duction[49] of the corresponding ketone, afforded **62b** (also 84% ee),[50] which upon benzenesulfenyl chloride treatment afforded **63** with the same optical purity[51] as starting material. It is presumed that the stereo-specifically produced intermediate **64** electrocyclizes disrotatorily to afford the less hindered *E* isomer **63** possessing the *R* bridgehead carbon.[49] Had disrotatory electrocyclization occurred in the opposite allowed sense, then the corresponding *Z,S* combination should have resulted. In other words, a novel situation emerges wherein *geometric* diastereomers correspond to optical antipodes.

Conclusion

Factors that influence *E* to *Z* pathways in the [1,5] hydrogen shift of vinylallenes of the general type **16** are not well-understood, but this process provides an efficacious route to the 1-hydroxyvitamin D system, certain

(49) Yamaguchi, S.; Mosher, H. S. *J. Org. Chem.* **1973,** *38,* 1870. The configuration is predicted to be that shown for **62** and this stereochemistry is assumed to be transferred to **63** and **64** as shown.

(50) Determined by using ¹H NMR with a chiral shift reagent [Eu-(hfc)₃] sold by Aldrich.

(51) The separated diastereomeric sulfoxides were analyzed by high pressure LC (chiral column, Regis *Chemical* Co.), but only one disastereomer could be resolved. See: Pirkle, W. H.; Finn, J. M.; Schreiner, J. L.; Hamper, B. C. *J. Am. Chem. Soc.* **1981,** *103,* 3964.

11-*cis*-retinoids, and other polyenes. Further exploratory investigations, both experimental and theoretical, should be useful and are continuing. The unexpected formation of drimatrienes, resulting from electro-cyclization rather than [1,7]-sigmatropic hydrogen shifts of an allenyl diene, offers a new method for the stereospecific asymmetric synthesis of polycyclic ring systems. It is easy to envisage an extension of the transformation **62b** → **[64]** → **63** to a variety of substitution patterns including other sized rings. This Account clearly describes how new research areas may emerge from others, namely, from vitamin D to retinoids and drimanes.

Infrared Fluorescence: A Versatile Probe of State-Selected Chemical Dynamics

Stephen R. Leone

Joint Institute for Laboratory Astrophysics, National Bureau of Standards and University of Colorado, and Department of Chemistry, University of Colorado, Boulder, Colorado 80309

Early studies on chemical reactions were limited to measurements on the nature of the reaction products and the total reaction rate. Now chemists have many elegant methods for analysis of specific excited electronic, vibrational, and rotational states. These techniques have amply demonstrated the ability to analyze chemical reactions in much greater detail, from a state-selected point of view. Understanding the participation of excited states in a chemical reaction and the partitioning of energy among various states of the products provides a wealth of sensitive information pertaining to the dynamics, i.e., the molecular motions and forces that play a role in the reaction. Thus, the study of state-selected reactive and inelastic energy transfer collision events has come to form a cornerstone

Stephen R. Leone is a staff member of the Quantum Physics Division of the National Bureau of Standards, where he is currently a Fellow of the Joint Institute for Laboratory Astrophysics and a Professor Adjoint in Chemistry at the University of Colorado. He received his B.A. in Chemistry from Northwestern University in 1970 and his Ph.D. degree under the direction of C. Bradley Moore at the University of California, Berkeley, in 1974. From 1974 to 1976 he was a faculty member at the University of Southern California; he assumed his present position in Boulder in 1976. He is the 1982 recipient of the American Chemical Society Pure Chemistry Award, which recognizes his work employing state-of-the-art infrared techniques to the study of chemical dynamics.

of modern chemical dynamics and kinetics.

The infrared emission technique was one of the earliest to be applied to detailed measurements of molecular states involved in reactions.[1] The infrared spectral region provides a means of analyzing vibrational state populations, and under high resolution, rotational state details as well. Overall, it has been a tremendously powerful technique for analysis of individual states in simple $A + BC \rightarrow AB(v,J) + C$ reaction dynamics[2] and in laser-excited vibrational energy transfer studies.[3] It is fair to say that the infrared studies completely opened up these fields, obtaining massive amounts of high quality detailed data and providing deep insights into the detailed mechanisms of these simple processes. State-selected optical studies and molecular beam scattering experiments provide ideal complements to each other in the study of collisional events. The former obtains precise information on product state popula-

(1) Smith, I. W. M. "Kinetics and Dynamics of Elementary Gas Reactions"; Butterworths: London, 1980.

(2) (a) Polanyi, J. C.; *Acc. Chem. Res.* **1972,** *5,* 161. (b) Anlauf, D. G.; Horne, D. S.; Macdonald, R. G.; Polanyi, J. C.; Woodall, K. B. *J. Chem. Phys.* **1972,** *57,* 1561.

(3) (a) Moore, C. B. *Acc. Chem. Res.* **1969,** *2,* 103. (b) Chen, H. L.; Moore, C. B. *J. Chem. Phys.* **1971,** *54,* 4072, 4081.

tions and the participation of excited reagent states, and the latter provides details on the potentials of interaction and the durations of the collisions, as well as information on internal excitation.

The state of the art in infrared detection skills has clearly advanced in the last 10 years.[4] Improvements in fabrication of large area detectors and in amplifier electronics now make it possible to detect emissions that are 10–100 times weaker than before. Similarly the response time of these sensitive detection systems has been improved an order of magnitude or more. Coupling such detectors with other new tools, such as powerful lasers, has qualitatively changed the types of experiments that are possible. Impressive new experiments can be carried out on all kinds of phenomena that were previously accessible only by more classical techniques.

