

Efficient multiphoton dissociation of CF_3I^+ in the metastable $\tilde{X}^2E_{1/2}$ excited state using cw infrared laser radiation

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Evidence for the multiphoton dissociation of an electronic metastable state of CF_3I^+ with CO_2 laser radiation is presented. Only those ions possessing sufficient internal excitation before irradiation can be dissociated. Photodissociation results primarily from resonant absorption by the ν_1 vibrational mode of CF_3I^+ in the higher of the two, spin-orbit levels of the ground electronic state $\tilde{X}^2E_{1/2}$. Only the lowest energy decomposition channel is observed; this yields CF_3^+ and I. Spin-orbit and vibrational relaxation compete with photodissociation. At CF_3I pressures below 2×10^{-7} Torr, the collisional relaxation rate is proportional to CF_3I pressure $k_c = (3.1 \pm 0.4) \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$ with a zero pressure rate of $11.3 \pm 1.3 \text{ sec}^{-1}$. The latter rate sets an upper limit on the spin-orbit relaxation rate. The photodissociation probability varies with laser frequency, exhibiting a broad, structureless peak near 960 cm^{-1} . The initial photodissociation rate is proportional to laser irradiance $k_D = 0.80 \pm 0.08 \text{ sec}^{-1} \text{ W cm}^{-2}$. The photoproducts and laser frequency dependence are the same using either cw or pulsed irradiation. Ions were exposed to irradiances up to 120 W cm^{-2} cw and fluences up to 1.6 J cm^{-2} pulsed. Ion cyclotron resonance (ICR) techniques were used to store and detect the ions.

I. INTRODUCTION

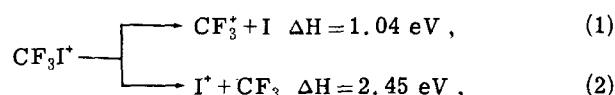
The combination of ion cyclotron resonance (ICR) and laser techniques has proved to be an effective means of studying multiphoton dissociation (MPD) of molecular ions. Both cw¹ and pulsed² lasers have been used. With the very low operating pressures used in ICR, pulsed lasers make possible the study of MPD under truly collisionless conditions; cw lasers can be used to study photodissociation kinetics and collisional effects. In the present study, both pulsed and cw CO_2 lasers are used to investigate MPD of the CF_3I molecular ion.

Until this study, molecules which have been dissociated using low power cw CO_2 lasers fell into two categories: (1) molecules with at least one weak bond, such as the van der Waals molecule $(\text{C}_2\text{H}_4)_2$ ³, and (2) large molecules such as $[(\text{C}_2\text{H}_5)_2\text{O}]_2\text{H}^+$ ⁴ which are in or near the vibrational quasi-continuum before laser excitation. By contrast, the present work is aimed at understanding the MPD of "small" molecular ions which have bond strengths greater than van der Waals molecules and which are further from the quasicontinuum than the large molecules previously studied. A survey of possible candidates for study led to the expectation that CF_3I^+ would conform to these criteria. Preliminary experiments were surprisingly successful, revealing that up to 60% of the CF_3I^+ ion population formed by electron impact can be efficiently dissociated with low-power CO_2 laser radiation. Further, the MPD studies of neutral CF_3I ^{5,6} provide a basis for comparison with the present results.

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For ground state ions the maximum number of photons required for dissociation is set by the dissociation energy of the lowest energy fragmentation channel.⁴ For CF_3I^+ , breaking the C–I bond,



gives the two lowest energy channels as determined from available thermochemical data for processes (1)⁷ and (2).⁸

The lowest energy ionization process for CF_3I involves removal of an electron from one of the nonbonding iodine p orbitals. As a result the ground state of CF_3I^+ is split into two, doubly degenerate spin-orbit doublets $\tilde{X}^2E_{3/2}$ and $\tilde{X}^2E_{1/2}$. These are clearly revealed in the photoelectron spectrum of CF_3I ^{9,10} as shown in Fig. 1. The energy required to produce $\text{CF}_3\text{I}^+(\tilde{X}^2E_{3/2})$ from neutral CF_3I is 10.29 eV, and 10.91 eV is required for $\text{CF}_3\text{I}^+(\tilde{X}^2E_{1/2})$.¹¹ These energies and the energy of process (1) are shown in Fig. 1. All of the $\tilde{X}^2E_{3/2}$ and part of the $\tilde{X}^2E_{1/2}$ Franck-Condon envelopes are at energies below the lowest energy fragmentation process. Thus, the CF_3I^+ population which survives electron impact and fragmentation comprises primarily the $\tilde{X}^2E_{1/2}$ and $\tilde{X}^2E_{3/2}$ states. That these two states have the same degeneracy and similar intensities in the photoelectron spectrum of CF_3I suggests that CF_3I^+ produced by electron impact populates $\tilde{X}^2E_{1/2}$ and $\tilde{X}^2E_{3/2}$ equally. Like CF_3I^+ , the ground state of I is split by strong spin-orbit coupling, into the $^2P_{3/2}$ state and, at 0.94 eV higher energy, the $^2P_{1/2}$ state. Thus the question arises as to the spin-orbit state of I produced from photodissociation of

