

# Time-Resolved FTIR Emission Studies of Molecular Photofragmentation

STEPHEN R. LEONE

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

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Fourier transform infrared (FTIR) spectroscopic techniques have revolutionized the field of infrared chemical analysis. The high resolution of the FTIR, short time scales for accumulation of spectra, and greater sensitivity of the Fourier transform technique make this method extremely useful in routine analysis as well as in high-performance research applications. Examples of some recent, nontraditional research applications include cold-jet absorption spectroscopy of stable molecules,<sup>1</sup> high-resolution studies of free-radical structures,<sup>2</sup> and emission spectra of ions.<sup>3</sup>

Fourier transform infrared instruments have also been used extensively to study the dynamics of simple gas-phase bimolecular reactions by analyzing the infrared chemiluminescence, or emissions, from product vibrational and rotational states.<sup>4-6</sup> These experiments are traditionally carried out in a flow tube or high-vacuum chamber under steady-state reaction conditions. Single collision product state distributions are often obtained.

A potentially powerful way to extend the range of dynamical information that can be obtained in chemical systems involves the use of time-resolved FTIR techniques. Although a number of time-resolved FTIR methods have been described in the literature over the years,<sup>7-13</sup> it is only very recently that practical experiments in time-resolved gas-phase molecular dynamics have been demonstrated.<sup>14,15</sup> These new experiments take advantage of the short pulse duration, high energy, and high repetition rate of pulsed laser sources, which are used to photolyze a precursor molecule to generate atoms or radicals for reaction. The laser is synchronized to the sweep of the mirror in the FTIR instrument, so that well-characterized, time-resolved interferograms of the emitting species can be accumulated.

In an earlier Account,<sup>16</sup> a number of dynamical experiments were described in which low-resolution, time-resolved infrared fluorescence detection was employed. These experiments used 30-60 cm<sup>-1</sup> resolution tunable interference filters for wavelength selectivity. Unfortunately, the lack of rotational resolution in those experiments sometimes limited the dynamical detail. In the present Account, new experiments are described, which utilize a high-resolution, time-resolved FTIR emission method to study photofragmentation dynam-

ics of large polyatomic molecules. The capability to obtain vibrational- and rotational-state details of the excited products in the dissociation reveals intriguing new features about the dynamics of simple bond-breaking processes. The results include information about the time scales for breaking several bonds in a single molecule and the constraints on rotational motion due to steric hindrance and energy and angular momentum considerations.

The study of photodissociation dynamics in simple systems is undergoing a tremendous resurgence of interest.<sup>17-20</sup> With the advent of powerful laser tools that can interrogate the vibrational- and rotational-state distributions of numerous fragments in simple dissociation processes, a deep understanding of the dynamics of dissociating bonds is being achieved. Velocity distributions and spatial directions of dissociating fragments are being probed. Polarized laser light is also used to measure the directions of the planes of rotation of dissociating fragments in order to learn about the twisting of molecular frameworks before decomposition.

With the FTIR method described here, large polyatomic radical fragments that are produced upon dissociation of complex molecules can be studied. Many species that are not readily amenable to the typical laser-based detection methods, e.g., laser-induced fluorescence and multiphoton ionization, are sometimes

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Stephen R. Leone was born in New York City in 1948. He is presently a Fellow of the National Institute of Standards and Technology (formerly the National Bureau of Standards) in the Quantum Physics Division. He is concurrently a Fellow of the Joint Institute for Laboratory Astrophysics and a Professor Adjoint in the Department of Chemistry and Biochemistry at the University of Colorado. He received his B.A. degree in Chemistry from Northwestern University in 1970, where he worked with Duward F. Shriver, 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, before assuming his present position in Boulder, Colorado.

