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MOLECULAR BEAM STUDIES AND HOT ATOM CHEMISTRY

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MOLECULAR BEAM STUDIES AND HOT ATOM CHEMISTRY

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1. Introduction

1.1. Molecular Beam Approaches to Hot Atom Chemistry

Molecular beam techniques play an important role in the elucidation of the detailed dynamics of hot atom chemical reactions. A great deal has been learned about the kinetics of hot atom reactions using traditional techniques in which reactant atoms generated by either radioactive decay or the photodissociation of an appropriate precursor molecule are allowed to react in a bulk, multi-collision environment with subsequent product yield analysis. Recent advances in time-resolved laser-based detection schemes have produced more detailed information on state-to-state rate constants for energy transfer and reactive processes in a variety of chemical systems. However, for the direct measurement of product velocity and angular distributions, identification of the primary products of chemical reactions, and the overall partitioning of energy in chemical reactions, a crossed molecular beams experiment using electron-impact ionization mass-spectrometric detection is the most versatile technique available for acquiring dynamical information.

Experimental measurements of the dynamical attributes of chemical reactions can help us answer not only the question of how fast a reaction proceeds, but what type of collisions lead to reaction. For example, observation of forward-backward symmetry in the center-of-mass (CM) angular distribution about the relative velocity vector reveals the presence of an intermediate collision complex that is long-lived compared to the typical $10^{-12}$ sec rotational period of the complex. If a long-lived complex is
formed, the exact shape of the angular distribution can even reveal the degree of correlation between reactant and product angular momenta. In the case of a direct elementary reaction which does not proceed through a long-lived complex, the form of the CM angular distribution reveals which reactant geometries favor reaction, providing insights into the angular dependence of the potential energy surface. Measurements of product velocity distributions reveal the extent to which energy is shared within the collision complex, or, for an elementary reaction, can provide state-resolved data on the CM angular distribution.

To demonstrate the application of molecular beam techniques to hot atom chemical reactions, two recently studied systems will be discussed here; (1) a study of the influence of translational energy in the 0.6 to 1.5 eV range on the endoergic reactions

\[ \text{Br} + \text{R-Cl} \rightarrow \text{R-Br} + \text{Cl} \]  

(1)

where R = o-, m- and p-chlorotoluene (CT) and 1,1- and 1,2-trans-C2H2Cl2 (DCE) and (2) an experimental study of the detailed dynamics of the elementary reaction

\[ \text{D} + \text{H}_2 \rightarrow \text{DH} + \text{H} \] 

(2)

at translational energies of 0.53 and 1.01 eV. The first example illustrates the contributions molecular beam experiments can make in the understanding of endoergic substitution reactions. The second example illustrates the role such studies can play in evaluating 'exact' three-dimensional (3-d) quantum scattering calculations and ab initio potential energy surfaces for chemical reactions. Other examples of the application of molecular beam techniques to HAC may be found in two earlier articles.

2. Experimental Techniques

The crossed beams technique involves crossing two well-defined atomic or molecular beams in a vacuum chamber under single-collision conditions, with subsequent analysis of the distributions of the velocity and laboratory (LAB) scattering angle of the reaction products. Although significant progress has been made in laser-based state-selective detection schemes for reaction products in recent years, the application of such techniques to the measurement of product velocity and angular distributions has been limited. The most useful technique for such measurements is still mass-spectrometric detection using electron-impact ionization of the scattered products in a crossed beams experiment. The principles of a successful crossed molecular beams scattering apparatus have been previously discussed in detail, but the important points will be reviewed here.
Fig. 1. Scale drawing of a continuous atomic-molecular beam reactive scattering apparatus, showing the high temperature halogen atom beam source and the rotatable mass spectrometer detector.

An experimental setup crossing a molecular beam with a high-energy halogen atomic beam is shown in Fig. 1. Energetic atoms are produced in a high-temperature oven and collimated as they pass through two regions of differential pumping into the main scattering chamber, which is maintained at a pressure of \(1 \times 10^{-7}\) torr. Molecular beams of stable species are conveniently produced by supersonic expansion through a small aperture (dia. \(= 100 \mu m\)), with subsequent collimation by skimmers and defining apertures. Products scattered from the beam interaction region at a specific LAB angle then enter the detector, are ionized by electron impact, mass selected in a quadrupole mass spectrometer, and then counted as ions with a rotatable mass spectrometer detector. In the ionizer region, the steady state density of products is as low as 10 to 1000 molecules per cubic centimeter. For this reason, sophisticated differential pumping for both the molecular-beam sources and the ultra-high vacuum mass spectrometric detector is required to reduce the background, allowing detection of the scattered products. Angular distribution measurements are typically made by modulating one of the beams with a tuning-fork chopper and measuring the signal at the product
mass with phase-sensitive detection. Product velocity distributions at specific LAB angles can be obtained by modulating the scattered products with a high-speed chopper wheel mounted on the rotatable detector and measuring the time-of-flight (TOF) spectra from the chopper to the point of ionization.

