Efficient multiphoton dissociation of CF$_3$I$^+$ in the metastable $X^2E_{1/2}$ excited state using cw infrared laser radiation

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Evidence for the multiphoton dissociation of an electronic metastable state of CF$_3$I$^+$ 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 $v_1$ vibrational mode of CF$_3$I$^+$ in the higher of the two, spin–orbit levels of the ground electronic state $X^2E_{1/2}$. Only the lowest energy decomposition channel is observed; this yields CF$_3$ and I$^-$. Spin–orbit and vibrational relaxation compete with photodissociation. At CF$_3$I pressures below $2 \times 10^{-7}$ Torr, the collisional relaxation rate is proportional to CF$_3$I pressure $k_c = (3.1 \pm 0.4) \times 10^{-7}$ cm$^3$ molecule$^{-1}$ sec$^{-1}$ with a zero pressure rate of $1.13 \pm 1.3$ 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 $k_d = 0.80 \pm 0.08$ sec$^{-1}$/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 cw$^3$ and pulsed$^4$ 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 are 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$_3$I 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 (C$_2$H$_2$)$_2$I$^+$; and (2) large molecules such as [(C$_2$H$_4$)$_3$O]$_2$I$^+$ 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$_3$I$^+$ would conform to these criteria. Preliminary experiments were surprisingly successful, revealing that up to 60% of the CF$_3$I$^+$ ion population formed by electron impact can be efficiently dissociated with low-power CO$_2$ laser radiation. Further, the MPD studies of neutral CF$_3$I$^+$ provide a basis for comparison with the present results.

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$_3$I$^+$, breaking the C–I bond,

$$\text{CF}_3^+ + \text{I}^- \xrightarrow{\Delta H = 1.04 \text{ eV}} \text{CF}_3 + \text{I}^-$$

(1)

$$\text{CF}_3^+ + \text{CF}_3 \xrightarrow{\Delta H = 2.45 \text{ eV}}$$

(2)

gives the two lowest energy channels as determined from available thermochemical data for processes (1)$^5$ and (2).$^6$

The lowest energy ionization process for CF$_3$I involves removal of an electron from one of the nonbonding iodine $p$ orbitals. As a result the ground state of CF$_3$I$^+$ is split into two doubly degenerate spin–orbit doublets $X^2E_{3/2}$ and $X^2E_{1/2}$. These are clearly revealed in the photoelectron spectrum of CF$_3$I$^{13,14}$ as shown in Fig. 1. The energy required to produce CF$_3$I$(X^2E_{3/2})$ from neutral CF$_3$I is 10.29 eV, and 10.91 eV is required for CF$_3$I$(X^2E_{1/2})$. These energies and the energy of process (1) are shown in Fig. 1. All of the $X^2E_{3/2}$ and part of the $X^2E_{1/2}$ Franck-Condon envelopes are at energies below the lowest energy fragmentation process. Thus, the CF$_3$I$^+$ population which survives electron impact and fragmentation comprises primarily the $X^2E_{3/2}$ and $X^2E_{1/2}$ states. That these two states have the same degeneracy and similar intensities in the photoelectron spectrum of CF$_3$I suggests that CF$_3$I$^+$ produced by electron impact populates $X^2E_{1/2}$ and $X^2E_{3/2}$ equally. Like CF$_3$I$^+$, the ground state of I$^-$ is split by strong spin–orbit coupling, into the $^3P_{1/2}$ state and, at 0.94 eV higher energy, the $^3P_{3/2}$ state. Thus the question arises as to the spin–orbit state of I produced from photodissociation of
CF$_3$I$^*$. Using state symmetries, the noncrossing rule, and assuming C$_3v$ symmetry is preserved, we find that both CF$_3$I$^*(2E_{1/2})$ and (2E$_{1/2}$) correlate to the products CF$_3$I$^*(A_1) + $I(P$_{2/2}$). A similar result was reported for CH$_3$I dissociation. 12

