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Photodissociation dynamics of CF_3I investigated by two-color femtosecond laser pulses

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Abstract. We report an experimental study of the multiphoton dissociation dynamics of CF_3I performed on a home-built femtosecond laser pump-probe system, with time-of-flight mass spectrometer. The first repulsive `A` band and the $5p\pi^3 7s\sigma$ $v_2 = 1$ Rydberg state of CF_3I were accessed by one- and two-photon transitions at 267 nm, respectively, with the latter two-photon absorption followed by a further two-photon probe transition at 401 nm to the $\widetilde{B}$ state of the parent ion. The observed signals from the CF_3^+ and I^+ fragments show similar multi-component exponential decay patterns but the former is 4 times stronger than the latter. However, the parent CF_3I^+ signal was observed to evolve in a very different manner, decreasing sharply when probed in the first 289 fs following excitation and subsequently rising again after 860 fs to a constant level below that measured at negative pump-probe delay times when the pump and probe pulses exchange roles. This dip observed in the parent ion profile, is very different from that previously reported at shorter pump wavelengths of 264 nm or 265 nm, and is interpreted as the competition between two different ionization channels. One from the vibrationally excited $v_2 = 1$ of the irradiated Rydberg state and the other from the dissociative vibrational origin of the same electronic state which is populated by internal vibrational relaxation.

PACS. 33.70.Ca Oscillator and band strengths, lifetimes, transition moments, and Franck-Condon factors – 33.80.Rv Multiphoton ionization and excitation to highly excited states – 33.80.Gj Diffuse spectra; predissociation, photodissociation – 82.53.Eb Pump probe studies of photodissociation

1 Introduction

Since the first femtosecond time-resolved photodissociation study of ICN by Zewail and coworkers [1], the pump-probe technique has been widely applied in fragmentation research of molecular photodissociation combined with resonance-enhanced multiphoton ionization (REMPI) and imaging techniques. Intense femtosecond laser pulses can easily induce multiphoton excitation and can also provide the high temporal resolution needed to study the associated dissociation dynamics in real time [2–4]. These direct time-resolved measurements can give a more straightforward and less ambiguous picture for the photodissociation process and provide detailed information on molecular interactions and bondbreaking dynamics.

In the past, extensive research has been carried out on CH_3I and CF_3I due to their prototypical importance in polyatomic molecular dissociation studies. Using tunable deep-UV femtosecond photoionization spectroscopy, the predissociation of the $\widetilde{B}$ (6*s* Rydberg) state of CH_3I and CD_3I has been studied and the lifetimes of several predissociated states were measured [5,6]. Similar lifetime measurements have also been carried out through the analysis of the spectral profile of the relevant dissociative states [7–9]. In 1998, Poth et al. studied the photodissociation dynamics of methyl iodide clusters using two-color femtosecond laser pulses ($\lambda = 270$ nm as pump and $\lambda = 405$ nm as probe) on their reflection time–of–flight mass spectrometer [10]. One of the most interesting results from their work relates to the unusual pump–probe profile which they observed. This profile was composed of a fast decay and a subsequent dip in ion signal followed

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by a rise for pump–probe delay times greater than 2 ps, which was interpreted in terms of the unusual electronic structure of the methyl iodide monomer and effects resulting from clustering of this species, such as shifts of the electronic energy levels and caging of excited molecules in the cluster. As for CF_3I, research has mostly focused on the photodissociation of the first `A` band to $CF_3 + I(^2P_{1/2}, ^2P_{3/2})$, which was considerably more complicated than initially expected [11]. After the work of van Veen et al. [11], the 248 nm photodissociation of CF_3I to $CF_3 + I(^2P_{1/2}, ^2P_{3/2})$ was re-investigated by high-resolution photofragment translational spectroscopy [12,13] with a rotating source chamber, to reveal the importance of translation-vibration coupling on the repulsive excited state potential energy surfaces, and the significant influence of the dissociation dynamics, near the Franck-Condon region on the energy transfer into the photofragments. The photodissociation of CF_3I has also been investigated at 304 nm and the results reported by Hwang and El-Sayed [14]. Following this, Felder studied the influence of the molecular beam temperature on the photodissociation of CF_3I at 308 nm [15]. A branching change study in the photodissociation of vibrationally excited CF_3I at 248.5 nm has also been performed showing that the $I(^2P_{3/2})$ product enhancement is due to an increased contribution from direct absorption to the correlated electronic state [16]. In 1996, Kim et al. investigated the photodissociation of CF_3I, cooled in a supersonic molecular beam, at 277 nm by state-selective photofragment imaging [17]. The anisotropy parameter $\beta(I^*)$ for the excited iodine atom $I^*(^2P_{1/2})$, which was determined from this work, deduced the dissociation lifetime of the state $\widetilde{\mathrm{A}}$ to be of the order of 150–350 fs. Using polarized photofragment translational spectroscopy, a further detailed investigation of the photodissociation process in the `A` absorption band between 275 nm and 303 nm was performed by Furlan et al., and the results were reasonably interpreted within a dynamic scheme involving a set of three potential energy surfaces [18].