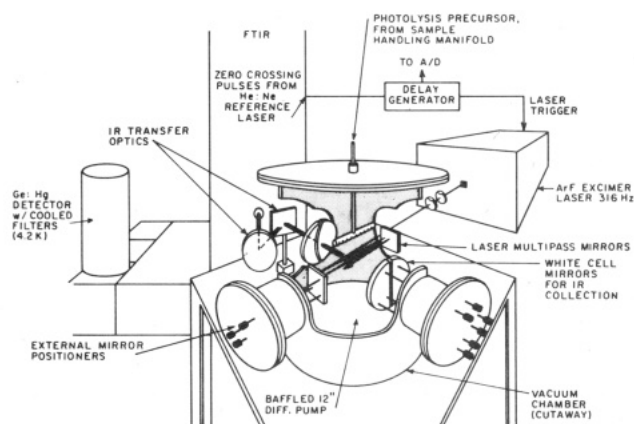
easily probed by infrared emission. The simplicity with which infrared emission line intensities are related to population distributions also affords a powerful means of studying a wide variety of product-state features in polyatomic photodissociation. A drawback of the FTIR emission experiment is that not all products are formed with vibrational excitation, and thus some states are not observed by this method.

The quality of some of the early results obtained by using time-resolved FTIR methods was somewhat discouraging because of artifacts in the spectra, which are caused by inadequate stability of either the time synchronization or the amplitude of the pulsed source.<sup>11,13</sup> Various time-resolved FTIR methods and the difficulties and subtleties of these techniques are described in excellent detail in a recent review.<sup>21</sup> In this Account, a method of achieving the timing synchronization is considered, which is simply arranged by minor modification of commercial equipment through the marriage of an FTIR instrument and a high repetition rate excimer laser. The remainder of this discussion considers the photochemistry of several polyatomic dissociation problems involving halogenated ethylenes, acetone, and acetylene.

### Experimental Arrangement for Time-Resolved FTIR Emission Studies

Fourier transform spectroscopic methods are thoroughly described in several excellent resources.<sup>22,23</sup> The basic advantages, which were originally described by Fellgett<sup>24</sup> and Jacquinot,<sup>25,26</sup> highlight the power of the method; these are, respectively, that all light frequencies are sampled simultaneously and that the optical throughput is greater than that in conventional dispersive, grating-based spectrometer systems, which use narrow, light-confining slits. The basic principle is to acquire an interferogram, that is, the light intensity as a function of the position of the moving mirror in one of the arms of a Michelson interferometer, and then to take the Fourier transform of the interferogram to obtain the light intensity as a function of frequency. In this way, high-resolution infrared spectra are obtained in very short times.

While there are many applications of FTIR methods using absorption spectroscopy, for low number densities of absorbing species, absorption measurements may require long path lengths and large quantities of gas. For some laser-initiated dynamical experiments, an alternative is to use emission spectroscopy, which can be very sensitive, even in the infrared region of the spectrum. With high quality mirror collection optics and improved, background-limited infrared detectors,<sup>16</sup> it is possible to obtain good signal-to-noise from as few as  $10^9$  emitting molecules per quantum state per  $\text{cm}^3$  in a pulsed experiment with a 1- $\mu\text{s}$  time response.<sup>27</sup> With the high pulsed energy from lasers, one can pho-



**Figure 1.** Overall schematic of the laser-photolysis, time-resolved FTIR emission apparatus. The photolysis laser is multipassed inside a vacuum chamber, and emission from the fragments is collected by mirrors into the FTIR instrument. The gas enters through a multiple pinhole effusor.

to dissociate a few percent of various molecules at an initial pressure of a milliTorr (1 mTorr = 0.133 Pa), resulting in more than  $10^{11}$  excited fragments  $\text{cm}^{-3}$ . Thus, photodissociation experiments can be carried out under collision-free conditions to probe the nascent vibrational and rotational states of the fragments by FTIR emission spectroscopy. Sloan and co-workers have also previously demonstrated use of the laser-photolysis, time-resolved FTIR technique to study reaction dynamics under single-collision conditions.<sup>14,15</sup> Good laser-based fluorescence techniques can detect as few as  $10^3$  molecules  $\text{cm}^{-3}$ ; however, the laser must then be scanned, sometimes for long times, to obtain a complete spectrum. In practice, the time required for the FTIR experiments is not essentially longer, but more care must be taken in signal collection and detection, in comparison to laser probing methods.

Figure 1 depicts the time-resolved FTIR emission apparatus used in the studies in our laboratory. It consists of a high repetition rate excimer laser operated at 193 nm in the ultraviolet, a commercial FTIR instrument, and a vacuum chamber with White cell mirror collection optics.<sup>27</sup> The laser photolyzes a precursor molecule which is flowed at low pressure through the vacuum chamber. Emission from the excited fragments of the dissociation is collected with the White cell mirror system into the interferometer. The laser is repetitively pulsed in synchronization with the sweep of the mirror in the FTIR instrument so that a pulse of emitting fragments is formed at a precise time just before the infrared detector is normally sampled at each mirror position. The resulting interferogram of the emitting fragments is thus generated at a specific time delay. The Fourier transform of the data yields the spectrum of the emitting fragments at a specific time after the laser pulse.