The lifetime of the $X^2E_{1/2}$ 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 $X^2E_{3/2}$. 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 $5P_{3/2} - 5P_{3/2}$ transitions in I and Xe$^*$, which are dipole forbidden. Thus the spontaneous emission rate for CF$_3$I$^*(X^2E_{1/2})$ might be close to those of $I(P_{3/2})$ and Xe$^*(P_{3/2})$, which are 9.3 and 18 sec$^{-1}$, respectively. Further indication of the metastability of CF$_3$I$^*(X^2E_{1/2})$ is the observed metaatability of CH$_3$I$^*(X^2E_{1/2})$ in the experiments of McGilvery and Morrison. 15 Thus, based on the expected lifetime and population of CF$_3$I$^*(X^2E_{1/2})$, observing MPD of both $X^2E_{1/2}$ and $X^2E_{3/2}$ by laser-ICR techniques appears possible. For $X^2E_{1/2}$, five CO$_2$ laser photons are required to reach the energy of process (1); ten photons are required for $X^2E_{3/2}$. Clearly, fewer photons are required if CF$_3$I$^*$ 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$_3$I, photodissociation occurs via the resonant absorption of CO$_2$ laser radiation by the $v_1$ mode at frequencies close to the small signal absorption peak at 1076 cm$^{-1}$. 18 In the ion, estimates of the $v_1$ frequency obtained from photoelectron spectra give 1090 cm$^{-1}$ for $X^2E_{3/2}$ and 940 cm$^{-1}$ for $X^2E_{1/2}$. Similar values are obtained from the vibrational spacings in the Rydberg spectra of CF$_3$I, which are closely related to the vibrational frequencies of the ion. Sutcliffe 19 first reported the band assignments and vibrational analysis of CF$_3$I Rydberg spectra. Subsequently Robin 20 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 $X^2E_{1/2}$ dissociation limit gives 970 cm$^{-1}$ for $v_1$. Thus, MPD of CF$_3$I involving the $v_1$ mode is expected to occur around 950 cm$^{-1}$ for $X^2E_{1/2}$ and 1090 cm$^{-1}$ for $X^2E_{3/2}$.

Recently, the photodissociation of CF$_3$I with low power cw CO$_2$ laser radiation in a fast (2–5 keV) ion beam was reported. 21 In these experiments CF$_3$I was produced by electron impact, and a small fraction of the total CF$_3$I*, presumably vibrationally hot, was photodissociated by a one-photon process. The yield of CF$_3$I$^*$, the only photoproduction 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 CF$_3$I$^*(X^2E_{1/2})$ 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$^3$ ions, formed by electron impact, were stored in crossed electric and magnetic fields for up to 5 sec, then mass-analyzed. Pressures of the neutral gases were varied from 10$^{-9}$ to 10$^{-6}$ Torr, as measured by a Schultz–Phillips type ionization gauge. The ionization gauge is calibrated against a MKS Baratron Model 901H-1 capacitance manometer. Absolute pressure measurements are accurate to ±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 90% 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 diameter. Thus, the irradiance (W cm$^{-2}$) to which the ions are exposed is 6.51 times the total power (W) of the incident laser beam. The fluences (J cm$^{-2}$) 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 W cm$^{-2}$ or fluences up to 1.6 J cm$^{-2}$ TEM$_{00}$. Irradiation of the ions with the cw laser is controlled by an Uniblitz Model 255 LOA14×5 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$_{1}$, 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.\textsuperscript{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\textsubscript{2} laser.

III. RESULTS

A. CO\textsubscript{2} cw laser photochemistry

As reported previously,\textsuperscript{4} CF\textsubscript{3}I, CF\textsubscript{4}I, and CF\textsubscript{3}I
are the major ions produced by electron impact on CF\textsubscript{3}I. Only
the concentrations of CF\textsubscript{3}I, CF\textsubscript{4}I, and CF\textsubscript{3}I
are affected by CO\textsubscript{2} laser radiation at CF\textsubscript{3}I pressures below
10\textsuperscript{-4} Torr. CF\textsubscript{3}I decreases, with a concomitant increase
in CF\textsubscript{4}I and CF\textsubscript{3}I. Ion cyclotron double resonance ex-
periments show the increase in CF\textsubscript{4}I is due entirely to the
increase in CF\textsubscript{3}I via its reaction with neutral CF\textsubscript{3}I.
This firmly establishes CF\textsubscript{3}I as the exclusive photopro-
duct, process (1). The reaction of CF\textsubscript{3}I to produce CF\textsubscript{4}I
is one of three processes which occur in the ion–mole-
cule chemistry of CF\textsubscript{3}I at low pressure.\textsuperscript{4} The other two
reactions involve I, which reacts with CF\textsubscript{3}I to produce
CF\textsubscript{3}I and CF\textsubscript{3}I.\textsuperscript{7} Since CF\textsubscript{3}I and CF\textsubscript{3}I were used to moni-
tor photodissociation, care was taken to reduce the con-
centration of I by either double resonance ejection or
operating with electron energies below 13 eV.

