Velocity map imaging of the photodissociation of CF$_3$I$^+$ in the $\tilde{A} \leftarrow \tilde{X}$ band

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The photodissociation dynamics of CF$_3$I$^+$ has been investigated within the $\tilde{A} \leftarrow \tilde{X}$ band by means of velocity map imaging. The CF$_3$I$^+$ cation is prepared by resonance-enhanced multiphoton ionization of CF$_3$I via the [X $^2E_{3/2}]^6p$, [2 $^2S^0$] band, and the (X $^2E_{3/2}$) ground-state population in the CF$_3$I$^+$ ion is unambiguously characterized by using photoelectron spectroscopy. Photodissociation of the state-selected CF$_3$I$^+$ ion results in fragmentation to both CF$_3$I$^+$ + I and CF$_3$I$^+$ + I$^-$. The translational energy distribution derived from the two-dimensional images of the CF$_3$I$^+$ fragments shows vibrational progressions that provide detailed information on the channeling of the parent internal energy into the dissociation process. The translational energy distribution of the CF$_3$I$^+$ fragment shows a one-to-one dependence on the excitation energy, which is typical of a single-photon dissociation process. The observation of a repeated pattern of rings in the CF$_3$I$^+$ images with an interval of $\sim$800 cm$^{-1}$ indicates that the $\nu_3$ umbrella mode of the CF$_3$I$^+$ fragment is excited upon dissociation. The low-kinetic-energy release observed in this channel indicates that substantial energy is deposited into the internal degrees of freedom of the CF$_3$I$^+$ fragment and suggests that the dissociation is controlled by the Franck-Condon factors between the parent ion and fragments. The translational energy distribution of the I$^+$ fragment is independent of the excitation wavelength and includes a feature peaking at near-zero kinetic energy. Plausible mechanisms for the CF$_3$I$^+$ and I$^+$ dissociation channels are discussed in terms of the observed kinetic energy and anisotropy distributions derived from the two-dimensional ion images. © 2003 American Institute of Physics. [DOI: 10.1063/1.1615523]

I. INTRODUCTION

The electronic structure of CF$_3$I$^+$ has been slowly unveiled by photodissociation$^1$–$^4$ and photoionization$^5$–$^8$ studies. The He(I) photoelectron spectrum (PES) of CF$_3$I recorded by Cvitas et al.$^5$ revealed a series of low-lying excited states. The ground electronic state of CF$_3$I$^+$ split into two spin–orbit components, with the $^2E_{3/2}$ level lying $\sim$5900 cm$^{-1}$ below the $^2E_{1/2}$ level. In the He(I) spectrum, both spin–orbit ionic states showed progressions in two vibrational modes that were assigned to the symmetric C–F stretch $\nu_1$ and the symmetric C–I stretch $\nu_3$. In the same study, the first low-lying excited state $\tilde{A}^2A_1$ was assigned to the C–I bonding orbital, while states at higher ionization energies were assigned to the excitation of electrons associated with the CF$_3$ group. The understanding of the ground electronic structure of the CF$_3$I$^+$ cation has been significantly improved by studies using resonant multiphoton ionization (MPI) via intermediate Rydberg states of neutral CF$_3$I.$^7$–$^9$ In particular, Macleod et al.$^7$ recently reported zero-kinetic-energy (ZEKE) photoelectron spectra of the CF$_3$I$^+$ (X $^2E_{3/2}$) state from several vibrational levels of the [X $^2E_{3/2}$]6$p$ Rydberg state of CF$_3$I, which were accessed by two-photon excitation. An accurate ionization energy of CF$_3$I was obtained from these high-resolution spectra, along with frequencies for a number of vibrational modes of the ground ionic state.

In contrast to the ground state of CF$_3$I$^+$, little is known about the excited electronic states and the dissociation dynamics of this cation. In the He(I) photoelectron spectrum, the broadband associated with the $\tilde{A}^2A_1$ electronic state of CF$_3$I$^+$ lies between $\sim$16 900 and 25 800 cm$^{-1}$ above the $^2E_{3/2}$ ground state. Although the $\tilde{A}^2A_1$ excited electronic state has been the center of some experimental studies,$^1$–$^2$ a clear description of this state has not been completed. The excitation of CF$_3$I$^+$ into the $^2A_1$ state results in the prompt dissociation into CF$_3$I$^+$ + I and CF$_3$I$^+$ + I$^-$. In a series of photoelectron–photoion coincidence experiments using single-photon ionization, Downie and Powis$^6$ characterized the correlations between the angular distributions of the ejected electron and the nascent CF$_3$I$^+$ and I$^+$ fragments. Additional information has been also obtained by preparing CF$_3$I$^+$ using resonant multiphoton ionization and, subsequently, photodissociating it through the absorption of an additional photon. Using this approach, Taatjes et al.$^8$ observed the rotational- and vibrational-state dependence in the photodissociation of CF$_3$I$^+$ via the $^C$ state of the neutral molecule. Similarly, Waits et al.$^1$ used translational spectroscopy to characterize the time-of-flight profiles of CF$_3$I$^+$ and I$^+$ ions formed following MPI via a series of vibrational levels of the [X $^2E_{3/2}$]6$p$ Rydberg state. Waits et al. suggested that some CF$_3$I$^+$ and I$^+$ fragments are produced by the dissociation of CF$_3$I$^+$ ions by absorption of an additional photon, while a second population of CF$_3$I$^+$ is produced by the unimolecular decomposition of vibrationally hot CF$_3$I$^+$ in the electronic ground state that are directly produced in the photoionization of the [X $^2E_{3/2}$]6$p$ state. Recently, we reported a similar bimodal velocity distribution of the CF$_3$I$^+$ fragments in a single-color ion-imaging study of the dissociation
The anisotropy parameters ($\beta$) determined from the angular distributions of the $CF_3^+$ and $I^+$ ions produced by the photofragmentation of $CF_3I^+$ are particularly interesting. Because the $\tilde{A}$ state of the $CF_3I^+$ ion has $2^2A_1$ symmetry or $2^E_{1/2}$ symmetry when spin–orbit coupling is included, the $\tilde{A} \rightarrow \tilde{X}^2E_{3/2}$ transition is perpendicular in character. For a fast dissociation process following excitation via a pure perpendicular transition, a limiting value of $\beta = -1$ is expected, while $\beta = 2$ is expected for a pure parallel transition. However, a value of $\beta > 1.1$ was observed in time-of-flight profiles\(^1\) and ion-imaging\(^2\) experiments, as well as in photoelectron–photoion coincidence experiments, which suggests a mostly parallel $\tilde{A} \rightarrow \tilde{X}^2E_{3/2}$ transition is responsible for the photodissociation transition. Orth and Dunbar\(^10\) observed a similar variation of the anisotropy value ($\beta > 1.5$) in the photodissociation of $CH_3Cl^+$ ions. They argued that this deviation is produced because a $\tilde{B} \rightarrow \tilde{X}$ transition, with its absorption dipole along the C–Cl bond, is initially excited and then an extremely rapid internal conversion to the $\tilde{A}$ state produced the observed $CH_3^+ + Cl$ photofragments. However, a similar mechanism is unlikely for the experiments on $CF_3I^+$, because the $\tilde{B}$ state of $CF_3I^+$ is not accessible with the excitation energies used. In addition, Low \etal\ have reported that the $\tilde{B}$ state of $CF_4I^+$ preferentially dissociates to $CF_3I^+ + F$, and no $CF_4I^+$ signal is observed in these experiments.\(^3\) Thus the origin of the positive value of the $CF_3^+$ and $I^+$ photofragment recoil anisotropies remains unclear, and new experimental and theoretical studies that improve our understanding of the electronic states and dissociation dynamics of $CF_3I^+$ ions are desired.