The timing of the laser initiation pulse to the sweep of the mirror is done conveniently by sampling the signal from the single-frequency He:Ne laser, which is customarily used to determine the precise mirror position in the FTIR instrument.<sup>27</sup> Figure 2 shows a schematic of a typical timing diagram. The He:Ne reference laser produces a sine wave as the mirror in the interferometer sweeps. The periodicity is determined by the wavelength of the laser light and the

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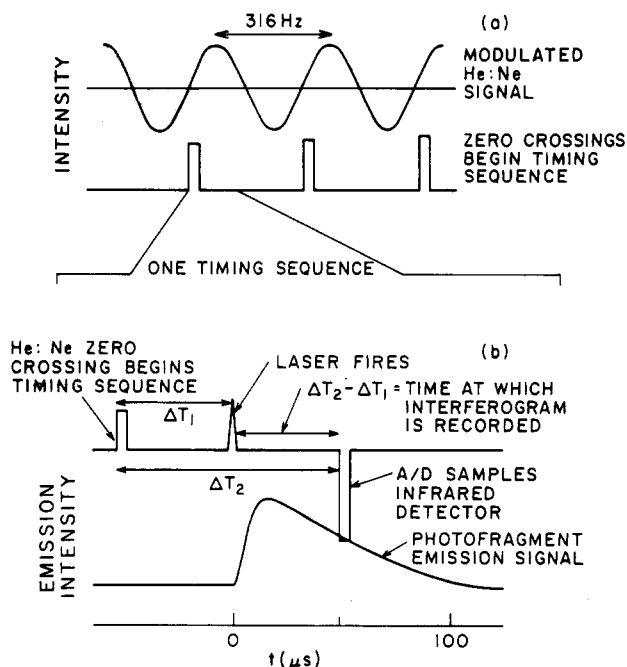
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**Figure 2.** Timing diagram for the synchronization of the laser pulse to the mirror sweep in the FTIR instrument. The laser is pulsed in synchronization with the He:Ne laser fringes, which establish the FTIR mirror position. Slightly later, the signal on the detector is sampled. A schematic of a decaying emission signal is shown at the bottom.

sweep speed of the mirror displacement. At each positive zero crossing of these He:Ne reference fringes, a timing pulse is used to start a delay generator. The pulsed excimer laser is triggered after some short delay time. Another, longer delay time is set with the FTIR software to sample the signal on the infrared detector at some time after the laser pulse. In this way, the entire interferogram is obtained at a user-determined delay time after the laser pulse. Typically, in our system, the mirror sweep speed is set to its slowest speed, which produces the He:Ne reference fringes at nominally 316 Hz. The delay times are adjusted so that interferograms are obtained anywhere from 1 to 20  $\mu\text{s}$  after the excimer laser photolysis pulse. In future versions of this experiment, interferograms will be collected at multiple time delays after the laser pulse.

High-speed, background-limited infrared detectors are employed,<sup>16</sup> which use cooled interference filters to eliminate some of the blackbody radiation falling on the detector element. This reduces the noise so that the weak infrared emission signals are more readily detected. After the raw spectrum is obtained, the background blackbody emission is subtracted, which is obtained by taking a spectrum while no precursor molecules are flowing. Then the spectrum is normalized for the detector sensitivity as a function of wavelength by calibrating the detector with the emission spectrum from a known high-temperature blackbody source.

At a few milliTorr of pressure of precursor molecules, the fragments survive for 5–10  $\mu\text{s}$  without appreciable collisions, which would deleteriously relax the rotational-state distributions that are formed in the dissociation. Vibrational distributions, especially in diatomics, are much more resistant to relaxation, and therefore it is much easier to obtain vibrational results without significant deactivation. Because the molecules are continuously being pumped through the narrow

detection zone, a fresh sample is photolyzed with each laser pulse, and some measure of insurance against relaxation is also achieved merely because the fragments are produced with a short laser pulse and they rapidly exit the viewing region.

