Infrared Photochemistry of $[(C_2H_5)_2O]_2H^+$ and $C_3F_6^+$. A Comparison of Pulsed and Continuous-Wave Laser Photodissociation Methods

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Abstract: A versatile technique employing pulsed ion cyclotron resonance spectroscopy and a pulsed CO_2 laser to study the megawatt infrared multiphoton dissociation of gas-phase ions under collisionless conditions is described. Wavelength and fluence dependences are reported for the ions $[(C_2H_5)_2O]_2H^+$ and $C_3F_6^+$. These results are compared with previous low-power infrared photodissociation studies of these ions carried out by using a continuous-wave CO_2 laser. The results for both continuous-wave and pulsed laser excitation are qualitatively similar; however, differences are found in the magnitude of the photodissociation cross sections for both ions and in λ_{max} of the photodissociation spectrum of $C_3F_6^+$. Possible reasons for these differences are discussed.

We have recently developed a method for studying the infrared (IR) multiphoton photochemistry of gas-phase ions.[1-4] A pulsed ion cyclotron resonance (ICR) spectrometer is used to generate, trap, and mass spectrometrically detect either positive or negative ions. Infrared photochemistry is induced by irradiating the trapped ions with the output from a pulsed TEA CO_2 laser. We have employed this technique in studying the photophysics of the multiphoton dissociation process,[1,2] in probing vibrational relaxation in gas-phase ions[2,3] and in demonstrating that some anions undergo an electronic transition, electron photodetachment, upon IR multiphoton absorption.[4] This paper provides a detailed description of the experimental techniques and data analysis employed in our photodissociation studies and presents data on the wavelength and fluence dependences of the ions $[(C_2H_5)_2O]_2H^+$ and $C_3F_6^+$.

Most of the information currently available on IR multiphoton processes comes from numerous studies on neutral systems employing a variety of experimental techniques for irradiation, product detection, and yield determination.[5] Such studies have elucidated a number of important aspects of the multiphoton absorption and dissociation process. They have also demonstrated the need for carefully controlled experimental conditions if the data obtained are to be useful in understanding the photophysics of IR multiphoton processes. In particular it is desirable to conduct experiments at low pressures, where collisional effects are unimportant, and under conditions where secondary reactions of photoproducts and wall-catalyzed reactions are minimized. Our technique provides these as well as several other desirable experimental features. Typical ICR operating pressures are in the 10^{-8}–10^{-5} torr range. At these pressures the time between ion-neutral collisions ranges from 3 s to 3 ms, much longer than the 3 μs laser pulse and in general longer than the relevant time scale for IR multiphoton dissociation induced by such a pulse.[6] Thus, to a very good approximation, we can study IR multiphoton dissociation in the absence of complicating effects due to collisions. Detection of products and determination of the photolysis yield is carried out after a single laser pulse, thus minimizing secondary reactions, and in most cases all ionic products can be readily identified. Furthermore, because the experiment is time resolved on a millisecond time scale, unimolecular decomposition products are easily distinguished from species formed bimolecularly. Wall-catalyzed processes are rigorously excluded since an ion-wall collision results in the ion being neutralized and removed from the experiment. Finally, because the duty cycle of the entire experiment is 1 s, species with rather low decomposition thresholds which would be impossible to work with under most conditions can be readily generated and photolyzed. This allows us to study IR multiphoton dissociation in the limit of extensive decomposition per pulse—a regime which is important in obtaining a complete understanding of multiphoton dissociation but which is often not accessible in experiments on more stable neutral species. In addition, we are able to employ a collimated laser beam of only modest peak intensity (10–15 MW cm^{-2}), thereby obviating many of the experimental difficulties inherent in the use of tightly focused laser beams.

In contrast to the large amount of work which has been done on IR multiphoton dissociation of neutrals, relatively few studies have thus far been carried out on gas-phase ions. Von Hellfeld et al. have reported data on the dissociation of SF_5^+ using a crossed ion beam-TEA CO_2 laser beam apparatus;[7] however, most pre-

(1) Rosenfeld, R. N.; Jasinski, J. M.; Brauman, J. I. *Chem. Phys. Lett.* **1980**, *71*, 400.

(2) (a) Rosenfeld, R. N.; Jasinski, J. M.; Brauman, J. I. *J. Am. Chem. Soc.* **1979**, *101*, 3999. (b) Rosenfeld, R. N.; Jasinski, J. M.; Brauman, J. I., *Ibid.*, following paper in this issue.

(3) Jasinski, J. M.; Brauman, J. I. *J. Chem. Phys.* **1980**, *73*, 6191.

(4) Rosenfeld, R. N.; Jasinski, J. M.; Brauman, J. I. *J. Chem. Phys.* **1979**, *71*, 1030.

(5) For recent reviews, see: (a) Schulz, P. A.; Sudbo, Aa. S.; Krajnovich, D. J.; Kwok, H. S.; Shen, Y. R.; Lee, Y. T. *Annu. Rev. Phys. Chem.* **1979**, *30*, 379. (b) Cantrell, C. D.; Freund, S. M.; Lyman, J. L. In "Laser Handbook"; Stitch, M. L., Ed.; North-Holland Publishing Co.: Amsterdam, 1979; Vol. III, p 485.

(6) This conclusion follows from the fact that in general the unimolecular dissociation rate will be greater than or equal to the rate of photon absorption at or above the dissociation threshold. The rate of photon absorption at typical pulsed CO_2 laser intensities (unfocused, in the megawatt range) is expected to be 10^6–10^9 s^{-1}. Thus for a typical 3-μs laser pulse most of the decomposition will occur during or shortly after the laser pulse.

(7) Von Hellfeld, A.; Feldmann, D.; Welge, K. H.; Fournier, A. P. *Opt. Commun.* **1979**, *30*, 193.
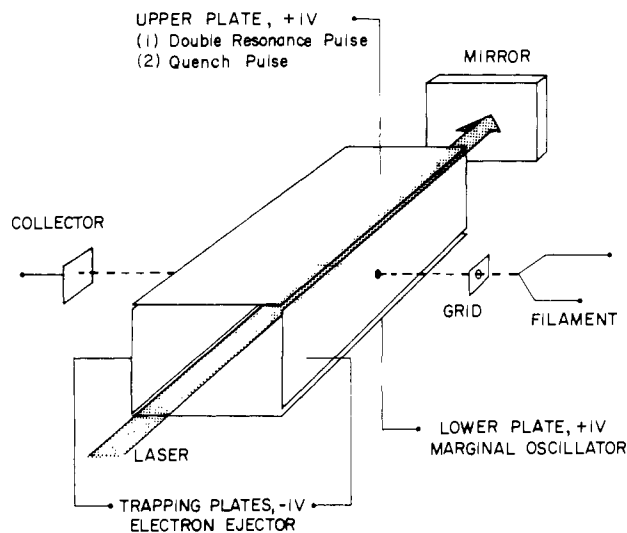
Figure 1. ICR cell modified for infrared photochemical studies.

