I. INTRODUCTION

The excitation of CF₃I⁺ into the A ²A₁ state results in dissociation to two different sets of products, corresponding to CF₃⁺ + I and CF₃ + I.¹⁻⁵ The details of this dissociation process have been elucidated primarily by studies of dissociative photoionization. In particular, Powis and co-workers¹⁻⁴ have performed a number of different types of coincidence experiments to characterize these processes, and they have found interesting correlations between the direction of the electron ejection and the direction of the nascent CF₃⁺ or I⁺ fragment. Additional information has come from studies in which multiphoton ionization was used to prepare ground state CF₃I⁺, and absorption of an additional photon led to photodissociation of the ion.⁵ Using this approach, Taatjes et al.⁶⁻⁷ have deduced information on the rotational and vibrational state dependence of the photodissociation of CF₃I⁺. Waits et al.⁵ also studied the competing photodissociation processes following two-photon resonant, three-photon ionization of CF₃I. Although these experiments accessed a somewhat higher energy in the A ²A₁ state than the coincidence measurements or those of Taatjes et al.⁶⁻⁷ both dissociation channels were observed, and many aspects of the dissociation were similar. In particular, the I⁺ was created with substantial translational energy, and the CF₃⁺ signal showed a component with high translational energy. However, Waits et al.⁵ also found an isotropic, low velocity component in the CF₃⁺ channel of their time-of-flight spectrum. While the fast CF₃⁺ signal was assigned to prompt dissociation following excitation into the A ²A₁ state, the slower component was assigned to dissociation of hot ground-state CF₃I⁺ molecules. These molecules were thought to be formed in the tail of the Franck–Condon distribution of the three-photon ionization process. The photoelectron spectrum reported by Waits et al.⁵ appeared to be consistent with this interpretation. Unfortunately, the value of the appearance energy of CF₃⁺ + I from CF₃I used by Waits et al.⁵ was ~0.4 eV lower than the subsequently revised value.⁸⁻¹⁰ With the improved appearance energy, the photoelectron spectrum of Waits et al. indicates that very few CF₃I⁺ ions are formed with sufficient energy to dissociate, and thus any significant dissociation process requires the absorption of an additional (fourth) photon.

In the present study, the experiments of Waits et al.⁵ have been reexamined by using velocity map ion imaging to extract angular distributions and velocity distribution following the photodissociation of CF₃I⁺ prepared by two-photon resonant, three-photon ionization of CF₃I via the same bands as in the earlier study. In addition, higher resolution photoelectron spectra have been recorded under similar conditions. The new results clarify a number of questions concerning the study of Waits et al.⁵ and provide new information of the dissociation dynamics of the A ²A₁ state. In particular, it is confirmed that both components of the bimodal velocity distribution in the CF₃⁺ + I channel must arise from a four-photon process. As suggested previously, the fast component is assigned to rapid dissociation to CF₃⁺ + I(²P ₁/₂), while the slow component may result from a rapid radiationless transition from the initially populated surface to the ground-state surface, followed by unimolecular decomposition to CF₃ + I(²P ₃/₂). In addition, the imaging results show that the I⁺ fragments in the alternate dissociation channel are produced in the ³P₂ ground state.

Figure 1 shows a schematic diagram of the energy levels and dissociation limits of CF₃I⁺ in the region of interest, and Table I gives the thresholds for the different ionization and dissociation processes.⁸⁻¹¹ The electronic states of the ion are generally assigned C₃v symmetry labels, and because the spin–orbit coupling is quite large in CF₃I, the states are also provided with symmetry labels from the appropriate double group.¹¹⁻¹² Both types of labels are given in Fig. 1. The X ²E ground electronic state of CF₃I is split into two spin–orbit components, with the ²E ₃/₂ level lying 0.73 eV below the
2$E_{1/2}$ level, both states dissociate adiabatically to CF$_3^+$($^1A_g$) + I($^2P_{3/2}$). In contrast, the CF$_3$I$^-$ $^2A_1$ state, which corresponds to $^2E_{1/2}$ in the double group, dissociates to CF$_3^+$($^1A_g$) + I($^2P_{1/2}$). These are the only states arising from these two dissociation limits. The origin of the CF$_3$I$^-$ $^2A_1$ state lies at nearly the same energy as the CF$_3$(A$_1$) + I($^2P_2$) limit, and both the CF$_3$(A$_1$) + I($^2P_1$) and CF$_3$(A$_1$) + I($^2P_0$) limits are below the energy region accessed in this study. Numerous electronic surfaces arise from these limits. In particular, the CF$_3$(A$_1$) + I($^2P_2$) limit gives rise to three $E_{1/2}$ levels and two $E_{3/2}$ levels, while the CF$_3$(A$_1$) + I($^2P_1$) limit gives rise to two $E_{1/2}$ levels and one $E_{3/2}$ level and the CF$_3$(A$_1$) + I($^2P_0$) limit gives rise to a single $E_{1/2}$ surface. Aside from these $E_{1/2}$ levels that arise from the CF$_3$(A$_1$) + I($^2P_2$) limit and correlate with the $^2B_2$ and $^2E$ states of CF$_3$I$^-$, the electronic states arising from CF$_3$(A$_1$) + I$^-$ are for the most part uncharacterized.

