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THE EFFECTS OF REAGENT TRANSLATIONAL AND VIBRATIONAL ENERGY ON THE DYNAMICS OF ENDOTHERMIC REACTIONS

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The endothermic reactions Br + CH3] \ast CH3 + IBr (aH_{c} = 13 kcal/mole) and Br + CF3I \ast CF3 + IBr (aH_{G} = 11 kcal/mole) have been studied by the cruced molecular beams method. Detailed center-of-mass contour maps of the IBr product flux as a function of recoil velocity and scattering angle are derived. For both systems it is found that the IBr product is sharply backward scattered with respect to the incident Br direction, and that most of the avai ble energy goes into product translation. Vibrational enhancement of the Br + CF3 reaction was investigated by using the infrared multiph on absorption process to prepare highly vibrationally excited CF3I. t a collision energy of 31 kcal/mole (several times the barrier heig reagent vibrational energy in promoting reaction. More forward scattered IBr is produced in reactions of Br with vibrationally hot CF3I.

INTRODUCTION

There have not been many direct experimental studies of subtantially endothermic chemical reactions. In the early dzys, using effusive beam sources, reactive scattering experiments were generally limited to collision energies in the thermal energy range. The development of seeded supersonic beams, I however, has largely removed this restriction. For reasonably heavy systems, it is easy to achieve collision energies.

In an early application of the seeded beam method to the study of endothermic reactions, Jaffe and Anderson² attempted to determine the cross section for the reaction HI + 10 + HO + I + 1. For collision energies between 20 and 109 kcal/mole, no HO attributable to reaction was detected ($q_r < 0.04$ Å²) suggesting that internal excitation of one or both reagents is required for this reaction to occur. The application of microscopic reversibility³ to the detailed rate constants obtained in infrared chemiluminescence studies of exothermic reactions has also been used to suggest that reagent vibrational energy (V') is vastly more effective than reagent translational energy (T') in crossing the endothermic energy barrier. Of course, since the exothermic reactions are used to suggest that resolution in the endothermic direction at energies just above threshold. Under these conditions, the preference for V' over T' will at least partially result from the requirement to conserve angular momentum in the collision. That is, for reaction just above threshold, if the reagent energy is present minity as translation an appreciable fraction of the translational energy will transform into rotational energy barrier. For collision energies is insufficient to overcome the potential energy barrier. For collision energies will inexcess of

This work was supported by the Assistant Secretary for Nuclear Energy, Office of Advance. Systems and Nuclear Projects, Advanced Isotope Separation Division, U.S. Department of Energy under Contract No. W-7405-Eng-48. role, and it is unclear whether or not V' will retain its overwhelming superiority in most endothermic reactions.

In fact, some endothermic reactions appear to proceed quite readily when the reagent energy is vested almost exclusively in translation. For exarcle, it has been shown⁶ that the collision-induced dissociation of alkali halides by rare gas atoms becomes very efficient when the collision energy is substantially higher than the endothermicity. Preliminary results on the endothermic reactions of 1 atoms with CH38r,⁵ reported at VII ICPEAC, provide additional evidence of the adequacy of translational energy in promoting endothermic reaction.

It has been recognized from early on⁶ that it woud be advantageous to have a direct comparison of the relative effectiveness of V' and T' in promoting substantially endothermic chemical reactions. This problem has been attacked both theoretically and experimentally. Polanyi and coworkers have performed an extensive series'.⁸ of classical trajectory calculations on what are thought to be "typical" endothermic potential energy surfaces. In one of their studies of AB * C reactions,⁷ they employed a potential energy surface which was endothermic by 35.7 kcal/mole and varied T' and V' in the range up to T' * V' = 90 kcal/mole. They found an orders-of-magnitude increase in the reaction cross section when energy was transferred from T' to V', until an optimal distribution over T' in promoting endothermic reaction was marked even at the highest reagent energy studied. One other interesting effect they observed is that while the molecular (BC) product was mainly backwards or sideways scattered, enhanced V' at the barrier crest (i.e., surfaces which exhipit a more gradual rise to the barrier crest (i.e., surfaces which exhipit a more of the barrier climb in the coordinate of approach), T' may compete much more effectively with V'. On extremely gradual endothermic surfaces they found that the best mix uf V' and T' may compete much more effectively with V'.

