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Imaging of Ultrafast Molecular Elimination Reactions

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Abstract: Ultrafast molecular elimination reactions are studied using the velocity map ion imaging technique in combination with femtosecond pump−probe laser excitation. A pump laser is used to initiate the dissociative reaction, and after a predetermined time delay a probe laser "interrogates" the molecular system. Ionic fragments are detected with a two-dimensional velocity map imaging detector providing detailed information about the energetic and vectorial properties of mass selected photofragments. In this paper we discuss the ultrafast elimination of molecular iodine, I_2, from IF_2C-CF_2I, where the iodine atoms originate from neighboring carbon atoms. By varying the femtosecond delay between pump and probe pulse, it is found that elimination of molecular iodine is a concerted process, although the two carbon−iodine bonds are not broken synchronously. Energetic considerations suggest that the crucial step in this fragmentation process is an electron transfer between the two iodine atoms in the parent molecule, which leads to Coulombic attraction and the creation of an ion-pair state in the molecular iodine fragment.

I. Introduction

In an elementary chemical reaction, the molecular system evolves continuously through a sequence of intermediate species that are neither reactants nor products, but the former turning into the latter.[1] Much research is focused on unraveling the transition states, because these intermediate states control the details of the reactant-to-product conversion process. One of the most elementary chemical reactions is the dissociation of a molecule, which can readily be triggered using light excitation. Indeed, photodissociation is particular suitable for experimental study, because the chemical reaction can be triggered at a preselected place and time in a highly controlled manner by a well-defined laser pulse. When a molecule photodissociates in the gas phase, its fragments fly apart in space. The trajectories and energies of these fragments are fully determined by the potential energy surfaces involved in the bond breaking process. Very detailed information on photodissociation dynamics has been obtained by mapping the angular distributions of fragments, after the dissociation is induced by a pulsed laser, by the ion imaging technique.[2,3] Most results of this type have been obtained with nanosecond lasers; however, the critical intermediate states evolve on a much shorter time scale, i.e. femtoseconds. In this paper, we study the elimination of molecular iodine from $C_2F_4I_2$ employing the femtosecond pump−probe technique in combination with time-of-flight velocity map imaging. Velocity map imaging measures the kinetic energy and the angular distribution of the photoions providing information about the dissociation pathways.[4]

When molecular bromine or chlorine adds to an alkene, the alkene polarizes the halogen bond and the reaction is classified as an electrophilic addition of the halogen cation; see Figure 1. In an electrophilic addition reaction, the π electron attacks the positive end of the polarized halogen molecule after which a bridged cation is formed.[5] A second mechanism involves radical formation, and in general there is a competition between the two; see, e.g., ref 6. Both these mechanisms are nonconcerted, i.e., a sequential addition of two halogen atoms. Using molecular beam techniques, the pathways relating reactants to products can be observed in either direction. Thus the two nonconcerted mechanisms have been studied extensively, in reverse, in the form of photodissociation reactions. Nathanson et al.[7] showed that the two-center elimination reaction $C_2F_4I_2 \rightarrow C_2F_4 + I + I$ is of nonconcerted character by using picosecond excitation of the dissociative A band, in combination with kinetic energy resolved time-of-flight mass spectrometry. The first iodine atom splits off within 200 fs. It takes 25 ps for the second iodine atom to be eliminated, from which a barrier of 0.6 eV was estimated. Zhong et al.[8] studied the elimination of halogen atoms from $C_2F_4I_2$ using femtosecond pulses centered at 277 nm to dissociate the parent molecule. A Resonance-Enhanced Multi-Photon Ionization (REMPI) scheme centered at 304 nm detecting the I atomic fragment was used in combination with kinetic energy resolved time-of-flight (TOF) spectroscopy. The recoil anisotropy was determined using polarized femtosecond pulses. These measurements conclusively excluded the possibility of breaking the two C−I bonds concertedly after excitation to the dissociative A band. This is in contrast to photodissociation at 248 nm of $C_2H_4Br_2$, where an asynchronous concerted mechanism was observed.[9] The structural dynamics of transient

