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Scope of Project

The major thrust of this research project is to elucidate detailed dynamics of simple elementary reactions that are theoretically important and to unravel the mechanism of complex chemical reactions or photochemical processes that play important roles in many macroscopic processes. Molecular beams of reactants are used to study individual reactive encounters between molecules or to monitor photodissociation events in a collision-free environment. Most of the information is derived from measurement of the product fragment energy, angular, and state distributions. Recent activities are centered on the mechanisms of elementary chemical reactions involving oxygen atoms with unsaturated hydrocarbons, the dynamics of endothermic substitution reactions, the dependence of the chemical reactivity of electronically excited atoms on the alignment of excited orbitals, the primary photochemical processes of polyatomic molecules, intramolecular energy transfer of chemically activated and locally excited molecules, the energetics of free radicals that are important to combustion processes, the infrared-absorption spectra of carbonium ions and hydrated hydronium ions, and bond-selective photodissociation through electric excitation.

Current Research and Recent Results

A. Primary Dissociation Processes

1. Photochemistry of NO_3 in a Molecular Beam (Lee,Johnston). The nitrate free radical (NO_3) is a key intermediate in thermal and photochemical reactions affecting the balance of atmospheric ozone and nitrogen oxides. Owing to its instability and the need for complex reaction mixtures in bulk analysis, NO_3 has remained poorly understood, and substantial uncertainties existed concerning its photochemistry and heat of formation.

We have employed the crossed laser-molecular beam method to study the photodissociation of NO_3 in the wavelength range 532-662nm under collision free conditions. Excitation to the $^2E'$ state followed by internal conversion to the vibrationally hot $^2A_2'$ ground state leads to dissociation by either of two mechanisms:

$$NO_3 \text{ -------> } NO_2 + O \qquad H \approx +46 \text{ kcal/mole} \quad (1)$$

$$NO_3 \text{ -------> } NO + O_2 \qquad H \approx 0 \text{ kcal/mole} \quad (2)$$

The branching ratio between these channels is strongly wavelength dependent. At 590nm, both channels compete about equally. Translational energy distributions of the products indicate that process (1) occurs with a barrier smaller than 0.5kcal/mole. A very high barrier (> 30kcal/mole) exists for dissociation channel (2) resulting in large translational energy released in the $NO + O_2$ products. The yield of $NO + O_2$ decreases sharply below 590nm, falling to zero at 584nm, while $NO_2 + O$ production remained nearly constant down to 532nm. At wavelengths longer than 590nm, a third channel is observed to compete with the above processes: absorption of a second photon followed by dissociation to $NO_2 + O$. Two photon excitation did not result in formation of $NO + O_2$.

The wavelength threshold for formation of $NO_2 + O$ indicates that NO_3 is approximately 5 kcal/mole less stable than previously believed, with a heat of formation of 21.6 ± 1 kcal/mole.

2. Heat of Formation of C_3H_2 and C_3 (Lee). Heat of formation of polyatomic radicals containing C atoms and smaller number of H atoms, such as C_3 and C_3H_2 ($:C{=}C{=}CH_2$) are not very well understood. The experimental studies for the purpose of producing intense C_3H_2 and C_3 beams and for obtaining the heat of formations of these species are highly desirable.

One possible approach for the investigation of C_3H_2 and C_3 is the photodissociation of allene ($H_2C{=}C{=}CH_2$) using 193 nm photons from the ArF laser. The heat of formation of C_3H_2 can be derived from the maximum translational energy release in the dissociation of $H_2C{=}C{=}CH_2 \dashrightarrow H_2C{=}C{=}C: + H_2$ using the well developed method of photofragmentation translational spectroscopy. The heat of formation for C_3 can also be derived from the studies of the secondary decomposition of $H_2C{=}C{=}C: \dashrightarrow H_2 + C_3$. The minimum vibrational energy required to induce the decomposition of $H_2C{=}C{=}C:$ radical can be derived from the minimum translational energy observed for the stable $H_2C{=}C{=}C:$ radicals produced.