Figure 1 shows the energy levels and dissociation limits of $CF_3I^+$ in the region of interest. The electronic states of the ion are assigned using $C_{1V}$ symmetry labels, but because of the large spin–orbit coupling in $CF_4I^+$, the states are also provided with symmetry labels from the double group. As described previously, the ground state of $CF_3I^+$ is split into $2^E_{3/2}$ and $2^E_{1/2}$ levels. Both states adiabatically dissociate into $CF_3^+(1^2A_1) + I(2^P_{3/2})$. The $CF_3^+ \tilde{A} 2^2A_1$ state, which corresponds to $2^E_{1/2}$ in the double group, dissociates into $CF_3^+(2^2A_1) + I(2^P_{3/2})$. The $I(2^P_{3/2})$ level lies 7603.15 cm\(^{-1}\) above the $2^P_{1/2}$ ground state. No other states correlate to these dissociation limits. Numerous electronic states correlate to dissociation limits involving an $I^+$ fragment. Although both the $CF_3^+(2^2A_1) + I^+(2^P_0)$ and $CF_3^+(2^2A_1) + I^+(2^P_2)$ limits are above the energy region accessed in this study, the $CF_3^+(2^2A_1) + I^+(3^P_2)$ limit is particularly interesting, as it lies at nearly the same energy as the origin of the $CF_3I^+ \tilde{A} 2^2A_1$ state. The $CF_3^+(2^2A_1) + I^+(3^P_0)$ limit leads to three $2^E_{1/2}$ levels and two $2^E_{3/2}$ levels. Among these levels, two $2^E_{1/2}$ levels correlate with the $\tilde{B} 2^2E_2$ and $\tilde{C} 2^2E$ states of $CF_4I^+$, while the other levels remain uncharacterized. These states may play an important role in the photodissociation dynamics of the $\tilde{A} 2^2A_1$ state. Because the $\tilde{A} 2^2A_1$ state is correlated with $CF_3^+(1^2A_1) + I(2^P_{1/2})$, it is clear that at least one additional surface is necessary to account for the observed $CF_2I^+$ products and that this state (or these states) may also be responsible for the observed angular distributions.

In the present study, state-selected $CF_3I^+$ ions are produced by single- and two-color, two-photon resonant, three-photon ionization [which are referred to as (2 + 1) and (2 + 1') ionization, respectively] via the $[2^E_{3/2}]6\rho, [2]5\delta_0$ band of $CF_3I$. A schematic diagram of the experimental approach is shown in Fig. 1. In what follows, the pump and probe beams are labeled UV and VIS, respectively. The state-selected $CF_3I^+$ ions produced by one- and two-color ionization are characterized by photoelectron spectroscopy. The state-selected $CF_3I^+$ ions are excited by an additional UV or VIS photon to the $\tilde{A} 2^2A_1$ electronic state (or to another state in this region), where they dissociate into $CF_3^+(1^2A_1) + I(2^P_{1/2})$, and $CF_3^+(2^2A_1) + I^+(3^P_2)$. The UV photodissociation process was discussed in an earlier study of $CF_3I$, and the present report focuses on the dissociation of the $CF_3I^+$ ions by visible light. The decoupling of the ionization and dissociation processes allows us to study the near-threshold photodissociation of state-selected $CF_3I^+$ ions as a function of the photodissociation wavelength.

