a differentially pumped chamber by the excimer laser photolysis of DI at 248 nm. The precursor beam is produced by a piezoelectric pulsed valve<sup>12</sup> modified to handle corrosive gases. Liquid nitrogen cryopanels in the source chamber assist in the pumping of the condensable precursor molecules, reducing the background gas load on the scattering chamber significantly. Polarized UV light (248 nm,  $\approx 150$  mJ/pulse, 100 Hz) is generated via a Brewster angle stack polarizer, which is then focussed to a 3 mm X 3 mm spot with two cylindrical lenses. The laser crosses the precursor beam at a distance of 5 mm from the 1 mm nozzle aperture. Instantaneous pressures approaching 1 torr of precursor may be easily generated with stagnation pressures of 140 torr in the pulsed valve. Under these conditions collisional broadening can occur in this localized high pressure region, and some reactive processes such as  $D + DI \rightarrow D_2 + I$  and  $D + HI \rightarrow DH + I$  occur. In practice, the timing of the dissociation laser relative to the precursor pulse is optimized to generate high intensity beams with minimal collisional interference. The atomic beam is defined by two collimators to  $\approx 6^\circ$  FWHM, and crosses a skimmed pulsed molecular beam of  $H_2$  (1200 torr stagnation pressure, 0.5 mm diameter nozzle) at a distance of 48 mm from the photodissociation source in an interaction volume of 27 mm<sup>3</sup>. DH product velocities are then measured as a function of laboratory scattering angle by the TOF method with a rotatable mass spectrometric detector. The products are ionized in a Brink-type ionizer after travelling 340 mm, mass selected by a quadrupole mass filter, and counted by a Daly-type detector.<sup>2</sup> A CAMAC interfaced custom multichannel scaler records the time of arrival of the products relative to the dissociation laser pulse. The data is then dumped to a LSI-11/73 microcomputer for subsequent analysis. Typical D atom photofragment beam TOF spectra are displayed in fig.(2).

The DCS measurements were performed by normalization to a common reference angle. Typically, spectra were averaged for 33 minutes per angle (200,000 laser shots at 100 Hz), with every fourth spectrum being the reference angle. The results reported here for  $D + H_2$  were performed with a para- $H_2$  beam. The detector background was kept to a minimum by use of a wide (6.4 mm) two slot chopping wheel rotated at 50 Hz mounted in front of the detector aperture with minimal clearance. This effectively gated the detector open when the product molecules were arriving, discriminating against the large pressure rise associated with

the intense pulsed  $H_2$  beam. This pressure rise is one important source of modulated background in the experiment, although this signal generally arrives at later times than the reactive signal. Modulated DH background is also produced by the hydrogen abstraction reactions in the D-atom source mentioned above. These reactions produce high velocity DH that scatters off the various defining apertures into the detector. This background limited measurements to laboratory angles greater than  $10^\circ$  from the primary (D) atom beam. Measurements of DH signal scattered from a He cross beam indicated that the broad DH velocity distribution present in the primary beam source did not give rise to any structure in the modulated background, and the integrated intensity of the DH background source was 100 times less than the D atom signal, making elastic scattering of this DH a minor contribution. TOF spectra were corrected for these background sources by careful measurement of the background due to the  $H_2$  beam and the laser + DI beams separately. These background contributions were then scaled to the TOF data at long times and subtracted, yielding the 'true' reactive scattering data.

### IV. Results:

#### A) $D + H_2 \rightarrow DH + H$

These pulsed reactive scattering measurements are characterized by small product signal count rates,  $\approx 0.02$  cts/laser shot x 100 shots/sec = 2 Hz. For this reason, long counting times and high apparatus reliability were required to allow the acquisition of high S/N data at individual laboratory scattering angles (up to a total of 30 hours per angle). At a collision energy of 0.98 eV, TOF data at 22 lab angles were measured, while at 0.51 eV, where the product is scattered into a smaller range of mass (COM) angles, only 12 lab angles were measured.

A raw TOF spectrum of DH at  $\theta_{lab} = 27.5^\circ$  representing 3 hours of data acquisition is shown in fig. (3a). After stripping the modulated background from the TOF, the true TOF spectrum is obtained as shown in fig. (3b). This spectrum, which represents 20 hours of signal averaging, shows resolved structure due to  $DH(v=1)$  and  $DH(v=0)$  product backscattered in the COM frame. The temporal resolution of the experiment is insufficient to resolve the forward scattered  $DH(v=1)$  and  $DH(v=0)$  which comprise the sharp, fast peak in the TOF spectrum.