Most of the spectra shown in this Account are acquired in a few hours' time or less, which allows for a very powerful means of surveying excited radical spectra or stable molecule fragment states. However, maintenance of the mirror and window cleanliness and the power of the high repetition rate excimer laser (400 Hz) throughout a long run presents the most serious limitation to the technique observed to date.

### Hydrogen Halide Eliminations from Halogenated Ethylenes: Steric Effects Involving Rotational Time Scales in a Statistical Decomposition

The photochemical elimination of hydrogen halide molecules (HX) from vinyl halides and dihalogenated ethylenes has been studied extensively in the past, and the vibrational-state distributions of the HX products for many systems have been summarized.<sup>28</sup> A feature that is characteristic of all these eliminations is the fact that the vibrational distributions can be characterized by a high temperature, suggesting a statistical partitioning of the energy in the dissociation. Similarly, time-of-flight measurements have characterized the velocities of the fragments in some of these systems, and the results show that the translational energy is much less than the maximum available.<sup>29</sup> Both results are interpreted to mean that the electronic excitation, which is initially on a  $\Pi$ - $\Pi^*$  transition, is converted to vibrational excitation in the ground electronic state, which then undergoes a unimolecular dissociation. A high barrier to dissociation, which might be typical of a four-center elimination, leads to the lower translational energy release and allows time for the energy to be partitioned throughout the vibrational manifolds.

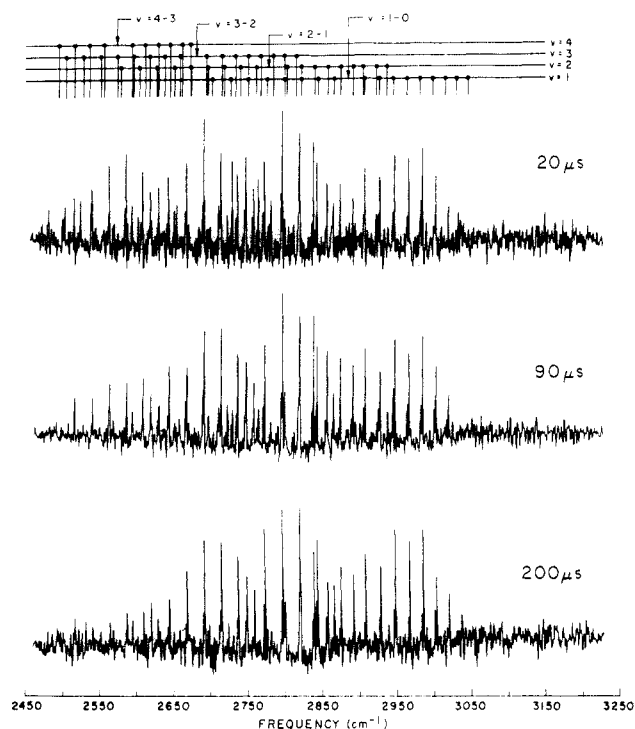
In Figure 3, a time sequence of spectra taken by the FTIR emission technique is shown for the vibrationally excited states of HCl produced in the photodissociation of 1,2-*trans*-dichloroethylene (*t*-DCE) at 193 nm.<sup>30</sup> Vibrational states up to  $v = 3$  are readily assigned in the spectra. These spectra are taken in the presence of argon buffer gas, so that the rotational manifolds are completely relaxed, but the vibrational states are not. At the longer times shown in the figure, the relaxation of the higher vibrational levels is apparent.

The intensities of the lines in such spectra are measured and normalized for the infrared emission strengths of the bands to determine the vibrational distributions. The vibrational distribution for *t*-DCE is found for  $v = 1, 2, 3,$  and  $4$  to be 0.49, 0.32, 0.19, and 0.0, respectively. This monotonically declining vibrational distribution is typical of those observed for HX eliminations from halogenated ethylenes,<sup>28,30</sup> and the result can be closely fit<sup>30</sup> with a modified statistical calculation using one adjustable parameter, namely, the vibrational frequency of the HX stretch in the complex. In these experiments, we did not attempt to obtain