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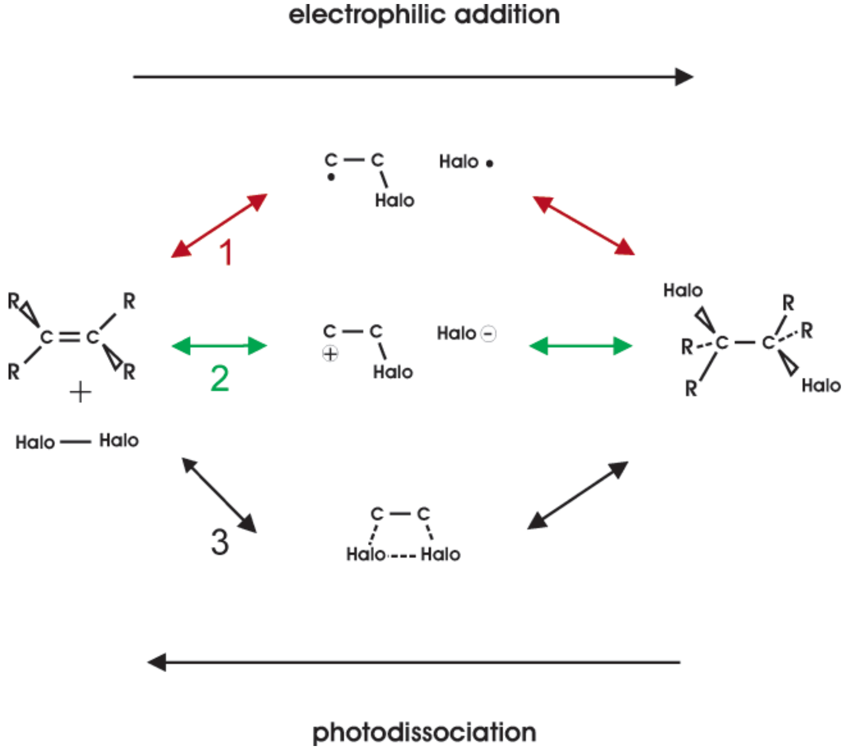

Figure 1. In general three different pathways in the route of an electrophilic addition can be followed, indicated with 1, 2, and 3. Channel 1 is a radical pathway, and channel 2 is an ionic pathway. Channel 3 is a four-center reaction. We can study channel 3 in the reverse direction using ultrafast velocity map imaging.

intermediates in the elimination reaction of $C_2F_4I_2$ was studied by Zewail and co-workers using ultrafast time-resolved electron diffraction.[10,11] Of special interest was the structure of the intermediate C_2F_4I radical. It was concluded that in the C_2F_4I intermediate radical, the iodine atom is not bridged between the two carbon atoms. This is in contrast to the analogous radical with hydrogen in place of fluorine. Recently, the photodissociation dynamics of $C_2F_4I_2$ in solution was reported.[12] In these experiments photodissociation at 266 nm resulted in the formation of molecular iodine within a few picoseconds. In this study it was concluded that in solution the main pathway was secondary dissociation of the haloethyl radical, formed after one-photon absorption at 266 nm, and geminate recombination of iodine atoms.

In this paper we report the dissociation of $C_2F_4I_2$ following two-photon excitation centered at 396 nm. We will present ion images of molecular iodine formed in a femtosecond pump−probe experiment. These experiments indicate the existence of a third channel (see Figure 1), which is the concerted elimination of molecular iodine and probably involves the formation of ion-pair states.

II. Experimental Section

The experimental setup has been described in full detail recently;[13] therefore we will only give a brief description here. The $C_2F_4I_2$ molecules (Fluorchem) are seeded (0.5%) in Ar and cooled by expansion through a pulsed nozzle operating at 1 kHz. After passing two skimmers, the molecular beam enters the ionization chamber. In this chamber the molecular beam is intersected by two collinearly propagating femtosecond laser pulses at a position midway between the repeller and extractor plates of a set of ion lenses. The ion optics are designed to map the velocity of the ionized fragments on a Micro-Channel-Plate (MCP)/Phosphor screen detector, located about 36 cm downstream of the ionization region. The gain of the MCP detector is pulsed at the arrival time of the ion mass of interest. In this way mass-selected ion images can be measured. The electrons emitted from the back of the chevron type MCP plates are accelerated toward a phosphor screen. The phosphorescence is imaged with a sensitive slow scan CCD camera and simultaneously by a photomultiplier to obtain the total ion yield.