To obtain a qualitative picture of the COM differential cross sections, the raw  $N(t)$  vs.  $t$  data may be converted with a single Newton diagram transformation to produce a 'Cartesian plot'<sup>13</sup> of the COM velocity flux intensity ( $I(u)/u^2$  vs.  $v_{lab}$ ). This approach does not take into account any experimental distributions of velocity, angle, or detection; however, for a kinematically well defined system such as this considerable insight may be obtained in this manner. Although these velocity weighted COM differential cross sections should not be over interpreted, the qualitative behavior of the DCS as a function of collision energy is clearly shown in the 0.51 and 0.98 eV contour maps in Fig.(4) and Fig.(5). The lower collision energy is only  $\approx 0.2$  eV above the energy threshold for the reaction and at this energy the strong collinear preference of the potential energy surface is clearly manifested in a strongly backscattered (peaking at  $\theta = 180^\circ$ , along the relative velocity vector) product flux contour map. As the collision energy is increased to 0.98 eV, a wider range of collision geometries can surmount the barrier, and the DH product is scattered over a wider range in the COM. The flux map at 0.98 eV indicates a peak in the DCS at  $\approx 130^\circ$  in the COM. The range of the product angular distribution is in qualitative agreement with recent exact quantum mechanical dynamics calculations by Zhang and Miller.<sup>14</sup> Rotational state differential cross sections for this reaction have also been calculated by Zhang and Miller<sup>14</sup> at the energies relevant to this experiment, and a detailed comparison of these calculations with the data is currently being made. A forward convolution procedure is used in this case which convolutes the COM DCS over the experimental velocity, angular, and temporal resolution functions to compare with the TOF data and laboratory angular distribution directly. This comparison is still in progress. As Fig.(6) indicates the theoretical DCS fits the laboratory angular distribution quite well. In Fig.(7), however, the fit to the TOF at  $\theta_{lab} = 27.5^\circ$  indicates that more slow rotationally excited DH product (at small COM velocities) is evident in the experimental results.

These measurements represent the most complete, highest resolution study of the DCS for this elementary reaction to date, and, as such, will provide an excellent test case for the abundant theoretical treatments of this system. Although this experiment cannot resolve individual rotational states, the TOF profiles of the vibrational state resolved backscattered DH product is quite sensitive to the form of the rotational distribution and the vibrational state branching ratio. Coupled with the high quality product state

distributions being measured in several laboratories,<sup>15,16</sup> these results will go a long way towards making this fundamental elementary reaction as well characterized experimentally as theoretically.

#### B) $D + C_2H \rightarrow C_2HD + H$ , Preliminary Study

The apparatus described here can, with only a few modifications, be used to study other systems where the dynamic behavior is expected to be strongly dependent on reagent translational energy. An example of such a case is a reaction that goes through a stable collision complex. As demonstrated with  $F + CH_3I$ , when the collision energy is much lower than the binding energy of such a complex, the reaction proceeds through a long-lived complex (long in terms of the rotational period). Experimentally, this often means that a COM DCS with forward-backward symmetry along the relative velocity vector is observed, as well as a statistical product translational energy distribution. As the reagent translational energy begins to approach and exceeds the complex binding energy, the lifetime of the collision complex becomes shorter and the DCS tends to become more and more asymmetric.

The energetics of the  $D + C_2H_2 \rightarrow C_2HD + H$  system have been studied both experimentally and theoretically;<sup>18</sup> a summary of this information is provided in Fig.(8). As this reaction diagram indicates, the expected binding energy of the  $C_2H_2D$  complex is approximately 1.8 eV. The collision energies that were obtained on the apparatus described are 0.9 eV (DI/laser polarized in the scattering plane), 1.7 eV (DI/laser polarized perpendicular to the scattering plane), and 2.4 eV (DBr/laser polarized perpendicular to the scattering plane), all of which are on the same order of magnitude as the complex binding energy. Complex formation was investigated by taking TOF data at 8 lab angles and using a forward convolution data analysis procedure to derive product energy and angular distributions in the COM reference frame.