II. EXPERIMENT

The experiments described in this paper were carried out in two different instruments. The photoelectron experiments were performed using a magnetic-bottle electron spectrom-
meters and subsequently dissociating the CF$_3$I

The gas sample of $\sim 3\%$ CF$_3$I seeded in He was supersonically expanded into the experimental chamber using a pulsed valve with a backing pressure between 1000 and 1500 Torr. The molecular beam is skimmed and introduced into the reaction chamber where CF$_3$I$^+$ ions are produced by multiphoton ionization via the $[2E_{3/2}]6p$, [2]5$^3_5$ band of the neutral molecule. The CF$_3$I$^+$ ions are produced by one-color, two-photon resonant, three-photon ionization with a photon energy of 32.954 cm$^{-1}$, which is generated by frequency doubling the output of a Nd:YAG pump dye laser. A second independently tunable laser was used to photodissociate the CF$_3$I$^+$ ions. It turns out that this second laser also ionizes the $[2E_{3/2}]6p$ state populated by the first laser and that this two-color process is more efficient than the one-color process. Thus the ions are produced by both one- and two-color processes.

The lasers were externally triggered and synchronized by a series of digital delay generators, with a delay of less than 10 ns between the pump and probe laser. The wavelength was calibrated by using the optogalvanic effect in neon and argon hollow cathode lamps and by using a commercial wavemeter. The wavelength was also calibrated by using known two-photon transition in atomic iodine. The linewidths of the lasers were approximately 0.03 and 0.1 cm$^{-1}$ for the pump and probe lasers, respectively. The intensity of the beams were $\sim 0.5$ and $\sim 2$ mJ per pulse for the ultraviolet and visible lasers, respectively. Both beams were collinearly focused into the interaction region of either the photoelectron or ion imaging spectrometers, and in the latter the beams are polarized parallel to the face of the imaging detector.

Photoelectron spectra were recorded following photoionization of CF$_3$I in a diverging magnetic field that traps and parallelizes the trajectory of the photoelectrons and allows $\sim 50\%$ collection efficiency while maintaining high velocity resolution. The resolution of the photoelectron spectra recorded is $\sim 60$ cm$^{-1}$ for electrons with energy less than 4000 cm$^{-1}$, which is sufficient to resolve the vibrational structure of interest. The photoelectron signal obtained from a dual-microchannel plate detector was sent to a digital oscilloscope and averaged for 5000 laser shots to obtain the final spectra. The spectra were then converted from the time to energy axis and were calibrated using a nonlinear parametrized fit to known energies of photoelectrons derived from the two-photon resonant, three-photon ionization of atomic iodine, which is produced by the neutral dissociation of CF$_3$I.

Ion images were recorded by photoionizing the CF$_3$I molecules and subsequently dissociating the CF$_3$I$^+$ ions between the repeller and extraction plates of the electrostatic lens. Once the masses of the photofragment peaks are identified, the gain of the microchannel plate (MCP) detector was gated for the mass of interest, and the image of the mass-selected photofragment was recorded by using a fast phosphor screen. The images of individual photofragments were optimized for size and sharpness by adjusting the repeller and extractor voltages ($V_R$, $V_E$) of the ion optics; optimal velocity mapping was obtained with $V_E/V_R=0.76$ ($V_R \sim 3400$ V). A charge-coupled device (CCD) camera mounted behind the phosphor screen recorded the images, which were accumulated in a computer for 20,000 laser shots. The velocity resolution is limited by the resolution of the MCP-CCD camera detection system, which corresponds to $\sim 0.10$ mm per pixel and results in $\sim 240$ cm$^{-1}$ resolution at $\sim 8000$ cm$^{-1}$ kinetic energy release. The velocities and, thus, the kinetic energies of the ions were calibrated by using images produced following the photodissociation of methyl iodide (CH$_3$I) as reported by Eppink and Parker. A magnification factor $N=1.18$ was derived from the CH$_3$I image by using the expression $R=NV_t$, where $R$ is the ring radius, $V$ the fragment recoil speed, and $t$ the ion time of flight. To ensure a uniform and constant magnification factor, all apparatus parameters were held constant while recording images of CH$_3$I and CF$_3$I. From time to time the $V_R$ and $V_E$ were adjusted a few volts to get the best focusing: however its effect on the translational energy distribution was insignificant. The original three-dimensional (3D) ion distribution was reconstructed from the raw 2D image by using both the interactive procedure developed by Vrakking and the Abel transform method reported by Dribinski et al. Similar translational energy distributions and anisotropy values were obtained from both inversion procedures.

III. RESULTS AND DISCUSSION

A. Mass spectrum

The mass spectra recorded following $(2 + 1')$ ionization of CF$_3$I and the subsequent photodissociation of CF$_3$I$^+$ show three peaks corresponding to the parent ion CF$_3$I$^+$ and the fragment ions I$^+$ and CF$_3^+$. As described above, the CF$_3$I$^+$ ions are produced using the $[2E_{3/2}]6p$, [2]5$^3_5$ intermediate state by resonant $(2 + 1)$ ionization by UV light and $(2 + 1')$ by UV + VIS light. By subtracting the mass spectrum obtained with a single-color (32.953.9 cm$^{-1}$) from that obtained in the two-colors experiment (the UV and VIS photon energies were 32.953.9 and 21.293.3 cm$^{-1}$, respectively), the signal resulting from the two-color process could be isolated. In general, the ratio of the CF$_3^+$ signal to the I$^+$ signal in the two-color experiment ranges from 0.70 to 0.90, which is towards the high end of the CF$_3^+/I^+$ ratio of 0.4–0.9 measured previously for the single-color experiment. In the two-color spectrum, the CF$_3^+$ and I$^+$ peaks are also considerably larger than those in the one-color spectrum, while the parent peak remains almost unchanged. The significant increase of the fragments signal indicates that a much higher population of CF$_3$I$^+$ ions is initially generated from the $(2 + 1')$ than from the $(2 + 1)$ process. In addition, the small change in the parent ion signal indicates that majority of CF$_3$I$^+$ ions produced from the $(2 + 1')$ process are photodissociated, indicating that the dissociation process is nearly saturated. Under different experimental conditions—e.g., reducing the laser power—the fraction of ions that are photodissociated remains approximately constant. As a result, it was not possible to record a meaningful spectrum of the photofragment signal as a function of the probe wavelength.
In the region investigated, the $I^+$ channel is the strongest, but this channel slowly decreases in importance at longer wavelengths. $I_2^+$ ions were observed under some conditions, but were eliminated by synchronizing the laser pulse with the early part of the molecular beam pulse. No cluster ions were observed under the expansion conditions used.