Recent studies on the two-photon resonant three-photon ionization spectrum of CF$_3$I by Macleod et al. indicate that the bands observed by Waits et al. correspond to the transitions to different vibrational and $\Omega$ levels of the CF$_3$I($^2X^2E_{3/2}$)6p Rydberg state that lie at two photon energies between 65496 and 67938 cm$^{-1}$. The strongest of these transitions were those to the $\Omega$=2 levels. Macleod et al. also recorded zero-kinetic energy (ZEKE) photoelectron spectra using a number of these bands as intermediate levels, and while these spectra provide some information on the vibrational character of the intermediate levels, some questions remain about the assignment of the vibrational quantum numbers. In particular, it was not clear if there were two $\Omega$=2 electronic origins in this region. In the present study, CF$_3^+$ and I$^-$ images have been recorded for a number of the $\Omega$=2 vibrational bands, and essentially the same behavior is observed for all of them.

II. EXPERIMENT

Two different instruments were used in the present study. The photoelectron spectra were recorded by using a magnetic-bottle electron spectrometer equipped with a pulsed, skimmed supersonic molecular beam source that has been described previously. The ion imaging studies were performed by using a modified time-of-flight mass spectrometer with an imaging detector that has also been described previously. The imaging signal was gated by applying a suitably timed voltage pulse to the front plate of the detector, so that separate images of the CF$_3^+$ and I$^-$ ions could be obtained without interference. A mixture of ~3%–6% CF$_3$I seeded in He with a backing pressure of 1 to 2 atm was expanded supersonically into a vacuum chamber by a pulsed valve. In these experiments, a single laser was used to ionize the CF$_3$I by two-photon resonant, three-photon ionization via the [$^2E_{3/2}$]6p Rydberg states and to photodissociate the resulting CF$_3$I$^+$ ions. Both ionization and dissociation occur within the same laser pulse. The light for these experiments was generated by frequency doubling the output of a Nd:YAG pumped dye laser. The resulting ultraviolet light was separated from the fundamental by using a series of dichroic mirrors, and focused into the imaging spectrometer (electron spectrometer) by using a 250 mm (75 mm) focal length lens. The polarization axis of the ultraviolet light was parallel to the face of the detector in the imaging spectrometer and perpendicular to the face of the detector in the electron spectrometer. The wavelength of the light was calibrated by using the optogalvanic effect in Ne and Ar and by using a commercial wavemeter. The wavelength was also calibrated by using known two-photon transitions in atomic iodine, which is produced by the neutral photodissociation of CF$_3$I in this wavelength region. The energy scale of the photoelectron spectrometer was calibrated by using the photoelectron spectrum resulting from two-photon resonant, three-photon ionization via these same resonances. As described previously, the ion images were calibrated by using resonantly enhanced multiphoton ionization to detect the CH$_3$ fragment produced by the photodissociation of CH$_3$I in this wavelength region. A magnification factor $N$=1.18 was derived from the CH$_3$I image by using the expression $R=Nvt$, where $R$ is the ring radius, $\nu$ 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.