Further interesting research on CF_3I, has focused on photodissociation involving the $\widetilde{A}$ state, and even the $\widetilde{B}$ state of CF_3I^+ [19–26]. The resonant multiphoton excitation of CF_3I between 300–306 nm turns out to be related to the photodissociation of CF_3I^+ into $CF_3 + I^+$ and $CF_3^+ + I$ with the latter of these two channels due to two different dissociation mechanisms with two ionic states involved [19,21,27]. The pump-probe technique has also been applied to direct temporal studies of the multiphoton dissociation of CF_3I [23–25,27], with the result that the CF_3^+ fragments are mainly formed by a two-photon pump excitation at 264–265 nm to the $5p\pi^3 7s\sigma$ Rydberg state, followed by one or two-photon probe excitation to the CF_3I^+ parent states with subsequent dissociation.

Recently we studied the multi-photon dissociative ionization dynamics of CF_3I via time-of-flight mass spectroscopy for a femtosecond pump pulse at 265 nm and a probe pulse at 398 nm [25], with results consistent with previous observations. In this paper, however, we report the observation of a very different pump-probe temporal profile for the parent ion under the same experimental scheme as in the previous work [25], but at the longer wavelength of 267 nm. In common with the work of Poth et al. on CH_3I [10], our experimental ionic signal of CF_3I^+ shows a profile consisting of a fast decay and a subsequent dip in ion signal followed by a rise to constant level as a function of the pump-probe delay time. This profile, however, was not observed for molecular clusters, as in the work of Poth et al., but for mono-molecular CF_3I. We therefore propose a new dissociation mechanism to explain our experimental observations.

2 Experimental

Although a detailed description of our experimental apparatus has been given previously [3,4], the essential elements will be summarized as the follows. The main component of our experimental apparatus is a home-built femtosecond laser system with frequency doubling and tripling, coupled to a standard Wiley-McLaren type time-of-flight mass spectrometer. The laser is composed of a seed oscillator and a regenerative amplifier with stretcher and compressor. The oscillator is a self-mode-locking Ti:sapphire cavity pumped by a 5 W argon ion laser (Coherent, Innova 300), which produces pulses of 20–30 fs duration at a repetition rate of 86 MHz and a central wavelength of 802 nm. The oscillator output is amplified by a chirped pulse regenerative Ti:sapphire amplifier pumped by a 3 kHz Nd:YAG laser. The final output from the amplifier is a 3 kHz train of 80 fs pulses with an energy of 200 μJ per pulse and is frequency doubled and tripled in a pair of BBO crystals, producing pump pulses at 267 nm and probe pulses at 401 nm with power of about 20 and 2–3 μJ, respectively.

The time-of-flight mass spectrometer used consists of three chambers: a source chamber, a field-free flight chamber and a detection chamber. The source chamber and the detection chamber are separately pumped by 1500 L/min and 800 L/min turbo pumps respectively. The pure CF_3I sample in saturated vapor tension is injected into the source chamber via a vitreous Hamamatsu capillary array operated in a continuous leakage regime. The molecular beam is crossed by the collinear pump and probe laser pulses, and the adjustment of the time delay between the two pulses permits the direct temporal measurement of the dissociation of highly excited CF_3I molecules with fs resolution. In our experiment the pump and probe beams share the same focusing lens (f = 29 cm), and care was taken to position the lens so that the pump and probe laser pulses have moderate intensities at the crossing point. This was achieved by reducing the energy of the laser pulses until the TOF peak of the CF_3^+ had almost disappeared for each single color excitation. Molecules ionized by the probe pulse in the source chamber fly freely through the flight chamber and are detected on a pair of micro-channel-plates (MCPs) in chevron configuration upon entering the detection chamber. The MCP signal is recorded via a computer controlled transient digitizer (Sonix STR81G) and the data are typically averaged over 3000 laser pulses.