In this Account, examples will be given in which state-of-the-art infrared fluorescence and chemiluminescence are used to study a broad spectrum of problems in chemical dynamics. The examples range from the simplest possible breaking of a molecular bond, called photofragmentation dynamics, to the complexities of laser-initiated chemical chain reactions. Several other examples will be given on the subtle competition between reactive and inelastic collision events, on intramolecular energy randomization, studies of ion–molecule reaction dynamics, and surface reaction phenomena. In many cases the application of state-resolved infrared fluorescence provides powerful new insights into important remaining problems in chemical dynamics.

Infrared Fluorescence Signal and Detection Limits

Infrared emission arises from transitions between an excited vibrational state and a next lower state. Typically the radiative lifetimes are long, ranging from 10^{-3} s up to 1 s. Often only a small fraction of the molecules emit before being deactivated, reacted, or swept out of view, so that the quantum yield of fluorescence is small. In addition, detection of longer wavelength photons is limited by infrared blackbody noise fluxes emitted by room-temperature objects. These factors add up to make infrared signals much more difficult to detect than visible or ultraviolet emissions. In addition, infrared detectors rarely have as fast a response as photomultipliers, so often the time resolution is more limited as well. Nevertheless, state-of-the-art detectors in a typical experimental setup can detect emission from 10^{12} or fewer excited molecules with a 10^{-7}-s response time. If time-response information is sacrificed, low resolution wavelength scans of emission can be made from fewer than 10^8 excited molecules with only a 1% light collection efficiency.

Thus, in emission the infrared region is remarkably more sensitive than might be thought based on the densities and path lengths required for absorption. For example, a low-resolution infrared absorption spectrum might take $>10^{17}$ molecules/cm^3 and a 10-cm path length, although high-resolution Fourier transform spectrometers may take many orders of magnitude less.

(4) (a) Wolfe, W. L., Zissis, G. J., Eds. "The Infrared Handbook"; Environmental Research Institute of Michigan: Ann Arbor, MI, 1978. (b) Keyes, R. J., Ed. "Optical and Infrared Detectors"; Springer-Verlag: Berlin, 1977.
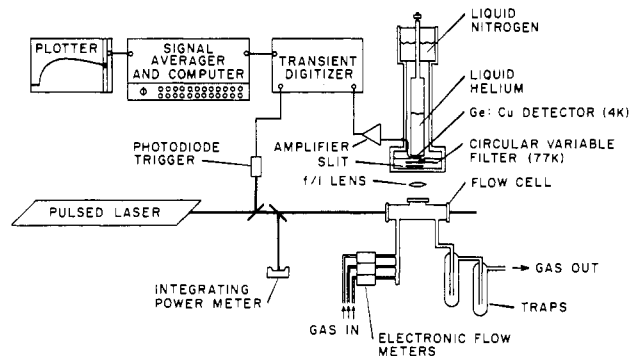

Figure 1. A typical experimental arrangement for laser-excited, time- and wavelength-resolved infrared fluorescence studies.

An important advantage of the infrared emission method is the long radiative lifetime and the relative resistance of the vibrationally excited state toward deactivation. These factors couple together to make the amplitude of the observed infrared signals easily relatable to the excited-state populations, so that it is relatively easy to extract kinetic time behaviors and state distributions properly.

Typical Experimental Arrangement for Laser-Excited Infrared Experiments

Figure 1 shows a typical experimental arrangement that incorporates pulsed-laser excitation or dissociation and detection of time and wavelength-resolved infrared emission. With such a setup, an impressive array of experiments in chemical dynamics are potentially possible. The apparatus consists of a tunable or fixed-frequency repetitively pulsed laser with pulse durations of $\sim$10–1000 ns and pulse energies of 1–100 mJ. Tunable dye lasers, rare-gas halide excimer lasers, frequency-doubled or Raman-shifted lasers, and infrared chemical lasers are the most common excitation sources. Short ultraviolet wavelengths are especially interesting for bond-breaking and time-resolved photochemical investigations. The laser irradiates a gas sample cell in which premixed and prepurified reagents are flowing. The light pulse initiates a reactive or inelastic collision process by dissociation or direct excitation, and the time developments of various vibrationally excited states are followed by recording their infrared emission through selected interference filters. The transient infrared signals are synchronized to the start of the laser pulse at time equals zero and are recorded digitally and then signal averaged by adding together repetitive pulses.

Several types of large area infrared detectors are used: e.g., 1.3-cm diameter InSb photovoltaic detectors or 0.3 × 1.0 cm Ge:Cu photoconductive detectors. The 4 K Ge:Cu detector is masked by cooled 77 K filters to reduce the blackbody noise flux and improve the signal-to-noise ratio. These filters have a continuously variable bandpass, so that they comprise a low-resolution monochromator (e.g., $\sim$40 cm^{-1} resolution at 5 μm). A similar, but more elegant, infrared filter spectrometer was used to detect planetary atmospheric absorptions in the early Mariner Mars space flights.[5]

The infrared signals in the experiments considered here arise from either vibrational fluorescence or chemiluminescence, the latter term being applied to chemically generated vibrational fluorescence. The

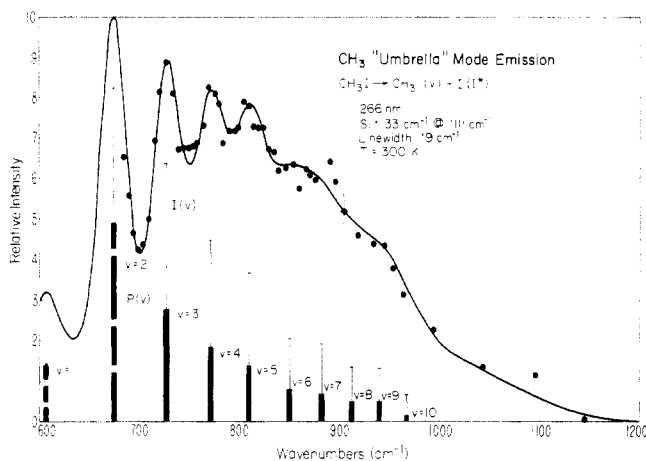(5) Herr, K. C.; Forney, P. B.; Pimentel, G. C. *Appl. Opt.* **1972**, *11*, 493.