Scattering experiments at thermal energies are readily performed with relatively simple beam sources. Extension of molecular beam experiments to the 0.5 to 20 eV kinetic energy range of most interest to the hot atom chemist require more sophisticated beam sources. Beams of reactive atoms can be produced by thermal dissociation of molecular precursors, however, the maximum kinetic energies achievable are limited by the thermal properties of source construction materials, such as tungsten, to less than \( \approx 0.5 \) eV. Some scattering experiments have been done with neutral beams produced by ion-beam neutralization at energies down to 10 eV\(^{12}\), however the intensity of such beams is low due to space-charge limitations on the incident ion beam current. Arc discharges, capable of reaching temperatures up to 30000 K, have been used extensively\(^{13,14,15}\) but such sources are plagued by short lifetimes and contamination of the neutral beam by ionic and metastable contaminants.

2.1. Seeded Atomic Beams

One of the most successful techniques for producing high energy beams of heavier atomic and molecular species with a narrow velocity spread has been the seeded-beam technique, which utilizes the aerodynamic acceleration of a dilute heavy species seeded in a light carrier gas in a supersonic expansion\(^{16,17}\). The average velocity of a dilute seeded beam using an inert carrier gas under extreme expansion conditions is given by

\[
V_{\text{seed}} = \sqrt{\frac{5kT}{m}}
\]

(3)

where \( m = x_1m_1 + x_2m_2 \) is the mean molecular weight of the gas mixture made from components of molecular weight \( m_1 \) and \( m_2 \) with mole fractions \( x_1 \) and \( x_2 \). For the heavy component, 2, the laboratory kinetic energy is given by

\[
E_2 = \frac{1}{2}m_2V_{\text{seed}}^2 = \frac{1}{2}\frac{m_2kT}{m}
\]

(4)

Thus, for large mass ratios \( m_2/m \), considerable acceleration can be achieved. Table 1 shows the upper limit to the kinetic energies achievable using this technique for halogen atoms in the limit of a hard expansion using He as a carrier gas with no velocity slip between the light and heavy atoms. Intense beams of I, Br and Cl can be conveniently generated by thermal dissociation of I\(_2\), Br\(_2\) and Cl\(_2\) in a graphite oven\(^{18}\). F atoms are very reactive, however, so Ni ovens must be used at temperatures less than \( \approx 1000K \). The seeded beam technique allows nearly continuous tuning of the collision energy over a wide
range for heavy particles, by merely changing the average molecular weight of the carrier gas by mixing a heavier rare gas with He.

Table 1  Seeded Atomic Beams

<table>
<thead>
<tr>
<th>Beam</th>
<th>T (°K)</th>
<th>$\frac{m_2}{m_1}$</th>
<th>E (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F/He(^a)</td>
<td>1000</td>
<td>4.6</td>
<td>1.0</td>
</tr>
<tr>
<td>Cl/He(^b)</td>
<td>1500</td>
<td>8.1</td>
<td>2.6</td>
</tr>
<tr>
<td>Br/He(^b)</td>
<td>1800</td>
<td>16.8</td>
<td>6.5</td>
</tr>
<tr>
<td>I/He(^b)</td>
<td>3000</td>
<td>24.3</td>
<td>15.7</td>
</tr>
</tbody>
</table>

\(^a\) Thermal dissociation of 0.5% F\(_2\)/He in a Nickel oven
\(^b\) Thermal dissociation of 0.5% X\(_2\)/He in Graphite ovens, where X\(_2\) = Cl\(_2\), Br\(_2\), I\(_2\)

Fig. 2. Schematic view of a photolytic atomic beams experiment. The output of an excimer laser, 1, was polarized with a transmission polarizer, 2. The laser beam then entered the molecular beam machine, crossing a pulsed beam of DI, 3. The DI/laser interaction region is in a differentially pumped chamber, with cryo-panels, 4, assisting in the evacuation. The recoiling D atoms were collimated, forming the D-atom beam, 6, which crossed the H\(_2\) molecular beam, 8, produced in a separate differential pumping chamber by the pulsed valve, 7. DH products, 10, scattered into the mass-spectrometric detector, and were ionized in the electron-impact ionizer, 9.
2.2 Photolytic Atomic Beams

For hydrogen atoms, the seeded-beam technique cannot be used since no lighter carrier gases are available. With the advent of high-power UV pulsed lasers, the classic hot-atom technique of H atom production by photolysis of hydride precursors19) has become applicable to the study of reactions of H and D atoms at high collision energies. Numerous time-resolved bulk experiments on energy transfer and reaction dynamics have made use of this approach1), however, only recently have such techniques been used to generate high-intensity 'monoenergetic' atomic beams for scattering studies.6,20) Fig. 2 shows a schematic diagram of the D + H2 \rightarrow DH + H scattering experiment using a pulsed photolytic D-atom beam.