At this point in the investigation, initial data on all three collision energies has been obtained along with a qualitative understanding of the dynamics in the COM frame. Fig.(9) shows a TOF spectrum of the  $C_2HD$  product at  $\theta_{lab} = 45^\circ$  after the secondary beam background has been stripped from the data; this spectrum was recorded at the lowest collision energy, 0.9 eV. Based on a preliminary forward convolution fit to data such as this, it appears that the  $C_2HD$  from this lowest energy reaction is somewhat back-scattered in the COM frame. The translational energy distribution is fairly broad, it peaks around 0.3 eV with a spread of 0.35 eV FWHM and

shows that on the average a fairly large fraction of the initial collision energy is going into product translation. The  $C_2HD$  produced in the higher energy reactions seem to be even more backscattered with a smaller fraction of the initial collision energy going into product translation. These results suggest that even with 0.9 eV collision energy, the  $D + C_2H_2$  reaction is not going through a long-lived collision complex. More data needs to be collected and further analyzed to confirm these initial observations. Although this work may not make it possible to estimate the  $C_2H_2D$  lifetime, the extent of energy sharing among vibrational degrees of freedom and the changes in dynamics of the system as the collision energy is changed from 0.9 to 2.4 eV will provide interesting information.

## V. CONCLUSION

Some of the earlier contributions the crossed molecular beams technique has made to the detailed understanding of the dynamics of hot atom chemical reactions have been reviewed. The recent experiments using the excimer laser generated photolytic D atom beams have provided exciting insights into the dynamics of the experimentally challenging hydrogen atom reactions which were previously inaccessible. The  $D + H_2$  studies provide a critical link between experimentally accessible reaction systems and those which are theoretically tractable. Preliminary studies on deuterium atom substitution reactions with polyatomic molecules were also presented. More work on energetic hydrogen atoms, and, in the future, methyl radicals, may be anticipated with the photolytic hot atom beam source.

## VI. ACKNOWLEDGEMENTS

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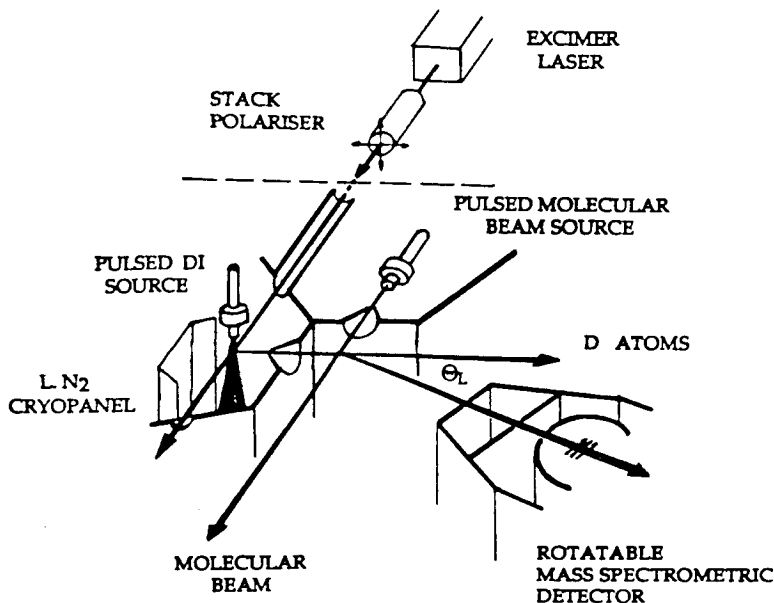


Fig. 1. Schematic diagram of the experiment as discussed in the text.