The extent of photodissociation varies with laser fre-
quency as shown in Fig. 2. These results were obtained
by monitoring the ratio of the CF\textsubscript{4}I ion signals for the
laser on and laser off (I/I\textsubscript{0}) with 80 W cm\textsuperscript{-2} irradiance
and 500 msec exposure time at a series of laser lines.
The photodissociation band (solid circles) peaks at 960
cm\textsuperscript{-1}, within the frequency region expected for the \nu\textsubscript{1}
absorption of CF\textsubscript{4}I(X\textsuperscript{2}E\textsubscript{1}\textsubscript{2}) and is about three times
wider than the \nu\textsubscript{1} absorption band of neutral CF\textsubscript{3}I.\textsuperscript{23} This

![FIG. 2. Dependence of CF\textsubscript{3}I photodissociation on laser fre-
quency using cw radiation. The extent of dissociation is moni-
tored by CF\textsubscript{4}I signal intensity. Experimental conditions are:
5×10\textsuperscript{-4} Torr CF\textsubscript{3}I pressure, 70 eV electron impact energy,
50 W cm\textsuperscript{-2} irradiance, 500 msec exposure time. Data are
shown for no delay (*) and 200 msec delay (o) between ion for-
mation and irradiation.](https://jcp.aip.org/jcp/fig/fig2.jpg)

band is also 1.2 times wider and at 13 cm\textsuperscript{-1} higher ener-
gy than the same band previously reported for CF\textsubscript{3}I
photodissociation.\textsuperscript{24} There is no detectable photodissocia-
tion in the 1030–1085 cm\textsuperscript{-1} region where the \nu\textsubscript{1} ab-
sorption of CF\textsubscript{4}I(X\textsuperscript{2}E\textsubscript{1}\textsubscript{2}) is expected to occur.
The limits of detectability for CF\textsubscript{3}I 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 results\textsuperscript{24} for CF\textsubscript{3}I which showed photodissocia-
tion is 40 times more efficient near 940 cm\textsuperscript{-1} than near
1080 cm\textsuperscript{-1}. In the present case, a delay of 200 msec be-
between ion formation and irradiation greatly reduces the
extent of photodissociation but the laser frequency de-
pendence is unchanged as shown by the open circles in
Fig. 2.

Photodissociation kinetics were investigated by re-
ording ln(I/I\textsubscript{0}) for CF\textsubscript{3}I as a function of exposure time
(Fig. 3). The photodissociation process does not follow
simple first order kinetics. The initial rate is 30 sec\textsuperscript{-1}
and drops to 0.2 sec\textsuperscript{-1} or less within 200 msec. This
indicates the presence of at least two populations of
CF\textsubscript{3}I, one which dissociates rapidly and another which
dissociates more slowly or not at all. If the delay be-
tween CF\textsubscript{3}I formation and irradiation is sufficiently long
(>300 msec) no photodissociation is observed. This sug-
gests that only CF\textsubscript{3}I 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\textsubscript{3}I which can be dis-
sociated does not increase beyond a limiting value of
0.59 for irradiances in excess of 110 W cm\textsuperscript{-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\textsubscript{3}I pressure of
5×10\textsuperscript{-5} Torr, the irradiance dependent rate constant is
k\textsubscript{D} = 0.80±0.08 sec\textsuperscript{-1}(W cm\textsuperscript{-2})\textsuperscript{-1}. This rate is weakly de-
pendent on CF\textsubscript{3}I pressure. Increasing the pressure by a
factor of 20, from 5×10\textsuperscript{-8} to 1×10\textsuperscript{-5} Torr, reduces the
rate by only a factor of 2.