The kinetic energy distribution of a photolytic atomic beam is determined by the laser photon energy, the bond-dissociation energy of the precursor, any distribution of internal energy in the precursor molecule, and the partitioning of the available energy between the photofragments. Since internally cold precursor molecules may be produced in a supersonic expansion, the CM translational energy in the photodissociation process is given by

$$E_{tr} = E_{hv} - D_0 - E_{int,prod} \quad (5)$$

where \(E_{int,prod}\) represents any energy in internal degrees of freedom of the photofragments, \(D_0\) is the bond dissociation energy and \(E_{hv}\) is the photon energy. Diatomic molecules make ideal precursors since the only form \(E_{int,prod}\) may take is that of electronic excitation, and they therefore typically provide 'cleaner' hot-atom velocity distributions. The use of polyatomic H atom precursors, such as H2S, inevitably will result in a broader kinetic energy distribution due to the distribution of vibrational and rotational excitation of the HS radical product. Additional complications can also arise due to H atoms produced by secondary dissociation of the HS radicals at high photolysis laser powers. Conservation of energy and linear momentum in the CM gives the kinetic energy of a photolytic H atom as

$$E_H = (1 - \frac{m_H}{m_{HX}}) \cdot E_{tr} \quad (6)$$

so, for disparate photofragment masses, nearly all of the translational energy will end up in H atom translation. By using HI, HBr, or H2S as precursors at the powerful excimer wavelengths of 193 and 248 nm, H atoms can be generated with translational energies from 0.95 to 3.3 eV.1)

Photodissociation of the hydrogen halides in the ultraviolet can produce both ground \(X(2P_{3/2})\) and spin-orbit excited \(X(2P_{1/2})\) halogen atoms. The branching ratio for the production of these atoms is wavelength dependent, a factor which can complicate bulk experiments in which the photodissociation laser wavelength is tuned to change the kinetic energy. For the production of
an atomic beam, however, use may be made of the fact that the electronic transitions associated with the two spin-orbit states have different symmetries with respect to the diatom bond. For the X(2P1/2) channel the transition moment is parallel to the bond, while for the X(2P3/2) channel, the transition moment is perpendicular to the bond. The angular distribution of photofragments produced with a polarized dissociation laser is given by

\[ I(\theta) = \frac{1}{4\pi} (1 + \beta \cdot P_2(\cos \theta)) \]  

(7)

In this equation\(^{21}\), \( \theta \) is the angle between the fragment recoil in the CM and the electric vector of the linearly polarized dissociation laser. \( P_2(\cos \theta) \) is an associated Legendre polynomial, and \( \beta \) is a form factor which ranges from 2 for a pure parallel transition (\( I = \cos^2 \theta \)) to -1 for a purely perpendicular transition (\( I = \sin^2 \theta \)). Fig. 3 shows the degree of separation which may be achieved under single collision conditions for the photodissociation of DI at 248 nm. In practice, the discrimination between the two channels is reduced by incomplete polarization of the laser, collisions in the photodissociation source volume and any curve crossing processes in the dissociation event.

Fig. 3. D atom (m/e=2) TOF spectra. Left frame: E parallel to the direction of detection in the top frame, discriminating against the fast atoms. Right Frame: E perpendicular to the direction of detection.

The atomic beam must also be well collimated in a scattering experiment. This constraint, however, is always in conflict with the desire to produce high intensity beams. To increase the intensity of a photolytic atomic beam, it is desirable to irradiate as many precursor molecules as possible, i.e., either irradiate a small volume with a high precursor number density or increase the size of the photolysis volume. Since the atomic beam crosses a secondary beam in a finite interaction volume (on the order of 0.03 cm\(^3\)), several centimeters away from the atomic beam source, the finite size of the
photodissociation source volume can cause a significant broadening of the atomic beam angular divergence. In principle, this problem can be solved by moving the photolysis volume arbitrarily far away from the cross beam, but, the decrease in beam intensity due to the smaller solid angle subtended at larger distances makes this impractical.