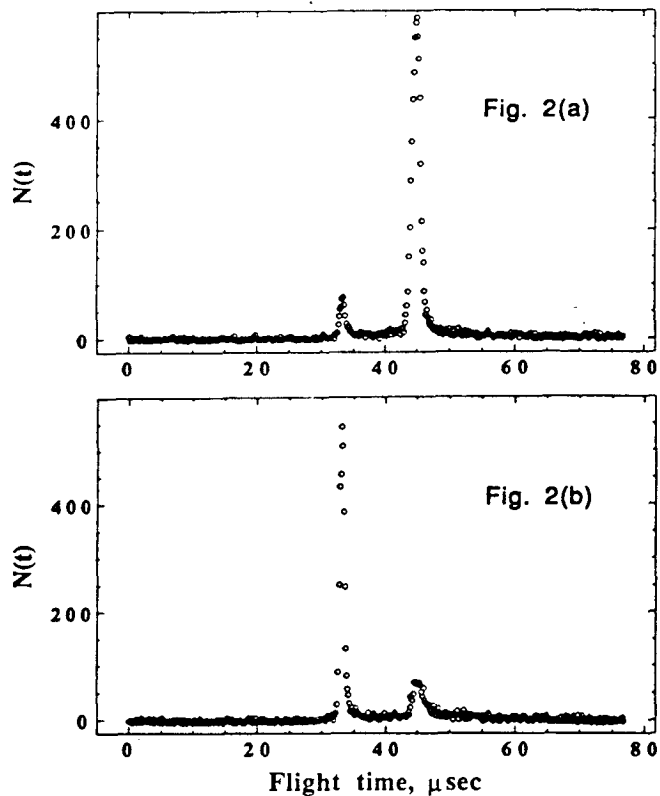
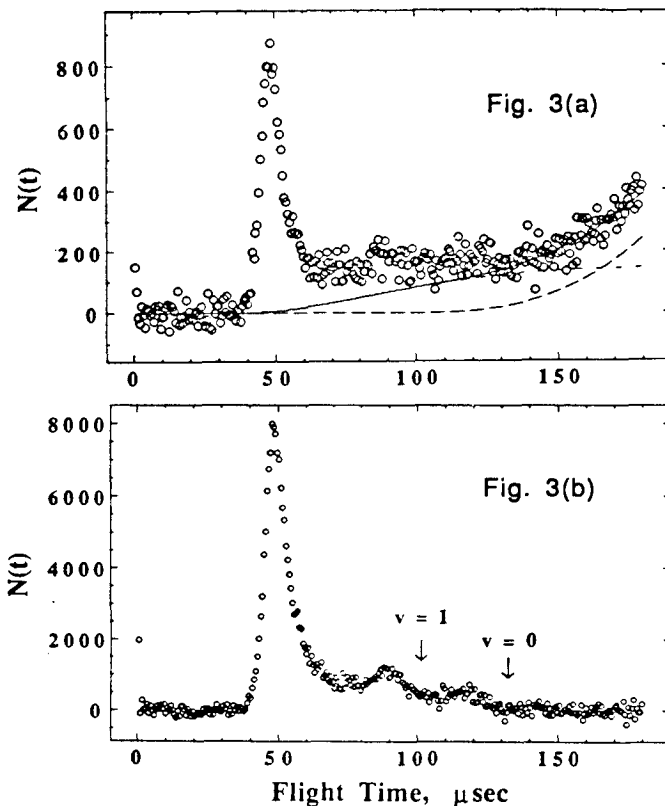
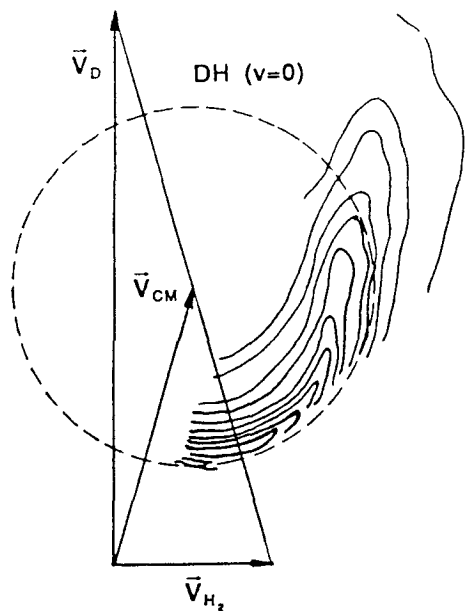


Fig. 2. D atom photofragment beam TOF spectra at 248 nm. (a) Laser polarized parallel to the detection direction, enhancing detection of the slow ( $V_D = 9.5 \times 10^5$  cm/sec) D atoms. (b) Laser polarized perpendicular to the detection direction, enhancing detection of the fast ( $V_D = 1.34 \times 10^6$  cm/sec) D atoms.