In the present study, the inversions of the two dimensional images were carried out by using the iterative procedure developed by Vrakking, resulting in a slice through the three-dimensional velocity distribution. Although it is possible to symmetrize the images prior to the inversion procedure to minimize effects of detector inhomogeneities, this
was not done for the present analysis. The velocity distributions were then converted to the kinetic-energy distribution of the fragment and, by using the conservation of linear momentum, into the total kinetic energy of the two fragments. An energy balance equation can then be written

\[ h\nu + E_{\text{int}}(\text{CF}_3 I^+) - D_0^p(\text{CF}_3 - I^+) = E_{\text{trans}} + E_{\text{int}}(\text{CF}_3), \]  

(1a)

\[ h\nu + E_{\text{int}}(\text{CF}_3 I^+) - D_0^p(\text{CF}_3^+ - I) - E_{\text{el}}(I) = E_{\text{trans}} + E_{\text{int}}(\text{CF}_3^+), \]  

(1b)

for dissociation to \( \text{CF}_3 + I^+ \) and \( \text{CF}_3^+ + I \), respectively. In these equations \( E_{\text{int}}(\text{CF}_3 I^+) \) is the internal energy of the initially prepared ground-state \( \text{CF}_3 I^+ \), \( D_0^p(\text{CF}_3 - I^+) \) and \( D_0^p(\text{CF}_3^+ - I) \) are the appropriate dissociation energies of \( \text{CF}_3 I^+ \), \( E_{\text{el}}(I) \) is the spin–orbit energy of the I fragment [i.e., 0.0 or 7603.15 cm\(^{-1}\) for \( I(2P_{3/2}) \) and \( I(2P_{1/2}) \), respectively], \( E_{\text{trans}} \) and \( E_{\text{int}}(\text{CF}_3) \) and \( E_{\text{int}}(\text{CF}_3^+) \) are the internal (vibrational and rotational) energies of the \( \text{CF}_3 \) or \( \text{CF}_3^+ \) fragment. The value of \( E_{\text{int}}(\text{CF}_3 I^+) \) is determined by the photoionization dynamics of the \([X^2E_{3/2}]6p \) Rydberg states used as the intermediates in the ionization scheme, and can be characterized using the photoelectron spectra. By using the literature value \(8\)–\(10\) for \( D_0^p(\text{CF}_3 I^+) \) or \( D_0^p(\text{CF}_3^+ - I) \), the only unknown is \( E_{\text{int}}(\text{CF}_3) \), and thus the image provides the internal energy distribution of the \( \text{CF}_3 \) or \( \text{CF}_3^+ \) fragment. On the other hand, if the internal energies of these fragments is known, Eqs. (1a) or (1b) can be used to determine the dissociation energy of the ion.

### III. RESULTS AND DISCUSSION

#### A. Wavelength scans and mass spectra

Figure 2 shows the one-color, two-photon resonant, three-photon ionization spectrum of \( \text{CF}_3 I \) obtained by monitoring the \( \text{CF}_3 I^+ \) signal. The spectrum is very similar to that of Waits et al.\(^5\) and to the spectrum of Macleod et al.\(^3\) who monitored the signal at the \( \text{CF}_3 I^+ \) mass. The spectrum is also similar to the spectrum obtained by monitoring the \( I^+ \) mass, but that spectrum also contains features resulting from neutral photodissociation of \( \text{CF}_3 I \) followed by two-photon resonant, three-photon ionization of \( I(2P_{3/2}) \) or \( I(2P_{1/2}) \). Selected features in Fig. 2 are labeled according to the assignments of Macleod et al.\(^8\) Note, however, that Macleod et al. have offered an alternative assignment for the \([2S_5], 0 \) and \([2S_5, 3] \) bands that corresponds to the \( 0^0_0 \) and \( 5^1_0 \) bands, respectively, of a second electron state. The present analysis does not resolve this question of assignment, and in what follows the former assignment is used.

Mass spectra were recorded at the wavelengths of the bands with assignments in Fig. 2. These spectra show features at the \( \text{CF}_3^+ \), \( I^+ \), and \( \text{CF}_3 I^+ \) masses. The relative intensities of these features depend somewhat on the resonance, and also depend quite strongly on the stagnation pressure in the molecular beam source. In general, at the lowest stagnation pressures (~700 Torr), the ratio of the \( I^+ \) signal to the \( \text{CF}_3 I^+ \) signal ranges from 1.1 to 2.6, while at high stagnation pressures (~1700 Torr) this ratio ranges from 1.4 to 5.0. Images obtained at both pressures are essentially the same in the \( \text{CF}_3^+ \) channel, but begin to show new features at high pressure in the \( I^+ \) channel. This is most likely the result of processes involving clusters of \( \text{CF}_3 I \). Under some conditions an \( I^+ \) ion signal was also observed. This signal may also arise from the fragmentation of clusters but it is more likely due to an \( I_2 \) impurity in the sample or contamination of the inlet line. The images discussed below were obtained in the low pressure regime, where no \( I^+ \) is observed and the contribution of clusters is expected to be minimal. Analysis of all of the images is consistent with single-photon dissociation of ground-state \( \text{CF}_3 I^+ \) monomers produced by two-photon resonant, three-photon ionization of \( \text{CF}_3 I \) monomers.