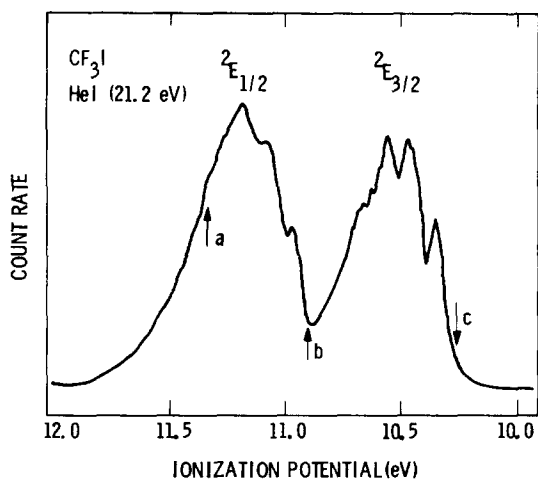


FIG. 1. Photoelectron spectrum of CF_3I^{11} showing the two lowest energy bands $\tilde{X}^2E_{3/2}$ and $\tilde{X}^2E_{1/2}$. (a) Thermodynamic dissociation limit (11.36 eV), (b) $\tilde{X}^2E_{1/2}$ adiabatic ionization potential (10.91 eV). (c) $\tilde{X}^2E_{3/2}$ adiabatic ionization potential (10.32 eV).

CF_3I^+ . Using state symmetries, the noncrossing rule, and assuming C_{3v} symmetry is preserved, we find that both $\text{CF}_3\text{I}^+(\tilde{X}^2E_{3/2})$ and $(\tilde{X}^2E_{1/2})$ correlate to the products $\text{CF}_3^+(^1A_1) + \text{I}(^2P_{3/2})$. A similar result was reported for CH_3I^+ dissociation.¹²

The lifetime of the $\tilde{X}^2E_{1/2}$ state is subject to speculation. In the absence of collisions two possible relaxation mechanisms are radiationless internal conversion or radiative transition, probably to low vibrational levels of $\tilde{X}^2E_{3/2}$. Although the radiative transition is dipole allowed by symmetry, it involves a change in only the j quantum number of an electron principally localized in the $5p$ nonbonding orbital of I. In this respect it is similar to the $5^2P_{1/2} \rightarrow 5^2P_{3/2}$ transitions in I and Xe^+ , which are dipole forbidden. Thus the spontaneous emission rate for $\text{CF}_3\text{I}^+(\tilde{X}^2E_{1/2})$ might be close to those of $\text{I}(^2P_{1/2})$ and $\text{Xe}^+(^2P_{1/2})$, which are 9.3 and 18 sec^{-1} ,^{13,14} respectively. Further indication of the metastability of $\text{CF}_3\text{I}^+(\tilde{X}^2E_{1/2})$ is the observed metastability of $\text{CH}_3\text{I}^+(\tilde{X}^2E_{1/2})$ in the experiments of McGilvery and Morrison.¹⁵ Thus, based on the expected lifetime and population of $\text{CF}_3\text{I}^+(\tilde{X}^2E_{1/2})$, observing MPD of both $\tilde{X}^2E_{1/2}$ and $\tilde{X}^2E_{3/2}$ by laser-ICR techniques appears possible. For $\tilde{X}^2E_{1/2}$, five CO_2 laser photons are required to reach the energy of process (1); ten photons are required for $\tilde{X}^2E_{3/2}$. Clearly, fewer photons are required if CF_3I^+ is vibrationally excited before laser irradiation.¹⁶

From the frequency dependence of MPD it is often possible to identify the vibrational modes which absorb radiation early in the dissociation process. For neutral CF_3I , photodissociation occurs via the resonant absorption of CO_2 laser radiation by the ν_1 mode¹⁷ at frequencies close to the small signal absorption peak at 1076 cm^{-1} .¹⁸ In the ion, estimates of the ν_1 frequency obtained from photoelectron spectra give 1090 cm^{-1} ⁹ for $\tilde{X}^2E_{3/2}$ and 940 cm^{-1} ¹¹ for $\tilde{X}^2E_{1/2}$. Similar values are obtained from the vibrational spacings in the Rydberg spectra of CF_3I , which are closely related to the vibrational frequencies of the ion. Sutcliffe¹⁹ first reported

the band assignments and vibrational analysis of CF_3I Rydberg spectra. Subsequently Robin²⁰ reassigned the bands to obtain more consistent term values. Using the vibrational analysis of Sutcliffe and the band assignment of Robin, the lowest energy band which correlates to the $\tilde{X}^2E_{1/2}$ dissociation limit gives 970 cm^{-1} for ν_1 . Thus, MPD of CF_3I^+ involving the ν_1 mode is expected to occur around 950 cm^{-1} for $\tilde{X}^2E_{1/2}$ and 1090 cm^{-1} for $\tilde{X}^2E_{3/2}$.