B. Photoelectron spectra

Figure 2(a) shows the two-color photoelectron spectrum of CF$_3$I via the $[2E_{3/2}]6p$, $[2]5_0^1$ band. The features at low energies correspond to photoelectrons produced from the (2+1) ionization of CF$_3$I molecules, while the peak at higher energy ($>10,000$ cm$^{-1}$) is produced by the (2+1) process. A detailed description of the single-color photoionization of CF$_3$I via the $[2E_{3/2}]6p$, $[2]5_0^1$ band and other Rydberg intermediate states has been reported previously.$^2$ The features derived from the (2+1) process, which are expanded in Fig. 2(b), are very similar, albeit with somewhat poorer resolution, to those in the ZEKE spectrum recorded by of Macleod et al.$^7$ The spectrum of Fig. 2(b) shows an intense peak corresponding to the origin band of the $^2F_{3/2}$ state along with a number of weaker features that correspond to excited vibrational levels. However, the present PES spans a greater range of energy than the ZEKE spectrum and allows the observation of a progression in the umbrella mode ($\nu_2$). The features observed in Fig. 2(b) are labeled according to the assignment of Macleod et al. The present spectrum was recorded with minimum retardation of the photoelectrons to ensure that the complete photoelectron spectrum was recorded. By integrating the individual photoelectron peaks, it is found that 63% of the ions are produced with less than 500 cm$^{-1}$ of internal energy and $\sim 91\%$ of them are formed with less than 1400 cm$^{-1}$. Because the fast photoelectron peak at $\sim 15,500$ cm$^{-1}$ in Fig. 2(a) is not resolved, it is difficult to extract the internal-state distribution of the ions formed by the one-color process. However, it is reasonable to expect that this distribution is determined primarily by Franck–Condon factors and thus is similar to that for the (2+1) process. This point is discussed in more detail in Sec. III D.

On the basis of the photoelectron energies and known photon energies, the photoelectron spectrum shows that CF$_3$I$^+$ ions were produced by absorption of a single visible photon from the resonant intermediate $[2E_{3/2}]6p$, $[2]5_0^1$ Rydberg state of the neutral molecule. The spectrum shows no evidence of electrons produced from dissociative ionization (DI), in which the CF$_3$I molecules would be excited to a neutral superexcited state by absorption of multiple photons and, subsequently, decay directly into CF$_3^+$+I or CF$_3$+I$^+$. In addition, the internal energy of the initially prepared parent ions is very small compared to the dissociation threshold for CF$_3$I$^+$, and as discussed previously, any significant dissociation process must involve the absorption of at least an additional visible photon.

C. Ion images: CF$_3$I$^+ + h\nu \rightarrow$CF$_3^+$+I

1. Total translational energy distribution

As shown in Fig. 1 and described above, the CF$_3$I$^+$ ions are produced by (2+1) and (2+1) ionization. The resulting ions can be photodissociated by either the pump or probe laser. Photodissociation of CF$_3$I$^+$ by the pump laser can be studied by performing the experiments with a single laser. Figure 3(a) shows a typical reconstructed CF$_3^+$ image derived from this process. As discussed previously, the image shows a bimodal distribution of energies, with a peak at near zero energy and a second peak at approximately 10,000 cm$^{-1}$. Figure 3(c) shows the total translational energy distribution (i.e., the sum of the translational energy of both the CF$_3^+$ and I fragments) derived from the image (dashed line). The distribution is generated by integrating the radial distribution over all angles and weighting the function as appropriate for polar coordinates. A detailed description of the image and total translational energy distribution derived from the single-color scheme has been reported previously.$^2$ In the two-color scheme, the state-selected CF$_3$I$^+$ ions are photodissociated by the probe laser; however, the images for this process also have a background that is produced by photodissociation by the pump laser alone. Figure 3(b) shows a
two-color reconstructed CF$_3^+$ image recorded at a probe wavelength of 19 969.8 cm$^{-1}$. The series of concentric rings result from photodissociation by the probe laser, while the dashed circle shows the position of a weak ring derived from photodissociation by the pump laser. The solid line in Fig. 3(c) corresponds to the total translational energy distribution derived from this image. The peak at high energies in the distribution is very similar to that obtained from the single-color experiment. Since this feature results from the dissociation of CF$_3$I$^+$ ions by a pump photon and the only difference is that some of the ions in the two-color image were produced by the two-color process, the similarity of the peaks indicates that the parent ions produced by the (2 + 1) and (2 + 1') processes have similar internal-state distributions.

The low-energy component of the total translational energy distribution derived from the two-color image is expanded in Fig. 3(d). This distribution shows a strong peak near zero kinetic energy and a series of weak features extending to higher energy. These features always lie at energies below 2000 cm$^{-1}$ for the probe wavelengths investigated, but the position and intensity of the peaks significantly change. In what follows, the energetics involved in the dissociation process and wavelength dependence of the kinetic energy distribution will be discussed, followed by an analysis of the vibrationally resolved features observed in the CF$_3^+$ kinetic energy distribution, Fig. 3(d).