#### B. Photoelectron spectra

Figure 3 shows the photoelectron spectrum obtained for single-color, two-photon resonant, three-photon ionization of \( \text{CF}_3 I \) via the \([X^2E_{3/2}]6p, [2S_5] \) band. The spectrum was recorded with minimal retardation of the photoelectrons to ensure that the complete photoelectron spectrum was ob-
The lack of retardation results in relatively poor resolution (~0.090 eV) for electrons with ~1.9 eV kinetic energy, as determined from photoelectron spectra recorded on atomic iodine resonances. This is considerably better than the resolution in the photoelectron spectrum of Waits et al.\(^5\) As concluded by Waits et al., the single strong peak at 1.92 eV in Fig. 3 is consistent with photoionization of the \([X^2E_{3/2}]6p\) Rydberg state to produce the \(X^2E_{3/2}\) ground-state ion.

The width of the photoelectron peak in Fig. 3 (~0.14 eV) is somewhat greater than the instrumental resolution, indicating that the ions are formed with a distribution of vibrational energy in the \(X^2E_{3/2}\) state. The ZEKE spectrum\(^8\) obtained via the \([X^2E_{3/2}]6p\), \([2]S^1\) band shows a strong peak corresponding to the origin band of the \(X^2E_{3/2}\) state, and weak progressions of other vibrational bands involving the excitation of the \(v_3\) and \(v_5\) modes. Unfortunately, the reported ZEKE spectra\(^8\) only extend ~0.125 eV above the origin, so it is not clear if other higher energy modes are excited. In any event, the photoelectron spectrum in Fig. 3 gives a good indication of the amount of internal energy in the initially prepared \(X^2E_{3/2}\) ion. In particular, by integrating the photoelectron signal, it is found that 93% of the ions are produced with less than 0.5 eV of internal energy, and greater than ~98% are formed with less than 0.9 eV of internal energy. Given that the dissociation threshold for CF\(_3\)I\(^+\) is somewhat greater than this, and that the mass spectra indicate that a significant fraction of the ions dissociate, it is clear that any significant dissociation process must involve the absorption of at least one additional photon. In addition, the threshold for the \(B^2A_2\) state of CF\(_3\)I\(^+\) lies ~4.63 eV above the ground state.\(^11\) Thus, for the range of photon energies used (4.06–4.10 eV), the \(B^2A_2\) state is only energetically accessible to a small fraction of the molecules. Given that Powis and co-workers\(^1\)–\(^4\) found that the \(B^2A_2\) state dissociates primarily to CF\(_2\)I\(^+\)+F, and that there is no evidence for CF\(_2\)I\(^+\) in the mass spectra recorded here, it is unlikely that excitation to this level is important for the present experiments.

With the observed electron energies and the known photon energy, the photoelectron spectra clearly show that photoionization of CF\(_3\)I occurs via two-photon resonant, three-photon ionization. The photoelectron spectra show no evidence for above-threshold ionization, in which the parent molecule absorbs a fourth photon before ionizing; such a process would result in considerably higher photoelectron energies than those observed. Similarly, all of the photodissociation results presented here are consistent with the parent ion absorbing a single photon, resulting in dissociation to CF\(_2\)I\(^+\)+I or CF\(_3\)I\(^+\)+I. As discussed below, the maximum observed translational energy releases are consistent with the energetic restrictions of one-photon dissociation. The absence of evidence for multiphoton absorption by the parent ion is likely a result of the relatively low intensities used in these experiments, and in the rapid dissociation of the states accessed by the absorption of one photon.
allow somewhat higher translational energies in the photofragments.