Experimentally, there have only been three attempts to directly compare the effect of V' and T' at the same total reagent energy. All of these involved reactions of alkali or alkaline earth atoms with hydrogen halide molecules and employed either pulsed chemical lasers or thermal heating to vibrationally excite the HX. Brooks and coworkers⁹ studied the approximately thermoneutral K + HCl reaction. They found that when HCl was excited to v = 1, the reaction cross section was around 10 times greater than when the same total reagent energy was supplied as translation. Gupta, Perry and $\rm Zare^{10}$ studied the Sr + HF reaction, which is endothermic by 6 kcal/mole. They found that reagent translation was quite effective in promoting this reaction. The reaction cross section for HF(v = 1) was only 1-10 times greater than when the same total energy was supplied as translation. Using thermal heating to excite vibrational motion, Heismann and Loesch¹¹ found that although vibrational excitation is more effective than translational energy in promoting the K + HCl reaction at lower collision energies, at collision energies higher than 0.5 eV translational energy becomes as effective as vibrational excitation. On the other hand, it the more endothermic K + HF reaction, vibrational excitation was found to be much more effective than translation even at collision energies as high as 1.7 e۷.

In this paper we will present some results of crossed molecular beams experiments on the following endothermic reactions:

 For each reaction, laboratory angular and velocity distributions of the IBr product (measured at a collision energy of approximately 60 kcal/mole) were used to deduce the center-of-mass (CM) product translational energy and angular distributions. The results, besides proving that both reactions proceed readily at enhanced collision energies without the aid of reagent vibration, provide a fairly detailed picture of the reaction dynamics. In addition, studies of vibrational enhancement of the Br + CF3I reaction were performed by using a CO2 TEA laser to prepare highly vibrationally excited CF3I molecules via the infrared multiphoton absorption process. These experiments revealed " qualitative effect of reagent vibration on the reaction dynamics, and allowed a comparison to be made of the relative efficiency of reagent translational and vibrational energy in prometing this endothermic reaction.

II. EXPERIMENTAL

The molecular beam apparatus used in these experiments has been described in detail previously- 1^2 Briefly, seeded supersonic beams of Br atoms and CHg1 (CFg1) molecules were crossed at right angles in a liquid nitrogen cooled interaction chamber maintained at ~5 x 10-7 torr. The products were detected in the plane of the atomic and molecular beams by a retatable, ultra-high vacuum mass spectrometer.

The atomic bromine beam was produced by thermal dissociation of a Br₂-rare gas mixture in a resistively heated graphite oven¹³ which was operated at about 1500°K. The hot gases expanded through a 0.18 mm diameter hole in the end of the even. The CH₃I and CF₃I beams were produced by expanding He- or Ar-seeded mixtures through a 0.13 mm diameter stainless steel nozzle. Both beam sources utilized two stages of differential pumping.

Beam velocity distributions were determined by standard time-of-flight .70F) measurements using an extended (80 cm) flight path. The CH₃₁ and CF₃₁ beams had FMHW velocity spreads of about 15%, while the velocity spread of the Br beam "aried between 15 and 25%, depending on the particular conditions. In general, the CH₃₁ (CF₃₁) beam velocity was held fixed, and the collision energy, $E_{\rm C}$, was varied by seeding the bromine in different carried pases or by changing the bromine and carrier gas partial pressures. The maximum Br velocity was obtained by passing 600 torr of He through a Br₂ reservoir held at -30C (bromine partial pressure \approx 5 torr). This resulted in a peak Br velocity of 2.90 km/s.

The Br + CH3I \Rightarrow CH3 + IBr and Br + ('3I \Rightarrow CF3 + IBr reactions were studied in the collision energy range 15-65 kcal/mole. The cross section for both reactions increased by more than two orders of magnitude over this energy range. Laboratory angular and velocity distributions of the IBr product were measured at three collision energies for the Br + CF3 reaction and at two collision energies for the Br + CF3 reaction. Here, only the best data for each reaction (obtained at the highest collision energy) will be presented, since this data allowed a direct deconvolut on to obtain the CM angular and velocity.