The intensities of the pump and probe laser beams are chosen such that about 10 parent ions per laser shot are formed when the pump and probe pulses are overlapped in time. The femtosecond chirped-regen laser system operates at 1 kHz. The pulse energies were typically 20 μJ for the 396 nm laser and 2 μJ for the 264 nm laser. The waists of both laser beams are measured with calibrated pinholes to be about 200 μm diameter. Images are taken at various delay times between pump and probe pulses. To account for background and one-laser contributions, images are measured with both laser pulses entering the ionization region, as well as images with pump and probe beams separately. The data treatment has been described previously.[13]

Results and Discussion

In general three different reaction pathways can be followed in the electrophilic addition of a halogen to an alkene; see Figure 1.[5,6] The reverse pathways can be conveniently studied using ultrafast photodissociation spectroscopy. For the model system $C_2F_4I_2$ the dissociation channels 1 and 2 have been extensively studied before.[7,8,10,11] In this paper we will study channel 3, a four-center reaction.

Figure 2a shows the TOF mass spectrum, using 20 μJ of 396 nm simultaneous with 5 μJ of 264 nm to ionize the fragments.

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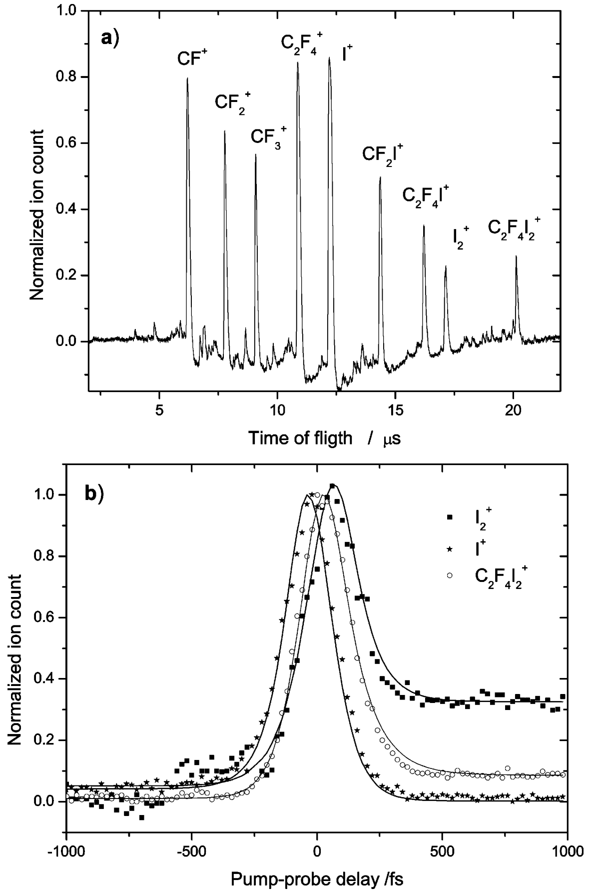

Figure 2. (a) Mass spectrum as observed at $\tau = 0$. The pump beam at 396 nm had an energy of 20 μJ, and the probe beam at 264 nm had an energy of 5 μJ. This probe energy is more than double the energy used in all other experiments reported here like the transients shown in panel (b). The undershoot of the ion signal below the baseline is an artifact of the preamplifier. (b) Pump probe transients of I_2^+, I^+, and $C_2F_4I_2^+$. A convolution of a Gaussian, with the sum of an exponential decay and an exponential rise, is used to determine the typical time scales of the dissociation reactions. The parent molecule and the I_2^+ fragment show an enhancement at positive times, indicating that for the formation of this channel the 396 nm laser is the pump laser. The baseline of the transients is the sum of the individual signals from each pulse separately.

The TOF spectrum is comparable to the spectrum observed by Zhong et al.,[8] who used a single laser beam of 277 nm. There is a slight difference in relative fragment intensities between our and Zhong's measurements, which might be caused by the difference in color used to ionize. After lowering the energy of the 264 nm beam to 2 μJ, the CF$^+$, CF$_2^+$, and CF$_3^+$ fragments disappeared. In all the experiments described here an energy of 2 μJ for the 264 nm laser is used.