The distribution function in Fig. 5 peaks at a value of $E_{\text{trans}} = 1.43 \pm 0.06$ eV, which is $\sim 0.25 \pm 0.08$ eV below the limiting value for dissociation to CF$_3$ + I$^-$ (3$P_2$), and has a full width at half maximum (FWHM) of $\sim 0.37$ eV, indicating that the photodissociation process results in considerable vibrational, and possibly rotational, excitation in the CF$_3$ fragment. These values are reasonably close to the values extracted from the time-of-flight data of Waits et al.,$^5$ which correspond to $E_{\text{trans}} = 1.26 \pm 0.1$ eV, with a FWHM of 0.60 $\pm 0.06$ eV. (This FWHM value was obtained by scaling the reported width in the I$^+$ channel and scaling it to that of the total translational energy.) Values of the total translational energy and peak widths for other intermediate levels are given in Table II. No structure is resolved in the distribution, which is not surprising given the initial distribution of vibrational energy in the ground-state CF$_3$I$^+$ ion. However, as in the case of the photodissociation of neutral CF$_3$I, it is likely that photodissociation results in the excitation of the $\nu_3$ umbrella vibration of CF$_3$. If this is the case, the peak in the distribution corresponds to $\sim 3$ quanta in the $\nu_3$ vibration. As discussed by Schinke and co-workers,$^{19-21}$ because both the CF$_3$ ground state and the CF$_3$ moiety in CF$_3$I are pyramidal, Franck–Condon factors alone could not account for the observed product state distribution in the CF$_3$I; this should also be the case for the photodissociation of CF$_3$I$^+$. Schinke and co-workers$^{19-21}$ performed model calculations to show that final state interactions, in particular the coupling between the umbrella motion and the bond-breaking motion, were responsible for the substantial excitation of $\nu_3$ in the photodissociation of CF$_3$I. The similarity of the present results with those on CF$_3$I suggests that the same type of final state effects are important in the photodissociation of CF$_3$I$^+$.

Figure 6 shows the photoion angular distribution obtained by integrating the reconstructed image for total translational energies between 1.2 and 1.8 eV and plotting the results as a function of the angle between the polarization axis of the laser and the detection angle on the image. The distribution is strongly peaked along the polarization direction. For photodissociation of an unaligned sample, the photofragment distribution can be expressed as$^{21,22}$

$$I(\theta) = (\pi^2)[1 + \beta P_2(\cos \theta)],$$  

where $I(\theta)$ is the signal intensity and $\theta$ is the angle between the polarization axis and the detection direction. $P_2(\cos \theta) = (3 \cos^2 \theta - 1)/2$ is the second Legendre polynomial, and $\beta$ is the anisotropy parameter. For instantaneous dissociation, the angular distribution is expected to reflect the character of the transition to the dissociative state. For a parallel transition, a limiting value of $\beta = 2$ is expected, while for a perpendicular transition, $\beta = -1$ is expected. These result in $\cos^2 \theta$ and $\sin^2 \theta$ distributions, respectively. Deviations from this limiting behavior are observed when the transition to the dissociative state has mixed character, which results in intermediate values of $\beta$ and when the dissociation is slow relative to the rotational period of the molecule (“rotational smearing”).$^1$ Fitting the distribution in Fig. 6 to the form of Eq. (2) yields a value of $\beta = 1.35 \pm 0.2$, indicating the transition is mostly parallel in character and that the dissociation is quite fast. The angular distributions for the I$^+$ images recorded using other pump transitions yield $\beta$ values between

![Fig. 5. The distribution function for the total translational energy (i.e., the sum of the translational energy of both fragments) for the photodissociation to CF$_3$ + I$^-$ following ionization of CF$_3$I via the 6$P$ transition.](image1)

![Fig. 6. The photoelectron angular distribution obtained by integrating the reconstructed image of Fig. 4 for total translational energies between 1.2 and 1.8 eV. Fits to Eqs. (2) and (3) are also shown (see text for details).](image2)
formed by three-photon ionization are not highly aligned. For dissociation, the distribution will in general have the form \(23\) more complicated form for the photofragment angular distribution. Based on rotational smearing would be similar as predicted based on rotational smearing would be similar as the decay rates. Thus, because the molecule dissociates on a time scale of one to a few vibrational periods, it is difficult to understand how the energy can be fully randomized in the activated molecule. It seems more likely that the dissociation is a direct process, either on a single potential surface involving a surface crossing. As in the case of the photodissociation of neutral CF\(_3\)I, the product state distributions and translational energy distributions would then be determined by the dynamics on these surfaces.