3. Decomposition of Tetralin via the retro-Diels-Alder Reaction (Lee). Tetralin (1,2,3,4-tetrahydronaphthalene, $C_{10}H_{12}$) is a hydroaromatic molecule which is a significant model coal compound. Its unimolecular decomposition was studied using photofragmentation translational spectroscopy after pulsed laser excitation. Following infrared multiphoton excitation the decomposition proceeds exclusively *via* the retro-Diels-Alder pathway, which produces benzocyclobutene (C_8H_8) and ethylene (C_2H_4). As in the unimolecular retro-Diels-Alder decomposition of cyclohexene, the center of mass translational energy distribution is peaked away from zero (suggesting a concerted reaction), at a value of 65% of the available energy. After excitation with 193 nm light the translational energy distribution for the retro-Diels-Alder channel is similar to that in the infrared experiment, indicating dissociation from the ground electronic state in both cases. The ultraviolet excitation produces a second primary channel for the decomposition of this compound, molecular elimination of H_2. Additionally, there is another, yet unidentified, secondary channel possibly reflecting the dissociation of the benzocyclobutene produced in the primary step.

4. Infrared Multiphoton Dissociation of Anisole and Phenol (Lee). Both anisole (methylphenyl ether, $C_6H_5OCH_3$) and phenol (C_6H_5OH) were used as precursors to the phenoxy radical (C_6H_5O), which is an important species in the combustion of benzene. The decomposition of the stable compounds as well as the radical were observed using photofragmentation translational spectroscopy after excitation with an intense pulse from a CO_2 laser. The use of a newly acquired high pulse

energy (1.2 J/pulse) laser facilitated the observation of the details of the decomposition of these species. In the decomposition of anisole a single primary reaction channel was observed: $C_6H_5OCH_3$ --> $C_6H_5O + CH_3$. An average of 5 kcal/mole was released into translational energy, and from the shape of the center of mass translational energy distribution, the existence of a small barrier to the reaction was observed. Under conditions of high laser fluence the phenoxy radicals formed in the first step absorbed additional photons and decomposed: C_6H_5O --> $C_5H_5 + CO$. A significant quantity of translational energy was released into recoil of the fragments and a sizable barrier was observed, which was consistent with earlier activation energy measurements (Lin and Lin).

In the phenol experiments the analysis is still not complete. However, there is a reaction sequence that corresponds to the anisole experiment: C_6H_5OH --> $C_6H_5O + H$, C_6H_5O --> $C_5H_5 + CO$. In addition there is another reaction that produces CO. This may be direct decarbonylation of phenol after isomerization, C_6H_5OH --> C_6H_6O --> $C_5H_6 + CO$, but this is yet to be confirmed.

B. Reaction Dynamics

1. <u>Reactions of Ba(^1S) and Ba(^1D) With Water and Methanol</u> (Lee). In order to explore the role of electronic energy on the chemical reactivity of divalent species, we have investigated the reactions of barium atoms in the ground (^1S) and electronically excited (^1D) states with water and methanol under single collision conditions. Most reactions of alkali and alkaline earth atoms with oxygen and halogen containing molecules are initiated by long range (r>4A) electron transfer. Owing to the negative electron affinities of water and methanol, their reactions with barium must involve a close collision (r≈2A), providing an opportunity to investigate reactions mediated by bond insertion or isomerization.

Ground state Ba atoms react with water to form $BaO + H_2$. Excitation to the (^1D) state by optical pumping of the ^1S-^1P resonance transition resulted in formation of BaOH + H with a twenty-fold enhancement of product intensity. No evidence was found for formation of $BaO + H_2$ from Ba(^1D). Both reactions are initiated by formation of Ba--OH_2. The $BaO + H_2$ products likely result from concerted elimination of H_2 whereas the BaOH + H channel involves H-atom migration to form the HBaOH intermediate followed by Ba-H bond rupture. Further experiments at varying collision energies will indicate whether this change in chemical products upon electronic excitation is due to the differing potential surfaces or from thermodynamic effects.