The partition of energy between the photofragments can be determined by the following energy balance equations:

$$h\nu + E_{\text{inf}}(\text{CF}_3^+) - D_0(\text{CF}_3^- - I) = E_{\text{trans}} + E_{\text{inf}}(\text{CF}_3^+) + E_{\text{el}}(I),$$

$$E_{\text{avail}} = E_{\text{inf}}(\text{CF}_3^+) + E_{\text{trans}} + E_{\text{el}}(I),$$

where $E_{\text{inf}}(\text{CF}_3^+)$ is the internal vibrational and rotational energy of the ground-state parent molecule, $D_0(\text{CF}_3^- - I)$ is the energy required for the dissociation of CF$_3$I$^+$ into CF$_3^+$($^1A_1$) + I($^3P_{1/2}$), $E_{\text{el}}(I)$ is the spin–orbit energy of the I fragment (i.e., 0 or 7603.15 cm$^{-1}$ for the I and I*, respectively), $E_{\text{inf}}(\text{CF}_3^+)$ is the internal vibrational and rotational energy of the CF$_3^+$ fragment, and $E_{\text{avail}}$ is the excess energy available following dissociation. In the previous single-color velocity map study of the dissociation of CF$_3$I$^+$ ions, dissociation was found to produce CF$_3^+$($^1A_1$) + I($^3P_{1/2}$), which is consistent with the direct dissociation on the $A ^2P_1$ electronic state surface. By solving Eq. (1a) using the literature value for $D_0(\text{CF}_3^- - I)$ and the $E_{\text{inf}}(\text{CF}_3^+)$ of 0–1400 cm$^{-1}$ derived above, $E_{\text{inf}}(\text{CF}_3^+) + E_{\text{trans}}$ ranges between 4000 and 7000 cm$^{-1}$ for photodissociation by the VIS laser in the region investigated here. The nonmaximal total translational energy extracted from the ion images indicates that most of the excess energy must be channeled into internal vibrational and rotational energy of the CF$_3^+$ fragments. Substantial excitation of the nascent CF$_3^+$ fragments is also implied by the fast component (UV photodissociation) of the total translational energy distribution shown in Fig. 3(c). As reported previously, this component peaks at a translational energy significantly lower than that expected if the CF$_3^+$ fragments were produced in the vibrationless ground state, indicating that vibrationally excited CF$_3^+$ ions were produced. In Fig. 3(c), the high-energy component of the single-color distribution extends to slightly higher energy than the corresponding feature in the two-color distribution. Since both features are produced from the dissociation of CF$_3$I$^+$ ions by absorption of a UV photon, this difference must be related to the vibrational distribution in the parent ions produced by the one- and two-color schemes. As discussed above, determination of the differences in the vibrational distributions for the (2 + 1) and (2 + 1') processes is not possible due to the difference in photoelectron energy resolution for the two schemes. In principle, however, the higher photon energy of the UV light could populate higher vibrational levels of the CF$_3$I$^+$, and this could ultimately result in higher total translational energies. In any case, Fig. 3 demonstrates that this is a relatively small effect, as the high-energy components of the two distributions only differ by a small amount.

**FIG. 3.** Reconstructed ion images of the photodissociation of CF$_3$I$^+$ into CF$_3^+$($^1A_1$) + I($^3P_{1/2}$). The CF$_3^+$ images are recorded from a (a) single-color (32 953.9 cm$^{-1}$) and (b) two-color (32 953.9 + 19 969.8 cm$^{-1}$) schemes. The lower figures correspond to the total translational energy distribution derived from the images. The distribution from the single-color image (dashed line) is superimposed to that obtained from the two-color image (solid line) to stress similarities between the distributions. (d) shows an expanded portion of two-color distribution where the low-energies features are observed.
2. \( \text{CF}_3^+ \) vibrational distribution

Figure 4 shows the total kinetic energy distributions derived from images recorded at a series of probe photon energies spaced by approximately 80 cm\(^{-1}\). The position and shape of the features observed in the distributions clearly depend on the excitation energy. For each 80-cm\(^{-1}\) decrease in the photon energy, the position of the most intense feature in the distribution also decreases by 80 cm\(^{-1}\), indicating that the photodissociation process is almost certainly a direct, one-photon process, and that a single vibrational level of the fragment is preferentially populated. At lowest excitation energy, the intense peak near zero kinetic energy corresponds to vibrationally excited \( \text{CF}_3 \) ions with excitation in the umbrella mode of the \( \text{CF}_3 \) moiety in \( \text{CF}_3\text{I}^+ \) and the planar \( \text{CF}_3 \) cation. For the free \( \text{CF}_3 \) radical, the vibrational distribution peaks around \( v = 20 \) for a transition involving a pyramidal to planar geometry change.\(^{21}\)