Figure 2b shows the pump−probe transients of I_2^+, I^+, and $C_2F_4I_2^+$. The parent ion shows a small enhancement at positive delay times, indicating the excitation of a long-lived state after interaction with the pump laser. Two or more 396 nm (pump) photons have to be absorbed because no resonant state can be excited with one 396 nm photon. The lowest electronically excited state of $C_2F_4I_2$, the A band, is located around 266 nm.[14] The molecular iodine fragment also shows a much stronger enhancement at large positive times. This also indicates the absorption of at least two 396 nm pump photons, followed by the absorption of at least one 264 nm probe photon. The transient of the atomic iodine fragments, however, shows only a very small enhancement at negative delay times; i.e., the roles of the pump and probe laser are reversed.

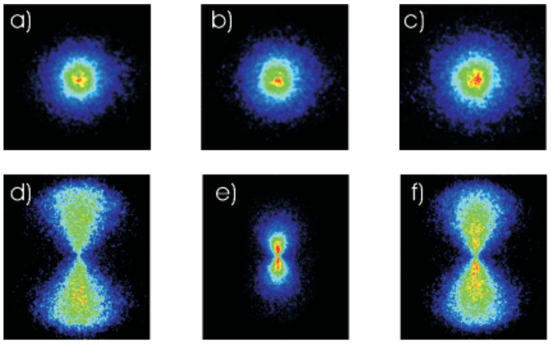

Figure 3. Velocity map images of the I_2^+ fragment at (a) 0 fs, (b) 250 fs, and (c) 750 fs. Almost no anisotropy is observed, indicating a high rotational excitation of the transition complex, due to an asynchronous concerted dissociation mechanism. Velocity map images of the I^+ fragment at (d) 0 fs, (e) −250 fs, and (f) −750 fs. Note that the 264 nm laser behaves as the pump laser. At $\tau = 0$ and high recoil energy, a high anisotropy is observed, corresponding to a two-photon parallel type excitation.

The pump−probe transients are fitted with the expression:

$$I(t) = \int_{-\infty}^{t} [e^{-(t'-t_0)/\tau_1} + c[1 - e^{-(t'-t_0)/\tau_2}]]e^{-(t'-t)^2/2\sigma^2}\,dt' \quad (1)$$

This formula represents an exponential decay and an exponential rise convoluted with a Gaussian pulse shape. τ_1 can be interpreted as the lifetime of the state excited by the pump laser. The typical value found for τ_1 is 100 fs. τ_2 can be interpreted as the time needed to create the fragments. With the time resolution of the laser system, 140 fs (fwhm), only an upper limit for τ_2 could be determined. This makes it difficult to derive from the pump−probe transients whether the state excited by the pump laser decays directly into the observed fragment channel or that there are more intermediate states involved: velocity map images are needed to provide more detailed information on intermediate states. However, the short buildup time of the molecular iodine, <150 fs, does indicate that the elimination is concerted.

Figure 3 shows the velocity map images recorded at three different pump−probe delay times. In the top row, panels (a), (b), and (c), the ion images of the molecular iodine fragment, are shown at 0, 250, and 750 fs pump−probe delays, respectively. Using the selected photon-ion drift time (Figure 2a) and the radial size of the velocity map image (Figure 3a−c), the kinetic energy of the fragments can be determined.[13] The kinetic energy distributions obtained are displayed in Figure 4a.