Angular distributions were obtained by modulating the Br beam with a 15C Hz tuning fork chopper. For each laboratory ang e, 0, data was collected for equal times during the open and closed portions of the tuning fork cycle by a dual channel scaler. The difference of the conts in the "open" and "closed" channels constituted the angular scan signal, N(O). For the experiments reported here, counting times of 1-2 minutes at each angle were sufficient to reduce the error bars (resulting from statistical counting error) to less than 1%. The IBr" signal rate at the peak of ne angular distribution was 4800 counts/s for Br + CH31 at $E_{\rm C}=65$ kcal/mole, with a background contrate of 200 counts/s.

Velocity analysis for the Br + CH3I reaction was performed by the standard TOF method. The 17.8 cm diameter wheel had four 0.75 mm slots on its perimeter. A 0.58 mm high reducing slit was mounted in front of the first 3 mm x 3 mm detector aperture. The wheel was rotated at 450 Hz, resulting in a shutter opening time of 5.3 us. Following each wheel opening the TOF distribution, N(t), of reactively scattered IBr was collected by a 255-channel multichannel scaler using a 2 us dwell time per channel. The distance from the wheel to the detector was 18.0 cm. Counting times were 1-3 hours at each angle.

For the Br + CF31 reaction, IBr velocity distributions were obtained by the cross-correlation TOF method.¹⁴ Our cross correlation wheel utilizes a 255-channel sequence. The wheel was rotated at 326.8 Hz, corresponding to a dwell time per channel of 12 μ s. The distance from the wheel to the detector was 18.3 cm. Counting times were 30-60 minutes at each angle.

The studies of vibrational enhancement of the Br + (FG] reaction were performed using a high repetition rate CO2 TEA laser (Genter DD-250). The laser beam crossed the CF31 beam at 90° inside the second differential pumping chamber of the CF31 beam source. (I.e., the molecular beam was irradiated after it passed the source skimmer but before it entered the main interaction chamber.) To improve the duty cycle, a cylindrical lens was used to focus the laser beam to a 2 mm high x 21 mm long rectangular spot at the point where it intersected the molecular beam. All of the experiments were performed at a laser frequency of either 1074.6 or 1076.0 cm⁻¹ and an energy fluence of 0.5-0.7 J/cm². The laser was typically operated at a repetition rate of 70 Hz. By pointing the mass spectrometer directly into the CF31 beam and measuring the amount of depletion of the CF31 signal following each laser pulse, we inferred that approximately 12-15% of the CF31 molecules in the irradiated zone were being dissociated. Most of the remaining CF31 molecules is the state of the cF31 beam and the proximately the state approximately the state of the cF31 molecules in the irradiated zone were being dissociated.

The reaction of Br atoms with these hot CF31 molecules was studied at two collision energies, 31 kcal/mole and 11.7 kcal/mole. At each collision energy, TOF distributions of IBr" were recorded at various lab angles by using a reference pulse from the CO2 laser to trigger the multichannel scaler. The dwell time per channel was 10 us. The distance from the interaction center to the detector was 21.2 cm. These TOF distributions were then integrated and the background subtracted to obtain the laboratory angular distribution of the laser-correlated Br product. At $E_{\rm c}=31$ kcal/mole, signal was collected for 6 x 10⁵ laser pulses at each of 10 angles. The maximum IBr* signal level was 0.018 counts/pulse. At $E_{\rm c}=11.7$ kcal/mole, signal was collected for 9 x 10⁵ laser pulses. No laser-correlated CF3Br or BrF product was detected at either collision energy.

III. RESULTS AND ANALYSIS

A. Br + CHal + CHa + 1Br

The laboratory angular distribution of $1Br^*$, obtained at a collision energy of 61 kcal/mole, is shown in Fig. 1 together with the nominal Newton diagram. The circle on the Newton diagram corresponds to the maximum CM velocity of the IBr product allowed by energy conservation. The TOF distributions of $1Br^*$ at 6 lab angles are shown in Fig. 2. The time scale in Fig. 2 has not been corrected for the flight time of the $1Br^+$ ions through the mass spectrometer (about 45 µs).