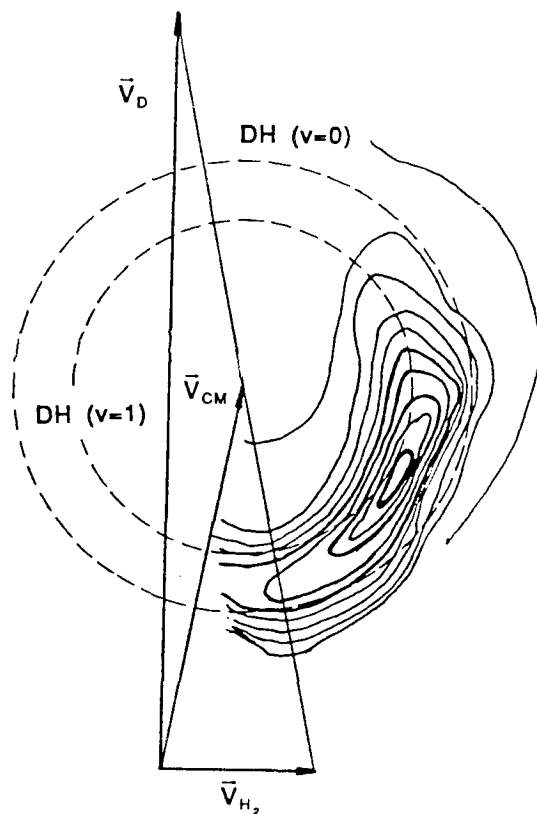
Fig. 3. (a) Raw DH product TOF spectrum at  $\theta_L = 27.5^\circ$ , representing 3 hours of signal averaging. Modulated background contributions discussed in the text are shown as lines fit to the data. (b) Stripped TOF spectrum  $\theta_L = 27.5^\circ$  representing 30 hours of signal averaging. Backscattered DH( $v=1$ ) and DH( $v=0$ ) product states are resolved, with the maximum allowable flight times for these states indicated by the arrows.





0.51 eV Collision Energy

Fig. 4. 0.51 eV collision energy Cartesian plot of the COM differential cross section, with the kinematic diagram for the collision process superimposed. Note peak of DCS is  $\approx 180^\circ$  in the COM frame.



0.98 eV Collision Energy

Fig. 5. 0.98 eV collision energy Cartesian plot. Peak of DCS is now  $\approx 130^\circ$  in COM.

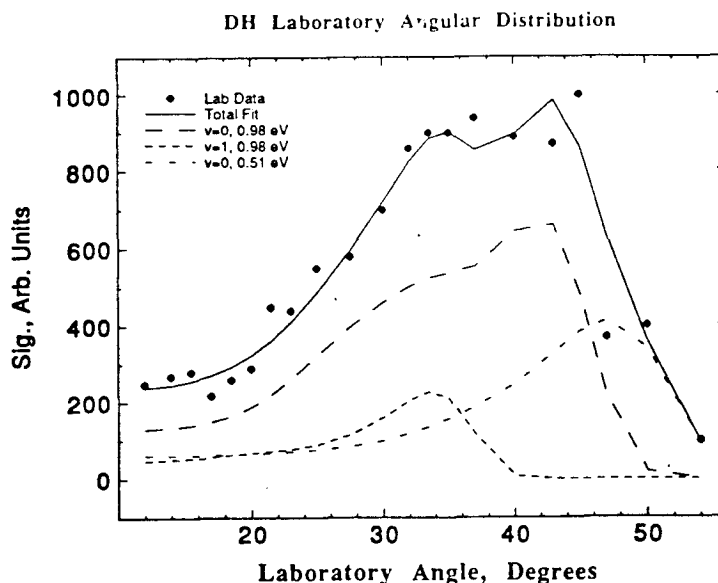


Fig. 6. Laboratory angular distribution of the DH product at 0.98 eV collision energy. The contribution at large lab angles is due to DH(v=0) from reaction at 0.51 eV which is not completely discriminated against. The fits are calculated by forward convolution of the theoretical DCS calculated by Zhang and Miller.

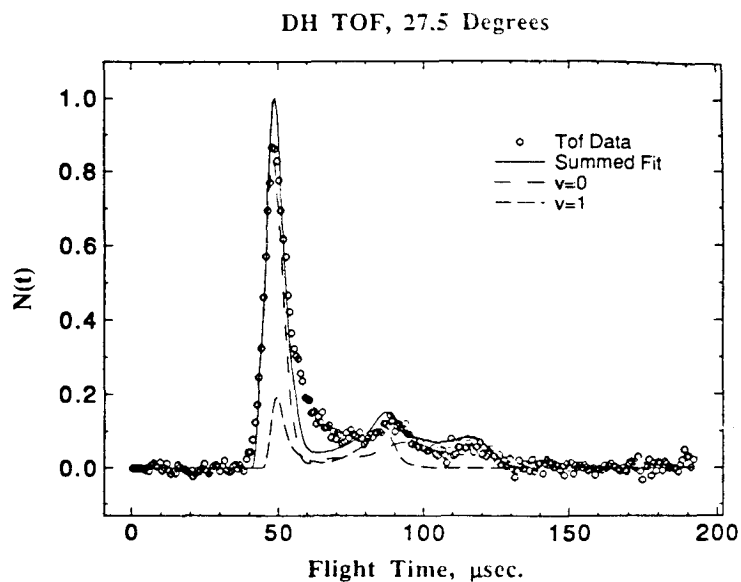


Fig. 7. Preliminary fit to the TOF spectrum  $\theta_L = 27.5^\circ$ . Note deficiency of theoretical DCS in fitting the contribution from high J DH product at small COM velocities.