The \(A^2\) state dissociation limit, which raises two possible explanations for the observed dissociation to \(CF_3^+ + I^+(3P_2)\). The first possibility is that two different electronic states are excited in this energy region, one of which is correlated to \(CF_3^+ + I^+(3P_2)\) and the other to \(CF_3^+ + I^+(3P_2)\), and the second possibility is that \(A^2\) state surface is coupled strongly to, or crosses a second surface corresponding to an electronic state correlated with \(CF_3^+ + I^+(3P_2)\). If there were two states that were accessed directly by the photoexcitation process, the He I photoelectron spectrum \(13\) would be expected to show evidence for two bands in this energy region. The observed He I spectrum \(13\) shows what appears to be a single band with a very regular shape. However, the wavelengths used in the present study access energies in the high energy tail of the \(A^2\) state band, and in this region another surface could contribute to the signal. In any event, if two surfaces are excited at these energies, they must have very similar shapes in the Franck–Condon region. Given that the dissociation limits are well separated, this seems somewhat unlikely. It is possible that the state responsible for dissociation to \(CF_3^+ + I^+(3P_2)\) is not accessible in a one-electron transition from the ground-state neutral, but that it is accessible in a one-electron transition from the ground state of the ion. However, Powis and co-workers \(1–4\) see dissociation to \(CF_3^+ + I^+(3P_2)\) in their single-photon dissociative ionization studies, so this explanation also appears unlikely. The branching between the two dissociation channels strongly favors dissociation to \(CF_3^+ + I^+(3P_2)\) at the energies studied by Powis et al., but at the energies of the present study, dissociation to \(CF_3^+ + I^+(3P_2)\) becomes the dominant process.

The second possibility involving the coupling between two surfaces also introduces some requirements about the \(CF_3^+ + I^+(3P_2)\) surface. In particular, either this surface must be optically forbidden, or the crossing must take place outside the Franck–Condon region. Otherwise, transitions to both the \(CF_3^+ + I^+(3P_2)\) and \(CF_3^+ + I^+(3P_2)\) surfaces would be expected. In addition, if the \(CF_3^+ + I^+(3P_2)\) is produced by curve switching, the switching probability must increase substantially with increasing energy in the \(A^2\) state because at the highest energies dissociation to \(CF_3^+ + I^+(3P_2)\) is the dominant process. At this point the knowledge of the potential surfaces correlated with the \(CF_3^+ + I^+(3P_2)\) dissociation limit is insufficient to determine which explanation is correct. However, a number of different mechanisms exist for the three \(E_{1/2}\) and two \(E_{3/2}\) states correlated with this limit to interact with the \(A^2\) state.
D. Ion images for dissociation to CF$_3^+$ +I

Figure 7 shows the CF$_3^+$ image obtained by tuning to the [X$^2E_{3/2}$]$6p$, $[2]5^1_0$ transition, that is, the same transition used for the I$^+$ image in Fig. 4. Although the CF$_3^+$ images recorded by using different intermediate states are all similar, some variations are observed. All of the images show a bimodal distribution of energies, with a peak near zero energy, and a second peak at $\sim$1.3 eV. The discussion of the high energy peak in this distribution will be discussed first, followed by a discussion of the low-energy peak. The high energy edge of the high energy peak is essentially the same in all of the images. However, the width of the outer ring is significantly greater for the $[2]0^1_0$ and $[2]5^1_0$ resonances than for any of the other resonances. Figure 8 illustrates this observation by showing two examples of the distribution function for the total translational energy for the photodissociation to CF$_3^+$ +I, which were obtained using the [X$^2E_{3/2}$]$6p$, $[2]5^1_0$ and $3^1_0$ resonances. Also shown in Fig. 8 are the maximum possible value for the total translational energy for dissociation to CF$_3^+$ +I($^2P_{3/2}$); the maximum value for dissociation to CF$_3^+$ +I($^2P_{1/2}$) is 0.943 eV higher in energy. While the high energy peaks are at approximately the same energy in the two distribution, the width of this peak is substantially greater for the $[2]5^1_0$ resonance. It is somewhat surprising that the two bands that show the greatest width are those for which the ZEKE spectrum$^8$ shows a strong origin band and little intensity in any vibrationally excited states of the ion, at least up to 1000 cm$^{-1}$ above threshold. (Indeed, the alternate assignment of the $[2]5^1_0$ band in the work of Macleod et al.$^8$ is that this band corresponds to an origin band of a second electronic state.) The observed total translational energies in Table II for the CF$_3^+$ +I channels are somewhat greater than the value of 1.11 $\pm$ 0.10 determined by Waits et al.$^5$ and the widths of the narrower distributions are in reasonable agreement with their value 0.32 $\pm$ 0.03 for the full width at half maximum (FWHM) of the total translational energy distributions.