Figure 2. Experimental configuration.

vious studies of the IR photochemistry of ions have employed continuous-wave IR lasers of much lower intensity than the pulsed lasers typically used in IR multiphoton studies on neutrals. Wing and co-workers studied the IR photodissociation spectroscopy of some diatomic cations using a coaxial ion beam–IR laser beam apparatus.[8] Very high resolution was obtained by exploiting the Doppler tuning capabilities of such an appatatus. A similar technique was used by Coggiola et al.[9] in studying the IR photodissociation of some highly excited polyatomic radical cations. Beauchamp and co-workers[10-14] have used a pulsed ICR spectrometer in conjunction with a continuous-wave CO_2 laser to study the low-power IR multiphoton dissociation of a number of polyatomic ions. This work is the most convincing demonstration that IR multiphoton dissociation is basically an incoherent process which can be induced even at rather low laser intensities under appropriate conditions.

A major reason we have chosen to study the ions $[(C_2H_5)_2O]_2H^+$ and $C_3F_6^+$ is that these ions have been studied by Beauchamp and co-workers using continuous-wave CO_2 laser activation.[10-12] We therefore have an opportunity to compare results obtained by using low-power irradiation for long times (several seconds) with our results obtained by using a much higher intensity pulsed CO_2 laser for a much shorter irradiation period (several microseconds). Thus we can determine any differences in photochemical and photophysical behavior which might result from a change in irradiation intensity of 5–6 orders of magnitude. Such a comparison is important in understanding the mechanism of IR multiphoton absorption. Early work by Yablonovitch and co-workers suggested[15] that IR multiphoton dissociation yields should scale linearly with laser fluence (integrated intensity) and depend only weakly, if at all, on laser intensity. Some confirmation of this suggestion was obtained in experiments on SF_6 where the laser intensity was varied over 3 orders of magnitude by varying the pulse width while keeping the fluence constant.[15,16] More
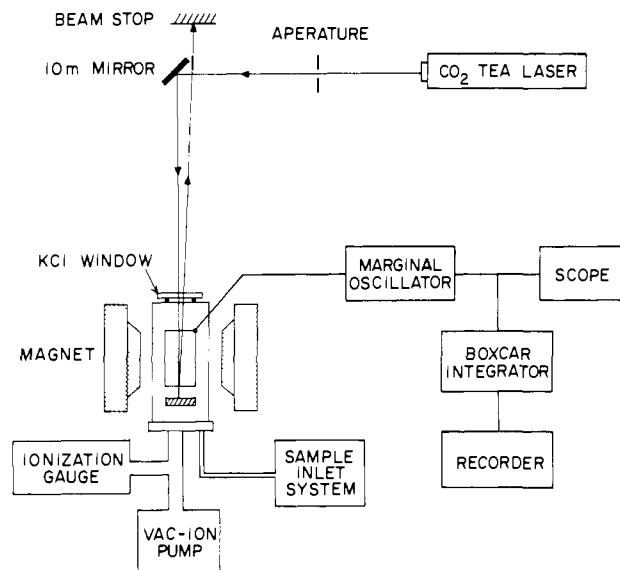
recent results on other molecules, however, suggest that intensity can in fact be quite important in determining the photodissociation yield.[17,18]

Our experimental results as well as a simple physical model for sequential multiphoton absorption are presented below. The results for both continuous-wave and pulsed laser irradiation of $[(C_2H_5)_2O]_2H^+$ and $C_3F_6^+$ are qualitatively similar; however significant quantitative differences in the magnitude of the photodissociation cross sections for both ions and in λ_{max} of the photodissociation spectrum of $C_3F_6^+$ are found. These differences are interpreted in terms of collisional and radiative relaxation effects which are present in the continuous-wave laser activation experiment, owing to the relatively long time period required for activation, but which are absent in the pulsed laser experiment.

Experimental Section

The theory and instrumentation for the type of pulsed ICR spectroscopy employed in our experiments have been described elsewhere in detail.[19,20] Our apparatus uses a trapped ion analyzer cell specially designed and constructed for IR photochemical experiments. The cell, shown schematically in Figure 1, is of standard design except that no end plates are employed and a flat mirror is mounted 4 cm behind one end of the cell. The cell plates and mirror are constructed of OFHC copper and gold plated. The cell plates are mounted on Vespel supports, and the cell and mirror are mounted on a stainless steel frame which holds them stationary in the vacuum chamber of the ICR. The absence of end plates does not noticeably reduce the trapping efficiency of the cell for the longest period investigated, 1 s. Light is admitted to the cell through a 50 mm × 6 mm KCl window mounted on the vacuum chamber by means of a Varian Conflat flange with Viton O-rings. The vacuum chamber is bakeable and is routinely pumped to a background pressure below 5×10^{-8} torr. The experimental configuration is shown in Figure 2.

The laser beam, which is a 3 cm × 3 cm square, passes through an aperture with a 2.5-cm diameter opening. A 10-m radius-of-curvature gold-coated copper mirror, placed 2.5 m from the ICR cell, steers the laser beam toward to cell. This mirror reduces the cross-sectional area of the laser beam to 1 cm^2 in the region of the ICR cell (as determined by burn patterns on thermal imaging paper) and results in a collimated laser beam passing down the 9-cm length of the cell. The flat mirror inside the vacuum chamber reflects the laser beam back through the cell and out of the vacuum chamber to a beam stop. In Figure 2 the outgoing

(8) Tolliver, D. E.; Kyrala, G. A.; Wing, W. H. *Phys. Rev. Lett.* **1979**, *43*, 1719.

(9) Coggiola, M. J.; Cosby, P. C.; Peterson, J. R. *J. Chem. Phys.* **1980**, *72*, 6507.

(10) Woodin, R. L.; Bomse, D. S.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1978**, *100*, 3248.

(11) Bomse, D. S.; Woodin, R. L.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1979**, *101*, 5503.

(12) Woodin, R. L.; Bomse, D. S.; Beauchamp, J. L. *Chem. Phys. Lett.* **1979**, *63*, 630.

(13) Bomse, D. S.; Woodin, R. L.; Beauchamp, J. L. In "Advances in Laser Chemistry 3"; Zewail, A. H., Ed.; Springer-Verlag: New York, 1978; p 362.