Recently, the photodissociation of CF_3I^+ with low power cw CO_2 laser radiation in a fast (2–5 keV) ion beam was reported.²¹ In these experiments CF_3I^+ was produced by electron impact, and a small fraction of the total CF_3I^+ , presumably vibrationally hot, was photodissociated by a one-photon process. The yield of CF_3^+ , the only photoproduct ion, showed a peak at 947 cm^{-1} and a much less intense peak at 1080 cm^{-1} . No mention was made of the role of $\text{CF}_3\text{I}^+(\tilde{X}^2E_{1/2})$ in the photodissociation. These results are discussed further below in comparison with the present results.

II. EXPERIMENTAL

The instrument used in this study has been described in detail in the literature.²² The ICR spectrometer was built in the Caltech shops and is of standard design with a variable 23.4 kG electromagnet and marginal oscillator detector. Approximately 10^5 ions, formed by electron impact, are stored in crossed electric and magnetic fields for up to 5 sec, then mass-analyzed. Pressures of the neutral gases are varied from 10^{-8} to 10^{-6} Torr, as measured by a Schulz-Phelps type ionization gauge. The ionization gauge is calibrated against a MKS Baratron Model 90H1-E capacitance manometer. Absolute pressure measurements are accurate to $\pm 20\%$; pressure ratios are somewhat more accurate.

Either an Apollo 550 A line-tunable cw CO_2 laser or a Tachisto 215 G line tunable CO_2 TEA laser is used as the radiation source. The laser beam is directed through a 92% transmittance mesh into the ICR cell and reflected back by a mirror finish on the back source plate. Assuming the source plate to be 100% reflective, the beam irradiance inside the cell is 1.84 the incident irradiance. Both the cw and pulsed (operated TEM_{00}) laser beam intensity profiles are nearly Gaussian (FWHM = 6 mm). For the cw laser, reported irradiances are calculated by dividing the total beam power in the cell by the area of the 6 mm diam beam. Thus, the irradiance (Wcm^{-2}) to which the ions are exposed is 6.51 times the total power (W) of the incident laser beam. The fluences (Jcm^{-2}) to which the ions are exposed by the pulsed laser are calculated in a similar way. Both laser beams are used unfocused so that the ions are uniformly irradiated. The ions can be exposed to irradiances up to 120 Wcm^{-2} or fluences up to 1.6 Jcm^{-2} TEM_{00} . Irradiation of the ions with the cw laser is controlled by an Uniblitz Model 255LOA14 \times 5 mechanical shutter having a 5 msec opening time. The effect of the laser radiation on the ion signal intensity is measured by a dual-channel box car integrator which time averages the ratio of the signal intensity with the laser on, I, and off, I_0 . The frequency of the laser radiation is measured with an Optical Engineering Model 16A spec-

trum analyzer. Additional experimental details are given elsewhere.⁴ For the experiments requiring visible laser radiation, a coherent radiation CR-2000K cw Krypton ion laser was used. The beam diameter is 2 mm, and the effective irradiance was calculated in the same manner as for the cw CO_2 laser.

III. RESULTS

A. CO_2 cw laser photochemistry

As reported previously,⁷ CF_3I^+ , CF_2I^+ , and CF_3^+ are the major ions produced by electron impact on CF_3I . Only the concentrations of CF_3I^+ , CF_2I^+ , and CF_3^+ are affected by CO_2 laser radiation at CF_3I pressures below 10^{-6} Torr. CF_3I^+ decreases, with a concomitant increase in CF_2I^+ and CF_3^+ . Ion cyclotron double resonance experiments show the increase in CF_2I^+ is due entirely to the increase in CF_3^+ via its reaction with neutral CF_3I . This firmly establishes CF_3^+ as the exclusive photoproduct, process (1). The reaction of CF_3^+ to produce CF_2I^+ is one of three processes which occur in the ion-molecule chemistry of CF_3I at low pressure.⁷ The other two reactions involve I^+ , which reacts with CF_3I to produce CF_3^+ and CF_3I^+ .⁷ Since CF_3^+ and CF_3I^+ were used to monitor photodissociation, care was taken to reduce the concentration of I^+ by either double resonance ejection or operating with electron energies below 13 eV.