Although it is not clear why some of the translational energy distributions are significantly broader than others, the position of the high energy peaks in Fig. 8 clearly suggest that the dissociation process must be to CF$_3^+$ +I($^2P_{3/2}$). This is consistent with direct dissociation on the A $^2A_1$ state surface, which correlates with these dissociation products. The peak of the fast component in all of the distributions is also shifted to the low-energy side of the limit corresponding to the production of vibrationless CF$_3^+$, indicating that there is substantial vibrational excitation in the CF$_3^+$ fragment. Unlike CF$_3$, CF$_3^+$ is planar. Thus, the Franck–Condon factors between the CF$_3^+$ fragment and the CF$_3$ moiety in CF$_3$I are expected to favor the production of vibrationally excited fragments, which is consistent with the observed distributions. The similarity of the high energy peaks in Fig. 8 with those in the photodissociation of neutral CF$_3$I photodissociation and in the photodissociation of CF$_3$I$^+$ to CF$_3$ +I$^+$ channel also suggests that final-state effect, in particular the cou-
pling of the CF$_3$ vibrations and the C–I$^+$ reaction coordinate.\textsuperscript{19–21} An assessment of the role of final-state effects in the CF$_3^+ + \text{I}(^2P_{1/2})$ must await more extensive modeling of the electronic surfaces involved in the photodissociation process.

Figure 9 shows the CF$_3^+$ angular distribution for the fast component in Fig. 6, following excitation via the $6p[2]5\Sigma_1^+$ band. This distribution was obtained by integrating the observed signal between 0.65 and 1.75 eV in the translational distribution at each angle. The corresponding angular distributions for the other resonances are very similar. The $\beta$ values obtained by fitting the distribution in Fig. 9 using Eq. (2) is $1.3 \pm 0.2$, and the values for the other resonances range from $1.3 \pm 0.2$ to $1.4 \pm 0.2$. Figure 9 shows this fit along with the fit to both the $\beta$ and $\gamma_1$ terms in Eq. (3). As in the CF$_3^+ + \text{I}^+$ distributions, the latter fit is somewhat better than the fit to $\beta$ alone, supporting the conclusion that the CF$_3$ I$^+$ ground state is aligned following multiphoton ionization. The $\beta$ values observed in the CF$_3$ $+ \text{I}(^2P_{1/2})$ channel are similar to those in the CF$_3$ $+ \text{I}^+$ channel, and indicate that the transition moment is primarily parallel to the molecular axis. Because the $\beta$ values are similar to those in the CF$_3$ $+ \text{I}^+$ channel, estimates based on rotational smearing result in similar values of the dissociation rates. Thus, dissociation is quite fast and likely occurs directly on the $A^2A_1$ surface. This conclusion is also consistent with the $\text{I}^+$ to CF$_3^+$ branching ratio in the mass spectra, which range from $\sim 1.1$ to 2.6 and thus also suggest similar rates for the two processes.

The slow component of the translational energy distribution in Fig. 8 is particularly interesting. This distribution peaks near zero energy and has a tail that extends out to 0.6–0.7 eV. Waits \textit{et al.}\textsuperscript{7} observed a similar slow isotropic component in their translational energy distribution, but attributed it to dissociation of vibrationally excited ground-state CF$_3$ I$^+$ produced in the three-photon ionization process. The present results clearly show that this is not energetically possible, and that this distribution must result from the absorption of a fourth photon by the ground state ion. Figure 10 shows the CF$_3^+$ angular distribution for excitation via the $6p[2]5\Sigma_1^+$ band obtained by integrating the observed signal between 0.00 and 0.22 eV. The $\beta$ values obtained by fitting the distributions for all of the intermediate levels using Eq. (2) range from $0.0 \pm 0.2$ to $0.3 \pm 0.2$, and the value in Fig. 10 is $\beta = 0.2 \pm 0.2$. Because the distributions are nearly isotropic, no attempt was made to fit both $\beta$ and $\gamma_1$. It is interesting to note, however, that within the low-energy component of the translational energy distribution, the $\beta$ value appears to increase with increasing energy. For example, the integrated distribution between 0.0 and 0.05 eV yields $\beta$ values between $0.1$ and $0.3$, whereas the integrated distribution between 0.05 and 0.22 eV yields $\beta$ values between $0.2$ and $0.5$.