By using pulsed molecular beam techniques\(^ {22}\), high precursor number densities may be established, allowing generation of high intensity atom beams from small source volumes. Under such conditions, however, some collisions may occur in the source volume, causing the beam velocity distribution to broaden, and producing possible beam contaminants by chemical reactions in the source volume. In the reactive scattering experiments we have performed on the \( \text{D} + \text{H}_2 \rightarrow \text{DH} + \text{H} \) reaction, beam intensity requirements dictated that the D atom beam had to be formed under such conditions, leading to a broadening of the velocity distribution.\(^ {6}\)

Chemical reactions such as \( \text{D} + \text{D} \rightarrow \text{D}_2 + \text{I} \) and \( \text{D} + \text{HI} \rightarrow \text{DH} + \text{I} \) in the source also produced fast \( \text{D}_2 \) and \( \text{DH} \) impurities in the atomic beam. Under the conditions of the experiments done on the \( \text{D} + \text{H}_2 \rightarrow \text{DH} + \text{H} \) reaction, a number density of \( \text{D}_2 \) of \( \sim 1 \times 10^{14} \) molec/cm\(^3\) in a photolysis volume of \( \sim 0.03 \) cm\(^3\) was achieved. Dissociation of 75% of these molecules produced \( 1 \times 10^{12} \) D atoms, of which \( 1 \times 10^9 \) D atoms/pulse were then delivered to a crossed beam interaction region 4.8 cm away, with a beam angular divergence of \( \sim 6^\circ \).

3. Endoergic Substitution Reactions

The study of endoergic reactions has a fundamental role in hot atom chemistry, however, these reactive scattering experiments on the Br substitution reactions (1) provide some of the first detailed insights into the role translational energy plays in promoting these polyatomic endoergic reactions, the degree to which energy is randomized in the transient collision complexes, and the influence of steric effects on the reactivity.

Using a seeded Br atom beam produced by thermal dissociation in a graphite oven, these substitution reactions were studied in the 0.65-1.50 eV range. These reactions are endoergic by 0.5-0.65 eV. The collision energies were tuned by changing seeding ratios and carrier gases and the source temperatures of both reactant beams. The measured cross sections at the different collision energies were normalized by measuring the elastic scattering of the reactants. A typical set of product LAB angular distributions for the \( \text{Br} + \text{o-CT} \) reaction are shown in Fig. 4. Product TOF spectra were also measured at several angles. The angular distributions and TOF spectra were simultaneously fit with an algorithm which convoluted input CM energy and angular distributions over the apparatus function. The collision energy resolution in these experiments was typically \( \Delta E/E = 30\% \), chiefly determined by the spread in reactant beam velocity and angular distributions. To fit the data, the CM energy and angular distributions are iteratively varied until a
good fit was achieved. The product translational energy distributions $P(ET)$ were fit using a functional form;

$$P(E) = (E' - B)P(E_{avl} - E')^q$$

in which $B$ is related to any barrier in the exit channel, which would force the $P(ET)$ to peak away from the statistical limit of zero, and $E_{avl}$ is the total energy available to the products. The parameters $p$, $q$, and $B$ were optimized to give the best fit to the data. The product CM angular distributions were parameterized with Legendre polynomials.

![Graph](image)

Fig. 4. LAB angular distribution for the o-BT product of the Br + o-CT reaction at energies of 1.34 eV ( ), 1.08 eV ( ) and 0.91 eV ( ). Solid lines are fits to the data (see text).

3.1. Br + o-m-p-CT

A direct visualization of the results in a crossed-beams experiment is given by the CM product velocity-flux contour map, as shown in Fig. 5 for the para-bromotoluene (p-BT) products. The strong forward scattering observed indicates that the transient collision complex survives for less than one rotational period. The CM product angular distributions for both the o-BT and p-BT products were found to be forward-peaked. The product CM translational energy distributions for these reactions are peaked near zero translational energy, with approximately 30% of the available energy appearing in product translation. The o-BT translational energy distributions
were peaked at a slightly smaller translational energy than the p-BT products.

Fig. 5. p-BT product CM velocity-flux contour map, showing a forward peaking CM angular distribution (in the direction of the Br atom in the CM). Scale is for contours; scale for kinematic diagram is half of the contour scale.

Fig. 6. Excitation Functions, $S_r(E)$, for the p-BT (——) and o-BT (— —) products. Arrows indicate the most probable experimental collision energies. Shaded regions indicate uncertainty in $S_r$ at high energies. The points represent predicted excitation functions using a reduced-mode model of energy sharing in the collision complexes.
The excitation functions, $S_r(E)$, found for these reactions are shown in Fig. 6. $S_r(E)$ for the o-BT products rises sharply with energy, while for p-BT, $S_r(E)$ is flatter. The p-BT cross section is larger at the lower collision energies, however. The higher cross section for p-BT at the lower collision energies may be due to the fact that the methyl group ortho to the Cl position in o-CT sterically hinders the Br attack. The excitation functions and $P(E_T)$'s observed indicate that more modes are active in the Br-o-CT collision complex. The larger reaction cross section for Br + o-CT may be due to the larger number of active modes in the transient collision complex, which may serve to dissipate the translational energy of the collision better, allowing Br to add more readily to o-CT than to p-CT and subsequently react.