The extent of photodissociation varies with laser frequency as shown in Fig. 2. These results were obtained by monitoring the ratio of the CF_3I^+ ion signals for the laser on and laser off (I/I_0) with 80 W cm^{-2} irradiance and 500 msec exposure time at a series of laser lines. The photodissociation band (solid circles) peaks at 960 cm^{-1} , within the frequency region expected for the ν_1 absorption of $\text{CF}_3\text{I}^+(\bar{X}^2E_{1/2})$ and is about three times wider than the ν_1 absorption band of neutral CF_3I .²³ This

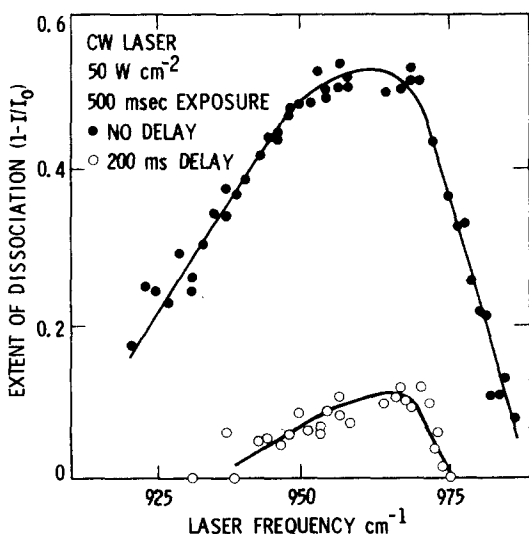


FIG. 2. Dependence of CF_3I^+ photodissociation on laser frequency using cw radiation. The extent of dissociation is monitored by CF_3I^+ signal intensity. Experimental conditions are: 5×10^{-6} Torr CF_3I pressure, 70 eV electron impact energy, 50 W cm^{-2} irradiance, 500 msec exposure time. Data are shown for no delay (\bullet) and 200 msec (\circ) delay between ion formation and irradiation.

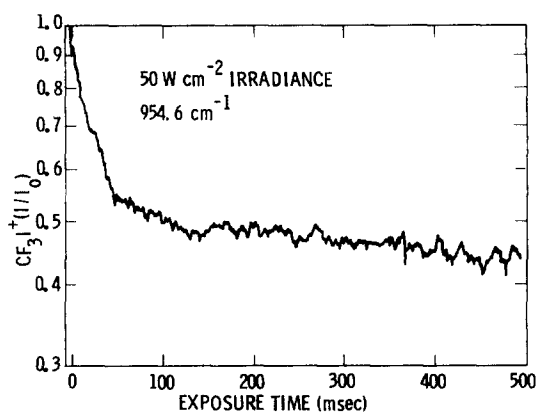


FIG. 3. Photodissociation kinetics of CF_3I^+ at 70 eV electron impact energy, 1.5×10^{-7} Torr CF_3I pressure and 50 W cm^{-2} laser irradiance at 954.6 cm^{-1} . The slope of the line at a given point gives the apparent photodissociation rate constant.

band is also 1.2 times wider and at 13 cm^{-1} higher energy than the same band previously reported for CF_3I^+ photodissociation.²¹ There is no detectable photodissociation in the $1030\text{--}1085 \text{ cm}^{-1}$ region where the ν_1 absorption of $\text{CF}_3\text{I}^+(\bar{X}^2E_{3/2})$ is expected to occur. The limits of detectability for CF_3I^+ loss in these experiments place an upper limit of 2% on the extent of dissociation in this frequency region. This is in agreement with the previous results²¹ for CF_3I^+ which showed photodissociation is 40 times more efficient near 940 cm^{-1} than near 1080 cm^{-1} . In the present case, a delay of 200 msec between ion formation and irradiation greatly reduces the extent of photodissociation but the laser frequency dependence is unchanged as shown by the open circles in Fig. 2.

Photodissociation kinetics were investigated by recording $\ln(I/I_0)$ for CF_3I^+ as a function of exposure time (Fig. 3). The photodissociation process does not follow simple first order kinetics. The initial rate is 30 sec^{-1} and drops to 0.2 sec^{-1} or less within 200 msec. This indicates the presence of at least two populations of CF_3I^+ , one which dissociates rapidly and another which dissociates more slowly or not at all. If the delay between CF_3I^+ formation and irradiation is sufficiently long (~ 300 msec) no photodissociation is observed. This suggests that only CF_3I^+ having sufficient internal energy before irradiation can be photodissociated (population 1). Evidence for an ion population stable with respect to dissociation (population 2) is given by the results shown in Fig. 4. Here, the fraction of CF_3I^+ which can be dissociated does not increase beyond a limiting value of 0.59 for irradiances in excess of 110 W cm^{-2} , indicating that population 1 and population 2 are approximately equal.