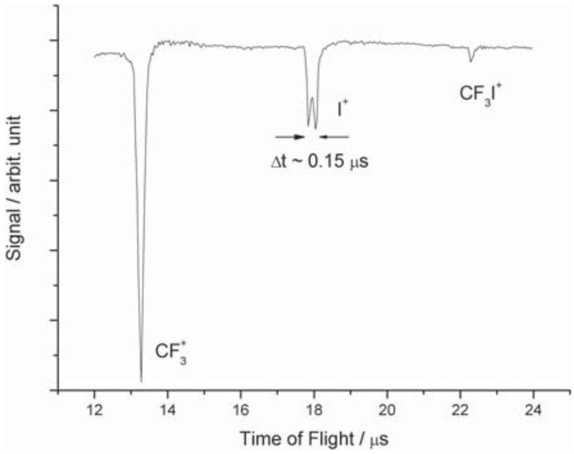

Fig. 1. Typical experimental time-of-flight spectrum at 267 nm pump and 401 nm probe. The ionic signal of iodine is split into two components with $\Delta t = 0.15$ μs.

3 Results and discussion

As presented in Figure 1, our time-of-flight mass spectrum of CF_3I is composed of three main features. These can be identified as arising from the CF_3^+ fragment, the I^+ fragment and the parent ion, CF_3I^+. What is immediately clear from the data in Figure 1 is that the signal from the CF_3^+ fragments is considerably stronger than that for the other two fragments (about 4 times that of the I^+ fragment), and the parent CF_3I^+ signal is the weakest at only one-fifth of the I^+ signal. This spectral intensity distribution indicates that the dissociation to CF_3^+ is dominant, a result which differs somewhat from previous observations at a pump wavelength of 265 nm [25]. We have also observed a splitting of the feature associated with the I^+ fragment indicating I^+ production at two different initial kinetic energies. The separation of the two time-of-flight peaks is ~0.15 μs, which corresponds to an initial kinetic energy difference of 4.46 eV when approximated using the formula $\Delta E = m(l/t)^2 \Delta t/t$.

Many previous authors have discussed the processes of photoexcitation and deexcitation that are relevant to the present work [19–26], thus an energy-level diagram for the specific electronic states and dissociation channels adapted from references [23–25,28] is reproduced in Figure 2 to assist in the discussion of our results. As can be seen from this figure, the total photon energy involved in our experiment can reach almost 15.5 eV arriving at the CF_3I^+, $\widetilde{B}^2A_2$ state. Upon further inspection of this energy-level diagram, one can see that both the CF_3I^+, $\widetilde{A}^2A_1$ state and the $\widetilde{B}^2A_2$ state can dissociate to produce ionic iodine through the channels: $CF_3 + I^+(^3P_2)$ and $CF_3 + I^+(^3P_{0,1})$ respectively. In our experiment, no CF_2I^+ signal was observed as was the case in the work of Aguirre and Pratt [28], however, our use of a two-photon probe ensures that the dissociation process is confined to the channels $CF_3^+(^1A_1) + I(^2P_{1/2})$ and $CF_3^+(^1A_1) + I(^2P_{3/2})$ with total required energies of 12.33 eV and 11.38 eV respectively.