(14) Woodin, R. L.; Bomse, D. S.; Beauchamp, J. L. In "Chemical and Biochemical Applications of Lasers"; Moore, C. B., Ed.; Academic Press: New York, 1979; Vol. 4, p 355.

(15) Black, J. G.; Yablonovitch, E.; Bloembergen, N.; Mukamel, S. *Phys. Rev. Lett.* **1977**, *38*, 1131.

(16) Black, J. G.; Kolodner, P.; Schultz, M. J.; Yablonovitch, E.; Bloembergen, N. *Phys. Rev.* **1979**, *A19*, 704.

(17) See, for example: King, D. S.; Stephenson, J. C. *Chem. Phys. Lett.* **1979**, *66*, 33.

(18) Rossi, M.; Barker, J. R.; Golden, D. M. *Chem. Phys. Lett.* **1979**, *65*, 523.

(19) McIver, R. T., Jr.; Dunbar, R. C. *Int. J. Mass Spectrom. Ion Phys.* **1971**, *7*, 471.

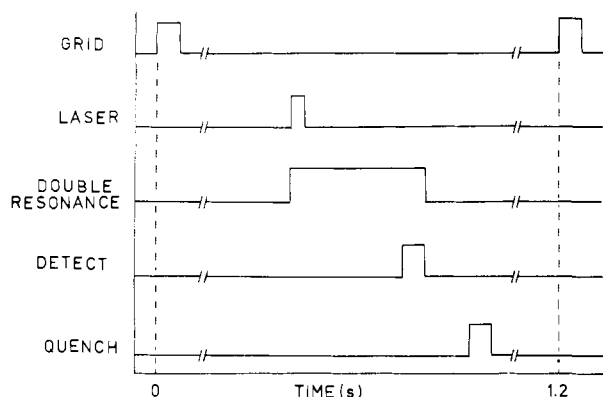(20) McIver, R. T., Jr. *Rev. Sci. Instrum.* **1978**, *49*, 111.

Figure 3. Pulse sequence.

Figure 4. Signal intensity with laser on and off. Each signal represents the average of approximately 70 duty cycles.

laser beam does not intersect the incoming laser beam near the 10-m mirror but passes above or below it in reaching the beam stop. The laser beam is aligned so that it does not impinge on any of the four cell plates and so that the incoming and outgoing beams are almost collinear inside the cell. This arrangement results in the fluence experienced by the ions trapped in the cell being equal to twice that calculated from the beam area and the laser pulse energy. The pulse energy is measured by a power meter (Scientech Model 36-0001) which is placed after the aperture in the optical train when the laser energy is measured. This method neglects any small reflection losses at the mirrors and KCl window. Because of the small distances involved, the incoming and outgoing laser pulses overlap in time as well as space inside the cell and at the KCl window. The optical train described above provides close to the maximum possible fluence at peak intensities which do not routinely damage the window. The fluence can be varied by attenuating the laser pulse with polyethylene sheets and/or CaF_2 flats placed in the optical train in front of the aperture. This method was employed in studies of the photodissociation yield vs. laser fluence described below.

The laser used is a grating tuned Lumonics TEA-103-2 CO_2 laser, operated multimode. The spatial distribution of energy across the beam, measured by scanning a 2-mm aperture across the beam as close to the KCl window as possible, is not Gaussian but is fairly uniform and shows no evidence of hot spots. The temporal profile of the laser pulse consists of an initial high intensity spike (150-ns fwhm) followed by a low intensity tail extending to 3 μs. The total energy is partitioned approximately equally between the spike and tail. When viewed with a fast pyroelectric detector, the initial spike is seen to consist of much shorter high intensity spikes separated by the 20-ns laser cavity round trip time. This temporal behavior, due to longitudinal mode beating, is a common feature of commercial CO_2 lasers. No attempt was made to smooth the laser pulse.[17] Exclusion of nitrogen from the laser cavity results in a laser pulse consisting of a 200-ns spike with no appreciable tail. This short pulse was used in studies of the dependence of the photodissociation yield on laser intensity. The laser was operated at a repetition rate of 0.8 s^{-1} in all experiments. The laser bandwidth is approximately 0.1 cm^{-1}.

The experiment is controlled by a series of five TTL pulses, shown in Figure 3. The duty cycle, typically 1 s, is determined by the time between the grid pulse, which begins the cycle, and the quench pulse, which terminates the cycle. The remaining pulses are completely variable in time between the grid and quench pulses. During the grid pulse, an electron beam passes through the ICR cell and forms primary ions. The ions are trapped in the cell by the crossed electric and magnetic fields and undergo cyclotron motion about the magnetic field axis at a frequency characteristic of their mass-to-charge ratio, m/e. During the trapping period and depending on the neutral gases present in the cell, the primary ions undergo reactive and/or nonreactive ion–molecule collisions. In this manner more complicated secondary and tertiary ions can be prepared via ion–molecule reactions and excess vibrational energy can be removed through collisional energy transfer. At any time during the trapping period the laser can be triggered by using the laser trigger pulse which is amplified to +20 V for this purpose. Any jitter in the firing of the laser after the leading edge of this pulse is insignificant on the millisecond time scale of the ICR. At some time after the laser pulse the detect pulse brings ions of a given m/e into resonance with a fixed frequency marginal oscillator. The transient signal from the marginal oscillator is integrated with a boxcar integrator and output to an x-y recorder. The integrated signal intensity at fixed magnetic field and marginal oscillator frequency is proportional to the number of ions of a given m/e present in the cell at the time the detect pulse is turned on. Following detection all ions are removed from the cell by the quench pulse, and the cycle begins again. The fifth pulse in Figure 3, labeled
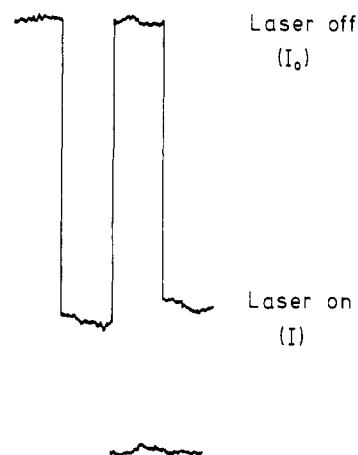
double resonance, can be used to perform ICR double resonance experiments.[19,20] The double-resonance pulse can be used to eject an ion of one m/e from the cell while an ion of a different m/e is observed. This technique is a powerful feature of ICR compared to most other mass spectrometric techniques and allows unambiguous identification of precursors to a given product ion in our photochemical studies.