Even though the photodissociation kinetics cannot be characterized by a single rate constant, the initial rate (during the first 20 msec) has a linear dependence on irradiance as shown in Fig. 5. At a CF_3I pressure of 5×10^{-8} Torr, the irradiance dependent rate constant is $k_D = 0.80 \pm 0.08 \text{ sec}^{-1} (\text{W cm}^{-2})^{-1}$. This rate is weakly dependent on CF_3I pressure. Increasing the pressure by a factor of 20, from 5×10^{-8} to 1×10^{-6} Torr, reduces the rate by only a factor of 2.

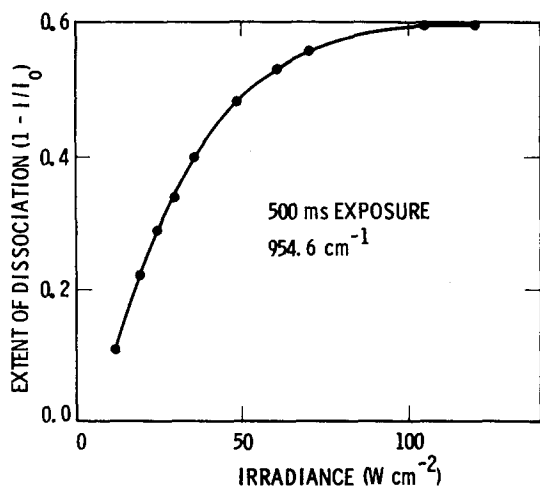


FIG. 4. Variation of the extent of dissociation on laser irradiance as monitored by the CF_3I^+ signal. Experimental conditions are: 70 eV electron energy, 6×10^{-8} Torr CF_3I pressure, 500 msec exposure time and 954.6 cm^{-1} laser frequency.

The influence of internal excitation of CF_3I^+ was investigated by measuring the maximum extent of dissociation for CF_3I^+ produced from various charge transfer agents. For CF_3I^+ produced by charge exchange with the molecular ion of perfluoropropylene $\text{C}_3\text{F}_6^+[\text{IP}(\text{C}_3\text{F}_6) = 10.3 \text{ eV}]$ the extent of dissociation drops by a factor of 3. No reduction is observed for CF_3I^+ produced from charge exchange with $\text{Xe}^+[\text{IP}(\text{Xe}) = 12.13 \text{ eV}]$. These results are consistent with $\text{CF}_3\text{I}^+(\tilde{X}^2E_{1/2})$ having a more rapid photodissociation rate than $\text{CF}_3\text{I}^+(\tilde{X}^2E_{3/2})$ since less $\text{CF}_3\text{I}^+(\tilde{X}^2E_{1/2})$ is produced from C_3F_6^+ than Xe^+ .

Motivated by a recent study of Superrex and van der Berg,²⁴ we investigated the effect of the magnetic field on the extent of CF_3I^+ dissociation. They report that photodissociation of CF_2HCl is enhanced by an external magnetic field. In the case of CF_3I^+ the photodissociation rate changed by less than 5% with magnetic fields in range between 11.2 and 19.6 kG. Lower fields were not examined due to poor ion trapping.

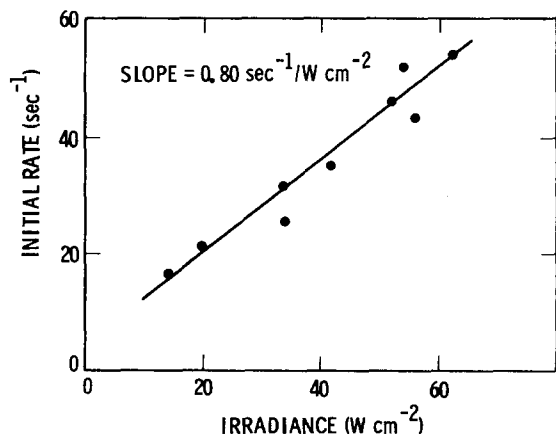


FIG. 5. Dependence of the initial CF_3I^+ photodissociation rate on laser irradiance at 954.6 cm^{-1} and 6.0×10^{-8} Torr CF_3I . The slope of the line gives $k_D = 0.80 \pm 0.06 \text{ sec}^{-2}$ for the irradiance dependent photodissociation rate constant.