The nearly isotropic angular distribution of the lower energy component in the translational energy distribution suggests that the process responsible for this component is significantly slower than that for the high-energy component, i.e., the isotropic distribution implies significant rotational smearing of the angular distribution. This is consistent with estimates based on the translational energy distributions. In particular, in Fig. 8 the integrated intensity of the low energy component of the translational energy distribution in the CF$_3^+ + \text{I}$ channel is $\sim 27\%$ of that in the high-energy peak. This observation indicates that the process responsible for the low-energy component is approximately four times slower than that for the high-energy component. It remains to determine the mechanism of the slower process and the state distribution of its products.

The appearance of the translational energy distribution, that is, the peak at zero energy and the approximately exponential fall to higher energy, is suggestive of a statistical dissociation process.\textsuperscript{24–27} Such a process could arise via a rapid radiationless transition to either the ground-state $^2E_{1/2}$CF$_3$ I$^+$ surface or to the spin–orbit excited $^2E_{3/2}$ component of the ground state, followed by statistical dissociation. In this case, the branching ratio between the slow and fast CF$_3^+$ component would be determined by the relative rates of the radiationless transition and the prompt dissociation giving rise to the high translational energy peak. As discussed above, however, the excitation energies are so far above the dissociation thresholds for either CF$_3^+$ $+ I (^2P_{3/2})$ or...
gies, but was significantly lower than predicted at higher energies. The observed translational energy release would be smaller than expected based on energy randomization. If that smaller amount of vibrational energy in the CH$_3$ radical was due to competing decay channels, in particular, dissociation processes that begin along the CH$_3$ + I$^-$ channel and then switch to the CH$_3$ + I, leaving a large amount of vibrational energy in the CH$_3$ fragment and a smaller than expected translational energy. The present experiments also suggest an alternative explanation. As discussed above, the dissociation rates calculated by using statistical theory are too fast to justify the assumption of total energy randomization. If the dissociation proceeds from the ground-state surface, and if the radiationless transition populating this state results in the preferential excitation of high frequency vibrations, a smaller amount of energy would initially be distributed into the reaction coordinate than expected based on energy randomization. If that smaller amount of energy is still sufficient to result in dissociation, the observed translational energy release would be smaller than expected. Whether this mechanism, the mechanism of Mintz and Baer, or some entirely different mechanism is operable in either of these systems will only be determined when more detailed information is available on the relevant potential energy surfaces.

IV. SUMMARY AND CONCLUSION

The present experiments provide new information on the dissociation of CF$_3$I$^+$ following excitation into the A $^2A_1$ state, and the data elucidate several questions resulting from earlier studies of this process. In particular, high resolution photoelectron shows that all of the dissociation processes observed must result from single-photon excitation of ground-state CF$_3$I$^+$ produced by two-photon resonant, three-photon ionization. Dissociation to CF$_3$ + I$^-$ results in the population of the I$^-$ $3P_2$ level, and this dissociation process is quite fast. Dissociation to CF$_3$ + I occurs via two mechanisms. The first corresponds to dissociation to CF$_3$ + I($^2P_{1/2}$), and results in a large translational energy release consistent with direct dissociation on the excited state surface. The second mechanism results in a small translational energy distribution that has an appearance similar to that expected for a statistical dissociation process, but statistical models predict a much larger translational energy than observed. Possible explanations for this behavior have been discussed, but none of these is completely satisfactory at this time. The present results suggest a number of future experimental and theoretical studies. In particular, experiments in which the ionization process is decoupled from the photodissociation process would allow a much more detailed study of the dissociation dynamics in the A $^2A_1$ state of CF$_3$I$^+$, and provide information on the internal energy dependence of the dissociation process. Theoretical calculations of the excited state potential surfaces of CF$_3$I$^+$ would be particularly useful, and it is hoped that the present experiments will provide the motivation for future work in this area.

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