3. Role of internal energy in the parent \( \text{CF}_3\text{I}^+ \)

The total kinetic energy spectrum shown in Fig. 3(d) clearly resembles the photoelectron spectrum shown in Fig. 2(b). Although the spectra were recorded at somewhat different excitation wavelengths, the spacings and intensities of the features between 0 and 1000 cm\(^{-1}\) of total translational energy are similar to those identified between the \( 0^0 \) and \( 1^1 \) peaks in the photoelectron spectrum. This clearly shows that the parent internal energy is channeled directly into the dissociation process. The peaks in Fig. 3(d) are labeled according to the assignment used in the photoelectron spectrum and previously reported by Macleod et al.\(^{7} \) For example, the intense peak near zero kinetic energy corresponds to vibrationally excited \( \text{CF}_3^+ \) ions \( (v_2^+ = 7) \) produced from the dissociation of parent ions in their vibrationless ground state. \( \text{CF}_3^+ \) ions with \( v_2^+ = 7 \) are also produced from the dissociation of vibrationally excited \( \text{CF}_3\text{I}^+ \) ions \( (e.g., v_5, v_5, v_2, v_1 = 1, v_2, v_1 = 1, 2) \), and these are indicated by the upper set of labels in Fig. 3(d). The peaks observed around 850 and 1000 cm\(^{-1}\) can be assigned to the dissociation of \( \text{CF}_3\text{I}^+ \) ions in the \( 2^1 \) and \( 1^1 \) states; however, they can be also assigned to \( \text{CF}_3^+ \) ions with \( v_2^+ = 6 \) that are generated from the dissociation of parent ions in the \( 0^0 \) and \( 3^1 \) states, as is indicated by the lower set of labels. Despite the significant change in the geometry of the \( \text{CF}_3 \) moiety, the vibrational frequency of the umbrella mode is almost the same in \( \text{CF}_3\text{I}^+ \) and \( \text{CF}_3^+ \). From their measured ZEKE photoelectron spectrum of \( \text{CF}_3\text{I}^+ \), Macleod et al. derived \( v_2^+ = 734 \) cm\(^{-1}\), while for the \( \text{CF}_3^+ \) ion Forney et al.\(^{22} \) obtained \( v_2^+ = 798 \) cm\(^{-1}\). Thus, owing to the limited resolution of the present ion images, an unambiguous identification of these peaks is not possible at this time. However, the peak at 1250 cm\(^{-1}\) in the total transla-
tional energy distribution does not have a counterpart peak in the photoelectron spectrum, but the spacing between it and the adjacent peak is close to the frequency of the $v_3$ mode of CF$_3$I$^+$. (The spacing is somewhat larger than expected but this is at least in part due to the difficulty in measuring the positions of the weak peaks at 1000 and 1250 cm$^{-1}$.) Thus it seems likely that the series of peaks at approximately 850, 1000, and 1250 cm$^{-1}$ correspond to the production of CF$_3$I$^+$ with $v_2 = 6$ from the photodissociation of a series of vibrational levels of CF$_3$I$^+$.

4. CF$_3$I$^+$ angular distribution

Figure 6 shows a typical angular distribution obtained by integrating the intensity of an individual ring in the reconstructed image and plotting the result as a function of angle between the polarization axis of the lasers and the detection angle of the image. The distribution in Fig. 6 was obtained from the intense peak in the total translational energy distribution recorded at 19 969.8 cm$^{-1}$ [see Fig. 3(d)]. As derived by Zare,$^{23}$ the angular distribution of photofragments produced by photodissociation of an unaligned sample with linearly polarized light can be expressed as

$$I(\theta) \sim (1/4\pi)\left[ 1 + \beta P_2(\cos \theta) \right].$$

(2)

However, ions produced by a multiphoton process can be significantly aligned, and the angular distribution for photodissociation of ions formed by a three-photon process using linearly polarized light is

$$I(\theta) \sim (1/4\pi)\left[ 1 + \beta P_2(\cos \theta) + \gamma_4 P_4(\cos \theta) + \gamma_6 P_6(\cos \theta) \right].$$

(3)

In Eqs. (2) and (3), $\theta$ is the angle between the polarization axis and detection direction, $\beta$ is the anisotropy parameter, and $P_n(\cos \theta)$ are the Legendre polynomials and $\gamma_n$ are the corresponding high-order anisotropy parameters. For instantaneous dissociation following excitation of an unaligned sample via a pure parallel transition, a limiting value of $\beta = 2$ is expected, which produces a $\cos^2 \theta$ distribution. For instantaneous dissociation of an unaligned sample via a pure perpendicular transition, $\beta = -1$ is expected, which produces a $\sin^2 \theta$ distribution. These limiting values are only obtained when the dissociation is much faster than the rotational period of the fragmenting molecule, and slower dissociation processes will result in more isotropic angular distributions—i.e., $\beta$ values closer to 0.

Fitting the distribution in Fig. 6 to the form of Eq. (2) yields a value of $\beta = -0.5$. As seen in the figure, this fit clearly does not represent the peaks of the distribution very well, suggesting that the sample is aligned. Unfortunately, the quality of the data is not sufficient for a meaningful fit of all four parameters in Eq. (3). However, Fig. 6 does show a fit of the first three terms in Eq. (3), which yields values of $\beta = -0.4 \pm 0.1$ and $\gamma_4 = 0.1 \pm 0.05$. This fit is significantly better near the peaks of the distribution and indicates that the three-photon ionization process does create some alignment in the CF$_3$I$^+$ ions. Table I summarizes the asymmetry parameters obtained by fitting the most intense feature in the images recorded at several different wavelengths.

In general, the negative $\beta$ values in Table I suggest that these features are produced by a perpendicular electronic transition. These values are consistent with the values of $\beta = -1$ expected for the perpendicular $\tilde{A} \leftrightarrow \tilde{X}$ transition. Deviation from this limiting value can be due to rotational smearing, which results when the dissociation process is on the order of, or slower than, the rotational period of the molecule. In addition, as has been observed in the dissociation of CF$_3$I, intermediate values of $\beta$ can be also observed if both parallel and perpendicular transitions contribute to the photodissociation process.$^{12,24,25}$ In a study of the photodissociation of analogous CH$_2$I$^+$ ions, Orth and Dunbar$^{16}$ suggested that contribution from the parallel $\tilde{B} \leftrightarrow \tilde{X}$ transition, which undergoes internal conversion to the lower-lying repulsive $\tilde{A}$ state and subsequently dissociates, accounts for the deviation from the limiting value $\beta = -1$. However, as discussed above, the parallel $\tilde{B} \leftrightarrow \tilde{X}$ transition in CF$_3$I$^+$ is energetically not accessible at the photon energies of the present study. It is particularly interesting that, in CF$_3$I$^+$, the $\beta$ value of $-0.5$ measured near the dissociation threshold increases dramatically when the dissociation laser is tuned to higher energies within the $\tilde{A} \leftrightarrow \tilde{A}_1$ excited state. For example, in our previous single-color ion imaging study of the photodissocia-

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TABLE I. Fragment recoil anisotropy parameter for the CF$_3$I$^+ (1$A_1$) $\rightarrow$ 1$^1P_{1/2}$ channel measured at different photon energies.