For the photodissociation yields to be measured, all pulses are fixed in time and a given reactant or product ion is tuned into resonance during the detect pulse. The signal intensity is then measured in the presence and absence of irradiation. For a reactant ion, the ratio of the signal intensity with irradiation (I) to the signal intensity without irradiation (I_0) determines the fraction of ions decomposed, $F_D = 1 - I/I_0$, by a single laser pulse. These intensities can be averaged over many cycles, greatly improving signal to noise ratios. An example of this type of data is shown in Figure 4 for irradiation of $[(C_2H_5)_2O]_2H^+$. With use of this technique, yields as small as 5–10% and as large as 90–95% can be accurately measured. All photodissociation yields reported below were obtained in this manner by monitoring the intensity of the reactant ion signal. For quantitative measurements it is important that all of the ions in the ICR cell be irradiated uniformly by the laser. The best indications that this condition can be reasonably well met is that for several ions we can decompose the entire sample, within experimental error, with a single laser pulse and that small changes in laser alignment do not measurably change the dissociation yield once it has been maximized.

Alternative modes of ICR operation include scanning the magnetic field to obtain a mass spectrum in the presence and absence of irradiation and scanning the detect pulse in time from grid to quench in the presence and absence of irradiation. Both of these modes of operation are used to elucidate various aspects of IR laser induced reactions such as the nature of the product ions and whether or not they undergo subsequent ion–molecule reactions and to check for possible experimental artifacts such as changes in the resonance position of a signal before quantitative photodissociation measurements are made.

Typical ICR operating conditions for the experiments described below included marginal oscillator frequencies of 122 and 153 kHz, magnetic fields of 4–14 kG, and grid pulses of 10–50 ms. Electron energies of 40 and 14 eV were used in the diethyl ether and perfluoropropene experiments, respectively. Unless otherwise noted, the detect pulse was placed 100 ms after the laser pulse when photodissociation yields were measured. Neutral gas pressures were measured with an ionization gauge and are estimated to be accurate to within a factor of 2. In all reactions discussed below, only ionic species are detected; neutral photoproducts are assumed on the basis of thermochemistry and mass balance. Diethyl ether and perfluoropropene were obtained from commercial sources and degassed on the ICR foreline by several freeze–pump–thaw cycles.

Results

A. $[(C_2H_5)_2O]_2H^+$. The positive ion chemistry of diethyl ether has been thoroughly studied.[10,11] Primary ions, generated by electron impact, react rapidly to produce protonated diethyl ether by chemical ionization. Protonated diethyl ether reacts with the neutral ether to form the proton-bound dimer (eq 1). Beauchamp

$$(C_2H_5)_2OH^+ + (C_2H_5)_2O \rightarrow [(C_2H_5)_2O]_2H^+ \qquad (1)$$
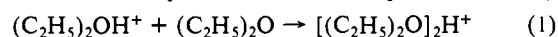
and co-workers have established that reaction 1 is a bimolecular association reaction as opposed to the more common three-body association reaction and have postulated that the dimer is stabilized
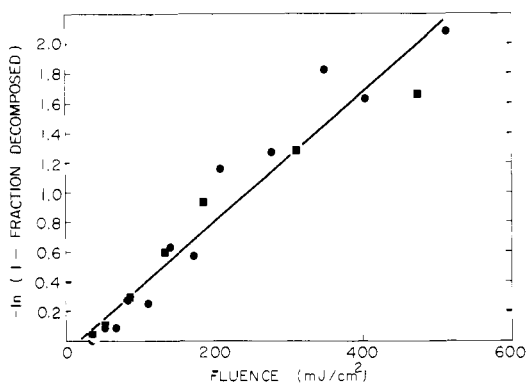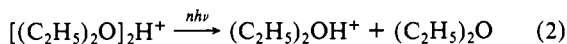
Photochemistry of [(C₂H₅)₂O]₂H⁺ and C₃F₆⁺

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Figure 5. Fluence dependence of the photodissociation yield of $[(C_2H_5)_2O]_2H^+$: (●) 3-μs pulse; (■) 200-ns pulse, 939-cm^{-1} irradiation.

radiatively.[11] Upon irradiation with the CO_2 TEA laser, the dimer ion readily undergoes photodissociation (eq 2). The endother-

$$[(C_2H_5)_2O]_2H^+ \xrightarrow{nh\nu} (C_2H_5)_2OH^+ + (C_2H_5)_2O \qquad (2)$$

micity of reaction 2 is estimated[11] to be 31 kcal mol^{-1}. Thus, on the average, the dimer ion must absorb at least 11 CO_2 laser photons to dissociate. We find that for a given laser wavelength and fluence the photodissociation yield is independent of pressure between 5×10^{-7} and 7×10^{-6} torr and independent of the time delay between the grid and laser pulses for delay times of 300–900 ms. These observations suggest that the dimer is thermalized prior to irradiation. A potential difficulty in determining quantitative photodissociation yields for reaction 2 arises since the photoproduct ion $(C_2H_5)_2OH^+$ reacts to regenerate the proton-bound dimer. Thus, if the concentration of the dimer is monitored too long after the laser pulse, the measured yield will be too small. This problem can be circumvented by ejecting the photoproduct ion using double resonance as was done by Beauchamp and co-workers.[10,11] In the present case, however, the rate of reaction 1 is suitably slow at the pressures employed that accurate yields can be obtained simply by placing the detect pulse within 100 ms of the laser pulse.

At constant fluence, we find the photodissociation yield to be relatively independent of laser wavelength. This was determined by irradiating with several different CO_2 laser lines. The result is consistent with the much more complete spectrum obtained by Beauchamp and co-workers using continuous-wave laser excitation.[11] The fluence dependence of the photodissociation yield, plotted as $-\ln (1 - F_D)$ vs. laser fluence for reasons discussed below, is shown in Figure 5. Note that similar results are obtained with either the long (3 μs) or the short (200 ns) laser pulses. The yield at the highest fluence shown is approximately 90%.