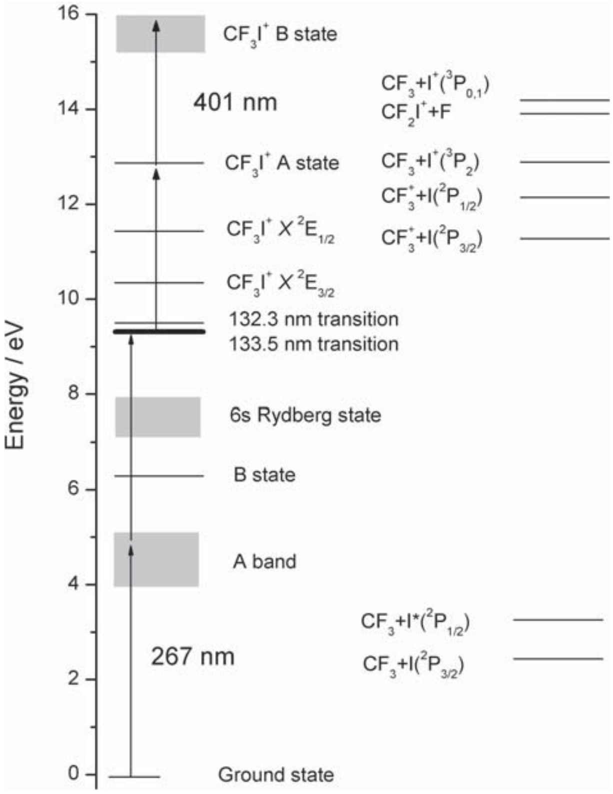

Fig. 2. Energy-level diagram of CF_3I and CF_3I^+. The lowest two channels are for the dissociation from the repulsive state A band and the upper channels for the ionic CF_3I dissociation giving CF_3^+ ions and I^+ ions. The diagram is redrawn according to references [23–25,28] and based on the spectral information in reference [29].

Due to the lack of information on the two-photon absorption spectrum of CF_3I related to our pump wavelength, we have assigned the pump pulse excited intermediate state with the aid of the far ultraviolet one-photon spectrum observation by Sutcliffe and Walsh [29]. In their work, the band at 132.3 nm was identified as to be one of the electronic origins of the $5p\pi^3 7s\sigma(^2\Pi_{1/2})$ configuration, which allowed Roeterdink and Janssen to assign their two-photon dissociation states at 264 nm [24]. This configuration gives rise to three electronic sub-states according to the Jahn-Teller theorem [29,30]. However, as our pump wavelength is longer than that of Roeterdink and Janssen, we cannot access the origin at 132.3 nm. In their work Sutcliffe and Walsh observed a strong diffuse band at 135.7 nm just under 132.3 nm, which is clearly the origin of a separate electronic transition but its vibrational pattern is concealed by other emission lines [29]. Our wavelength of 267 nm should access this area 670 cm^{-1} above the band origin at 135.7 nm, corresponding to the first symmetrical CF_3 deformation mode $\upsilon_2 = 680$ cm^{-1}, by two-photon absorption. The states of interest in this process are included on the right hand side of Figure 2. Thus, since the intermediate excited state is different in our work than in previous measurements [19,21,23,24,28], the dynamics