<table>
<thead>
<tr>
<th>Photon energy (cm$^{-1}$)</th>
<th>$\beta$</th>
<th>$\gamma_4$</th>
<th>$\beta^{ac}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>20 148.5</td>
<td>-0.5 ± 0.1</td>
<td>0.2 ± 0.05</td>
<td>-0.4 ± 0.1</td>
</tr>
<tr>
<td>19 969.8</td>
<td>-0.4 ± 0.1</td>
<td>0.1 ± 0.05</td>
<td>-0.2 ± 0.1</td>
</tr>
<tr>
<td>19 890.4</td>
<td>-0.2 ± 0.1</td>
<td>0.0 ± 0.05</td>
<td>-0.2 ± 0.1</td>
</tr>
<tr>
<td>19 351.6</td>
<td>-0.4 ± 0.1</td>
<td>0.0 ± 0.05</td>
<td>-0.4 ± 0.1</td>
</tr>
</tbody>
</table>

$^a$ Anisotropy value derived from the most intense peak in the images.
$^b$ Values obtained by fitting the first three terms in Eq. (3).
$^c$ Values obtained by fitting Eq. (2).
tion of CF$_3$I$^+$ ions, a $\beta$ value of 1.3 was derived from images recorded for the CF$_3$I$^+$($^1A_1$) + I($^2P_{1/2}$) channel at 32,953.9 cm$^{-1}$. This significant change in the $\beta$ value in the dissociation of CF$_3$I$^+$ ions as a function of the excitation energy clearly indicates that one or more additional electronic states contribute in the dissociation of CF$_3$I$^+$ ions in this energy region. As shown in Fig. 1, a number of low-lying electronic states must exist near the origin of the $\tilde{A}$ $^2A_1$ state, but these states are largely uncharacterized. The explanation for the anisotropy anomaly observed in the dissociation of CF$_3$I$^+$ ions will most likely only be found when more detailed information is available on these states.

D. Ion images: CF$_3$I$^+$ + $h\nu$ → CF$_3$ + I$^+$

Figures 7(a) and 7(b) show the reconstructed images for the I$^+$ signal generated by the dissociation of CF$_3$I$^+$ ions produced with the one- and two-color schemes, respectively. Figure 7(c) shows the total translational energy distributions derived from the one- and two-color images. At higher translational energies, the two distributions are very similar, but below $\sim$1000 cm$^{-1}$ the two-color distribution shows several additional peaks. In contrast to the CF$_3$I$^+$ images, the signal at high translational energies in the I$^+$ channel is significantly more intense than the signal at lower energies. The high-energy peak has been previously assigned to the UV dissociation of CF$_3$I$^+$ ions into CF$_3$($^2A_1$) + I($^2P_{1/2}$). We now focus on the less-intense two-color peaks observed at low energies in the distribution.

Figure 8 shows the low-energy portion of the total translational energy distributions derived from two-color I$^+$ images recorded at a series of probe energies. The positions of the dominant peaks appear to be essentially independent of energy, as seen from the two vertical lines at 340 and 2300 cm$^{-1}$. Similar invariant distributions were observed in images obtained at 40-cm$^{-1}$ intervals of the probe laser. The principal change in the distributions of Fig. 8 occurs between scans (e) and (f), where the peak at 2300 cm$^{-1}$ disappears.

Structured but wavelength-invariant translational energy distributions are somewhat difficult to rationalize for simple photodissociation processes, because they require any increase in photon energy to be absorbed into the internal degrees of freedom of the molecule and because there is not a continuum of energy levels in the molecule. However, wavelength-independent translational energy distributions have been observed in the dissociative ionization of some molecules, including I$_2$. Because dissociative ionization corresponds to a three-body breakup, the photoelectron can be produced with a continuous range of energies, allowing the summed translational energy of the two heavy products to remain constant. However, dissociative ionization can be ruled out in the present example because the photoelectron spectrum demonstrates that the ions are produced by (2 + 1) or (2 + 1') ionization.

A second explanation for the translational energy distributions in Fig. 8 is that they result from the UV photodisso-
cation of CF$_3$I$^+$ produced by (2 + 1$') ionization. This explanation requires that (2 + 1) and (2 + 1$')$ ionization result in somewhat different vibrational state distributions in the CF$_3$I$^+$ and that photodissociation from differentially populated levels of CF$_3$I$^+$ give rise to the features in Fig. 8. These differences must be relatively small, because the major portions of the one- and two-color distributions are nearly identical. This explanation accounts for several features of the distributions in Fig. 8. First, because the UV photon energy is constant, the positions of the peaks in the distribution should not depend on the VIS energy, as is observed. Second, the disappearance of the 2300-cm$^{-1}$ peak is consistent with the VIS photon energy being reduced below the ionization threshold for a particular vibrational level of CF$_3$I$^+$. Specifically, the ionization threshold from the [3$^2E_{3/2}$]$_{6p}$, [2]$^5S_{0}$ state to the vibrationless ground state of CF$_3$I$^+$ is ~17 750 cm$^{-1}$. If it is assumed that the excited vibrational levels responsible for the features in Fig. 8 correspond to a progression in $v_2^+$, the threshold to produce CF$_3$I$^+$ $X\tilde{^2}E_{3/2}$, $v_2^+$ = 3 is ~20 000 cm$^{-1}$, which is very close to the photon energy at which the 2300-cm$^{-1}$ feature disappears. Finally, the thermochemical threshold for photodissociation of CF$_3$I$^+$ into CF$_3$I$^+$ + I$^+$($3P_{2}$) is ~19 440 cm$^{-1}$, and there is little change in the intensity of the low-energy features across this threshold region. While photodissociation of hot CF$_3$I$^+$ could account for this observation, the intensity of the signal would still be expected to fall as the energy was tuned to longer wavelengths. Of course, photodissociation by the UV light is always energetically allowed. In principle, this explanation could be tested by delaying the VIS pulse to arrive after the UV pulse. Unfortunately, the lifetime of the intermediate state is short and there are insufficient ions produced by the UV pulse alone to record adequate two-color images when the pulses are not overlapped in time.