![FIG. 3. Photodissociation kinetics of CF\textsubscript{3}I at 70 eV electron
impact energy, 1.5×10\textsuperscript{-7} Torr CF\textsubscript{3}I pressure and 50 W cm\textsuperscript{-2}
laser irradiance at 945.6 cm\textsuperscript{-1}. The slope of the line at a given
point gives the apparent photodissociation rate constant.](https://jcp.aip.org/jcp/fig/fig3.jpg)
The influence of internal excitation of CF$_3$I$^*$ was investigated by measuring the maximum extent of dissociation for CF$_3$I$^*$ produced from various charge transfer agents. For CF$_3$I$^*$ produced by charge exchange with the molecular ion of perfluoropropane C$_3$F$_8$[IP(C$_3$F$_8$)]$^-$=10.3 eV the extent of dissociation drops by a factor of 3. No reduction is observed for CF$_3$I$^*$ produced from charge exchange with Xe[IP(Xe)]$^-$=12.13 eV. These results are consistent with CF$_3$I$^*$($\tilde{X}^2E_{1/2}$) having a more rapid photodissociation rate than CF$_3$I$^*$($\tilde{X}^2E_{3/2}$) since less CF$_3$I$^*$($\tilde{E}^2E_{1/2}$) is produced from C$_3$F$_8$ than Xe$^*$. Motivated by a recent study of Superrex and van der Berg, we investigated the effect of the magnetic field on the extent of CF$_3$I$^*$ dissociation. They report that photodissociation of CF$_3$HCl is enhanced by an external magnetic field. In the case of CF$_3$I$^*$ 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.

![Graph showing the variation of the extent of dissociation on laser irradiance as monitored by the CF$_3$I$^*$ signal.](image1)

**FIG. 4.** Variation of the extent of dissociation on laser irradiance as monitored by the CF$_3$I$^*$ signal. Experimental conditions are: 70 eV electron energy, 6×10$^{-8}$ Torr CF$_3$I pressure, 500 msec exposure time and 954.6 cm$^{-1}$ laser frequency.

![Graph showing the dependence of CF$_3$I$^*$ photodissociation on laser frequency using pulsed radiation.](image2)

**FIG. 6.** Dependence of CF$_3$I$^*$ photodissociation on laser frequency using pulsed radiation. Extent of dissociation is calculated from the measured yield of CF$_3$I. Experimental conditions are 5×10$^{-9}$ Torr CF$_3$I, 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$_3$I$^*$ 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$_3$I$^*$ and CF$_3$I$^*$ are influenced by pulsed CO$_2$ radiation; as with cw radiation CF$_3$I$^*$ is the exclusive photoprod. 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.

![Graph showing the dependence of the initial CF$_3$I$^*$ photodissociation rate on laser irradiance at 954.6 cm$^{-1}$ and 6.0×10$^{-8}$ Torr CF$_3$I. The slope of the line gives $k_0=0.80\times10^{-5}$ sec$^{-1}$ for the irradiance dependent photodissociation rate constant.](image3)

**FIG. 5.** Dependence of the initial CF$_3$I$^*$ photodissociation rate on laser irradiance at 954.6 cm$^{-1}$ and 6.0×10$^{-8}$ Torr CF$_3$I. The slope of the line gives $k_0=0.80\times10^{-5}$ sec$^{-1}$ for the irradiance dependent photodissociation rate constant.

![Graph showing the relaxation rate of CF$_3$I$^*$ at two different pressures as measured by CF$_3$I$^*$ 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$_3$I pressure as indicated, 1.6 J cm$^{-2}$, 40 nsec laser pulse at 952.9 cm$^{-1}$.](image4)

**FIG. 7.** Relaxation rate of CF$_3$I$^*$ at two different pressures as measured by CF$_3$I$^*$ 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$_3$I pressure as indicated, 1.6 J cm$^{-2}$, 40 nsec laser pulse at 952.9 cm$^{-1}$. 

\[SLOPE = 0.80 \text{ sec}^{-1}/\text{W cm}^{-2}\]

\[SLOPE = 16 \text{ sec}^{-1}\]

\[SLOPE = 25 \text{ sec}^{-1}\]

\[6.2 \times 10^{-8}\ \text{torr}\]

\[1.4 \times 10^{-7}\ \text{torr}\]
As with cw irradiation only internally excited CF$_3$I can be dissociated. As the delay between ion formation and pulsed laser irradiation increases the yield of CF$_3$I decreases. This is shown in Fig. 7 for two different CF$_3$I pressures. These results show that the relaxation of CF$_3$I can be described by a pressure dependent, first-order rate constant $k$, which is linearly dependent on CF$_3$I pressure (Fig. 8). These data yield $k = 3.1 \pm 0.4 \times 10^{9}$ cm$^3$ molecule$^{-1}$ sec$^{-1}$ with a zero-pressure inter- cept of 11.3 sec$^{-1}$. Apparently Xe is nearly as effective as CF$_3$I in causing relaxation of CF$_3$I.