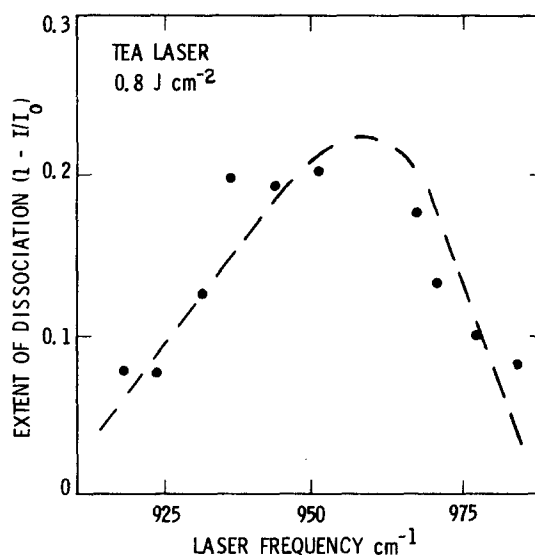


FIG. 6. Dependence of CF_3I^+ photodissociation on laser frequency using pulsed radiation. Extent of dissociation is calculated from the measured yield of CF_3^+ . Experimental conditions are 5×10^{-8} Torr CF_3I ; 1.0 J cm^{-2} , 40 nsec pulse. The broken line indicates the shape of the photodissociation band using cw radiation.

B. Pulsed CO_2 laser photochemistry

With pulsed CO_2 laser radiation, CF_3I^+ photochemistry occurs on a submicrosecond time scale. This permits the effects of laser irradiation to be detected before ion-molecule collisions can alter the results. Only the concentrations of CF_3I^+ and CF_3^+ are influenced by pulsed CO_2 radiation; as with cw radiation CF_3^+ is the exclusive photoproduct. The laser frequency dependence for pulsed and cw radiation are similar (Fig. 6). By contrast, however, the maximum extent of dissociation using a 1.6 J cm^{-2} , 40 nsec, pulse is 0.2 as compared with 0.6 for 110 W cm^{-2} , 0.5 sec exposure (55 J cm^{-2}) to cw radiation.

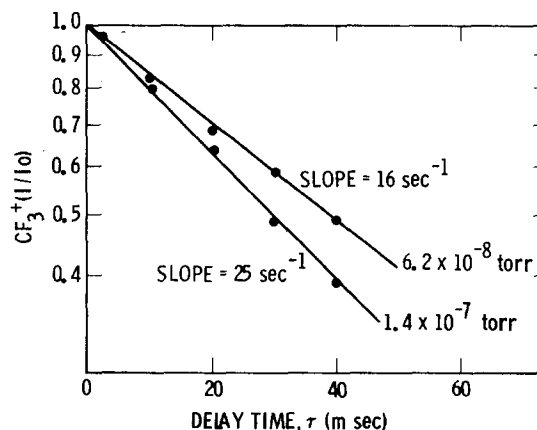


FIG. 7. Relaxation rate of CF_3I^+ at two different pressures as measured by CF_3^+ signal intensity. The delay time is the time between ion formation and irradiation. The slopes of the lines give the relaxation rates. Experimental conditions: 70 eV electron impact energy, CF_3I pressure as indicated, 1.6 J cm^{-2} , 40 nsec laser pulse at 952.9 cm^{-1} .

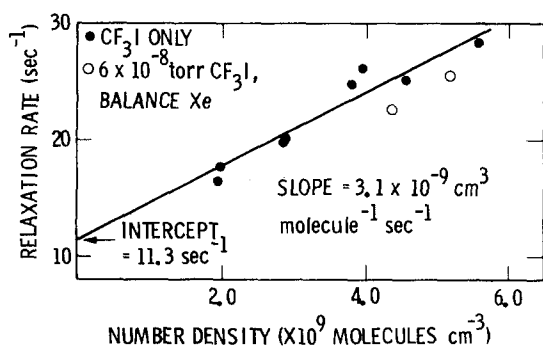


FIG. 8. Dependence of the CF_3I^+ relaxation rate on total pressure for CF_3I (●) and 6×10^{-8} Torr CF_3I with the balance Xe (○). The slope of the line gives a collisional relaxation rate constant of $3.1 \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$ and the intercept gives the zero-pressure relaxation rate constant of 11.3 sec^{-1} . Same experimental conditions as for Fig. 7.

As with cw irradiation only internally excited CF_3I^+ can be dissociated. As the delay between ion formation and pulsed laser irradiation increases the yield of CF_3^+ decreases. This is shown in Fig. 7 for two different CF_3I pressures. These results show that the relaxation of CF_3I^+ can be described by a pressure dependent, first-order rate constant k_r , which is linearly dependent on CF_3I pressure (Fig. 8). These data yield $k_r = 3.1 \pm 0.4 \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$ with a zero-pressure intercept of $11.3 \pm 1.3 \text{ sec}^{-1}$.