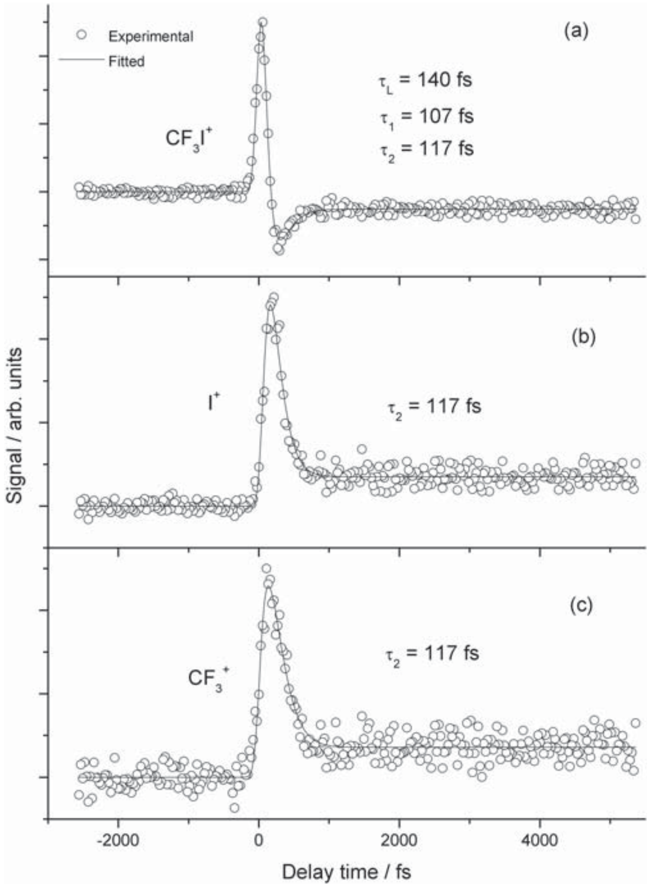

Fig. 3. Normalized pump-probe transients of CF_3I^+ and its fragments CF_3^+ and I^+. (a) The pump-probe signal of CF_3I^+. It can be seen that the signal peak is located around the zero delay time point but followed by a sharp dip although it comes back to a constant level. The signal is uniquely fitted to bi-exponential decays with time character parameters $\tau_1 = 107$ fs and $\tau_2 = 117$ fs. $\tau_L = 140$ fs is the instrumental response. (b) and (c) the pump-probe signal of fragments CF_3^+ and I^+. Although the signal magnitudes are different, they share the same dissociation pattern with the same decay time τ_1 and τ_2.

here might reasonably be expected to differ, as will be discussed in detail later in this section.

With our 267 nm pump and 401 nm probe laser pulses, we have recorded the signals from all of the photodissociation fragments of CF_3I as a function of the pump-probe delay time. However, as our pump wavelength differs from that employed in previously reported work, and results in a pump-probe profile which is different from that previously observed, one must conclude that the photodissociation mechanism occurring in our work is also different from that observed previously. In Figure 3 we present the pump-probe signals from the CF_3I^+ parent ion and each of the I^+ and CF_3^+ fragments. In each of these plots the data sets are individually normalized, but the pump-probe signal for the parent ion in Figure 3a is clearly very different from the profiles observed previously by us at a pump wavelength of 265 nm [25] and also by Roeterdink and Janssen at 264 nm [23,24]. The profile which we have observed for the parent ion peaks at around the point in time at which the pump and probe beams coincide, but this is followed by a sharp dip to a minimum at a delay time of 289 fs between the pump and probe pulses before then returning to a constant level after 860 fs. Most interestingly, the constant level to which the signal returns after 860 fs is lower than that recorded at the negative pump-probe delay time (i.e. when the pump and probe pulses exchange roles such that the 401 nm acts as the pump pulse and the 267 nm pulse acts as the probe). This implies that there should be a state involved which is excited by the 401 nm pulse when the pulses exchange roles, and is identified as the long-lived $\widetilde{B}$ state corresponding to two-photon absorption for 401 nm; thus accounting for the strong signal observed in the negative time direction, when followed by a one-photon ionization at 267 nm. These sequential processes will enhance the product of CF_3I^+ in $\widetilde{\mathrm{X}}^2E_{3/2}$ state, but will not dissociate into fragments in our observation time range.

In Figures 3b and 3c the peaks of the I^+ and CF_3^+ fragment signals appear at a pump-probe delay time of 145 fs, and decrease to a constant level for delay times greater than 1 ps. In each of these cases, the signal does not return to the same level as recorded when the molecules were probed before the zero delay time, as was the case in previous observations [25]. We account for this behavior by introducing a multiphoton process involving $\widetilde{\mathrm{B}}$ state excited by two 401 nm photons absorption and followed by one 267 nm ionization, as discussed before in this section, where only the CF_3I^+ in $\widetilde{\mathrm{X}}^2E_{3/2}$ state is accessed by probe pulse. From our measurements, the peaks of the I^+ and CF_3^+ profiles appear at the same pump-probe delay time, a result which differs from that obtained at a pump wavelength of 264 nm by Roeterdink and Janssen [23,24] where the I^+ peak lay ~120 fs after the CF_3^+ peak, which itself lay ~200 fs after that of the parent ion. The temporal parent ion profile, consisting of a fast decay and a subsequent dip in signal followed by a rise to constant level, is very similar to the dissociation of CH_3I at a pump wavelength of 270 nm, as reported by Poth et al. [10]. However, in their experiment, this parent ion profile was only observed when the dissociation of molecular clusters was probed rather than single molecules as is the case in our experiment [10]. In our previously published work on the photodissociation of CF_3I at a pump wavelength of 265 nm, each of the fragments observed including that of the parent ion exhibited a temporal profile which could be fitted by a monotonic exponential decay [25].