A deconvolution program 15 was used to directly obtain the CM differential cross section from the experimental results. Briefly, this program proceeds as follows: (i) A laboratory velocity-angle flux map is constructed from the measured angular and TOF distributions. (ii) An iterative ratio method developed

by Siska¹⁶ is used to deduce a "monochromatic" laboratory flux map, which is supposed to represent the result of an ideal experiment performed with monoenergetic molecular beams. (iii) This monochromatic LAB flux map is directly inverted to CM coordinates using a single (nominal) Newton diagram. The TOF distributions were smoothed by a 15-point filter before the lab flux map was constructed. Also, the collision energy dependence of the reaction cross section was taken into account when weighting the various Newton diagrams for the deconvolution in step (ii).



Fig. 1. Laboratory angular distribution of the IBr product from the Br + CHgI reaction at 61 kcal/mcle collision energy. The curve is drawn free-hand through the points.

Fig. 2. Time-of-flight analysis of the IBr product from the Br + CH31 reaction at 61 kcal/mole.

A rontour map of the resulting CM differential cross section in velocity space, $d^2\sigma/dud_{\alpha}$, as a function of IBr scattering angle, e, and recoil velocity, u, is shown in Fig. 3, superimposed on the nominal Newton diagram. (Note that dw represents the unit of solid angle in CM coordinates, and that $\theta = 0$ is defined to be the direction of the incident Br atom.) It is usually more meaningful to talk about the differential cross section in energy space, $d^2\sigma/dt_1^2$, where E_1 is the tota' CM translational energy of both products. The computer program also calculates this quantity at various IBr scattering angles. The results suggest that there is strong coupling of the product energy and angular distributions. The translational energy distribution broadens and

shifts to lower energies as the IBr scattering angle der ases. In Fig. 4 are shown the average CM translational emergy distribution (obtained by averaging $d^2_a/dE_1^d\omega$ over all solid angles) and the CM angular distribution (obtained by integrating $d^2_a/dE_1^d\omega$ over E_1^* at each scattering angle φ). These distributions are regarded as tentative, especially in view of the fact that the translational energy distribution is not entirily successful at conserving energy. The high energy tail which extends beyond the maximum available energy must be an artifact of the deconvolution procedure. This tail contains about 10% of the total product flux. Nevertheless, for the energy distribution shown, the mean product translational energy is 31 kcal/mole, or 64% of the available energy. The true values probably lie slightly lower. By applying the sine weighting factor to do/dw (to account for out-of-plane scattering), we calculate that 80% of the IBr product is scattere into the backward hemisphere.





 $\frac{4t}{4t_1}$

8r + CH31 ---- CH3 + 18r

E. + 61 keat/ants

Fig. 4. Center-of-mass product translational energy and angu'ar distributions for the Br + CHJ reaction at 61 kcal/mole, obtained by direct deconvolution. The shaded portion of the translational energy distribution is energet "ally forbidden.

B. Br + CFal + CFa + IBr

Laboratory angular and TOF distributions of $10r^+$, obtained at a collision energy of 65 kcal/mole, are shown in Figs. 5 and 6. TOF distributions were also measured at $\odot = 40^\circ$ and 50°, but these are not shown. The time scale of Fig. 6 has not been corrected for ion flight time. These data were input to the deconvolution program, after smoothing all of the TUF distributions with a 5-point filter. The calculated contour map of the CM differential cross section

in velocity space is shown in Fig. 7. The angle-averaged CM translational energy distribution and the CM angular distribution are shown in Fig. 8. (Since the total CM flux could not be sampled in the laboratory, only the data on the "far" side of the relative velocity vector was used to calculate $d\sigma/dE_1$ and $d\sigma/d\omega_{-}$). The mean product translational energy is 35 kcal/mole, or 65% of the available energy. The CM angular distributions falls off more gradually here than for the 8r + CH31 reaction. Also, there is no relative maximum in $d\sigma/d\omega$ at $\bullet = 0^{\circ}$. About 74% of the IBr product is scattered into the backward hemisphere.







Fig. 6. Time-of-flight analysis of the IBr product fom the Br + CFgI reaction at 65 kcal/mole.





Fig. 7. Center-of-mass IBr product flux contour map for the Br + CF3I reaction at $65 \, \text{kcal/mole}$, obtained by direct deconvolution of the data in Figs. 5 and 6.

Fig. 8. Center-of-mass product translational energy and angular distributions for the Br Cf31 reaction at 65 kcal/mole, obtained by direct deconvolution. The shaded portion of the translational energy distribution is energetically forbidden.