B. $C_3F_6^+$. The radical cation of perfluoropropene was formed by electron impact on the neutral species. Total pressures were in the range (1–5) $\times$ 10^{-6} Torr. Irradiation of $C_3F_6^+$ with the pulsed CO_2 laser leads to photodissociation (eq 3). The endo-

$$C_3F_6^+ \xrightarrow{nh\nu} C_2F_4^+ + CF_2 \qquad (3)$$
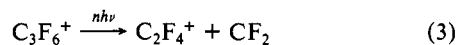
thermicity of reaction 3 is reported[12] to be 56 kcal mol^{-1}, so on the average at least 20 laser photons are required for dissociation. The ion $C_3F_5^+$ is also formed by electron impact on C_3F_6 but does not undergo IR photodissociation under our conditions, a result consistent with the findings of Beauchamp and co-workers.[12] Figure 6 shows the photodissociation spectrum of $C_3F_6^+$. At each wavelength a phenomenological cross section, σ_{ss}, was determined from the least-squares slope of the linear portion of a plot of $-\ln (1 - F_D)$ vs. fluence (vide infra). Examples of such plots at two different wavelengths are shown in Figure 7. All experiments on $C_3F_6^+$ were performed by using the 3-μs laser pulse. Also shown in Figure 6 are spectra previously reported[12,21] by Beau-
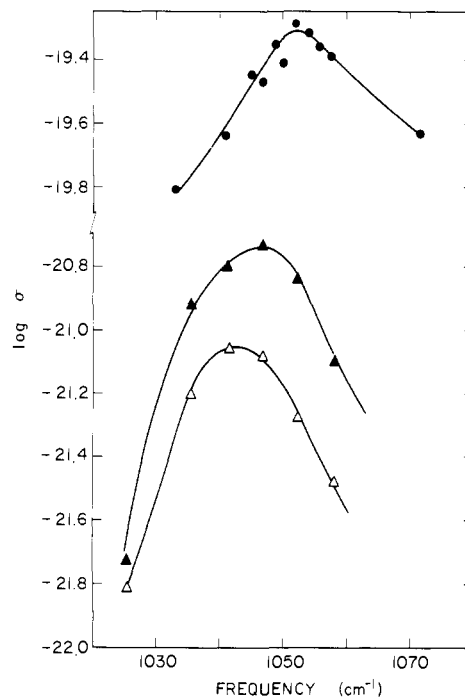

Figure 6. Photodissociation spectra of $C_3F_6^+$: (●) pulsed laser, ions formed at 14 eV; (△) continuous wave, ions formed at 20 eV;[12] (▲) continuous wave, ions formed at 70 eV,[12] σ in cm^2.
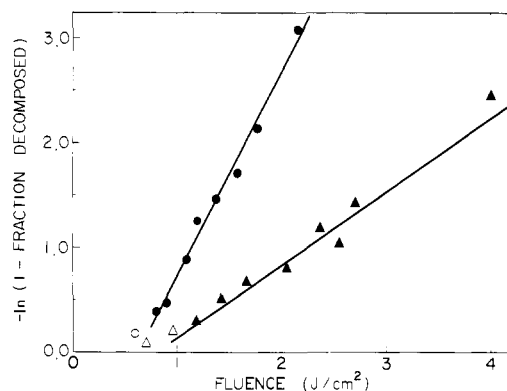

Figure 7. Fluence dependence of the IR photodissociation yield for $C_3F_6^+$ at (▲) 1033.5 cm^{-1} and (●) 1057.3 cm^{-1}. Lines are least-squares fits; data with open symbols (△, O) are not included.

champ et al. using continuous-wave laser excitation at an intensity of 34 W cm^{-2}.

Discussion

A. Kinetic Model for IR Multiphoton Dissociation. A simple physical model for IR multiphoton dissociation is represented schematically in Figure 8. This model, which has been described by several workers,[22–25] treats multiphoton activation in terms of a series of single photon absorptions from groups of molecular states, denoted as levels, separated by one photon in energy. Thus the population of molecules which have absorbed i photons, A_i, can be depleted by further photon absorption with intensity proportional rate constant $k_{i+1,i}$ or by stimulated emission to the

(21) We thank Dr. D. S. Bomse for providing the data necessary to determine the cross sections for continuous-wave activation. These cross sections were calculated from the fractional decomposition after 2-s irradiation at 34 W cm^{-2}.

(22) Baldwin, A. C.; Barker, J. R.; Golden, D. M.; Dupperex, R.; van den Bergh, H. *Chem. Phys. Lett.* **1979**, *62*, 178.

(23) Stephenson, J. C.; King, D. S.; Goodman, M. F.; Stone, J. *J. Chem. Phys.* **1979**, *70*, 4496.

(24) Grant, E. R.; Schulz, P. A.; Sudbo, Aa. S.; Coggiola, M. J.; Lee, Y. T.; Shen, Y. R. In "Laser Spectroscopy III"; Hall, J. L., Carlson, J. L., Eds.; Springer-Verlag: Berlin, 1977; p 94.

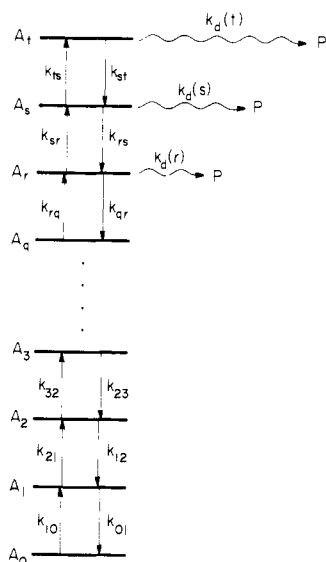(25) Quack, M. *J. Chem. Phys.* **1978**, *69*, 1282.

Figure 8. Linear rate law model for sequential multiphoton absorption.

next lower level with rate constant $k_{i-1,i}$. For levels with energy in excess of the unimolecular dissociation threshold ($E \geq rh\nu$ in Figure 8), population depletion can also occur via decomposition to products, P, with an internal energy dependent rate constant $k_d(i)$. The time dependent populations of the levels A_i and the dissociation yield can be calculated as a function of time for such a model by solving the set of coupled linear differential equations (the master equation) describing the processes depicted in Figure 8.

While most workers agree that some form of the linear rate law model described above is a good basic description of the photophysics of IR multiphoton dissociation, there is as yet little agreement on how best to present or compare experimental data within the framework of such a model. The difficulty arises because a typical experiment measures dissociation yield as a function of some experimental parameter such as pressure, fluence, intensity, or wavelength, whereas complete specification of the master equation requires determination of all of the rate constants shown in Figure 8. Since we wish to compare our results with those for continuous-wave irradiation of the same ions in as direct a manner as possible, we have chosen to follow the data treatment suggested by Quack. This approach allows us to characterize the overall absorption and dissociation process for both pulsed and continuous-wave experiments in terms of a single parameter, the steady-state cross section, which is readily obtained from the experimental data.