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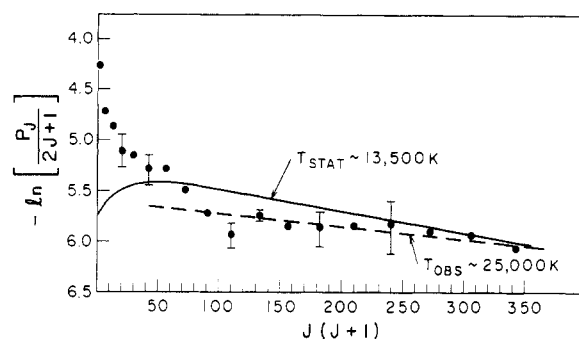
**Figure 3.** Time-resolved spectra from the vibrationally excited HCl product of the photolysis of *trans*-dichloroethylene. These emission spectra are taken with the FTIR instrument at time delays of 20, 90, and 200  $\mu$ s after the dissociating laser pulse. The grid at the top denotes the various vibrational and rotational lines observed. At longer time delays, the relaxation of the higher vibrational states is readily apparent. All spectra are rotationally relaxed to 300 K by a high pressure of Ar buffer gas.

information on the rotational distributions.

Because of the additional ambiguity of the  $\alpha\beta$ - versus  $\alpha\alpha$ -elimination in *t*-DCE, which depends on whether the elimination occurs across the double bond or from one end of the molecule, a more detailed experiment, which could detect rotational distributions, was performed on 1,1-chlorofluoroethylene.<sup>27</sup> The HF product, which is then most likely produced only by  $\alpha\beta$ -elimination, is detected with the FTIR apparatus. The results for the  $v = 1$ –5 vibrational states of the HF product again closely approximate a statistical behavior, at approximately 28000 K, suggesting a statistical breakup of the molecule. However, the rotational states of the HF, which were studied in this case, reveal new detail about the dynamics of the four-center elimination.

Figure 4 shows a semilogarithmic plot of the rotational population distribution that is observed for HF( $v=1$ ), compared to a calculation based on a modified statistical model for the dissociation.<sup>27</sup> The data show a high-energy component to the rotational distribution as well as a large population that is much lower in energy. The low-energy component is in strong disagreement with the rotational distribution predicted by the statistical model. This departure from the prediction suggests that there is some constraint or additional dynamics that affects the partitioning of energy among the rotational states.

One possibility for why the vibrational states fit so well to a statistical prediction, while the rotational states do not, may involve steric constraints on the rotational motion of the departing HF fragment. Energy can flow among vibrational levels on a time scale of a vibrational period, typically  $10^{-13}$ – $10^{-14}$  s. For a



**Figure 4.** Semilogarithmic plot of the rotational distribution of HF( $v=1$ ) from 1,1-chlorofluoroethylene, shown together with the prediction from a statistical model. The dramatic difference suggests that the HF molecules may recollide with the chloroacetylene fragment in attempting to depart through a four-center transition state.

highly excited,  $J = 15$  rotational state of HF, which is formed in this dissociation, the time scale for the light H atom to revolve around the relatively heavy F atom is also very similar,  $5 \times 10^{-14}$  s. However, from the typical translational energies for HX products in this type of elimination, during a time scale of  $5 \times 10^{-14}$  s, the relatively heavy HF can separate by only 0.13 nm from the acetylenic framework of the molecule. This distance of separation is equivalent to the length of a typical bond, and thus the HF fragment has not yet left the region of strong interaction during the time scale of one rotational period. The probability for there to be hindrance of the rotational motion in the escape, i.e., a rotational "recollision", is high. This would therefore serve to relax the rotational distribution substantially, producing the observed deviation from the statistical prediction.

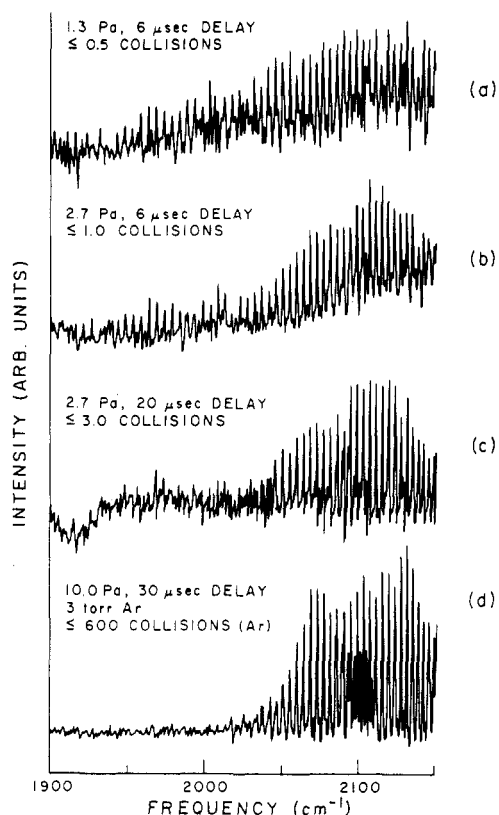
#### Acetone Decomposition: Concerted vs Nonconcerted Breaking of Two Bonds