C. Br + CF31⁺ + CF3 + IBr

The angular distribution of laser-correlated IBr product obtained at a collision energy of 31 kcal/mole is shown in Fig. 9. This signal is a result of reactive scattering events between Br atoms and vibrationally hot CF3I molecules produced by the infrared multiphoton absorption process. For comparison, the angular distribution of IBr obtained at the same collision energy but without the laser is also shown. As was the case at the higher collision energy, most of the IBr produced in collisions of Br atoms with cold CFal molecules is scattered backwards. However, Fig. 9 shows that there is much more forward scattered IBr produced in the reactions with vibrationally hot CF31. Fig. 10(a) shows the TOF distribution of laser-correlated IBr measured at 0 = 60which is close to the CM angle. Apart from a minor offset, t = 0 corresponds to the firing of the laser. The solid line in Fig. 10(a) is just a S-point smooth of the raw data. Fig. 10(b) shows the corresponding TOF distribution of IBr from the "cold" reaction as obtained by cross-correlation TOF. (Actually, this data was taken at a slightly lower collision energy, $E_{\rm C}$ = 27 kcal/mole, but at a lab angle of Θ = 50, which was near the CM angle for this experiment. Therefore, to the qualitative extent intended, Figs. 10(a) and (b) may be directly compared.) The similarity between the two TOF distributions suggests that the product translational energy distribution is not drastically altered when the CF3I reagent is vibrationally excited.



Fig. 9. Laboratory angular distribution of IBr produced in collisions of Br with vibrationally hot CF31. Error bars represent one standard deviation. ---- Laboratory angular distribution of IBr produced in collisions of Br with vibrationally cold CF31. Both distributions were obtained at a collision energy of 31 kcal/mole.

At the peak of the laser-on angular distribution, the IBr⁺ signal rate was 0.018 counts/laser pulse. In order to compare the signal levels from the "hot" and "cold" CF3I, we must correct for the duty cycle of the laser excitation. Each laser pulse excites a 2.1 cm long segment of the CF3I molecular beam, and the CF3I beam velocity in this experiment was 11.7 x 10⁴ cm/s. Therefore, the signal rate from the "hot" CF3I may be calculated to be be

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IBr signal rate = 0.018 counts/pulse x 11.7 x 10<sup>4</sup> c.m/s
(laser on)
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1000 counts/s.

† (ms)

Fig. 10. (a) Time-of-flight distribution of laser-correlated 18 product from the Br + CF31 reaction at a collision energy of 31 kcal/mole. This distribution was measured at C = 60. The solid curve is a 5-point smooth of the measured points. (b) Time-of-flight distribution of 18 product from the Br + CF31 reaction at 27 kcal/mole. This distribution was measured at $0 = -50^{\circ}$ by the cross-correlation method.

At the peak of the laser-off angular distribution, the IBr signal rate (after correcting for the duty cycle of the tuning fork chopper) was 2400 counts/s. The 1000 counts/s enhancement due to vibrational excitation is quite small; an equivalent enhancement could be achieved by merely increasing the collision energy by 2 or 3 kcal/mole. Due to our imprecise knowledge of the CF_{31} vibrational population distribution created by the CO_2 laser pulse, we cannot make an accurate quantitative statement concerning the relative effectiveness of reagent vibrational vs. translational energy in promoting this endothermic reaction. Nowever, we can still make some reasonable estimates. We know that I2-15% of the CF_31 molecules are being dissociated by the laser pulse. It seems likely that the average vibrational energy content of the remaining CF_31 molecules is around 30-40 kcal/mole. Even if we consider only that fraction of the total vibrational energy which lies in the reaction coordinate, i.e., the C-1 bond, it still appears that, at this collision energy (which is "3 times the endothermic barrier height), reagent vibrational energy is less effective than an equivalent amount of <u>additional</u> reagent translational energy in promoting

The angular distribution of laser-correlated IBr product obtained at a collision energy of 11.7 kcal/mole is shown in Fig. 11. (The laser conditions were unchanged from the previous experiment, so the CF_31 vibrational energy distribution should be identical.) For this experiment, the peak IBr signal rate was 0.012 counts/pulse and the CF_31 beam velocity was 6.5 x 10^4 cm/s. The IBr signal rate was calculated as before:

370 counts/s.