The appearance energy of I_2^+ can be calculated[15] to be $E_a = 10.0$ eV for the reaction:

$$C_2F_4I_2 \rightarrow C_2F_4 + I_2^+ + e \quad (2)$$

As discussed above for the parent ion, the enhancement at positive delay times of the I_2^+ transient indicates that at least two 396 nm photons are absorbed. The formation scheme of I_2^+ in which the minimum number of photons are absorbed is the (2 + 1′) photon process, where the prime indicates the absorption of 264 nm pump photons; see Figure 5. Previous time-resolved ion imaging studies have shown that in the case

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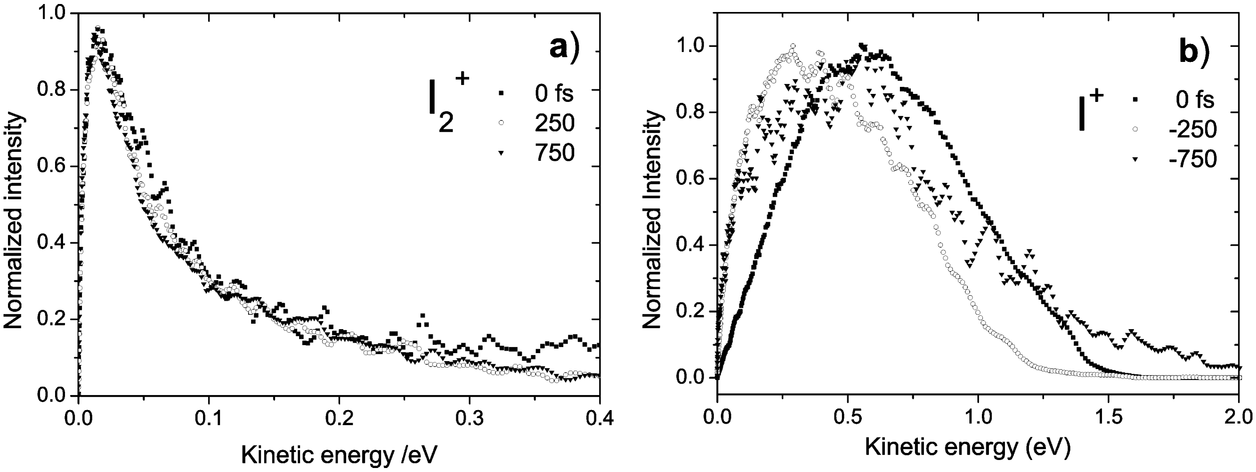

Figure 4. (a) Kinetic energy distribution of the I_2^+ fragment, derived from the velocity map images by radial integration. The most probable recoil energy is 0.017 eV. (b) Kinetic energy distribution of the I^+ fragment, derived from the velocity map images by radial integration.

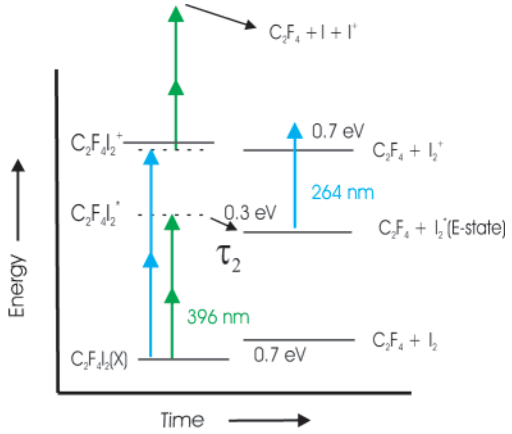

Figure 5. Schematic overview of the energetics of the formation of atomic and molecular iodine. In the case of molecular iodine, the parent molecule is excited with two 396 nm photons of which 0.7 eV is needed to break both iodine−carbon bonds. The atomic iodine ion is formed in the dissociation of the parent ion.

of CF_3I and CF_2I_2 the photon schemes using the minimum number of photons are the dominant channels.[13,22] This was confirmed by coincidence imaging measurements[21] and time-resolved electron measurements.[24] In the experiment we reduced the fluences of both the pump and probe laser to only produce the fragments of interest and to prevent photon processes involving more photons. The total photon energy of the (2 + 1′) process is 10.94 eV. The cutoff kinetic energy of the I_2^+ fragment can be calculated using the conservation of energy:

$$nh\nu_{\text{pump}} + mh\nu_{\text{probe}} - E_{\text{a}} = \sum_x E_{\text{kin,x}} + \sum_x E_{\text{int,x}} + E_{\text{electron}} \tag{3}$$

in which n is the number of pump photons, m is the number of probe photons, E_{a} is the appearance energy, and x is C_2F_4 and I_2. The conservation of momentum for this two body dissociation process implies:

$$E_{\text{kin},I_2} + E_{\text{kin},C_2F_4} = E_{\text{kin},I_2}\left(1 + \frac{m_{I_2}}{m_{C_2F_4}}\right) \tag{4}$$

in which m_x is the mass of fragment x. A cutoff kinetic energy for the I_2^+ fragment of 0.25 eV is calculated as an upper bound, i.e., when the internal and electron energies vanish and the available energy is completely converted into recoil energy. Experimentally we observe a peak at a kinetic energy around 0.02 eV with a tail to 0.2 eV (see Figure 4a) well below the cutoff energy of 0.25 eV.