Autoionization phenomena could result in somewhat different vibrational distributions for CF$_3$I$^+$ produced by (2 + 1) and (2 + 1$'$) photoionization. Because the photoelectron spectra are close to what is expected for direct photoionization of the intermediate state, electronic autoionization is probably not important, as this would most likely produce very different vibrational distributions for the two processes. However, vibrational autoionization could play a role in the (2 + 1$'$) process, because the ionizing photon accesses an energy that is within the Franck–Condon–Condor region of the ground-state ion. For example, at 20 148.5 cm$^{-1}$, the probe energy lies just above the CF$_3$I$^+$ $X\tilde{^2}E_{3/2}$, $v_2^+$ = 3 threshold, and thus could access neutral Rydberg series converging to the $X\tilde{^2}E_{3/2}$, $v_2^+$ = 4 threshold. The Franck-Condon factors for such transitions would be poor, but vibrational autoionization of these states would be expected to populate the CF$_3$I$^+$ $X\tilde{^2}E_{3/2}$, $v_2^+$ = 3 state preferentially. Although this is expected to be a small effect, it would result in a greater population of $X\tilde{^2}E_{3/2}$, $v_2^+$ = 3 in the (2 + 1$'$) spectrum than in the (2 + 1) spectrum, and could account for the observed results.

If the low-energy features in Fig. 8 arise from the UV photodissociation of vibrationally excited CF$_3$I$^+$, it remains to identify the mechanism by which the low-energy peaks are produced. Given the UV photon energy, there is substantial excess energy for photodissociation into CF$_3$($X\tilde{^2}A_1$) + I$^+$($3P_{2}$) that would have to go into vibrational excitation of the CF$_3$ fragment. If this is the case, it is difficult to rationalize the structure observed in the translational energy distributions. On the other hand, if the dissociation is to CF$_3$(X$^2A_1$) + I$^+$($3P_{0}$ or $3P_1$), there is a considerably smaller amount of excess energy, and the lower-energy features in the translational energy spectrum would be easier to understand. At this time, it is not possible to distinguish between these scenarios or to confirm a specific photodissociation mechanism. However, if the low-energy features in Fig. 8 are produced by the UV photodissociation of CF$_3$I$^+$, it is interesting to compare the $\beta$ values of the low-energy peaks with those of the high-energy feature. Figure 9 shows a plot of the $\beta$ values obtained by fitting the angular distributions to Eq. (2) at a number of translational energies. The $\beta$ values near zero energy are close to zero, but rise to almost 2 at the highest energies. This substantial change in $\beta$ indicates that the photodissociation mechanism is different for distributions with low and high translational energy, making it appear likely that different electronic states are responsible for the two components.

**IV. CONCLUSIONS**

The photodissociation dynamics within the $\tilde{A} \rightarrow \tilde{X}$ band of the trifluoromethyl iodide cation CF$_3$I$^+$ have been investigated by velocity map ion imaging. The CF$_3$I$^+$ ion was prepared by (2 + 1) and (2 + 1$'$) multiphoton ionization of CF$_3$I via the [$X\tilde{^2}E_{3/2}$]$_{6p}$, [2]$^5S_{0}$ band and characterized by using photoelectron spectroscopy. Additional CF$_3$I$^+$ ions are produced by a two-color (2 + 1$'$) process. The state-selected CF$_3$I$^+$ ions were photodissociated into CF$_3$(+$^3A_1$) + I$^+$($^3P_{2}$) and CF$_3$(+$^3A_1$) + I$^+$($^3P_{2}$) by the tunable probe laser. By decoupling the ionization process from the dissociation process, it was possible to vary the photodissociation wavelength and study the dynamics of the dissociation process near threshold. Vibrationally resolved translational energy distributions were recorded, which allows a characterization of the internal energy distribution of the nascent fragment. Dissociation into CF$_3$I$^+$ + I$^+$ results in a small trans-
lational energy release that shows a linear dependence with the photon energy, indicating that the dissociation process results from a single-photon excitation of the ground state of CF$_3$I$^+$. The reappearance of nearly identical translational energy distributions for every 800-cm$^{-1}$ change in the probe photon energy suggests that the umbrella mode of the CF$_3$ fragment is excited in the dissociation process and that there is a strong propensity to populate the highest energetically allowed $v_2$ level of CF$_3$I$^+$ upon dissociation. The substantial excitation of the fragments indicates that the dissociation process is governed by Franck–Condon factors between the CF$_3$ moiety in CF$_3$I$^+$ and the free CF$_3$ fragment. It is hoped that the present experiments will provide the motivation for theoretical calculations of the excited-state potential energy surfaces of CF$_3$I$^+$, as well as the photodissociation dynamics of this molecule.

In contrast to the CF$_3$ channel, dissociation into CF$_3$ + I$^+$ results in an invariant translational energy distribution as a function of the excitation energy. It is hypothesized that the two-color signal in this channel comes from the UV photodissociation of vibrationally excited ions produced by (2 + 1)’ photoionization. While this explanation appears to account for the observed results, additional experiments are necessary to confirm this assignment.

The present study demonstrates that the combination of resonant multiphoton-ionization and ion-imaging techniques provides a powerful method to study the photodissociation dynamics of state-selected ions. The observation of the effects of alignment of the CF$_3$I$^+$ parent ion in the photodissociation angular distributions also suggests a number of future experiments. For example, if the alignment of the parent ion can be extracted from the photofragment angular distribution, the present approach could be used to provide insight into the dynamics of the photoionization process. In addition, by using different combinations of linearly and circularly polarized light, it may be possible to study the photodissociation dynamics as a function of the alignment or orientation of the parent ion.

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