Since the collision energy was essentially equal to the barrier height in this experiment, there was almost no IBr signal with the laser off. We measured 45 \pm 11 counts/s at the CM angle. To achieve a signal rate of 370 counts/s with translational energy alone, the collision energy would have to be increased from 11.7 kcal/mole to around 20 kcal/mole. Therefore, vibration competes much more effectively with translation when the collision energy is comparable to the barrier height.



Fig. 11. Laboratory angular distribution of laser-correlated IBr product from the Br + CF31 reaction at a collision energy of 11.7 kcal/mole. IV. SUMMARY AND DISCUSSION

The dynamics of the Br + CH_3I and Br + CF_3I reactions appear to be quite similar. In both cases:

- (1) Reagent translational energy alone can adequately promote reaction.
- (2) The product energy and angular distributions are coupled. This is expected to be the rule rather than the exception in direct reactions. On the average, the products carry away about 2/3 of the available energy as translation.
- (3) The IBr product is mainly backward scattered with respect to the incident Br direction; about 3/4 of the IBr scatters into the hackward hemisphere, and the IBr angular distribution peaks at $\bullet = 180^{\circ}$.

Although the percentage of IBr scattered into the forward and backward hemispheres is about the same for both reactions, the shapes of the CK angular distributions are rather different (see Figs. 4 and 8). The angular distribution of IBr from Br * CFgI falls off rather gradually and monotonically on moving frm $\theta = 180^\circ$ to $\theta = 0^\circ$. In contrast, the IBr product from Br + CHgI is more strongly peaked on the relative velocity vector, and there is even a relative maximum in do/dw at $\theta = 0^\circ$. This small concentration of flux in the forward direction also appears in the contour map (Fig. 3). The fast peak in the TOF distribution at $\theta = 25^\circ$ (see Fig. 2) is mainly responsible for this feature. Sharp product peaking on the relative velocity vector suggests¹⁷ that there may be significant polarization (i.e., parallel or artiparallel alignment) of the initial and final orbital angular momenta, L and C', even though with CH3 depa ting L' must be rather small. If this interpretation is correct, then it implies that there is a stronger preference for conjuar reaction geometries in the H IBI and Final orbital angular momentum polarization effects have been noted in the Li + HI¹⁸ and F + D2¹⁹ reaction systems, which also have very light leaving groups.

The experiments on the vibrational enhancement of the 8r + $\mbox{CF3I}$ reaction reveal that:

- (1) Much more (around 50%) of the IBr product is forward scattered when Preacts with vibrationally hot CF31. This trend has also been observed in trajectory calculations.⁷ A large amount of vibrational energy in the bond under attack may allow larger impact parameter collisions to rear., giving rise to more forward scattering.
- (2) The product translational energy distribution is not greatly perturbed by the addition of large amounts of reagent vibrational energy; most of the reagent vibrational energy is retained as vibrational energy in the products.
- (3) When the collision energy is several times the barrier height, reagent vibrational energy appears to be less effective than an equivalent amount of additional translational energy in promoting reaction. This suggests that the reaction proceeds on an extremely gradual endothermic potential energy surface,⁸ with most of the barrier lying along the coordinate of approach.
- (4) When the collision energy is comparable to the barrier bought, vibrational energy in the bond under attack is more effective than additional translational energy in crossing the endothermic berrier. This preference for V' over T' at low collision energies results, at least in part, from simple angular momentum constraints.

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THE CURKENT STATUS OF REACTIVE SCATTERING EXPERIMENTS - A BRIZE INTRODUCTION TO THE SYMPOSIUM ON REACTIVE SCATTERING -

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Molecular beam studies of reactive scattering between neutral atoms and molecules is the main theme of this symposium. The polarization of product angular momentum, the dynamics of endothermic reactions between atoms and polyatomic molecules and the effect of reactant internal excitation on the product state distribution will be discussed in three lectures given by Rettner, Krajnovich and Pruitt. These three lectures represent some of the current activities of molecular beam studies of reactive scattering. It might be worthwhile to touch on some of the recent developments briefly before we start the main part of the symposium.