The reaction $C_2F_4I_2 \rightarrow C_2F_4 + I_2$ has an endothermicity of 0.7 eV,[16] indicating that after the absorption of two 396 nm photons the total energy of both fragments has to be 5.5 eV; see Figure 5.

To ionize the highly excited molecular iodine with one 264 nm photon, at least 4.6 eV from the total of 5.5 eV must be internal energy of the molecular iodine fragment. Ion pair states correlating to I^+ and I^- are strongly bound and therefore the best candidates when a lot of energy has to be deposited in the products.[17] Thus it is likely that molecular iodine is formed in the E-state (T_e = 5.2 eV), an ion-pair state. Under the assumption that the dissociation is an instantaneous process, i.e., the probe photon merely ionizes the molecular iodine fragment and does not contribute to the recoil energy, an excess energy of 0.3 eV would give an upper limit to the kinetic energy of 0.08 eV for the molecular iodine fragment. Of course part of the energy can be funneled into vibrational or rotational energy of the products, which makes this 0.08 eV an upper limit. Furthermore, the distance between both iodine atoms in $C_2F_4I_2$ is 3.8 Å[11] which is close to the bond length of molecular iodine in the E-state, 3.5 Å. Although we use a seeded molecular beam expansion, which is estimated to be rotationally cold (perhaps tens of Kelvin), we do not know how well the gauge conformer freezes out to the anti confomer. The energy difference between the gauge and anti confomers is 5 kJ/mol, i.e., 600 K.[18] This makes it difficult to determine whether the C−C bond rotation takes place after the excitation or we select the gauge confomer.

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The formation of this ion-pair state also gives a logical explanation for the formation mechanism of the iodine molecule: despite the fact that the two molecular iodine atoms are separated relatively far, Coulombic attraction ensures that the two atoms attract each other.

From our data we cannot exclude the possibility of the formation of excited C_2F_4. The lowest lying electronically excited state in C_2F_4 is the $CFCF_3$ state, formed after a 1,2 fluorine migration. The energy of this state can be estimated to be 1.8 eV.[19] To access this state a $(3 + 1')$ transition is necessary, which gives a cutoff value of the kinetic energy around 0.6 eV. This high cutoff value for the kinetic energy is experimentally not observed which makes this channel less likely. The lowest electronically excited state in the $\pi\pi^*$ manifold of C_2F_4 is around 5.0 eV,[20] which can be accessed via a $(2 + 2')$ transition. This channel gives a cutoff kinetic energy of 0.17 eV, and therefore we cannot exclude this channel with our data. Electron energy measurements are needed to conclusively determine the operational channel. Photoion photoelectron coincidence imaging would be the ideal tool to further elucidate the formation mechanism for these fragments.[21]

The velocity map images, shown in Figure 3, not only provide information on the kinetic energy release in the ionic fragments but also, from the angular intensity distribution, contain information about the number of photons absorbed and the photodissociation dynamics. The angular distributions of the ions are fitted with

$$I(\theta_s) = \frac{\sigma}{4\pi}[1 + \beta P_2(\cos\theta_s) + \gamma P_4(\cos\theta_s)] \tag{5}$$