Figure 2. Low-resolution vibrational emission spectrum of the CH₃ "umbrella" mode, showing the vibrational distribution produced in the dissociation of CH_3I.

resultant signals are a record of fluorescence vs. time at a specific wavelength. They could be as simple as an exponential decay or more complicated, with multiple exponential or nonexponential behavior. Careful analysis of the signals with a suitable kinetic framework provides accurate rate coefficient data, and normalization of the signals for the intensities of different vibrational states in emission obtains population information.

Dynamics of Molecular Bond Breaking

The breaking of a chemical bond is the simplest kind of reactive event we know.[6] In principle it should be possible to calculate the relevant forces and geometry changes in order to accurately describe the precise mechanics of the bond-breaking process and the internal states in the fragments. Absorption of a photon of light is the most convenient means of preparing the system in a repulsive, dissociative state. Methyl iodide is a classic example of a simple, direct dissociation, where the photoabsorption promotes a nonbonding electron on the iodine into an antibonding σ^* orbital on the C–I bond.

$$CH_3I \xrightarrow{h\nu} CH_3 + I$$
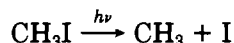
The initial geometry of the methyl group in the molecule is pyramidal, while the final geometry of the methyl radical is planar.[7] Thus, simple physical arguments suggest that some of the excess photon energy will go to make the methyl radical excited in its out-of-plane "umbrella" bending vibration. Recent time and wavelength-resolved infrared experiments directly confirm this excitation[8] and provide an accurate test for theoretical calculations[9] that have considered the dissociation dynamics and the precise population distributions that result.

Figure 2 shows the spectrum of the CH₃ "umbrella" vibrational progression that is observed immediately after dissociating methyl iodide at 266 nm. The peaks in the spectrum are Q-branch features of various vibrational bands in emission ($v = 1$–0 at 606 cm⁻¹, $v = 2$–1 at 682 cm⁻¹, $v = 3$–2 at 730 cm⁻¹, etc.). A computer
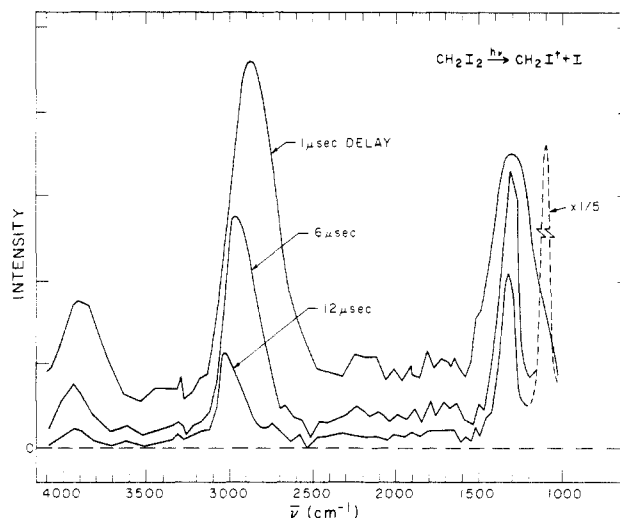

Figure 3. Time sequence spectra from the vibrationally excited CH_2I radical after photolysis of CH_2I_2.

fit to the spectrum (solid line) yields the raw intensity contributions of the different bands, which are shown as the thin bars in Figure 2. Normalization of the raw intensities for the relative strengths of the different vibrational bands gives the relative populations, which are shown as the wide bars. For a portion of the spectrum that is not covered by the available circular variable filter, data from molecular beam time-of-flight experiments[10] are used to complete the analysis (dashed bars at $v = 1$ and 2).

The interesting result in the methyl iodide dissociation is the remarkable specificity of excitation in the "umbrella" mode of the methyl radical. The infrared experiments[8] confirm that the only significant internal excitation is in this out-of-plane bend. Most of the excess photon energy goes into the translational velocity of separation of the two fragments.[10,11] However, the "umbrella" vibration is excited up to levels as high as $v = 10$. The distribution is complicated by the fact that two electronic channels occur simultaneously for the I atom product: $I^*(^2P_{1/2})$ and $I(^2P_{3/2})$, $\Delta E = 7603$ cm⁻¹. In addition, there is a variety of evidence[11] to suggest that these two channels arise from a curve crossing in the dissociation process.

It is clear from the time-of-flight data[10,11] that the major I* channel produces a maximum in the "umbrella" mode distribution around $v = 2$. A quantum mechanical calculation[9] predicts a large shift in the maximum of this distribution up to the $v = 5$ level upon dissociation with a shorter wavelength (248 nm). The infrared experiments[8] confirm a significant enhancement of excitation in the higher levels at 248 nm, but not this dramatic shift in the maximum of the distribution. This is one of the few such state-specified infrared results for a polyatomic free radical and represents a major step forward in capability. Difficulties with the theoretical description of the dissociation process may arise from the choice of potential energy surfaces for ground and electronically excited states of CH_3I. The disagreement of the experimental results with theory points out the high degree of complexity

(6) Leone, S. R. *Adv. Chem. Phys.*, **1982**, *50*, 255.
(7) Yamada, C.; Hirota, E.; Kawaguchi, K. *J. Chem. Phys.* **1981**, *75*, 5256 and references therein.
(8) Hermann, H. W.; Leone, S. R. *J. Chem. Phys.* **1982**, *76*, 4759, 4766.
(9) Shapiro, M.; Bersohn, R. *J. Chem. Phys.* **1980**, *73*, 3810.