Although the collision of Ba with CH_3OH could be expected to lead to 1) BaOH + CH_3, 2) BaO + CH_4, or 3) $BaOCH_3$ + H, only reaction 3) was observed for both ground and electronically excited Ba atoms. The reaction occurs weakly for the ground state and is enhanced by a factor of ten upon electronic excitation of the reactant metal atom. It is initiated by formation of a weakly bound adduct involving interaction of Ba with the oxygen atom in CH_3OH. Formation of $BaOCH_3$ rather than BaOH indicates that H migration to form $HBaOCH_3$ followed by hydrogen atom elimination is fast, whereas migration of the bulkier CH_3 to form the $HOBaCH_3$ intermediate does not occur.

Parallel experiments involving D_2O and CH_3OD show that the deuterated species are approximately three times less reactive, indicating that quantum mechanical tunneling plays an important role in atom migration in these reactions. No reaction occurs for Ba(^1S) or (^1D) with CH_3OCH_3, confirming the necessity for H-atom migration in reactions of divalent metals with water and its derivatives.

2. Reaction of Sodium Dimer with O_2 (Lee). Reaction of ground state sodium atoms with oxygen molecules is not thermodynamically possible at room temperature. The reaction is possible for sodium excited to the (4D) or (5S) electronic states, yet it is only seen in the case of Na(4D). For sodium dimer, however, two distinct reaction channels are thermodynamically accessible from the ground state:

$$Na_2 + O_2 \;\text{-->}\; NaO + NaO \qquad \Delta H = -3 \text{ kcal/mole} \qquad (1)$$

$$Na_2 + O_2 \;\text{-->}\; NaO_2 + Na \qquad \Delta H = -18 \text{ kcal/mole} \qquad (2)$$

Our preliminary studies indicate a substantial cross section for the latter reaction, with the translational energy distribution peaked at low energy and the NaO_2 product backscattered relative to the sodium dimer beam. No evidence was found for reaction (1) above. Further studies will be conducted to explore the possibility of sideways scattered NaO_2 product and obtain more accurate flux distributions.

3. The Reaction of Ground State Barium Atoms with Cl_2 (Lee). The BaCl product from the reaction of barium with chlorine showed a significant contribution in the backward hemisphere in its symmetric center of mass angular distribution. This is in marked contrast to the reactions of alkali metals with chlorine, known to occur via a stripping mechanism which results exclusively in forward scattered products. Backward scattered base should be related to two electron transfer intermediate and that is turn should be related to $BaCl^+ + Cl^-$ channel which is now under investigation.

4. Dynamics of the Reaction $D + H_2 \text{ -> } DH + H$ (Lee). One of the central goals of chemical dynamics, the comparison of detailed experimental measurements with first-principles theoretical predictions, has begun to be realized. Differential cross section measurements for the $D + H_2 \text{ -> } DH + H$ reaction at collision energies of 0.53 and 1.01 eV have been compared with fully converged, three-dimensional reactive scattering calculations by Zhang and Miller using a Monte Carlo simulation. These experiments constitute the first extensive differential cross section measurements for this elementary reaction with DH product vibrational-state resolution. Although the comparison between theory and experiment is generally very good, significant differences in the angular distribution of rotationally excited DH products were observed. These experimental results indicate that quantum chemists may need to perform further studies of the $D + H_2$ bending potential, which should have the largest influence on the angular distribution of rotationally excited DH products.

Future Plans

A. Intramolecular Dynamics, Spectroscopy and Primary Dissociation Processes

1. IR Absorption Spectroscopy of CH_5^+ (Lee). Important roles played by polyatomic ions in combustion processes started to be recognized in recent years, yet the information on these carbonium ions are still rather limited. In our recent investigation of $C_2H_7^+$, it has been shown that in addition to a more stable bridged structure in which H^+ is bonded to both C atoms, there is a less stable structure in which a weakened H_2 molecule bound to one of the carbons is $C_2H_5^+$ forming the three center two electron bond. CH_5^+, on the other hand, should have only one stable structure which can approximately be described as CH_3^+ bound to H_2 with a near tetrahedral structure. We intend to investigate the CH_5^+ ion through vibrational spectroscopy using the powerful consequence spectroscopy technique developed in our laboratory. IR photon absorption by CH_5^+ will be detected by dissociating vibrationally excited CH_5^+ in a radiofrequency octopole ion trap using the multiphoton dissociation method.