Using Xe as a buffer gas gives similar results. Adding up to 2×10^{-7} Torr Xe to 6×10^{-8} Torr CF_3I^+ gives $k_r = 2.5 \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$. Apparently Xe is nearly as effective as CF_3I in causing relaxation of CF_3I^+ .

C. Visible laser photochemistry

Attempts were made to cause single photon photodissociation of CF_3I^+ using visible laser radiation to promote CF_3I^+ from $\tilde{X}^2E_{3/2}$ or $\tilde{X}^2E_{1/2}$ to $\tilde{A}^2E_{1/2}$. The analogous transition in CH_3I^+ , $\tilde{X}^2E_{1/2}$ to $\tilde{A}^2E_{1/2}$, for example, leads to photodissociation.¹⁵ In CF_3I^+ the $\tilde{A}^2E_{1/2}$ state is 2.07 and 2.76 eV above the $\tilde{X}^2E_{1/2}$ and $\tilde{X}^2E_{3/2}$ states, respectively.⁹ Krypton ion laser radiation with photon energies (and laser irradiances) of 2.65 eV (19 Wcm^{-2}), 2.33 eV (71 Wcm^{-2}), 1.92 eV (95 Wcm^{-2}), and 1.83 eV (22 Wcm^{-2}) were used. No photodissociation was observed. These results place an upper limit of $5 \times 10^{-22} \text{ cm}^2$ on the photodissociation cross section at the photon energies mentioned. Simultaneously exposing CF_3I^+ to CO_2 and Kr laser radiation did not increase the extent of photodissociation beyond that observed for CO_2 radiation alone.

IV. DISCUSSION

The photodissociation of CF_3I^+ by infrared radiation clearly involves ions which are internally excited. Thus a detailed treatment of the photodissociation requires knowing the amount and distribution of internal energy and the mechanism by which it is lost by relaxation or gained by laser irradiation.

There are two possibilities for the initial state of the CF_3I^+ fraction which undergoes photodissociation. Either

it is (a) in the $\tilde{X}^2E_{3/2}$ state with up to 1.04 eV of vibrational energy or (b) it is in the $\tilde{X}^2E_{1/2}$ state with up to 0.45 eV of vibrational energy. Coggiola, Cosby, and Peterson advance possibility (a).²¹ However, the present results support (b) for the following reasons. The extent of photodissociation peaks around 960 cm^{-1} , near the 940 cm^{-1} range expected for the ν_1 mode of $\text{CF}_3\text{I}^+(\tilde{X}^2E_{1/2})$ and 130 cm^{-1} lower than the same transition for $\text{CF}_3\text{I}^+(\tilde{X}^2E_{3/2})$. This 130 cm^{-1} difference could be explained if the absorption is due to one of the other fundamental modes of CF_3I^+ . However all of the other modes are much further from the observed absorption than is the ν_1 mode as estimated from the absorption frequencies of CF_3I . It is possible but unlikely that the entire photodissociation band is due to a combination mode. Thus the 960 cm^{-1} peak is probably due to absorption by the ν_1 mode in $\text{CF}_3\text{I}^+(\tilde{X}^2E_{1/2})$ or by the same mode in $\text{CF}_3\text{I}^+(\tilde{X}^2E_{3/2})$, where the vibrational energy shifts the ν_1 frequency from 1090 cm^{-1} to 960 cm^{-1} via the anharmonicity of the modes. The latter explanation can be correct only if CF_3I^+ has enough vibrational energy and the anharmonicities are large enough to account for a 130 cm^{-1} shift. This shift can be estimated from the dissociation limit which sets an upper limit on the vibrational energy of 1.04 eV and the anharmonicities which can be obtained from published values²⁵ or estimated from combination spectra of CF_3I .¹⁸ Based on the population of the various vibrational modes and the first order anharmonicity constants, the average ν_1 transition frequency is expected to shift by no more than 50 cm^{-1} when CF_3I^+ has up to 1.04 eV of vibrational energy. This suggests that photodissociation does not involve the ν_1 mode of $\text{CF}_3\text{I}^+(\tilde{X}^2E_{3/2})$ but rather the ν_1 mode of $\text{CF}_3\text{I}^+(\tilde{X}^2E_{1/2})$. Further evidence for this is that the photodissociation peak is not observed to shift to higher frequency as a result of relaxation (Fig. 2). A small shift probably does occur, however, and is likely the reason for our results giving a peak 13 cm^{-1} higher than that previously reported where CF_3I^+ was known to be within 0.12 eV of the dissociation limit. Further evidence for photodissociation of $\text{CF}_3\text{I}^+(\tilde{X}^2E_{1/2})$ and not $\text{CF}_3\text{I}^+(\tilde{X}^2E_{3/2})$ is the reduced extent of dissociation of CF_3I^+ produced from a charge transfer agent which preferentially produces $\text{CF}_3\text{I}^+(\tilde{X}^2E_{3/2})$.