One of the most striking observations in this study, however, was that no reaction was observed for Br + m-CT at collision energies up to 1.26 eV. This negative result indicates that the substitution cross section for m-CT is at least a factor of ten lower than for o-CT. This o,p directing behavior of CH$_3$ substituents is well documented in condensed-phase organic chemistry, and is usually explained in terms of the electron donating capability of the methyl group, which stabilizes the o- and p- adducts by either increasing the o- and p- frontier electron populations in the reactant molecule or by lowering the total $\pi$ electron energy of the o- and p- adducts relative to the m- adduct. Although no rigorous quantum mechanical calculation of the heats of formation of the isomeric radical intermediates through which these reactions proceed have been done, the energy associated with removing an electron from conjugation with the $\pi$ cloud of the ring and localizing it at the o-, m- and p- positions of various aromatic molecules has been calculated.$^{23}$ For toluene, only 0.03 eV difference was found between the o- and m- localization energies, a number which we may associate with the stability of the radical adduct intermediate. Such a small energetic difference cannot explain the differences in the dynamics of these reactions.

These gas-phase results may indicate that the reactivities of the isomers of CT in the gas phase are governed by the shape, especially the slope of the entrance channel, of the Br-CT potential energy surface (PES) along the reaction coordinate. The increased electron populations o- and p- to the methyl group in CT could enhance the attraction between Br and these sites during the approach. Such an effect would make the PES rise more gradually in the entrance valley, allowing translational energy to couple more readily with the reaction coordinate and promote the reaction. Effects of this sort have been seen in classical trajectory studies of atom-diatom systems by Polanyi and coworkers$^{24}$, and may well explain the striking differences in reactivity between the isomers of CT.

### 3.2. Br + 1,1- and 1,2-trans-DCE

The product translational energy distributions found for the Br + DCE reactions were very similar to those for the Br + CT reactions. Once again,
approximately 30% of the available energy appears in product translation. The product CM angular distributions, however, are indicative of a much longer-lived collision complex in these reactions compared with the Br + CT reactions. This is shown by the near forward-backward symmetry in the CM-frame velocity-flux contour maps for the Br + chloro-olefin reactions, as shown for the Br + 1,2-trans-DCE reaction in Fig. 7, which implies that the lifetime of the collision complexes in these reactions is longer than a rotational period. This is due to the fact that formation of the bromodichloroethyl radical adduct is exoergic by approximately 0.35 eV, resulting in a longer adduct lifetime when compared with the Br + CT adducts, which are endoergic by ≈ 0.09 eV.5)

Fig. 7. Product CM velocity-flux contour map for the Br + t-DCE reaction, showing a more nearly forward-backward symmetric product t-BCE CM angular distribution. See caption for Fig. 5.

The shape of the excitation functions for the Br + DCE reactions were also found to be consistent with a mechanism in which vibrational energy in the complex is shared in few of the available modes. The excitation functions for the Br + DCE reactions also showed striking differences in reactivity for the two isomers studied. The cross section for the Br + 1,2-trans-DCE reaction is significantly larger than that for 1,1-DCE reaction. This result is consistent with the traditional theory of anti-Markovnikov addition, which predicts that radical attack at the least-substituted carbon will be favored due to resonance stabilization of the resulting radical adduct.25) However, the simplest
explanation for these results, as well as a large body of gas-phase radical-alkene addition reactions, is that for Br + 1,1-DCE, the Cl substituents hinder the approach of the attacking atom, reducing the probability of addition and subsequent reaction.

3.3. Conclusions about Endoergic Reactions

Several unifying features were observed in these studies of the dynamics of endoergic Br substitution reactions. In both the aromatic and alkene reactions, endoergic substitution occurs in a quasi-direct fashion as shown by measurement of the \( P(E_T) \)'s and excitation functions for the reactions. In fact, the number of active modes remains approximately the same for both the Br + DCE and Br + CT reactions. This offers the intriguing possibility that the dynamics of endoergic aromatic substitution reactions can be modeled by the simpler analogous atom-alkene reactions. Steric effects were also shown to play a significant role. Earlier studies of the exoergic reactions of F atoms with similar compounds\(^ {26} \)) indicated that the F atom addition reactions are not very site-selective, which is not surprising in light of their exoergicity. In the case of Br addition, which is much less exoergic and therefore proceeds with less long-range attractive forces, subtle differences between isomeric potential energy surfaces can manifest themselves much more strongly in the reaction cross sections.

4. Dynamics of the Elementary Reaction D+H\(_2 \)→DH+H

High resolution scattering experiments on atom-diatom systems can play a critical role in the evaluation of theoretical chemical dynamics calculations and \textit{ab initio} PES's for chemical reactions. For example, work done on the F + H\(_2\), HD, and D\(_2\) systems provided some of the first experimental evidence for the role that quasi-bound states due to quantum mechanical resonances play in otherwise 'direct' chemical reactions.\(^ {27} \) The F + H\(_2\) system is, however, several years away from being treated exactly with quantum scattering calculations, although the PES for this system has been improved significantly in recent years.\(^ {28} \) The three-electron, three-proton hydrogen exchange reaction, on the other hand, can now be treated exactly quantum mechanically over a wide energy range. Although measurements of product angular distributions in this system are difficult because of the substantial potential energy barrier, the recent advances in the production of high kinetic energy photolytic atomic beams have now made such measurements possible.