The applicability of the linear rate law model to IR multiphoton dissociation and solutions to the resulting master equation have been discussed at length by Quack.[25] In particular, he has shown that when such a master equation involving only incoherent single photon transitions between levels is a good description of the process, the overall rate of photodissociation is given by a unimolecular rate coefficient defined by eq 4. After a suitable

$$-d \ln (1 - F_D)/dt = k_{uni}(t) \qquad (4)$$

irradiation period, $k_{uni}(t)$ approaches a true constant, k_{uni}^{ss}, where ss denotes steady state. This corresponds to the internal energy distribution among levels, determined by the relative values of the A_i, becoming time invariant. Quack further defines a bimolecular rate constant $k_1^{ss} = k_{uni}^{ss}I$, where I is the laser intensity. If we note that $Idt = dF$, where F is the laser fluence, then at steady-state eq 4 reduces to eq 5. Equation 5 implies that the

$$-d \ln (1 - F_D)/dt = k_1^{ss} = \sigma_{ss}\Phi \qquad (5)$$

slope of the *linear portion* of a plot of $-\ln (1 - F_D)$ vs. laser fluence can be used to obtain the phenomenological steady-state cross section, σ_{ss}, by dividing k_1^{ss} by the photon flux, Φ.

Although eq 5 was derived by assuming a laser pulse of constant intensity and variable length, model calculations show that k_1^{ss} is often insensitive to intensity.[26] Thus, meaningful values of σ_{ss} can be obtained from plots of $-\ln (1 - F_D)$ vs. fluence regardless of whether the fluence is changed by varying the irradiation period at fixed intensity as is done in the continuous-wave laser experiments or the fluence is changed by changing the intensity of a fixed length irregularily shaped TEA laser pulse as is done in our pulsed laser experiments.

While model calculations for some neutral systems suggest that steady state is often not reached until 20–40% of the sample has decomposed,[25,26] this value should depend on the particular system under consideration. Figure 5 demonstrates that for $[(C_2H_5)_2O]_2H^+$ the plot of $-\ln (1 - F_D)$ vs. fluence is linear to the smallest dissociation yield we can measure. Figure 5 also demonstrates that there is no measurable intensity effect on σ_{ss} for $[(C_2H_5)_2O]_2H^+$ when the laser pulse is shortened from 3 μs to 200 ns, corresponding to 1 order of magnitude change in average intensity and a factor of 2 change in peak intensity. Figure 7 demonstrates that $C_3F_6^+$ exhibits the more usual shape[28] for a plot of $-\ln (1 - F_D)$ vs. fluence, showing a nonlinear portion characteristic of an induction period (open symbols) followed by linear behavior (filled symbols). The continuous-wave data of Beauchamp et al.[10-14] also generally exhibit the expected behavior of an induction period followed by steady-state dissociation which in their case is observed directly as an exponential decay of reactant ion signal with irradiation time.

The principal advantage in plotting fluence dependence data in the manner discussed above is that the data can be characterized by a single parameter, σ_{ss}, which can then be used to compare the pulsed laser and continuous-wave laser results. Moreover, photophysical information can, in principle, be obtained by noting deviations in the shape of such plots from the normal behavior.[1,28]

B. $[(C_2H_5)_2O]_2H^+$. With use of eq 5, a steady-state photodissociation cross section can be calculated for $[(C_2H_5)_2O]_2H^+$ from the data in Figure 5. A linear least-squares fit to the data gives $\sigma_{ss} = 1 \times 10^{-19}$ cm^2. The x intercept determines a fluence threshold of 40 mJ cm^{-2}. On the basis of the model discussed above, however, it is possible that if our technique were capable of measuring smaller yields, the straight line in Figure 5 would be seen to curve and tend smoothly toward a lower fluence threshold. The x intercept in Figure 5 is perhaps more correctly interpreted as a measure of the induction period required before the onset of steady-state behavior. Solution of the master equation using smoothly varying absorption rate constants results in flluence plots with larger induction periods than we observe here. The source of the discrepancy between calculated and observed time to onnset of steady state is currently under active investigation.[29] In their continuous-wave laser study of $[(C_2H_5)_2O]_2H^+$, Beauchamp and co-workers find[10] an apparent cross section of 2×10^{-20} cm^2 and a fluence threshold of 300 mJ cm^{-2}. A possible origin of the discrepancy between these data is the 10^5–10^6 difference in intensity between the pulsed and continuous-wave laser sources. However, linear dependences of yield on fluence are obtained in both cases and neither experiment shows any measurable intensity effect on the yield over the ranges accessible to each experiment. These results suggest that no major difference in the photophysics of the activation process is occurring; i.e., the linear rate law model with intensity proportional single-photon absorption rate constants appears to be valid in both cases.

A more likely explanation for the cross section and fluence threshold differences may be found in relaxation effects. Because of the differences in the laser intensities, the time scale for activation in the two experiments is drastically different. In the pulsed experiment, a typical rate constant, k_{ij}, for pumping from level i to level j (given by $\sigma_{ij}\Phi$, where σ_{ij} is a one-photon IR

(26) Quack, M. *J. Chem. Phys.* **1979**, *70*, 1069.
(27) Quack, M. *Ber. Bunsenges. Phys. Chem.* **1979**, *83*, 1287.
(28) Quack, M.; Humbert, P.; van den Bergh, H. *J. Chem. Phys.* **1980**, *73*, 247 and references therein.
(29) This discrepancy has been noted by Dr. A. C. Baldwin (S.R.l. International), see also: Troe, J. *J. Chem. Phys.* **1980**, *73*, 3205.

Photochemistry of [(C₂H₅)₂O]₂H⁺ and C₃F₆⁺

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absorption cross section and Φ is the photon flux) is 1×10^7 s^{-1} when a reasonable value of $\sigma_{ij} = 1 \times 10^{-19}$ cm^2 is used and Φ is the appropriate value of 10^{26} photons cm^{-2} s^{-1}. The unimolecular decomposition rate must be comparable to this (at least during the laser pulse), or the ion will simply absorb more photons until the discussion rate becomes comparable. This suggests that the entire activation and dissociation process using pulsed laser excitation is complete on a submillisecond time scale. This time is much shorter than the average time between ion–molecule collisions and spontaneous IR emission lifetimes. In the case of low-power excitation, the activation process is comparable to or slower than the time between ion–molecule collisions and of the same order of magnitude as IR radiative lifetimes. In their data analysis,[11,13] Beauchamp and co-workers account for collisional effects by extrapolating their data to low pressure, which they define as the pressure at which the time between collisions is long compared to the induction period they observe before any dissociation takes place. If one views this induction period as the time required to reach steady state rather than the average time required for complete activation of an ion, then such an analysis does not necessarily remove collisional relaxation and/or spontaneous emission effects during laser pumping from the reported cross section and threshold values. Although we have not attempted a quantitative evaluation of such effects, it seems apparent that the qualitative effect of such processes will be to reduce the observed cross section and increase the fluence threshold compared to those obtained in a pulsed laser experiment. In spite of these small quantitative differences, the results show that the linear rate law model, predicting fluence rather than intensity dependent yields, is a good description of the IR photophysics of $[(C_2H_5)_2O]_2H^+$ over an intensity range of 6 orders of magnitude.