(10) Sparks, R. K. Shobatake, K.; Carlson, L. R.; Lee, Y. T. *J. Chem. Phys.* **1981**, *75*, 3838.
(11) (a) Riley, S. J.; Wilson, K. R. *Faraday Discuss. Chem. Soc.* **1972**, *53*, 132. (b) Dzvonik, M. J.; Yang, S. C. *Rev. Sci. Instrum.* **1974**, *45*, 750.

involved in an accurate description of this simple molecular dissociation process.

The photofragmentation of methylene iodide is dramatically different from methyl iodide.[12]

$$CH_2I_2 \xrightarrow{h\nu} CH_2I + I$$
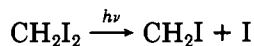
The CH_2I radical is born with a high degree of internal excitation, in both vibration and rotation. Figure 3 shows a series of spectra from the CH_2I radical taken at various times after the dissociation of CH_2I_2 with 248-nm light.[12a] One notes immediately that the radical initially emits at all wavelengths. This is ascribed to the large amount of internal excitation ($\sim 20\,000$ cm^{-1}) and the high density of states in CH_2I at this energy, giving rise to a more or less continuous spectrum of possible overtone, combination, and difference band emissions. Peaks in the spectrum correspond to the CH_2 bend (1000–1500 cm^{-1}), the C–H stretches (2500–3000 cm^{-1}), and a combination band of these two modes (~ 3900 cm^{-1}). These peaks are unusually broad and shifted, as can be seen from the sharpening that occurs in the later time spectra when the radical is partially relaxed.

The tremendous broadening of the CH-stretch region has been attributed to excitation of a series of anharmonic levels extending up to $v = 5$. The rapid collapse of the feature in the CH_2-bending region appears to be due to an initial high degree of rotational excitation. The spectra have been successfully modeled with a statistical partitioning of an average internal vibrational energy in the radical of $\sim 18\,000$ cm^{-1}. Qualitatively, it can be shown that a high degree of vibrational and rotational excitation will result from both the geometry change of the CH_2I and the repulsive "kick" that the carbon atom receives in the bond breaking while it is still constrained by the bond to the other iodine atom. A detailed theoretical treatment of this more complex fragmentation process is somewhat further from realization.[6,12]

Highly Excited Polyatomic Molecules and Vibrational Relaxation

The time-resolved spectra of the CH_2I radical in Figure 3 have been used to obtain some of the few measurements on vibrational relaxation in a free radical species.[12a] In addition, the observation of the continuous emission from CH_2I sheds light on the important problem of intramolecular vibrational relaxation in highly excited polyatomic molecules and the onset of the so-called "quasicontinuum".[13] In a separate set of experiments to study intramolecular vibrational relaxation, polyatomic molecules with varying complexity were directly excited to their CH-overtone levels (~ 6000 cm^{-1}).[14] The molecules under investigation were methane, ethylene, ethane, cyclopropane, propane, propene, and *n*-butane. It was found that in all but the smallest molecules (methane and ethylene), rapid intramolecular relaxation occurs out of the CH-stretch modes.

The results can be interpreted in terms of rapid randomization of the energy without collisions on the
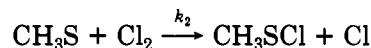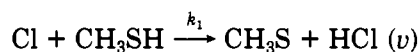
time scale of the detection (1 μs). In this case, intramolecular vibrational relaxation occurs for these molecules when the typical density of states is greater than or equal to 15 vibrational states per cm^{-1}. In another laboratory, elegant infrared fluorescence experiments with more complete spectral resolution have independently confirmed similarly rapid intramolecular vibrational relaxation effects in a collision-free molecular beam environment.[15] It is clear that such infrared experiments provide a new way to look at intramolecular vibrational relaxation, especially in systems that will one day be tractable theoretically.

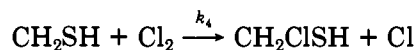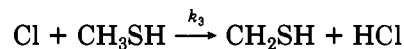## Laser-Initiated Chain Reactions—A Link between Complex Combustion and Elementary Reactions

Infrared fluorescence from laser-initiated chain reactions[16,17] provides an interesting possibility for probing the details of more complex kinetic systems such as combustion chain reactions. By careful choice of the photolysis wavelength and precursor molecule, the laser can introduce selected free radicals in order to initiate the chemistry. Varying the power density of the laser varies the initial radical density. This in turn determines whether the chain will burn linearly, in which case radicals collide only with excess reagent molecules, or whether nonlinear radical–radical collision processes will be important. A complete mathematical description of the chain combustion system has been made and applied to extract a wealth of kinetic rate information.[16,17] In some cases, exceedingly complex chemistry can be followed, and a bridge can be built between the study of elementary reaction steps on the one hand and complex combustion phenomena on the other.

The chain chlorination of methyl mercaptan is an excellent example of the potential of the time-resolved method for more complex systems. This chain reaction has two simultaneous chain cycles and a cross chain propagation step:
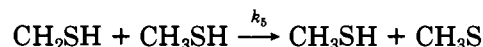
chain 1

$$Cl + CH_3SH \xrightarrow{k_1} CH_3S + HCl\ (v)$$

$$CH_3S + Cl_2 \xrightarrow{k_2} CH_3SCl + Cl$$

chain 2

$$Cl + CH_3SH \xrightarrow{k_3} CH_2SH + HCl$$

$$CH_2SH + Cl_2 \xrightarrow{k_4} CH_2ClSH + Cl$$

cross chain

$$CH_2SH + CH_3SH \xrightarrow{k_5} CH_3SH + CH_3S$$

Solution of the set of differential equations for these five main propagation steps shows that the signal of the product HCl(v), which is formed only in the k_1 process, will have three distinct time regions.[17] These are the time for chain 1 to come into steady state, the time for chain 2 to come into steady state, and the vibrational deactivation of HCl($v = 1$) (mainly by CH_3SH):

$$HCl(v = 1) + CH_3SH \xrightarrow{k_6} HCl(v = 0) + CH_3SH$$
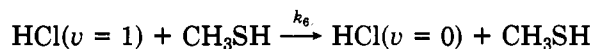
(12) (a) Baughcum, S. L.; Leone, S. R. *J. Chem. Phys.* **1980**, *72*, 6531. (b) Kroger, P. M.; Demou, P. C.; Riley, S. J. *J. Chem. Phys.* **1976**, *65*, 1823.
(13) Mukamel, S.; Jortner, J. *J. Chem. Phys.* **1977**, *65*, 5204.
(14) Nesbitt, D. J.; Leone, S. R. *Chem. Phys. Lett.* **1982**, *87*, 123.