where θ_s is the laboratory fixed scattering angle between the recoil velocity and the polarization of the photolysis laser, P_2 and P_4 are the second- and fourth-order Legendre polynomial. β and γ are the recoil anisotropy parameters representing a measure of correlation between the direction of the transition dipole moment of the molecule μ and the fragment velocity vector $\mathbf{v}$. In the limit that the probe pulse merely ionizes the I_2^* molecule a $\beta = 2.86$ is expected for a two-photon parallel transition.[13] However, no anisotropy ($\beta \approx 0$) in the angular distribution of I_2^+ is observed. In analogous systems such as CF_2I_2[22] and CH_2I_2,[23] also a reduced β parameter was observed. Using symmetry arguments it can be shown that after the absorption of only one 264 nm photon by the parent molecules, CF_2I_2, CH_2I_2, and $C_2F_4I_2$, no stable state of I_2 can be accessed; i.e., the symmetry of the electronic wave function is such that there is no electron density between the two iodine atoms. This symmetry barrier causes an asynchronous bond breaking and consequent high rotational excitation.[22,23] Indeed, a high barrier for the elimination of molecular iodine from $C_2F_4I_2$ is observed, reflected in the fact that at least two 396 nm photons must be absorbed to form molecular iodine and not just one 264 nm photon. Our data suggest that the elimination of molecular iodine starts with an electron transfer between the two iodine atoms. The Coulombic interaction between the atoms causes the formation of the molecule despite the large distance between them.

Velocity map images of the atomic iodine fragment are shown in Figure 3d−f. In contrast to the I_2 fragment a clear change in the velocity map image with delay is observed. Around −250 fs the ion image is much smaller, and this indicates that the fragment is produced with a lower kinetic energy. The kinetic energy distributions are shown in Figure 4b. Presently, it is unclear what causes this minimum in the kinetic energy release around −250 fs. It may be a fingerprint of the C−I bond as such a strong reduction in the recoil energy was observed before in the photodissociation of CF_3I,[13] were it attributed to a $(1+3')$ transition, and in the dissociation of CF_2I_2.[22] However, at this moment we cannot conclusively determine the mechanism of the process resulting in a reduced kinetic energy.

The I^+ fragments are produced at negative delay times, i.e., the 264 nm laser beam acts as a pump laser. Therefore, we can exclude the possibility that, after the formation of molecular iodine, one additional 264 nm photon is absorbed to form I^+. The photon scheme which requires the minimal number of photons are two 264 nm photons as pump followed by two 396 nm photons as probe. The two-photon absorption at 264 nm excites to a longer lived (Rydberg) state in the parent molecule, which may internally convert to lower lying electronic states. The further absorption of two 396 nm photons brings the excited parent molecule into an excited parent ionic state, which dissociates yielding I^+. This scheme is analogous to the formation of I^+ in CF_3I and CF_2I_2;[13,22] see also Figure 5. This multiphoton pathway was also studied in CF_3I using coincidence imaging[21] and time-resolved electron measurements.[24] The long lifetime of this state is reflected in the small enhancement at negative times of the I^+ transient; see Figure 2b. Such a $(2 + 2')$ photon scheme gives a photon energy of 15.7 eV. The photon induced reaction, $E_a = 13.0$ eV:

$$C_2F_4I_2 + h\nu \rightarrow C_2F_4I + I^+ + e \tag{6}$$

which thus has an excess energy of 2.7 eV. Using eqs 3 and 4, a cutoff kinetic energy of 1.7 eV can be calculated. Experimentally we observe a peak at a kinetic energy around 0.6 eV with a tail to 1.5 eV; see Figure 4a. This is below the cutoff energy of 1.7 eV. The I^+ fragment has an anisotropy close to the value expected for a two-photon parallel transition. This suggests that the probe laser merely ionizes the iodine atoms and the angular distribution is determined by the actual dissociation process. The high anisotropy is a strong indication for a prompt dissociation, which is corroborated by the short buildup time of less than 150 fs derived from the pump−probe transient.

IV. Conclusion

In summary, with femtosecond pump−probe spectroscopy in combination with velocity map imaging, information about transition states from molecular elimination reactions was obtained. The studied reaction shows the elimination of molecular iodine where the two iodine atoms originate from neighboring carbon atoms. This reaction has a high symmetry barrier of more than 4.7 eV for the formation of molecular iodine. It is proposed that the molecular iodine is created in an electronically highly excited state, most probably an ion-pair state. This suggests that the elimination reaction starts with an electron transfer between the two iodine atoms, which gives rise to a Coulombic attraction between the atoms. This facilitates the creation of molecular iodine in an ion-pair state.

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