The decomposition of acetone by a single photon at 193 nm occurs primarily by the breaking of both C–C bonds to produce two methyl radical fragments and CO.<sup>31</sup> In a low-resolution infrared emission experiment performed several years ago,<sup>32</sup> emissions were identified from both the CO and CH<sub>3</sub> fragments, and it was determined that the CO fragment was apparently unusually highly excited in rotation. However, it was not possible to quantify the degree of rotational excitation.

The acetone system offers an intriguing possibility to investigate whether the three body dissociation process occurs in a precisely concerted fashion or there is some degree of nonconcerted breaking of the two bonds. From the symmetry of the methyl radicals about the CO fragment in the acetone molecule, if both bonds were to break at precisely the same time, there would be no mechanism to impart rotational angular momentum to the CO fragment. In contrast, if one methyl radical were to depart first, it would leave a highly excited acetyl radical fragment. In the breakup of the bent acetyl fragment, the CO would receive significant torque from the impulsive kick of the departing methyl radical, which would result in high rotational excitation of the CO.

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**Figure 5.** Rotationally resolved spectra of the CO fragment from the photodissociation of acetone. Predominantly the P branch is shown. Various time delays a–d show the dramatic rotational excitation that is produced in the nascent distribution (a). Trace d is nearly room temperature in rotation.

Figure 5 shows sequences of spectra of the vibrationally and rotationally excited CO fragment from acetone, which are taken at various pressures and time scales after the dissociating laser pulse with the FTIR apparatus.<sup>33</sup> As the pressure is lowered and the time scale shortened, more and more rotational excitation is observed. Rotational levels as high as  $J = 50$  are detected in several vibrational states of CO. While the vibrational distribution of the CO fragment can be closely approximated by a temperature of 2000 K, the rotational excitation is much higher and is not as good a fit to a Boltzmann distribution.<sup>33</sup> The amount of energy partitioned into vibration and rotation can be successfully modeled by an impulsive dissociation starting with a bent, highly excited acetyl radical fragment. Thus, the results are in excellent agreement with a mechanism in which the breaking of the two C–C bonds is nonconcerted. The nonconcerted dissociation mechanism is also corroborated by multiphoton ionization studies, in which acetyl ion fragments are observed when the laser power density is high enough to make the acetyl radical ionization rate competitive with the rate of the acetyl decomposition.<sup>34</sup>

Recently, the methyl radical fragment has also been observed with the high-resolution FTIR experiment, and work is in progress to characterize the rotational excitation in at least some of the  $\text{CH}_3$  fragments.<sup>35</sup> If the nonconcerted bond breaking mechanism is correct,

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then it may be possible to detect two different degrees of internal excitation for the sample of methyl radical fragments.

### Acetylene Dissociation: A Case for Energy and Angular Momentum Constraints

As a final example of the power of the FTIR method, the CCH radical fragment from the dissociation of acetylene is probed. Once again we can analyze for the subtle features of the dissociation dynamics through the details of the rotational states produced. The dissociation of acetylene has been studied by low-resolution infrared emission<sup>36</sup> and by the molecular-beam time-of-flight technique.<sup>37</sup> In addition, the infrared-absorption features of CCH have been characterized by tunable F-center laser spectroscopy.<sup>38</sup> The CCH radical has a low-lying electronic state which mixes in with the nearby vibrational levels, producing a strong infrared emission or absorption, especially from the  $\tilde{A}^2\Sigma^- - \tilde{X}^2\Pi$  transition in the region around  $3700\text{ cm}^{-1}$ . Use of the assignments from the laser spectroscopy measurements allowed the rotational dynamics of this dissociation to be studied for the first time by the FTIR method.