(15) Stewart, G. M.; McDonald, J. D. *J. Chem. Phys.* **1981**, *75*, 5949.
(16) Nesbitt, D. J.; Leone, S. R. *J. Chem. Phys.* **1980**, *72*, 1722.
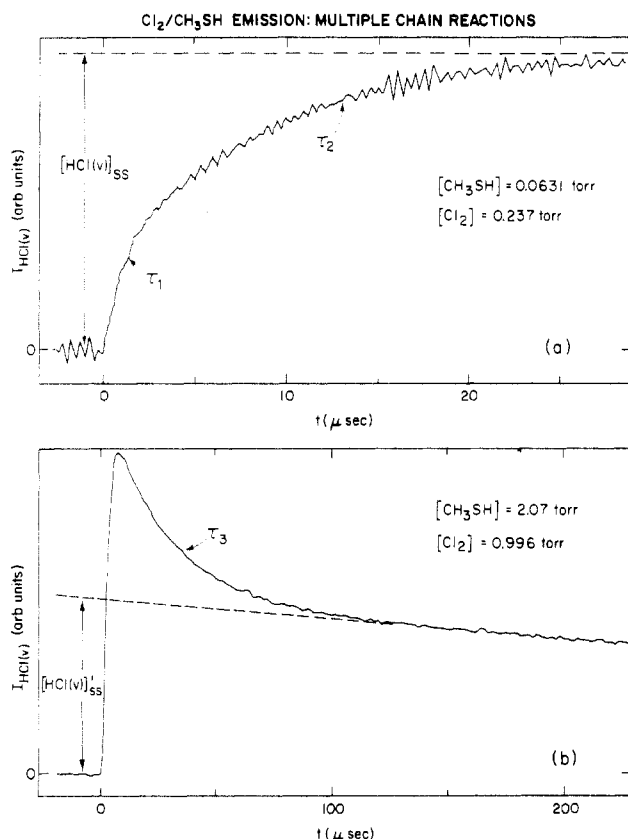(17) Nesbitt, D. J.; Leone, S. R. *J. Chem. Phys.* **1981**, *75*, 4949.

Cl₂/CH₃SH EMISSION: MULTIPLE CHAIN REACTIONS

Figure 4. Detailed time-resolved signals of HCl(v = 1) fluorescence from the Cl₂/CH₃SH chain reaction.

Figure 4 shows that each of these distinct time regimes is observed. However, the correlation of each time regime with each kinetic event is counterintuitive. It turns out that the rise τ_1 corresponds to the onset of the chain 1 process, the rise τ_2 corresponds to the competition between vibrational deactivation of HCl and the linear production of HCl(v) by chain 1, and τ_3 corresponds to the onset of the slow chain 2. Note that τ_3 is a decay because chain 2 siphons away chain carriers from the chain 1 process, which is the only source of vibrationally excited HCl, and therefore causes the signal to diminish. A detailed analysis leads to excellent values for the rate coefficients of all k_1 through k_6.[17] The rate for abstraction of the methyl hydrogens by chlorine atoms is found to be 20 times slower than the rate for abstraction of the SH hydrogen. This result would be difficult to obtain in any other way, and it falls rigourously out of the chain analysis. The rate constant for the cross chain reaction k_5 is found to be very small ($<10^{-15}$ cm³ molecule⁻¹ s⁻¹).

The chain analysis has been applied to a variety of other chlorination type reactions.[18] Complete time-resolved vibrational emission spectra have now been taken in systems such as Cl₂/butane.[18a] These spectra together with independent radical reaction studies[19] indicate that a large fraction of the overall exothermicity is partitioned into polyatomic vibrational excitation. This vibrational energy is rapidly shared among the vibrations of all the products and reagents in the system and appears to be only more slowly degraded into translational heating. Thus, there is evidence for
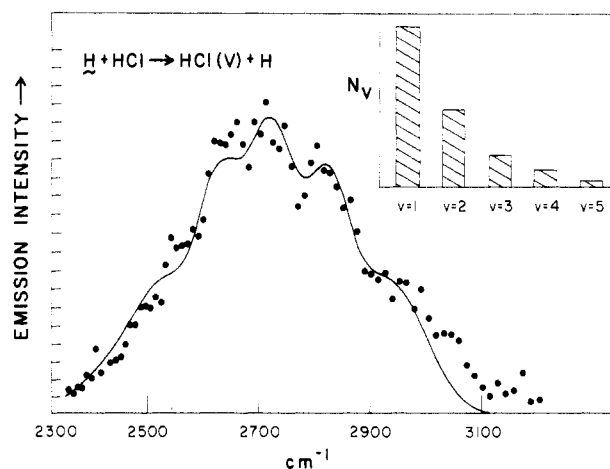
Figure 5. Early time low-resolution HCl(v) spectrum from the T–V excitation of HCl by translationally fast H atoms (**H**). The spectrum includes the contributions of various $v \rightarrow v - 1$ bands, which are anharmonically shifted to longer wavelengths. The inset shows the vibrational distribution of the best fit.

an initial disparity between the internal vibrational excitation, which is approximately a factor of 2 hotter, and the translational temperature. This has important consequences for the modeling of combustion phenomena, since rate coefficients often depend markedly on vibrational excitation, and the results indicate that there may be a disequilibrium between vibration and translation over much of the course of the chain reactions thus far investigated.