C. Visible laser photochemistry

Attempts were made to cause single photon photodisso- ciation of CF$_3$I using visible laser radiation to pro- mote CF$_3$I from $X^2E_{1/2}$ or $X^2E_{3/2}$ to $A^2E_{1/2}$. The analogous transition in CH$_3$I, $X^2E_{1/2}$ to $A^2E_{1/2}$, for example, leads to photodissociation. In CF$_3$I, the $A^2E_{1/2}$ state is 2.07 and 2.76 eV above the $X^2E_{1/2}$ and $X^2E_{3/2}$ states, respectively. Krypton ion laser radiation with photon energies (and laser irradiances) of 2.65 eV (19 W cm$^{-2}$), 2.33 eV (71 W cm$^{-2}$), 1.92 eV (95 W cm$^{-2}$), and 1.83 eV (22 W cm$^{-2}$) were used. No photodissociation was observed. These results place an upper limit of $5 \times 10^{22}$ cm$^{-3}$ on the photodissociation cross section at the photon energies mentioned. Simultaneously exposing CF$_3$I 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$_3$I 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$_3$I fraction which undergoes photodissociation. Either it is (a) in the $X^2E_{1/2}$ state with up to 1.04 eV of vibrational energy or (b) it is in the $X^2E_{3/2}$ state with up to 0.45 eV of vibrational energy. Cogola, Cosby, and Peterson advance possibility (a). 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 $v_1$ mode of CF$_3$I($X^2E_{1/2}$) and 130 cm$^{-1}$ lower than the same transition for CF$_3$I($X^2E_{3/2}$). This 130 cm$^{-1}$ difference could be explained if the absorption is due to one of the other fundamental modes of CF$_3$I. However all of the other modes are much further from the observed absorption than is the $v_1$ mode as estimated from the absorption frequencies of CF$_3$I. 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 ab- sorption by the $v_1$ mode in CF$_3$I($X^2E_{1/2}$) or by the same mode in CF$_3$I($X^2E_{3/2}$), where the vibrational energy shifts the $v_1$ frequency from 1000 cm$^{-1}$ to 960 cm$^{-1}$ via the anharmonicity of the modes. The latter explanation can be correct only if CF$_3$I 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 values or estimated from combination spectra of CF$_3$I. Based on the population of the various vibrational modes and the first order anharmonicity constants, the average $v_1$ transition frequency is expected to shift by no more than 50 cm$^{-1}$ when CF$_3$I has up to 1.04 eV of vibrational energy. This suggests that photodissociation does not in- volve the $v_1$ mode of CF$_3$I($X^2E_{1/2}$) but rather the $v_1$ mode of CF$_3$I($X^2E_{3/2}$). 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$_3$I was known to be within 0.12 eV of the dissociation limit. Further evi- dence for photodissociation of CF$_3$I($X^2E_{3/2}$) and not CF$_3$I($X^2E_{1/2}$) is the reduced extent of dissociation of CF$_3$I produced from a charge transfer agent which preferentially produces CF$_3$I($X^2E_{3/2}$).

If photodissociation of CF$_3$I($X^2E_{1/2}$) 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$_3$I might be higher due to delocalization of the iodine 5$p^-$ electrons. Countering this effect, however, is the smaller spin-orbit splitting in CF$_3$I which would give a lower rate for CF$_3$I 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$10$^{20}$ cm$^{-2}$ molecule$^{-1}$ sec$^{-1}$ for CF$_3$I is three times the ion-neutral collision rate calculated from ADO theory. The relaxation rate is also large compared to resonant charge transfer rates. This leaves collision induced radiative transition or collision induced crossing to the $X^2E_{3/2}$ state as possible relaxation mechanisms.

A remarkable aspect of CF$_3$I photodissociation is...
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$_3$I$^\ast$.

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11. I. Novak (private communication).


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