4.1 \textit{Ab Initio} Reaction Dynamics

Fundamental to the prediction of the dynamics of a chemical reaction is the quantitative calculation of the forces which determine the outcome of a collision. Due to the simplicity of the H\(_3\) system, the PES for this system is known with greater accuracy than for any other reactive system. It has long
been known that the hydrogen exchange reaction proceeds via a collinear minimum energy path. Sophisticated ab initio calculations of the energy of H₃ in several hundred configurations have been done. An analytic fit, based on calculations by Liu and Siegbahn²⁹) was done by Truhlar and Horowitz³⁰) in 1978. This surface has been used in many dynamics calculations, and is referred to as the LSTH surface. The LSTH surface heavily weights collinear H₃ geometries, and gives a barrier in the minimum-energy collinear configuration of 0.425 eV. The more recent Double-Many-Body Expansion, or DMBE representation of the PES includes more non-collinear configurations and has a collinear barrier of 0.419 eV³¹), in accordance with the most recent ab initio³²) and quantum Monte Carlo calculations³³,³⁴).

The H₃ system was the first reaction for which detailed dynamical predictions were possible using quasi-classical trajectory calculations.³⁵) These early studies showed that the DH products for the D + H₂ reaction, for example, were directly backward-scattered at low collision energies, with progressively more forward scattering occurring as the collision energy increases, allowing more non-linear configurations to react. QCT calculations are economical to perform, and still play an important role in the evaluation of experimental results.³⁶)

Schatz and Kuppermann performed the first fully converged three-dimensional quantum scattering calculations on the H + H₂ reaction in 1975 up to collision energies of 0.5 eV.³⁷) Extension of such calculations to other isotopic combinations and to the higher energies of more significance to experimentalists did not become possible until 1988, however, with the work of Zhang and Miller³⁸) and Manolopolous and Wyatt.³⁹) Recently, Zhang and Miller (ZM) ⁴⁰), and subsequently Zhao, Truhlar, Schwenke and Kouri (ZTSK) ⁴¹) have calculated differential cross sections (DCS's) for the D + H₂ reaction on both the LSTH and DMBE surfaces, respectively. These extensive calculations provide the first accurate detailed picture of the reaction dynamics for any chemical reaction.

4.2. Critical Experimental Tests

Considerable effort has been made to obtain experimental results to test the extensive theoretical predictions available for the H₃ system. In the 1960's, bulk photochemical hot atom techniques were first applied to the D + H₂ reaction to measure the total reactive cross section by White and Kuppermann.⁴²) Crossed molecular beams studies, using thermal dissociation of D₂ or H₂ to make the atomic beams, were also initiated by Datz and Taylor⁴³) and Fite and coworkers.⁴⁴) Kwei and coworkers used radiochemical techniques to obtain the TH product angular distribution of the T + H₂ reaction.⁴⁵) These early scattering experiments verified that the products were backward scattered in the CM at low collision energies, as dynamics calculations had predicted.

In recent years significant progress has been made in detailed measurements on the H₃ reaction. Advances in both the production of
energetic H or D atoms by photodissociation and laser-based spectroscopic detection techniques have enabled the product vibration-rotation state distributions to be measured for several isotopic variants of the hydrogen exchange reaction using both Coherent Anti-Stokes Raman Scattering (CARS) by Valentini and coworkers\textsuperscript{46) and Resonance Enhanced Multiphoton Ionization (REMPI) by Zare and coworkers.\textsuperscript{47}) In these studies, pulsed UV lasers are used to generate energetic H atoms, with subsequent time-resolved probing of the products allowing product-state distributions to be effectively recorded under single collision conditions. At the level of product-state distributions, good agreement between theory and experiment has now been observed for the D + H\textsubscript{2} reaction.\textsuperscript{48}) Total cross section measurements using vacuum ultraviolet laser induced fluorescence measurements of the H and D atom products have been made by Bersohn's group, also using photolytic methods of atomic beam generation.\textsuperscript{49})

The first crossed beams scattering experiments in which the DH product velocity distributions were measured were reported by Toennies and coworkers for both D + H\textsubscript{2}(v=0) and D + H\textsubscript{2}(v=1).\textsuperscript{50,51}) For the H\textsubscript{2}(v=0) reaction, energetic D atoms were produced with a high-temperature arc discharge, with a very broad D atom velocity distribution, which precluded resolution of the DH vibrational states in the experiment.