Competition between Reaction and Energy Transfer Channels

One of the simples possible energy transfer processes involves the excitation of a diatomic vibration by collision with a high-speed atom.[20] This process is called translation-to-vibration (T–V) excitation and is the subject of numerous theoretical treatments. The predominant collision force in simple models is the repulsive hard-sphere interaction. An analysis of the excitation probability shows that high-speed projectiles are more efficient in exciting a given oscillator. For a given speed projectile, the lower frequency oscillator will be more efficiently excited. This criterion is called the "impulsive" limit. Excitation can occur by multiple quantum jumps, and usually the probability for excitation falls off rapidly above some level for a given energy.

A variant of the T–V process can now be studied by using laser photolysis to produce the high-speed atom and infrared fluorescence to detect the vibrational excitation. In these experiments, however, the atom is not simply a repulsive hard sphere but rather a highly reactive hydrogen atom. The H atoms are produced with high translational excitation by photolysis of a precursor molecule such as H₂S with a short wavelength, 193 nm, from an ArF excimer laser. The H atom has ∼2.5 eV of energy, which is sufficient to excite typical molecules to v = 10. Collisions of the "hot" H atom with HCl result in substantial vibrational excitation in the HCl up to v = 5 (Figure 5).[21] Since the system is interacting on a reactive potential surface, the T–V collisions could

(18) (a) Nesbitt, D. J.; Leone, S. R. *J. Phys. Chem.* **1982,** *86*, 4962. (b) Dolson, D. A.; Leone, S. R. *J. Chem. Phys.* **1982,** *77*, 4009.
(19) Kovalenko, L. J.; Leone, S. R., to be published.

(20) Lambert, J. D. "Vibrational and Rotational Relaxation in Gases"; Clarendon Press: Oxford, 1977.
(21) Magnotta, F.; Nesbitt, D. J.; Leone, S. R. *Chem. Phys. Lett.* **1981,** *83*, 21.

also result in a significant fraction of reactive H atom exchange, providing an opportunity to probe the interplay between reaction and energy transfer channels.

Experiments with H on DCl and D on HCl reveal the consequences of carrying out a T–V energy transfer process on a reactive surface.[22] The T–V excitation efficienty (η_{T-V}) is dramatically enhanced by pairing the higher speed projectile with the lower frequency oscillator:

$$H + DCl \rightarrow DCl(v) + H \qquad \eta_{T-V} \cong 1.0$$

$$D + HCl \rightarrow HCl(v) + H \qquad \eta_{T-V} \cong 0.06$$
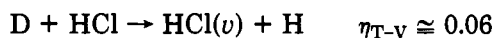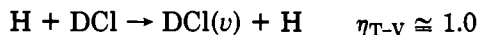
However, the fraction of reactive exchange resulting in a vibrationally excited product is substantial and similar in both cases:

$$H + DCl \rightarrow HCl(v) + D \qquad \eta_{T-V} \cong 0.2$$

$$D + HCl \rightarrow DCl(v) + H \qquad \eta_{T-V} \cong 0.2$$
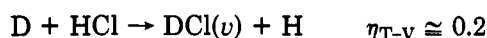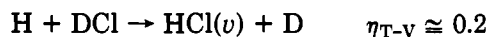
These results confirm the substantial role that reactive collisions play in the energy transfer process. There appears to be a steep dependence in the seemingly "pure" T–V process upon the degree of "impulsive" collision, but there is little dependence of the reactive process upon the vibrational frequency and projectile speed within the range thus far studied. The results bring to mind the possibility that the two different channels might occur by collisions of the H atom with different ends of the HCl molecule. Thus far we have no data on the extent of an additional reactive channel that should also be important:

$$H + HCl \rightarrow H_2 + Cl$$
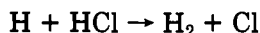
As a second example of the subtle interplay between reactive and inelastic collision processes, a study has been carried out on the collision between excited bromine atoms, $Br^*(^2P_{1/2})$, and vibrationally excited H_2.[23] Pulsed dissociation of Br_2 produces Br^* atoms, and upon collisions with H_2, a rapid electronic-to-vibration (E–V) energy transfer takes place:

$$Br^* + H_2(v = 0) \rightleftarrows Br + H_2(v = 1)$$
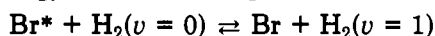
At high laser power densities, it is possible to generate significant concentrations of Br^* and $H_2(v = 1)$, so that collisions between these two excited species can occur. The first expectation might be that Br^* would again transfer its energy to H_2 by a second E–V transfer:

$$Br^* + H_2 (v = 1) \rightleftarrows Br + H_2(v = 2)$$
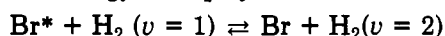
This should be favorable because the resonance mismatch is even smaller than in the $v = 0 \rightarrow 1$ case. However, at this total energy a reactive channel also opens up:

$$Br^* + H_2(v = 1) \rightarrow HBr + H$$
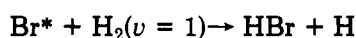
This reactive channel can be detected by subsequent reaction of the H atoms with excess Br_2 to produce vibrationally excited $HBr(v)$.