For the numerical analysis of the observed ion temporal profiles, we have fitted the data points with a function of the form:

$$I(t) = \begin{cases} C_1 e^{-t/\tau_1} + C_2(1 - e^{-t/\tau_2}) + D & (\text{for } t \geq 0) \\ C_3 e^{t/\tau_3} + D & (\text{for } t < 0), \end{cases} \tag{1}$$

where τ_1 represents the time constant for the fast decay close to a pump-probe delay of zero, τ_2 the constant for the fast component responsible for the subsequent rise in intensity at longer pump-probe delay times, and τ_3 is an additional fitting parameter for the transient process of CF_3I^+ in the negative pump-probe direction as discussed previously in this part. It should be noted that to give a physically meaningful result, the coefficients C_1, C_2, C_3 of each exponential decay term must be positive. The function given in equation (1), when convoluted with the temporal profile of the laser pulse, can be used to describe the data recorded in our experiments. It is worth noting that the slow varying component in equation (1), τ_3, is very large, $\gtrsim$10 ps, corresponding to the lifetime of $\widetilde{\mathrm{B}}$ state. We have determined the decay parameters, τ_1 and τ_2 to be 107 fs and 117 fs respectively, with the coefficients $C_1 = 0.1596$, $C_2 = 0.1403$ and $C_3 = 0.00057608$, consistent with the physical consideration. Since the fitted profile in the first ~1 ps is dominated by the parameters τ_1 and τ_2, there should exist a fast dissociation process which occurs on the $\tau_1 = 107$ fs timescale and a subsequent process which occurs on the $\tau_2 = 117$ fs timescale and results in the increase in signal strength following the initial dip.

The mechanism which gives rise to the dip structure in the temporal profile of the parent ion signal must be interpreted as either being a feature of the two-photon pump excitation to the CF_3I $5p\pi^3 7s\sigma$ Rydberg state, or the interaction between both of this state and the one-photon pump excitation to the repulsive state $\widetilde{\mathrm{A}}$. However, this parent ion temporal profile cannot be explained purely by the excitation to the repulsive state $\widetilde{\mathrm{A}}$.

To date no clear dissociation mechanism giving rise to a temporal ion profile such as that in Figure 3a has been identified, although some proposals have been put forward. In 1992 Guo made a theoretical time-dependent wavepacket calculation for the CX_3I (X = H, D, F, etc.) dissociation from the A band after absorbing UV light at a wavelength near 266 nm [31]. For this dissociation, resulting in the fragments $I + CX_3$ or $I^* + CX_3$, Gao found that the parent molecule bending motion could influence the nonadiabatic transitions during photodissociation giving rise to a different I/I^* branching ratio [31]. The value of these research efforts was confirmed by the afterwards investigation of the vibrational and rotational effects upon the fragmentation of CF_3I by Taatjes et al. [32].

From the spectral analysis presented in the early part of this section, the 267 nm pump pulse excites the ground state CF_3I into the first $\upsilon_2 = 1$ mode of the electronic state at 135.7 nm via a two-photon process. This vibrational mode then undergoes deexcitation through internal vibrational relaxation until it reaches the band origin $\upsilon_2 = 0$. We propose that the 401 nm probe excitation from these two vibrational states will competitively contribute to give the dip structure observed in the parent ion temporal profile at a pump-probe delay time of 289 fs. At longer delay times (i.e. > 1 ps), the feature of time-sensitive ionization contribution will disappear to give flat signal observed. These processes are illustrated in Figure 4.

Although the dip feature observed in the CF_3I monomer signal in our experiment is similar to that observed for the CH_3I clusters by Poth et al. at a pump wavelength of 270 nm [10], the dissociation mechanisms are different. In their two-color pump-probe experiment, the CH_3^+ fragment took on a single exponential decay with a short time response of 185 fs, the same time response as CH_3I^+. This behaviour was accounted for by considering a one channel ionization from 6s Rydberg state. However, when the supersonic expansion was adjusted to preferentially lead to the formation of clusters, the sharp pump-probe response at time zero of the CH_3I^+ ion signal was followed by a sharp dip and a subsequent rise for times greater than 2 ps, with a typical time scale of 234 fs and 1.1 ps respectively. The cluster-induced dip structure is the result of the energy surface shift brought on by clustering. Typically the CF_3I energy surfaces for the ground state and 6s and 10s Rydberg states, are lowered in energy by 500 cm^{-1} upon dimerization and up to 1000 cm^{-1} in larger clusters while the fast dissociative $\widetilde{\mathrm{A}}$ state is only shifted by ~10 cm^{-1}. This opens up another ionization channel from 10s Rydberg state, competing with the ionization from 6s Rydberg state, and these two channels are correlated by the dissociation from 10s Rydberg state to the 6s Rydberg state due to caging effects occurring in molecular clusters. The ionization competition between the different Rydberg states gives a longer rising time

