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Summary

Time-resolved Fourier transform infrared emission experiments are used to study photofragmentation processes, single collision reactions, energy transfer events, and laser-initiated radical-radical reactions. The apparatus unites a commercial FTIR spectrometer with a high repetition rate excimer laser. Fringes of the He:Ne reference laser are used for the time synchronization of the FTIR as the mirror sweeps. The zero crossings of these fringes are also used to trigger the variable repetition rate laser with a chosen delay time. Following a short delay after the laser pulse, the analog-to-digital converter samples the signal on the infrared detector. Thus emissions from the excited fragments of the photolysis event are recorded with the FTIR at specific time delays after the laser pulse. We also utilize the capability to multiplex time delays after the laser pulse to obtain several sequential time-resolved spectra at once.

The studies focused specifically on collision processes, such as single collision energy transfer, multiple collision reaction dynamics, and radical-radical reactions. We employed the FTIR technique in the study of single collision energy transfer processes using translationally fast H atoms, as well as radical-radical reactions, e.g. $CH_3 + O$, $CF_3 + H(D)$, and $Cl + C_2H_5$. The fast atoms permit unique high energy regions of certain transition states of combustion species to be probed for the first time. A few examples of the results of this work are given here.

Experiments were carried out on radical-radical reactions. We characterized the CO(v) product from the $CH_3 + O$ reaction, which had not been reported before. In a collaboration with Larry Harding, he calculated all the possible transition states deriving from the CH_3O and CH_2OH species. Thus far the calculations do not find pathways that are favorable to produce CO(v), for example by elimination of H_2 from CH_2OH followed by decomposition of HOC. The pathways do exist, but they are sufficiently high in energy that other pathways might typically be more favored. The group of Dave Gutman completed new studies on this reaction to probe the quantum yields of various products, which showed that the yield of formaldehyde is nearly 100%. This far, there is no consistent explanation for our observation of a high yield of vibrationally excited CO from the $CH_3 + O$ reaction.

The reaction of $Cl + C_2H_5$ was studied to obtain a complete analysis of the HCl(v) product distribution as well as the rate coefficient. The excimer laser is used to form an initial high density of Cl atoms and a smaller density of ethyl radicals simultaneously from a variety of precursors. We studied the time evolution of the HCl product from the addition-elimination process: $Cl + C_2H_5 \rightarrow [C_2H_5Cl] \rightarrow C_2H_4 + HCl(v)$. By using two lasers and suitable time delays, we are able to demonstrate that the vibrationally excited HCl is formed by the interaction of Cl with ethyl radicals. Sequences of time-resolved FTIR emission spectra were acquired, and the risetime of the v=4 state was analyzed to obtain the reaction rate constant for the radical-radical process. The estimated result is $3.0 \pm 1.0 \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1}, in good agreement with a previous determination of Kaiser, Rimai, and Wallington,

but in strong contrast to the much slower value of Dobis and Benson. The Benson group has since repeated their measurements, and a different group at Ford has also repeated theirs, but with a diode laser technique. A major controversy is shaping up over the rate coefficient of this reaction, since both groups now insist they are correct. The monotonically decreasing HCl vibrational distribution is characteristic of an addition elimination reaction (v=1-4 = 0.39±0.04/0.29±0.03/0.22±0.02/0.10±0.02).

Recently, we experimented with combinations of discharge flow apparatus and pulsed laser methods, to increase the range of possible studies of radical-radical reactions. One species can be formed with the discharge flow and the other by the laser, for example. The radical-radical reaction, CF_3CH_2 + D, was studied completely in a discharge flow apparatus. This study was carried out to provide a clear example of a radical-radical reaction which proceeds through an addition-elimination mechanism. The CF_3CH_2 radicals are produced by initial reaction of D atoms with CF_3CH_2I, and these radicals then react with the excess D atoms. A direct abstraction mechanism would form DF(v) exclusively, but the HF(v) product can arise from the addition of D atoms to form $[CF_3CH_2D]^‡$ followed by elimination of HF. The vibrational population distributions are measured to be: HF(v=1-4) 0.63 : 0.29 : 0.07 : 0.01 and DF(v=1-4) 0.58 : 0.30 : 0.10 : 0.02. Taking into account the difference in Einstein A factors between HF and DF, the vibrationally excited HF product is formed 2.8 times more frequently than the DF(v) product. This gives strong evidence for an addition-elimination pathway. Purely statistical weighting for elimination from the $[CF_3CH_2D]^‡$ transition state might suggest an HF : DF ratio of 2 : 1. Thus the larger ratio of 2.8 must indicate additional enhancement of the rate of elimination of HF versus DF in the transition state because of tunneling or some other mechanism.