It was found that the reactive channel has a substantial rate constant, nearly similar to that for the $v = 0 \rightarrow 1$ E–V process.[23] This is surprising since the $Br^* + H_2(v = 1)$ pair does not correlate directly to ground-state products and might have exhibited a barrier to reaction. It is possible that the presence of

the E–V transfer channel plays a significant role in enhancing the reactive channel. The E–V process could convert the spin–orbit electronic excitation into vibrational motion of the H_2 nuclei in the entrance channel of the reactive encounter. This would convert the electronic energy into a coordinate which would greatly facilitate reaction.

There are likely to be numerous other examples in which the presence of an energy transfer pathway might alter the outcome in a reactive encounter, either by modifying the incoming states to a more favorable location on the reactive potential surface or by altering final product state distributions. An elegant study of the Br/Br^* yield in the F + HBr reaction has already demonstrated what appears to be an energy transfer pathway in the exit channel of a reaction.[24] This should lead to an active area of theoretical investigation, in which it will be valuable to consider the time-dependent excitation of different nuclear motions over the course of a transition state in a reaction.

Ion–Molecule Reaction Dynamics—Probing a New Subset of Chemical Dynamics

A few years ago the first observation was made of infrared chemiluminescence from a thermal-energy ion–molecule reaction.[25] These early experiments on the associative detachment reaction, $O^- + CO \rightarrow CO_2(v) + e^-$, were limited in scope. More recently, a number of elegant product-state studies of thermal energy ion-molecule reactions have been completed.[26–30]

One system of particular interest is:[29]

$$F^- + HX \rightarrow HF(v) + X^- \qquad X^- = Cl^-, Br^-, I^-$$
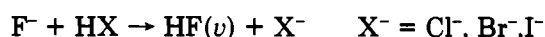
which is exactly analogous to the neutral reactions:

$$F + HX \rightarrow HF(v) + X \qquad X = Cl, Br, I$$
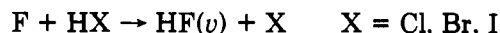
In fact, these reactions are so similar that the overall exothermicity for each corresponding pair of ion and neutral reactions are nearly identical. Combining that with the identical mass combinations in each pair gives the experimentalist a rare opportunity to study a series of reactions that are similar in many respects but occur over very different potential energy surfaces. The major difference in the potential energy surfaces is that the neutral reactions have a small activation barrier to reaction, while the ion reactions have very strong ion–dipole and ion–induced dipole attractive forces that draw the ion and molecule together from very long range and ensure reaction upon every collision.

Up until a few years ago, it would not have been possible to study such ion reactions because the typical densities of ions attainable are 10^3 times smaller than neutral radicals, making the signals prohibitively weak. However, with the best available infrared detectors, it is now possible to perform infrared emission experi-

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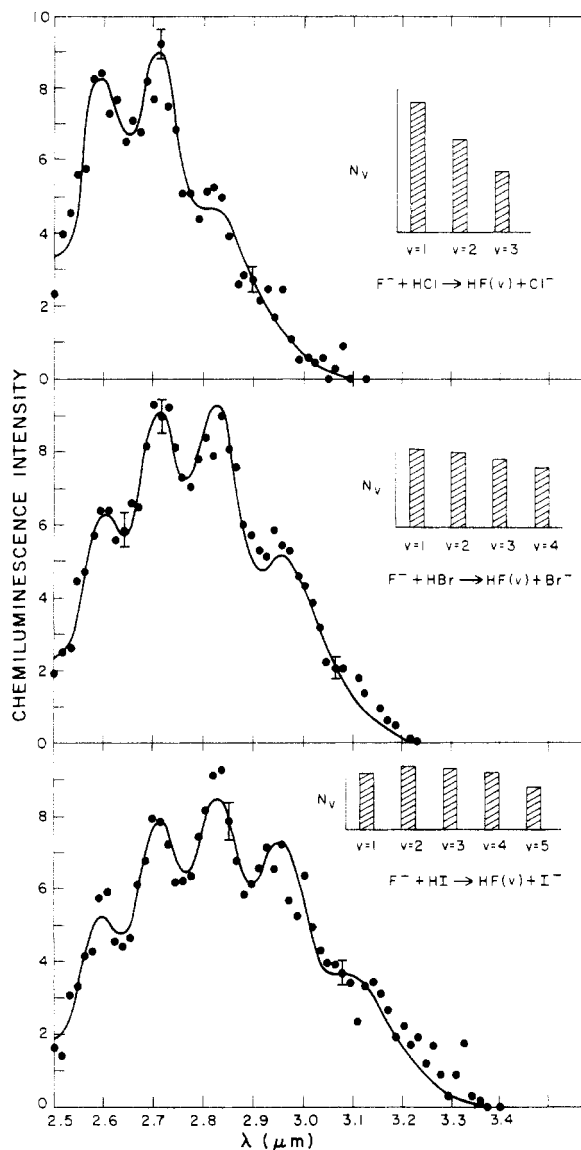(30) Zwier, T. S.; Weisshaar, J. C.; Leone, S. R. *J. Chem. Phys.* 1981, 75, 4885.

Figure 6. Low-resolution HF(v) spectra and their best fit vibrational distributions after radiative cascade corrections for the $F^- + HX \rightarrow HF(v) + X^-$ reactions.

ments on as few as 10^8 ions/cm^2 without cumbersome white cell light-collection optics. The apparatus used for this work[27] is a device called a flowing afterglow. It is a large diameter flow tube, in which ions are created in a flow of helium buffer gas. The ions are thermalized by collisions before being modulated and then reacted. The product-state emission from the ion–molecule reaction is spectrally resolved and deconvoluted to obtain the population distribution. Experiments thus far have only been made with high light collection and low resolution, i.e., small f number optics and the low resolution circular variable filters described earlier.