STATE-TO-STATE CHEMISTRY

Lasers are playing increasingly more important roles in the state preparation of reactants and state identification of products, especially for small molecules. Pruitt's lecture entitled "State Resolved Products from High Reagent Vibrational Levels" exemplifies the utility of these methods. The recent development of various vacuum UV laser has started to considerably expand the chemical scope of state resolved product detection by laser induced fluorescence. I The availability of high power visible and UV laser has also made the multiphcion ionization process a practical alternative to laser induced fluorescence in some of the experiments. Using a plane polarized laser beam, it has been induced mourt angular momentum. This subject will be dealt with in Rettner's lecture on "Product Polarization in Reactive Systems."

One aspect of state-to-state reactive scattering which is of special importance and which has been attracting both theoretical and experimental attention is the dynamic resonance in the reaction of atom-diatomic molecule systems containing hydrogen atoms. This quantum phenomenon involving the motion of three "atomic" particles : extremely sensitive to the details of the potential energy surface, and should provide a most stringent and mean ingful comparison between theory and experiment in the coming years. Some encouraging progress has already been made on the $F + H_2 \rightarrow HF(v-n) + H$ reaction both experimentally2 and in three dimensional quantum mechanical calculations. 3,4 At this conference, Kuppermann will review the theoretical aspects of this phenomenon in a lecture entitled "Reactive Scattering Computations; Dynamic Resonances in Chemical Reactions."

INTERACTION OF LASERS AND REACTION COMPLEXES

Extensive theoretical studies have been carried out on the interaction of high power lasers with reaction complexes. The promotion of the reaction probability, the opening up of new and desiraule reaction channels and obtaining spectral information of reaction complexes are some of the goals of the interaction of the lasers and reaction complexes.5,6 Some vigorous experimental activity is also expected in this interesting area in the near future, but it will remain a difficult experimental problem. The deposition of

photons in the short lived reaction complexes is far less efficient than the resonant excitation of reagent atoms or molecules and the absorption spectra of reaction complexes in the "continuum" are expected to be broad. It remains to be seen whether the interaction of high p wer lasers and reaction complexes will become a useful tool for either the modification of chemical reactions or obtaining information on the structure and the potential energy surface of reaction complexes. Polariyi's progress report in this conference entitled "Probing the trasition state in Chemically Reactive Collisions" is relevent to this subject.

ENDOFRGIC REACTIONS BETWEEN ATOMS AND POLYATOMIC HOLECULES.

The relation between the location of the potential energy barrier and the effectiveness of vibrational and translation excitation of the reagents in promoting endothermic reactions of atoms with diatomic molecules has been promoting enduthermic reactions of acting with diactime motions in social studied quite extensively in a series of classical trajectory calculations carried out by Polanyi and coworkers.⁷ Recently, several experiments on the reactions of alkali atoms and alkaline earth atoms with hydrogen halides have been carried out for the purpose of making a detailed comparison between translational and vibrational excitation.⁸ Krajnovich's lecture entitled "The Effects of Reagent Translational and Vibrational Energy on the Dynamics of Endothermic Reactions" will summarize some recent studies on reaction atoms with polyatomic molecules, Br + CH3I + CH3 + IBr and Br + CF3I + CF3 + IBr. The IR multiphoton excitation process was used to excite a beam of CF3I to a very high vibrationally excited state in these experiments.

FUCIDATION OF REACTION MECHANISM FROM DYNAMIC AND KINEMATIC RELATIONS

Crossed molecular beams experiments have been used mainly for the study of reaction dynamics of known chemical reactions. In recent crossed molecular beams studies of oxygen atoms with unsaturated hydrocarbons, it has been shown that the difficult task of determining the reaction mechanism and primary products of these reactions can be solved by using dynamic information and kinematic relations of primary products. The identification of radical products in these reactions has been frustrated in the past due to the lack of parent ions or excessive fragmentation of radical products in the mass spectrometric detection. By carrying out measurements of product angular and velocity distributions with sufficiently high resolution and by monitoring all the ions which are observable, it has been possible to convincingly derive reaction mechanisms for a series of reactions involving oxygen atoms with unsaturated hydrocarbo:s.⁹ For example, the substitution of oxygen for a methyl radical or a hydrogen atom were found to be the major channels in the reaction of an oxygen atom with a propylene molecule 10

These are some of the current molecular beam studies of reactive scattering which attracted my attention. Omission is inevitable, no attempt was made to cover all important areas and I am sure the situation will change rapidly in the coming years.

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