One further comparison between the two activation techniques deserves comment. If the unimolecular rate constant for decomposition of the proton-bound dimer is estimated as a function of internal energy by using quantum RRK theory,[30] assuming a mean vibrational frequency of 1000 cm^{-1} and an A factor of 10^{16}, the criterion that decomposition be faster than further photon absorption is not fulfilled until the internal energy reaches 46 kcal mol^{-1} when pulsed excitation is used. This is in contrast to the result for continuous-wave excitation which indicates that dissociation is already rapid compared to further photon absorption at 31 kcal mol^{-1}. Thus the average energy of ions decomposing as a result of pulsed excitation is estimated to be 15 kcal mol^{-1} greater than that of ions decomposing as a result of continuous-wave excitation. For species with more than one unimolecular decomposition channel these considerations suggest that chemically distinct products may sometimes result from the two different activation techniques.[31]

C. C₃F₆⁺. The steady-state cross sections for pulsed IR photodissociation of $C_6F_6^+$, calculated from eq 9 by using data such as that shown in Figure 7, are as follows [frequency in cm^{-1} (σ_{ss} $\times 10^{20}$ cm^2)]: 951.2 (0); 966.2 (0); 981.0 (0); 985.5 (0); 1033.5 (1.54 ± 0.1); 1041.2 (2.27 ± 0.1); 1045.0 (3.59 ± 0.1); 1046.8 (3.04 ± 0.3); 1048.6 (4.48 ± 0.5); 1050.4 (3.80 ± 0.4); 1052.1 (5.08 ± 0.6); 1054.0 (4.74 ± 0.2); 1055.6 (4.30 ± 0.4); 1057.3 (4.14 ± 0.2); 1071.9 (2.32 ± 0.2) (errors quoted are standard deviations). All variable fluence plots were linear above 20% of decomposition. Points below that value tend smoothly toward the origin and were not included in the least-squares treatment.

The average fluence threshold, determined as for $[(C_2H_5)_2O]_2H^+$, lies around 500 mJ cm^{-2} and is about 10 times larger than that for $[(C_2H_5)_2O]_2H^+$. This is not surprising since, if the single-photon absorption cross sections are comparable, one would expect a longer induction period prior to the onset of steady state for a system with a higher dissociation threshold. Again the cross sections observed in the pulsed laser experiment are about 1 order of magnitude larger than those observed by using con-

tinuous-wave excitation, and again the most plausible explanation for this appears to be collisional and radiative relaxation in the continuous-wave experiment.

An interesting feature of the pulsed photodissociation spectrum shown in Figure 6 is a blue shift of the maximum with respect to the continuous-wave spectra. The value of this shift is 6–10 cm^{-1} depending on the electron energy at which the ions were formed in the continuous-wave experiment. There appears to be little if any power broadening. In order to explain the spectral shift, we note that the photodissociation maximum for SF$_6$ is red shifted by 7 cm^{-1} with respect to the Q branch maximum of the ν_3 mode in the low-power IR absorption spectrum.[32] The position of the photodissociation maximum depends both on pressure and laser intensity—higher pressure or lower intensity cause an increased red shift.[33] A red shift in the photodissociation spectrum is an expected consequence of anharmonic shifts in the combination bands associated with IR absorption from levels in the quasi-continuum. The absorption should be increasingly red shifted with increasing level, and the phenomenological cross-section maximum for IR multiphoton dissociation should occur at a frequency which optimizes the overall pumping, trading off the resonant ground-state absorption and resonant population against the red-shifted upper level pumping. Because only some rotational levels of the ground-state population may be pumped, rotational hole burning may play an important role in determining the photodissociation maximum. Collisions during the laser pulse will repopulate depleted rotational levels and thus allow a larger fraction of the ground state to be accessed. Since resonant pumping from the ground state is less critical, this in turn will shift the photodissociation maximum further to the red. Thus, compared to the continuous-wave results the observation of a blue shift in the pulsed experiment is consistent with other experimental results. This suggests that the maximum in the 0–1 (ground-state) absorption of C$_3$F$_6^+$ lies to the *blue* of our pulsed experiment maximum and that the observed agreement[12] between the continuous-wave laser photodissociation maximum with an absorption band of neutral C$_3$F$_6$ may be coincidental. Simple MO considerations suggest that as a result of changes in the bond orders on ionization of C$_3$F$_6$ the maximum for this band, which is a CF$_3$ group stretching motion, should be blue shifted in the ion relative to the neutral.[34] The small blue shift observed in the 70-eV continuous-wave spectrum is not fully understood.

Conclusions

We have shown here that pulsed ICR spectrometry is a useful tool for studying the infrared photochemistry of gas-phase ions. When a pulsed CO$_2$ laser is employed as the excitation source, collision-free photodissociation processes can be studied. The IR photochemistry of two ions, $[(C_2H_5)_2O]_2H^+$ and C$_3$F$_6^+$, is reported. In both cases, dissociation yields near unity are obtained at fluences less than 1–2 J/cm^{-2}. The results reported here are compared with those obtained by using continuous-wave irradiation and indicate that collisional and radiative processes may complicate the interpretation of the results of the cw experiments. Moreover, the two activation methods may lead to somewhat different photodissociation spectra, as was found with C$_3$F$_6^+$. Finally, a simple kinetic model for photodissociation induced by sequential IR multiphoton absorption is discussed. This model indicates that the average internal energy of a decomposing ion is typically larger when a pulsed, rather than continuous-wave, laser is used as the excitation source.

(30) Robinson, P. J.; Holbrook, K. A. "Unimolecular Reactions"; Wiley-Interscience: New York, 1972.

(31) Rosenfeld, R. N.; Brauman, J. I.; Barker, J. R.; Golden, D. M. *J. Am. Chem. Soc.* **1977**, *99*, 8063.

(32) Ambartzumian, R. V.; Letokhov, V. S. In "Chemical and Biochemical Applications of Lasers"; Moore, C. B. Ed.; Academic Press: New York, 1977; Vol. III, p 167.

(33) Gower, M. C.; Dillman, K. W. *Opt. Commun.* **1980**, *20*, 123.