2. Vibrational Spectroscopy of CH_3OH^+ and CH_3CHO^+ (Lee). For many organic molecules, it is well known that the fragmentation pattern of the dissociative ionization processes changes drastically when molecules are vibrationally excited. For example, both CH_3OH and CH_3CHO molecules give parent ions when ionized from the ground state, but if these molecules are excited by ~20 kcal/mol, no parent ions are observable, the dissociative ionization breaking the C-H bond dominates in both cases. The main reason for these phenomena to occur is because after one electron is removed from the bonding orbital of these molecules, the C-H bond rupture will be stabilized by the formation of a delocalized π orbital, much similar to the dissociation of CH_3CH radicals, and cause one of the C-H bonds to be very weak. The vibrational spectroscopy of these molecules is extremely interesting, because two quanta of O-H stretching vibration will exceed the dissociation energy of these molecules and from the vibrational predissociation spectroscopy one can learn the coupling of discreet energy levels to the continuum.

3. High Resolution Spectroscopy of Benzene (Lee). In order to further understand the mechanism of intramolecular energy transfer from the local excitation of C-H stretching overtone, it is desirable to obtain high resolution, higher overtone spectra of rotationally cold benzene molecules. Recently, we have successfully carried out a high resolution spectroscopic study of the first overtone (v=2) transition of benzene by using the recently developed transform-limited pulsed laser system. We adapted the molecular beam infrared-UV double resonance ion-dip technique and extended it to high resolution, nearly single transition detection. The following preliminary experimental results are obtained; a) the single peak observed by the previous works has been rotationally resolved to hundreds of lines. The linewidth of each transition is limited by the laser bandwidth of 120 MHz which indicates that the lifetime of v=2 vibrational state is at least longer than 0.01 microsecond. b) first overtone transition of benzene is strongly coupled by many adjacent transitions which are observed through the line progression with approximately 0.01 cm^{-1} separation.

These observations will set the stage for our pursuit of high resolution C-H stretching overtones at the v=4 and 5 level. Using a flop in technique to detect v=4 and 5 using the dissociative photoionization technique.

4. <u>The Photochemistry of Methyl Acetylene at 193 nm</u> (Lee). The investigation of reactions, thermochemistry and photochemistry of small hydrocarbon molecules and radicals with high carbon atoms to hydrogen atoms ratio are very important in combustion chemistry. In our recent investigation of the photodissociation of allene at 193 nm, a question arises on the possible facile isomerization of the excited molecule. The question can be answered if we compare the results of the allene experiment with those of another C_3H_4 isomer, namely methylacetylene (propyne). If the H atom migration is facile in the electronically excited state, many common features will be detected between these two systems.

B. Reaction Dynamics and Energy Transfer Processes

1. <u>Collision Dynamics of Highly Vibrationally Excited Molecules on Surface</u> (Lee). Previous studies in our group have shown that the excitation of the internal degrees of freedom of polyatomic molecules such as, SF_6 and CCl_4 can inhibit the molecule's probability of condensation. A more complete understanding of the gas-surface energy transfer mechanisms can be gained by extending the studies to determine which internal degree of freedom, vibration or rotation is more likely to change the sticking probability. Measuring the distribution of translational energy of those molecules that inelastically scatter off the surface will also further clarify the dynamics of gas-surface interactions.