Figure 6 shows the typical low-resolution spectra of the HF product from the three ion reactions and their deconvoluted vibrational distributions. Both the ion and corresponding neutral reactions deposit a substantial fraction of their exothermicity into product vibration.[29] In both cases the reactions populate the HF product up to the maximum vibrational level accessible by the exothermicity. In all cases, however, the ion product distributions are slightly less inverted than the neutrals. It can be shown that the ion vibrational distributions are still far from statistical, but that they

are slightly more statistical than the neutral reactions. This could be a consequence of the strongly attractive ion–dipole and ion-induced dipole forces, which might result in a tendency for a long-lived intermediate.

Trajectory calculations indicate that the transfer of the light atom in both cases probably has a significant influence in the predisposition to put energy into vibration.[29,31] Thus it may not matter greatly whether the potential energy surface has a deeply attractive well or not. The dynamics of the reaction may be determined more by the kinematics of the light atom transfer than by the potential surface. These results are just the first of their kind, and the infrared chemiluminescence approach to the study of ion–molecule chemistry promises to provide further general insights into the nature of reactive dynamics.

The Future: Infrared Chemiluminescence of Surface Reactions

Infrared fluorescence methods have been described that are applied to a tremendous range of different dynamical experiments. With the impressive sensitivity demonstrated in detecting ion–molecule reaction products, it is appropriate to ask whether infrared methods might now be applied to surface reaction studies. The answer is definitely yes. It has now been demonstrated that it is possible to detect directly the product molecules emerging in various excited states off a catalytic surface.

In two recent experiments,[32,33] vibrationally excited CO_2 molecules have been observed from the oxidation of CO on a platinum surface. Experiments were performed in a flow tube apparatus very similar to that used for the ion–molecule experiments.[32] The CO_2 was characterized and found to be much more highly excited than the surface temperature. In a series of more elegant experiments at Yale,[33] the CO_2 emission was spectrally resolved with a Fourier transform infrared spectrometer, and the internal excitation in various vibrational modes and in rotation were obtained. This paves the way for many new and imaginative studies of surface reaction phenomena. The uniquely interesting aspect of the surface system is its potential for generating highly ordered and constrained geometries of the reactive transition state. Such studies are sure to be of practical interest in the formation of molecules on interstellar grains and from a more fundamental standpoint in trying to learn about reaction dynamics.

Conclusion

In this Account, infrared fluorescence and chemiluminescence are shown to be versatile probes for a wide variety of chemical dynamics problems. Improvements to state-of-the-art infrared detection and the availability of powerful new tools, such as lasers, are making fundamentally new experiments possible every day. Experiments can now be carried out with unprecedented time and state resolution. Work thus far provides several conceptually new ways of thinking about reaction dynamics and energy transfer. The experimental results are pressing the state of current theoretical interpretation as well. The prospects for future innova-

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tions in the study of chemical dynamics by infrared fluorescence are excellent, and several major new directions are already off the drawing board and into the laboratory.

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Structural and Electronic Properties of Linear Chain Compounds and Their Molecular Analogies

MYUNG-HWAN WHANGBO

Department of Chemistry, North Carolina State University, Raleigh, North Carolina 27650

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The electronic structures of extended linear chain compounds are characterized by their energy bands, in contrast to the discrete energy levels in molecular systems. Energy bands are continuous regions of allowed energy values for an extended system, and are often indicated by rectangular blocks as shown in **1a** and **1b**.
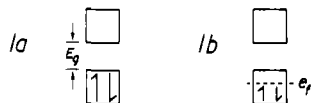

For an extended system of N repeat unit cells, where $N \rightarrow \infty$, any of its energy bands consists of N band orbital levels. Since each of those levels can accommodate two electrons, a given band is completely filled if each unit cell contributes two electrons to the band. The band orbitals of the highest occupied band may be either completely or partially filled as illustrated in **1a** and **1b**, respectively.

Many physical properties of an extended system are largely governed by the highest occupied and the lowest unoccupied bands, just as those of a molecule are influenced by the highest occupied and the lowest unoccupied molecular orbitals. The highest occupied band level at the absolute zero temperature is commonly referred to as the Fermi level e_f, while the energy gap between the highest occupied and the lowest unoccupied band levels is known as the band gap E_g. Thus, the band gap is nonzero in **1a** but vanishes in **1b**, so that the band structures **1a** and **1b** represent typical insulating (or semiconducting if E_g is small but nonzero) and metallic states, respectively.

One of the important quantities in describing the electronic structure of a molecule or an extended system is the so-called density of states. Consider, for example, a hypothetical molecule that has the allowed orbital

energy levels shown in **2**, where the e_2 level is doubly
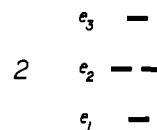
degenerate. Thus in **2**, the number of allowed orbital levels (or density of states) with the energy e_2 is two, while that with the energy e_1 or e_3 is one. Of course, the density of states with the energy value other than the allowed energy levels is zero. Similarly, the density of states $n(e)$ in an extended system is the number of allowed band orbital levels having the energy value e per unit cell or per unit volume. In an extended system the density of states is generally a complicated function of energy, and its value at the Fermi level, $n(e_f)$, is important in describing the physical properties arising from a partially filled band.

A linear chain in a metallic state is susceptible to a structural distortion that introduces a band gap at the Fermi level.[1a] This metal-insulator transition is known as a Peierls distortion, and is also called a $2k_f$ distortion. A nonlinear polyatomic molecule whose highest occupied level is degenerate but incompletely filled undergoes a structural distortion that lowers the molecular symmetry and thus removes the degeneracy. This phenomenon in molecules is called a Jahn–Teller distortion,[1b] and is similar in nature to a Peierls distortion in extended linear chains.

A partially filled band results typically when a chain has an odd number of electrons per repeat unit cell. A chain with an even number of electrons per unit cell may also lead to a partially filled band when the chain structure has a special symmetry element[2] or when the chain is partially oxidized (reduced) by good electron acceptors (donors).[3] From the viewpoint of one-elec-

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