(34) **Note Added in Proof:** Kelsall and Andrews have recently reported the IR absorption spectrum of C$_3$F$_6^+$ isolated in rare gas matrices (Kelsall, B. J.; Andrews, L. *J. Phys. Chem.* **1981**, *85*, 1288). They find that the the absorption band of neutral C$_3$F$_6$ (1033 cm^{-1} matrix, 1037 cm^{-1} gas phase) is blue shifted to 1062 cm^{-1} for the C$_3$F$_6^+$ ion. This observation is in complete agreement with our discussion of the shift in λ_{max} in the continuous wave and pulsed IR multiphoton dissociation spectra of C$_3$F$_6^+$.

Infrared Multiphoton Dissociation of the Methanol Solvate of the Fluoride Ion, CH_3OHF^-

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Abstract: The infrared multiphoton dissociation of the methanol solvate of the fluoride ion, CH_3OHF^-, has been studied under collisionless conditions using pulsed ion cyclotron resonance spectroscopy in conjunction with a pulsed TEA CO_2 laser. Photodissociation spectra and fluence dependences for both chemically activated and collisionally relaxed CH_3OHF^- as well as an estimate of the number of ion–molecule collisions required to relax the chemically activated ion are presented. The data suggest that 40–80 ion–molecule collisions are required to relax excess vibrational excitation in the ion and that a species which is estimated to be in the vibrational quasi-continuum can retain structured features in its infrared absorption spectrum.

The activation of gas phase ions via infrared (IR) multiphoton absorption can, as in the case of neutral molecules, result in collision-free photodissociation.[1] This technique provides a novel and useful method for studying the dynamics of unimolecular ion decomposition and permits the vibrational spectroscopy of ions to be investigated in the absence of solvent and counterions. We have recently demonstrated that the IR multiphoton dissociation of gas-phase ions can be useful in studying the collisional relaxation of internal energy in vibrationally excited ions,[2,3] and we have shown that the dependence of the IR photodissociation yield on laser fluence can serve as a probe of some important aspects of the photophysics of IR multiphoton absorption.[1,4] In the case of the ion CH_3OHF^-, our results showed[4] that structured absorption features are found in the rovibrational spectrum even when excess vibrational energy is present in the ion. This paper provides a detailed discussion of our studies of the IR photodissociation of CH_3OHF^-.

The photodissociation of gas-phase ions induced by single UV–visible photon absorption has been studied by using ion beam and trapped ion techniques.[5] Both methods provide information on the electronic spectroscopy of ions, assuming that the quantum yield for photodissociation is independent of irradiation wavelength. The use of lasers as the excitation source permits high-resolution spectroscopic data to be obtained from such experiments.[6] In cases where the dissociation threshold exceeds the energy of a single photon, dissociation due to two-photon absorption,[7] and more recently four-photon absorption,[8] has been observed. Two-photon activation occurs via a sequential absorption process proceeding through a long-lived intermediate state generated after one photon has been absorbed. Ion–molecule collisions are observed to reduce the photodissociation rate by quenching the intermediate.[9]

Beauchamp and co-workers have demonstrated that ion photodissociation can be induced by sequential IR multiphoton absorption of tens of photons when a continuous-wave CO_2 laser is used as the excitation source.[10–13]

Most studies of IR multiphoton dissociation reported to date involve the irradiation of neutral molecules with the output of a pulsed TEA CO_2 laser.[14–16] These studies are generally interpreted in terms of a model for molecular rovibrational level structure similar to that shown in Figure 1. At low energies (the discrete level regime) the number of photons absorbed by a molecule may be sensitive to irradiation wavelength and laser intensity. At sufficiently high internal energies, the spacing between rovibrational energy levels is less than or equal to the laser bandwidth. This condition is usually used to define the quasi-continuum.[14a] It has been suggested that absorption in this regime is not strongly dependent on the laser wavelength and that photon absorption in the quasi-continuum depends primarily on laser fluence (integrated intensity) but is independent of laser intensity.[14b] This model provides a useful starting point in characterizing some of the photophysical details of IR multiphoton absorption, but important questions remain beyond the scope of this simple scheme. For example, what role do rotational selection rules play in vibrational transitions in the discrete level regime and in the quasi-continuum? Do all rovibrational transitions in the quasi-continuum have equal oscillator strengths, or does the absorption

(1) Jasinski, J. M.; Rosenfeld, R. N.; Meyer, F. K.; Brauman, J. I. *J. Am. Chem. Soc.*, preceding paper in this issue.

(2) Rosenfeld, R. N.; Jasinski, J. M.; Brauman, J. I. *J. Am. Chem. Soc.* **1979**, *101*, 3999.

(3) Jasinski, J. M.; Brauman, J. I. *J. Chem. Phys.* **1980**, *73*, 6191.

(4) Rosenfeld, R. N.; Jasinski, J. M.; Brauman, J. I. *Chem. Phys. Lett.* **1980**, *71*, 400.

(5) Dunbar, R. C. In "Gas Phase Ion Chemistry"; Bowers, M. T., Ed.; Academic Press: New York, 1979; Vol. 2, p 181.

(6) Dunbar, R. C.; Teng, H. H. *J. Am. Chem. Soc.* **1978**, *100*, 2279.

(7) Freiser, B. S.; Beauchamp, J. L. *Chem. Phys. Lett.* **1975**, *35*, 35.

(8) Kim, M. S.; Dunbar, R. C. *J. Chem. Phys.* **1980**, *72*, 4405.

(9) Kim, M. S.; Dunbar, R. C. *Chem. Phys. Lett.* **1979**, *60*, 247.

(10) Woodin, R. L.; Bomse, D. S.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1978**, *100*, 3248.

(11) Bomse, D. S.; Woodin, R. L.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1979**, *101*, 5503.

(12) Woodin, R. L.; Bomse, D. S.; Beauchamp, J. L. *Chem. Phys. Lett.* **1979**, *63*, 630.

(13) Woodin, R. L.; Bomse, D. S.; Beauchamp, J. L. In "Chemical and Biochemical Applications of Lasers"; Moore, C. B., Ed.; Academic Press: New York, 1979; Vol. 4, p 355.

(14) (a) Ambartzumian, R. V.; Letokhov, V. S. In "Chemical and Biochemical Applications of Lasers"; Moore, C. B., Ed.; Academic Press: New York, 1977; Vol. 3, p 167. (b) Bloembergen, N.; Yablonovitch, E. *Phys. Today* **1978** (May), 23.

(15) Cantrell, C. D.; Freund, S. M.; Lyman, J. L. In "Laser Handbook"; Stitch, M. L.; Ed.; North-Holland Publishing Co.: Amsterdam, 1979; Vol. 3, p 485.

(16) Schulz, P. A.; Sudbo, Aa.; Krajnovich, D. S.; Kwok, H. S.; Shen, Y. R.; Lee, Y. T. *Annu. Rev. Phys. Chem.* **1979**, *30*, 379.