2. <u>Rotationally State Resolved Angular Distributions of DH Products in D + H_2 --> DH + H Reaction</u> (Lee). During the last year a rigorous comparison between theoretical calculations and experimental results became possible due to the advances of quantum scattering calculation and various microscopic experimental methods. Although theoretical calculations compare reasonably well with experimental results, some questions still remained on the accuracy of the potential energy surface and on the aspects of dynamic resonances. These questions can be best resolved by carrying out a "perfect experiment" with complete specifications of reactants and product quantum states and measuring the angular distribution of each quantum state of products formed.

The experiments that we are currently planning to do are threefold:

- First of all, we would like to set up a crossed beam arrangement (for $D+H_2$), where, downstream from the crossing region, we will set up a counterpropagating uv beam arrangement, which will allow us to efficiently detect DH(v,J) products in a Doppler-free (2+1) REMPI scheme through the E- and F-states. By varying the delay between the detection and the D-atom generation (HI-photolysis), and using position-sensitive detection for the DH^+ produced, we hope to map out the angular distribution for a specific rovibrational product state.

- Using (1+1) REMPI through the B- and C-states or (2+1) REMPI through the E- and F-states, we want to determine the rovibrational product state distribution (detection of total product at the crossing region).

- Using (2+1) REMPI we can lock in on a rovibrational product state, and using a tunable photolysis laser we want to tune the collision energy, and look for the occurrence of dynamical resonances.

3. The Chemi-ionization Reaction of Barium Atoms with Halogen Molecules (Lee). The reactions of alkaline earth atoms with halogens are a striking illustration of how dynamical factors can determine the course of a reaction when more than one potential hypersurface is involved. Both ground state and electronically excited barium atoms are known to react with halogen molecules to yield neutral products in ground and excited electronic states. In addition there is a significant channel yielding ionic products BaX^+ and X^- seen even in the case of ground state reactants. Previous studies have resulted in considerable insight, but a comprehensive understanding of these reactions is still lacking. A modification of the crossed molecular beams apparatus will allow for angle- and energy-resolved detection of ionic reaction products under conditions identical to those under which we observe the neutral products. The use of supersonic beams under single-collision conditions, laser preparation of reactants in well-defined electronic states and a versatile universal detection system will provide unprecedented insight into these revealing reactions.

4. Reaction of Transition Metal Atoms with Alkyl Halide (Lee). In the catalytic reaction of hydrogen halide elimination from alkyl halide by transition metal atoms, the insertion of transition metal atom into C-X bond is thought to be the first step. The second step involves the migration of one of the H atoms to the transition metal and eliminates either an olefine or a hydrogen halide. Whether a hydrogen halide or an olefin will be eliminated depends on which hydrogen atom migrates and on the nature of the transition metal and carbon atom interaction. The detailed mechanistic and dynamic question can now be answered by investigating these reaction under single collisions of molecular beams. Molecular beam study of the transition metal chemistry has been our dream for many years and the recent development of a molecular beam source of transition metal will allow us to do so.

5. Reaction of OH Radicals with Unsaturated Hydrocarbons (Lee). Crossed molecular beams studies on the reactions of radical species have been shown to be difficult. Reaction cross sections are small and the production of high intensity radical beams has not been easy. Over the last several years, some significant progress in the development of radical beam sources using both the thermal dissociation and the photodissociation technique has been made. The recent successful crossed molecular beam studies on $CH_3 + CF_3I \rightarrow CF_3$ are certainly very encouraging, since this is a reaction of a radical with a polyatomic molecule and has a very small cross section.

It is now possible to produce radical beams with a relatively high intensity of OH radicals. These radicals are produced quite efficiently by dissociating HNO_3 at 193 nm.

The first series of reactions to be investigated are the addition and the subsequent substitution or elimination reactions of unsaturated hydrocarbons including aromatic hydrocarbons. Since a pulsed radical beam source will be used for this reaction, a pulsed beam of unsaturated hydrocarbons will also be used. Product velocity distribution will be measured by the time-of-flight method.

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*The applications of VUV on spectroscopy and dissociation dynamics are described under separate entry by Lee and Kung.

**Because of limited space, papers coauthored with R. Saykally and D. Shirley are not listed.

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