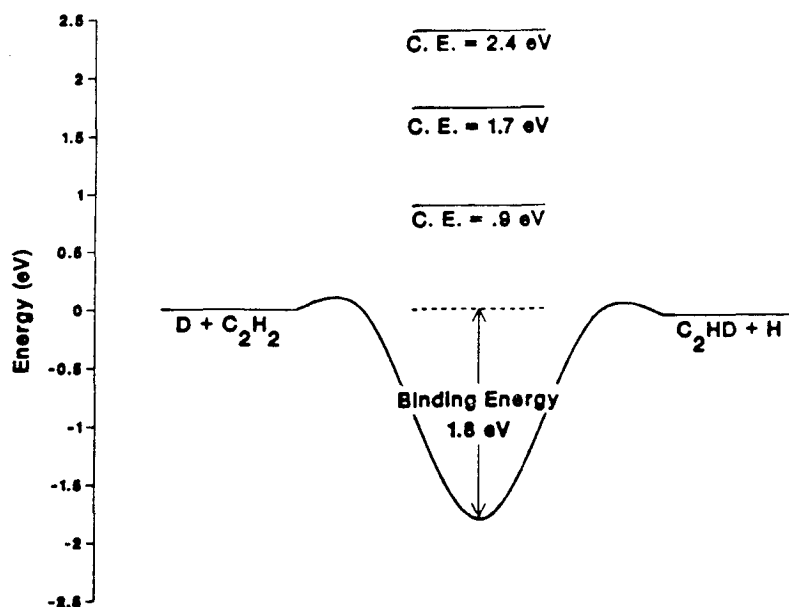


Fig. 8. Energy diagram showing the  $D + C_2H_2$  substitution reaction along with the collision energies experimentally accessible. The activation energy is expected to be  $\approx 0.1$  eV and the reaction exothermicity  $\approx 0.07$  eV.

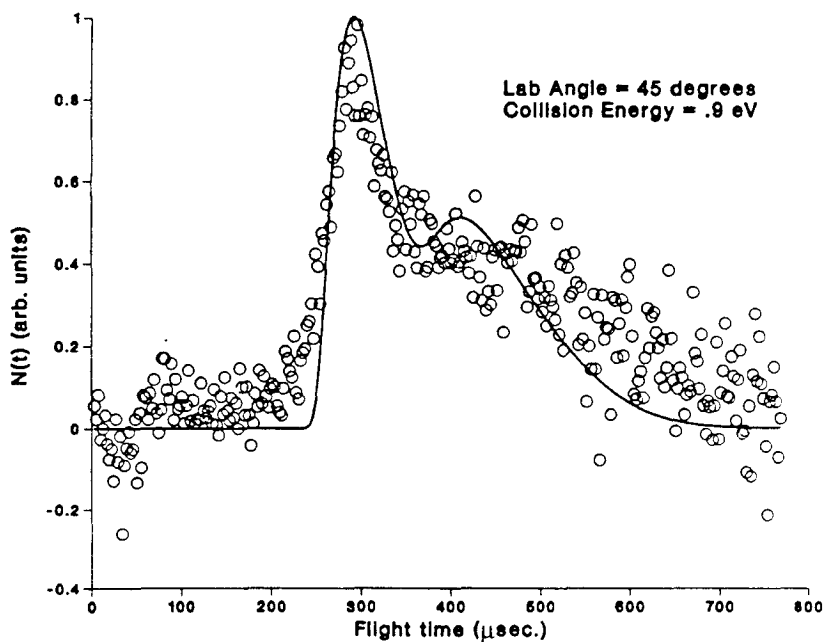


Fig. 9. TOF spectrum of  $C_2HD$  product scattered at  $\theta_L = 45^\circ$  and 0.9 eV collision energy. The fit to the data is generated by forward convolution of a product angular and translational energy distribution as discussed in the text.

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