\subsection{4.3 Vibrational State-Resolved Differential Cross Sections}

By application of the photolytic atomic beam technique, Gentry and coworkers first reported product vibrational state-resolved DCS measurements for the D + H\textsubscript{2} reaction.\textsuperscript{20}) By photolyzing D\textsubscript{2}S at 193 nm and making use of rotatable beam sources to tune the collision energy by changing the beam intersection angle, product velocity distributions were measured at single LAB angles as a function of collision energy from 0.85 to 1.05 eV with an energy resolution of \( \pm 20\% \). The LAB angles were chosen to allow measurement of the backward scattered DH(v=0) and DH(v=1) as a function of collision energy.

In our laboratory, measurements of state-resolved DCS's as a function of LAB scattering angle have been made on the D + H\textsubscript{2} reaction at energies of 0.53 and 1.01 eV with an energy resolution of \( \pm 10\% \). As Fig. 2 shows, these experiments were done by photolyzing DI at 248 nm, making use of a polarized laser to allow spatial separation of the D atoms to change the collision energy. The pulsed D-atom beam crossed a pulsed H\textsubscript{2} beam, with product velocity distributions measured as a function of LAB scattering angle. A typical raw DH TOF spectrum is shown in Fig. 8. As shown in the figure, the raw TOF spectra had to be corrected for modulated background inherent in the pulsed beams technique. Careful measurement of the background signals associated with the D-atom and H\textsubscript{2} beams allowed the TOF spectra to be corrected, yielding the spectra shown in Fig. 9.
**Fig. 8.** Raw TOF spectrum (m/e = 3) for the $E_c = 1.01$ eV D + H$_2$ reaction at a LAB angle of 27.5°. The curves fit to the data represent the modulated background contributions to the signal: ---; total modulated background: · · · · · ·; D-atom-beam modulated background: - - - -; H$_2$-beam modulated background.

**Fig. 9.** Comparison of representative DH TOF spectra with the theoretical predictions of Zhang and Miller (top frames) at 27.5° and 32°. The bottom frames show the comparison using the best-fit DCS. The circles represent the TOF data, the solid line is the results of the Monte Carlo simulation summed over all DH(v,j) states. The ----- line is for DH(v=0,j) products; the - - - - line is for DH(v=1,j) products. A small contribution from DH(v=2,j) is seen near 60 µsec in the 27.5° spectra.
Consideration of the kinematic diagram in Fig. 10 shows that at a LAB angle of 27.5°, for example, four peaks might be observed in the TOF spectrum in the limit of no rotational excitation; fast, forward scattered DH(ν=0) and DH(ν=1) and slower, backward scattered DH(ν=1) and DH(ν=0). In the spectra shown in Fig. 9, the backward scattered DH(ν) states are resolved. Once the corrected product TOF spectra and LAB angular distributions were obtained, a direct comparison of the experimental results with the dynamical predictions of ZM and ZTSK was possible using a Monte Carlo simulation code to perform the CM to LAB transformation of the theoretical DCS's to the LAB frame for comparison with the experimental results.

![Kinematic diagram for the D + H₂ → DH + H reaction at 1.0 eV](image)

**Fig. 10.** Kinematic diagram for the D + H₂ → DH + H reaction at 1.0 eV, showing the relationship between the CM and LAB reference frames. The concentric circles centered at the origin of the CM frame represents the maximum CM recoil velocities for DH products in ν = 0, 1 and 2. The CM recoil velocities for DH(ν=0, j=10 and 11) products are also shown.

Representative results of the Monte Carlo simulation of the TOF spectra for D + para-H₂ → DH + H at a collision energy of 1.01 eV are shown in the top frames of Fig. 9. The theoretical DCS's used in these simulations were the D + H₂(j=0) DCS calculations of ZM. Little difference was observed between the calculations of ZM and ZTSK for the D + H₂(j=0) reaction. A significant discrepancy is seen between theory and experiment at flight times from 50 to 80 μsec corresponding to DH products with small CM velocities. Qualitatively, though, the agreement between theory and experiment is quite good. Integration of the normalized TOF spectra obtained gives the LAB angular distribution shown in Fig. 11 at a collision energy of 1.01 eV. At this level of comparison, no major discrepancies are seen between theory and experiment. ZTSK have also done calculations for H₂(j=1) reagents, which show a more significant difference than that between the two separate calculations for H₂(j=0) on the two PES's. Scattering experiments with D + normal-H₂ did not
show a significant difference from the D + para-H$_2$ results, however, so mere inclusion of more reactant H$_2$ rotor states probably does not account for the observed differences between theory and experiment.

Fig. 11. LAB angular distribution at $E_c = 1.01$ eV generated by integrating the corrected TOF's. The solid line shows the results of the Monte Carlo simulation of the experiment using the theoretical predictions summed over vibrational states. The contributions from the DH vibrational states are shown as; DH(v=0) - - - - - ; DH(v=1) - - - - ; DH(v=2) - - - - .