If photodissociation of $\text{CF}_3\text{I}^+(\tilde{X}^2E_{1/2})$ does indeed occur, then the zero-pressure relaxation rate of 11.3 sec^{-1} is an upper limit on the ground state spin-orbit relaxation rate. This value seems reasonable compared to the same rate for atomic iodine of 5.9 sec^{-1} . The rate for CF_3I^+ might be higher due to delocalization of the iodine $5p$ electrons. Countering this effect, however, is the smaller spin-orbit splitting in CF_3I^+ which would give a lower rate for CF_3I^+ than for I. A surprising result is the effectiveness of collisions in increasing the relaxation rate. The pressure dependent relaxation rate of $3.1 \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$ for CF_3I^+ is three times the ion-neutral collision rate calculated from ADO theory.²⁶ The relaxation rate is also large compared to resonant charge transfer rates.²⁷ This leaves collision induced radiative transition or collision induced crossing to the $\tilde{X}^2E_{3/2}$ state as possible relaxation mechanisms.

A remarkable aspect of CF_3I^+ photodissociation is

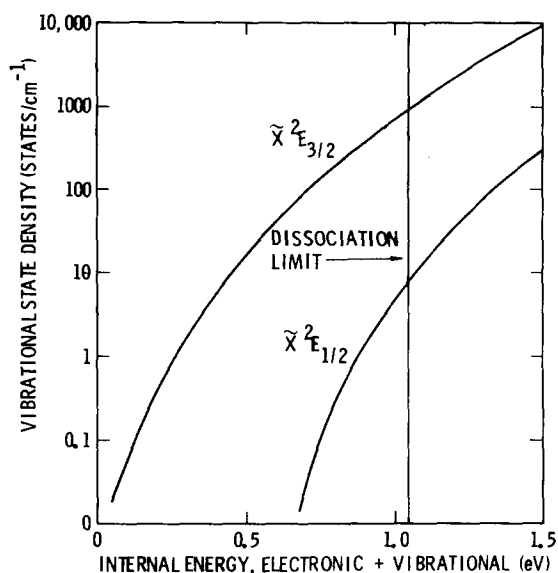


FIG. 9. Dependence of the density of vibrational states of CF_3I^+ on total internal energy, vibrational plus electronic. Data is based on the vibrational frequencies of CF_3I^{18} using the direct count method (Ref. 28). The enthalpy of Reaction (1) is taken as the dissociation limit.

that nearly 60% of the entire population can be photodissociated at a single frequency. The average density of vibrational states alone is not sufficient to account for this high yield. The energy at which the vibrational state density is equal to or greater than the laser bandwidth (50 MHz) occurs at a vibrational energy of 1.1 eV for $\tilde{X}^2E_{3/2}$, which is above the dissociation limit (Fig. 9). The situation is less favorable for $\tilde{X}^2E_{1/2}$. Thus, in terms of the average vibrational state density, efficient laser pumping is not expected to occur below the dissociation limit. A recent study,¹⁷ however, has shown that a single CO_2 laser line may be simultaneously resonant with the ν_1 mode and various combination modes of CF_3I . This was shown for five different CO_2 laser lines. Thus, even though the average vibrational state density may be low, the density of states in regions near integral multiples of the CO_2 laser frequency may be high enough for efficient photodissociation. This is probably true for CF_3I^+ also because of the similarity in vibrational frequencies. Other factors serving to increase the density of states are the coupling of the iodine nuclear spin angular momentum and the spin angular momentum of the iodine unpaired electron to the molecular rotational angular momentum. These couplings serve to split the rotational energy levels and can dramatically enhance the photodissociation, as was suggested for $\text{CF}_2\text{HCl}^{24}$ to explain magnetic field effects on dissociation probability.

What appears to be different about cw laser photodissociation of CF_3I^+ and perhaps other small ions under collisionless conditions, as compared to ions containing ten or more atoms, is the competition of rapid relaxation processes with photodissociation. Large molecules, in general, have many, low-frequency vibrational modes which have correspondingly low spontaneous emission rates. These modes serve as an intramolecular heat bath into which energy gained from absorption of laser

radiation can be accumulated until the dissociation limit is reached. Without many low-frequency modes, energy storage in small molecules is not efficient on the time scale of the ICR experiment, and, consequently, relaxation competes favorably with photodissociation as in the case of CF_3I^+ .

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