We probed the vibrational and rotational excitation and alignment dynamics in a single collision experiment of 2.2 eV (in the center of mass) H atoms colliding with H_2O. The fast H atoms are produced by photolysis of H_2S and these atoms collide with H_2O in a jet. The water molecules are excited in many vibrational modes by the 2.2 eV H atom, including the symmetric and antisymmetric stretch and two quanta of the bend. In the antisymmetric stretch, there is a dramatic propensity to produce primarily motion about the K_c inertial axis, which is the axis perpendicular to the plane of the water molecule. This K_c motion strictly defines the collision geometry that leads to the antisymmetric stretch excitation. From the observed direction of the rotational angular momentum, the collision that produces the excitation must be constrained to occur approximately in the plane of the water molecule. Two new theoretical studies have confirmed the origin of the high degree of alignment in the collisions of H + H_2O. Theoretical work by both George Schatz and David Clary, and their associates, shows that the planar transition state that leads to the reaction to form OH + H_2 plays an important role in this dynamics.

Collisions of translationally fast $\underline{H}$ atoms with HF (2.2 eV in the center of mass frame) produce inelastic T-V excitation transfer as well as the H atom exchange reaction. Both of these processes can lead to vibrationally excited HF. Recent theoretical work by George Schatz has shown that when the H atom approaches the H atom end of the HF molecule it can produce primarily T-V excitation transfer, as well as very high rotational states. Collisions with the F atom end have a greater probability to undergo the exchange reaction, resulting in higher vibrational excitation, but lower rotational states. The exchange channel can be directly probed in the $\underline{D}$ + HF collision system. Recently we studied both $\underline{H}$ + HF and $\underline{D}$ + HF with the FTIR to elucidate these dynamics. In the latter system, both vibrationally excited DF(v) and HF(v) are observed. Extensive rotational excitation is also produced by these collisions. Experiments are performed with carefully selected timescales and densities to achieve nearly single collision conditions. One important result of the dynamics is the similar vibrational distributions observed for the HF and DF products of $\underline{D}$ + HF: *e.g.* 0.86 : 0.14 : 0.0 for v=1-3 of HF(v) produced by inelastic collisions and 0.82 : 0.14 : 0.4 for DF(v) produced by reactive exchange. This can also be compared to $\underline{H}$ + HF collisions, which include the sum of inelastic and reactive exchange: 0.76 : 0.19 : 0.05. Another important result is that the inelastic versus reactive exchange channels for $\underline{D}$ + HF give a ratio of vibrationally excited product molecules of 0.6 : 0.4. Work is now in progress to compare these results to theory.

We also discovered that the rotational distributions are a very sensitive function of the potentials used in the calculations. For example, the first calculations of Schatz on an older potential surface (Truhlar No. 5) indicated a dramatic bimodal distribution in rotation, which arises from collisions with different ends of the HF molecule. The experiments confirmed that there are two different rotational distributions, but not as pronounced as in the theory. Using an improved version of the semi-empirical H + HF potential surface (6SEC), the rotational results are found to be in better agreement with experiment. Detailed comparisons of the experimental and theoretical results this system will provide one of the most exacting tests of vibrational and rotational dynamics in a simple collision system.

New work is being carried out to study radical-radical collisions under single collision conditions, for example, $\underline{H}$ + NH_2. High resolution spectra of the A-X transition in NH_2 have been obtained in emission following the photodissociation of NH_3 at 193 nm. Many more lines have been observed with much higher signal-to-noise using the normalization technique mentioned above. The next step is to study the collision dynamics of a fast H atom colliding with the excited NH_2 to look for newly formed states in emission. New studies are also planned to produce H atoms by a discharge flow followed by laser-initiated reaction with CF_3, to obtain complete rotational distributions for the thermal radical-radical reaction.

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