To ascertain the magnitude of the discrepancies between theory and experiment, the Monte Carlo simulation was used to iteratively adjust the theoretical DCS's until the simulation fit both the LAB angular distribution and TOF spectra simultaneously.$^{52}$) The fits to the TOF spectra in the lower frames of Fig. 9 show the level of agreement obtained between simulation and experiment. The final best-fit state-to-state DH(v,j) DCS's are by no means unique, but they do provide a qualitative view of the region in which discrepancies are observed between theory and experiment. The most significant discrepancies were observed for the lesser-populated rotationally excited DH products at both collision energies. Cartesian CM velocity-flux contour maps showing the differences between theory and experiment are shown in Fig. 12 at both collision energies. The contour maps at 0.53 eV show that although the products were observed to be backward scattered in the CM, significant broadening of the DCS in the backward hemisphere was observed compared to the theoretical results. At 1.01 eV, the peak of the DCS is still
seen to be $\approx 125^\circ$ in the CM as predicted theoretically, but the DCS's are significantly broadened in the

![Cartesian CM velocity-flux contour maps for the D+H$_2$ $\rightarrow$ DH + H reaction at $E_c = 0.98$ eV.](image)

backward hemisphere, with more rotationally excited products observed in the experiment. Gentry's group has observed similar discrepancies. At a collision energy of 0.85 eV, they have also seen a significant discrepancy in the ratio of forward/backward scattered products.$^{53}$ Thus, the available high-resolution molecular beam experiments indicate that the theoretical predictions are not yet perfect.

4.4 Implications for the H$_2$ PES

Since two different groups have now done fully converged quantum scattering calculations on the D + H$_2$ reaction that qualitatively agree$^{40,41}$, the discrepancies between the DCS measurements and the dynamics calculations must reflect deficiencies in the PES's on which the calculations have been done. The PES's are fits to nearly the same set of $ab$ initio calculations, with the greatest emphasis placed on collinear arrangements of the three atoms. High energy bent configurations of the H$_3$ complex have
received little attention until recently\textsuperscript{5,4}. The fact that the largest discrepancies between theory and experiment were seen for rotationally excited DH products suggests that the bending potential is the source of the observed discrepancies. The bending potential governs the distribution of initial orbital angular momenta that lead to reaction. A softer bending potential in the vicinity of the lower collision energy of 0.53 eV could lead to substantially more sideways/forward scattering of products than predicted theoretically, as larger impact parameter collisions would react. A steeper bending potential at the higher energies near 1 eV could limit the extent to which the D-H\textsubscript{2} products can bend while in close interaction, giving more rotationally excited products, but with a broader angular distribution in the backward hemisphere, as observed in the contour maps in Fig. 11. At this stage, to get quantitative accord between theory and experiment, a more detailed, systematic study of the H\textsubscript{3} PES appears to be in order.

Fig. 12b. Cartesian CM velocity-flux contour maps for the D+H\textsubscript{2} \rightarrow DH + H reaction at E\textsubscript{c} = 0.51 eV. The top frame shows the best-fit DCS, while the bottom shows the contour map obtained from the theoretical predictions of ZM.
5. Conclusions

As illustrated by the examples in this chapter, crossed molecular beams experiments can probe the detailed dynamics of chemical reactions. In the case of elementary atom-diatom reactions these experiments provide critical tests of dynamical calculations and the PES's on which they are done. This is an important step in the verification of our \textit{ab initio} understanding of chemical reaction dynamics. Once quantitative agreement between theory and experiment has been reached for the simplest chemical reaction, efforts to extend dynamics calculations to more complex systems and to develop approximate, yet accurate, dynamical theories will be able to proceed with confidence.

In the area of polyatomic hot atom chemical reactions, such as the endoergic Br substitution reactions, crossed beams scattering with electron-impact ionization mass spectrometric detection will remain the most versatile technique for acquiring dynamical information, due to the difficulties associated with thorough spectroscopic probing of complicated polyatomic species. The molecular beam technique can be applied to virtually any material which can be introduced into a molecular beam, with the universal mass-spectrometric detection scheme providing information on the distribution of energy in the products and the lifetime of transient collision complexes.

In the area of elementary chemical reactions, the future holds great promise for obtaining more detailed experimental results on the dynamics of elementary reactions. The work on vibrational state-resolved DCS's for the hydrogen exchange reaction does not test the theoretical results to the limit of their predictions. Rotationally resolved DCS's will have to be measured to provide the final answers for this elementary reaction. Welge and coworkers have developed a technique which allows TOF spectra of H atoms to be measured, allowing better resolution of final product states due to the larger H atom recoil velocities.\textsuperscript{55} This technique should be able to achieve rotational state resolution if the reactant beams can be sufficiently collimated. In addition, the application of state-specific spectroscopic techniques, such as REMPI, to measuring DCS's for individual product quantum states should become more feasible in the near future for the hydrogen exchange reaction.

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