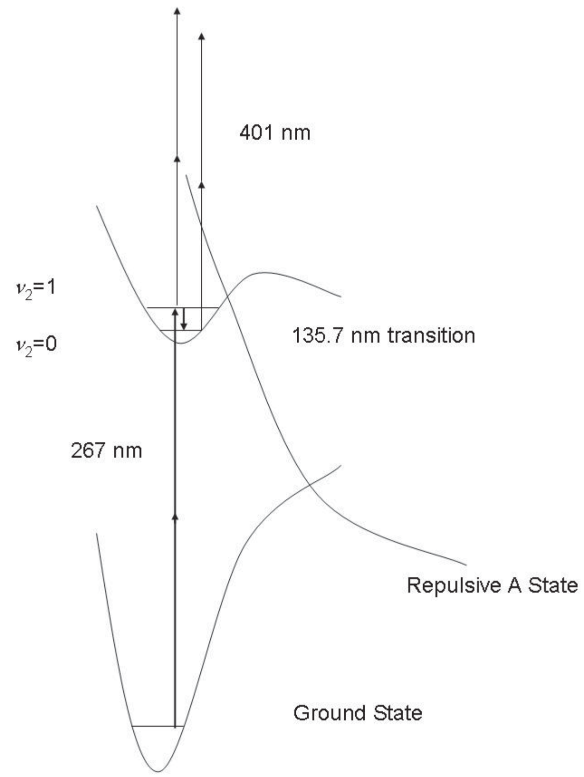

Fig. 4. Proposed mechanism for CF_3I dissociation at two 267 nm photons absorption excitation consistent with the experimental observation. The grounded CF_3I is excited onto the first vibrational state $\upsilon_2 = 1$ of the electronic state corresponding to 135.7 nm transition in reference [29] and then undergoes deexcitation through internal vibrational relaxation until it reaches the vibrational origin. The probe pulse 401 nm ionizations from these two vibrational states compete to give the dip structure at 289 fs delay time.

$\tau = 1.1$ ps, compared with our rising time $\tau = 117$ fs for the ionization from different vibronic states. This is easily understood by supposing that the 10s Rydberg state takes more time to dissociate and subsequently recombine into the lower lying 6s Rydberg state which is shifted due to the caging effects, than our direct dissociation from $\upsilon_2 = 1$ to $\upsilon_2 = 0$ by internal vibrational relaxation.

4 Conclusion

In this paper we reported new experimental results on the multiphoton dissociation dynamics of CF_3I using a standard Wiley-McLaren type time-of-flight mass spectrometer coupled to a homebuilt femtosecond laser pump-probe system. Signals from the CF_3^+ and I^+ fragments observed show a similar exponential decay profile when observed as a function of pump-probe delay time, while the corresponding signal from the parent ion has a clear dip structure. The ion fragments which we have observed are produced via the processes $(2+1')$ and $(2+2')$ through the dissociation of the ionic CF_3I^+ state. The first repulsive $\widetilde{\mathrm{A}}$ state and the $5p\pi^3 7s\sigma$ Rydberg state of CF_3I were accessed by one and two 267 nm pump photons respectively, but we propose that the latter channel provides the sole contribution to the ion signal. We attribute the dip structure observed in the parent CF_3I^+ ion signal at a pump-probe delay time of 269 fs to the competition of the ionization between from the vibronically excited $5p\pi^3 7s\sigma$ $\upsilon_2 = 1$ Rydberg state of CF_3I and from its subsequently dissociated vibrational origin $\upsilon_2 = 0$ by internal vibrational relaxation. This process will cause the excited states to be temporarily invisible to the probe pulse within the first few hundred femtoseconds of the dissociation.

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