Figure 6 shows a portion of the  $\tilde{A} - \tilde{X}$  transition originating from a state with one quantum of bending excitation in the excited manifold. When the data from this spectrum are plotted to ascertain the rotational excitation, it is found that the CCH radical is rotationally "colder" (225 K) than the parent acetylene (300 K).<sup>39</sup> This result was at first surprising, since it is thought that the dissociation of acetylene would take place from a trans-bent configuration, which might result in an impulsive kick from the departing H atom that would enhance the rotation in the radical.

A model that takes into detailed account the angular momentum and energy considerations in the dissociation of acetylene can rationalize the decrease in rotational excitation that is observed.<sup>39</sup> One mechanism for rotational cooling comes about from the loss of angular momentum due to the departing H atom from an initially rotating acetylene. This is much like a rotating ice skater who releases an object while spinning. The loss of rotating mass will reduce the ice skater's rotational energy. However, since the H atom is light compared to the C–C framework of the molecule, this effect is typically small (but actually enough to account for the rotational cooling if the acetylene remains linear).

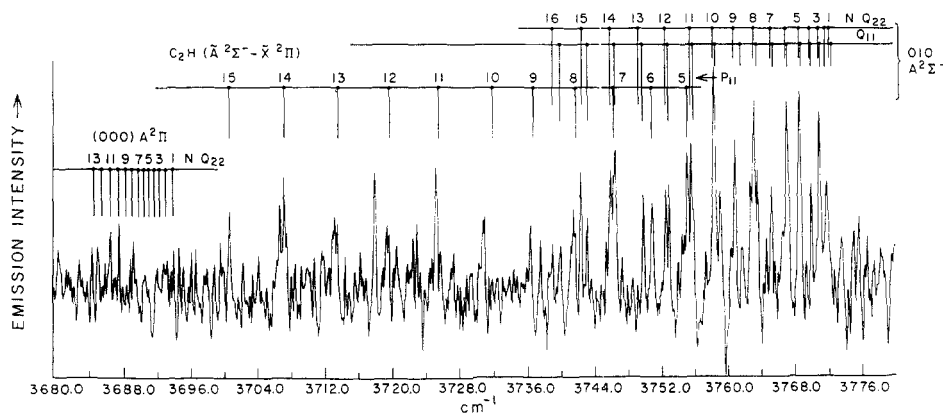
A second mechanism for rotational heating and cooling comes about when one considers the dissociation of acetylene in a trans-bent configuration. Here, the departing H atom will impart a "kick" to the C–C framework. However, since the kick due to the departing H atom can act either in the same direction or in the opposite direction to the initial acetylene rotation, the rotation of the C–C framework can either be enhanced substantially or slowed to a point where the initial rotation changes direction and leaves the C–C

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**Figure 6.** Rotationally resolved emission spectrum of CCH  $\tilde{A}(010)-\tilde{X}(000)$  from the photodissociation of acetylene. The grid at the top shows the assignments<sup>38</sup> of the vibrational and rotational lines. The terms 000 and 010 indicate the vibrationless electronic transition and the electronic transition with one quantum of bending excitation in the upper state, respectively. From the intensities of the rotational lines, an approximate rotational distribution produced in the dissociation is extracted.

framework in a low rotational state. By further consideration of the available energy in excess of breaking the C-H bond, it is found that many combinations of translational energy and angular momenta are not energetically allowed. Specifically, those dissociation events that would produce the highest rotational states require more energy than is available to the system if the H atom is born with significant kinetic energy.

Thus, the rotational cooling effect is presently interpreted as due to energy and angular momentum constraints which sometimes prevent dissociation of the trans-bent acetylene when the direction of the departing H atom would add significantly to the initial rotational energy. This exciting result suggests many intriguing experiments which can be used to probe the dynamics of the dissociating transition state, for example, by isotope substitution and variation of the photon energy.

## Conclusion

The time-resolved Fourier transform infrared method is shown to be a powerful new way to study dissociation dynamics in polyatomic systems. Through the rotational- and vibrational-state details and the capability to examine larger radical fragments, this technique will be potentially useful to unravel numerous new aspects of unimolecular and collisional problems in molecular dynamics.

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