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Ultrafast photodissociation dynamics in electronically excited CF_2I_2 molecules

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Abstract. Using the femtosecond pump-probe technique with photoion and photoelectron detection the ultrafast dissociation processes in excited CF_2I_2 molecules have been analyzed suggesting the dominance of a concerted three-body decay.

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A topic of interest in photodissociation is the three-body decay in which the excited molecule is subject to two bond-scissions yielding three final products [1, 2]. CF_2I_2 has proved to be a molecule with a particular richness of dissociation mechanisms including three-body decay. Using photofragment translational spectroscopy and REMPI-TOF with ns laser pulses [3] it has been found that at 248 nm a concerted three-body decay to $CF_2 + I + I$ is the dominant decay path while at 308 nm a sequential three-body decay to $CF_2I + I \rightarrow CF_2 + I + I$, and a two-body decay to $CF_2I + I$ are the main dissociation channels.

In the present work we applied the pump-probe technique with femtosecond laser pulses to study the ultrafast dynamics of the photodissociation of CF_2I_2 molecules. Combinations of three different wavelengths – 400, 267, and 200 nm – were used as pump and probe beam. The laser pulses with a pulse width of ~ 130 fs were obtained as the second, third and fourth harmonics of a commercial Ti:sapphire laser and amplifier system (Clark MXR) tuned to 800 nm. The parent molecule ion and product ions are detected by a time-of-flight mass spectrometer (TOF-MS). Figure 1 shows an example of the ion signal vs. the delay time between the pump pulse at 267 nm and the probe pulse at 400 nm with the solid lines representing the theoretical fit. The rapid decay of the parent ion signal with a time constant $\tau_R \sim 30$ fs is due to an ultrafast relaxation process whose nature is presently unknown. The successive fragmentation process, proceeding with a time constant $\tau_F \sim 100$ fs, leads to the formation of neutral fragments CF_2, I, and I_2. These products are ionised by the time delayed probe pulse and represent the small but finite ion signals at larger delay times τ (Fig. 1). The strength of the tails with respect to the peaks of the ion signals (Fig. 1) and also the significance of the fragmentation time $\tau_F \sim 100$ fs, is enlarged for lower probe laser intensities [5]. The peaks of the ion signals for the different masses (Fig. 1) are due to fragmentation of the parent ion molecules caused by the excess energy after the absorption of the pump and probe photons. Whereas the peaks of $CF_2I_2^+$ and CF_2I^+ result from ionization and dissociation via the primarily excited state of CF_2I_2, the distinct shift of the maxima for the products I_2^+, I^+, CF_2^+ to longer delay times demonstrates the ionization and fragmentation of CF_2I_2 after the transfer to a secondarily excited neutral state. Because the shift is identical for the three products a common source can be supposed which will be the excited state of the parent molecule populated with the time constant $\tau_R \sim 30$ fs [5]. The absence of this time shift for CF_2I^+ indicates that a sequential decay involving the CF_2I intermediate can be excluded at 267 nm excitation in agreement with the findings of [3]. This is supported by the missing of any finite CF_2I^+ signal at longer delay times (see Figs. 1, 2).

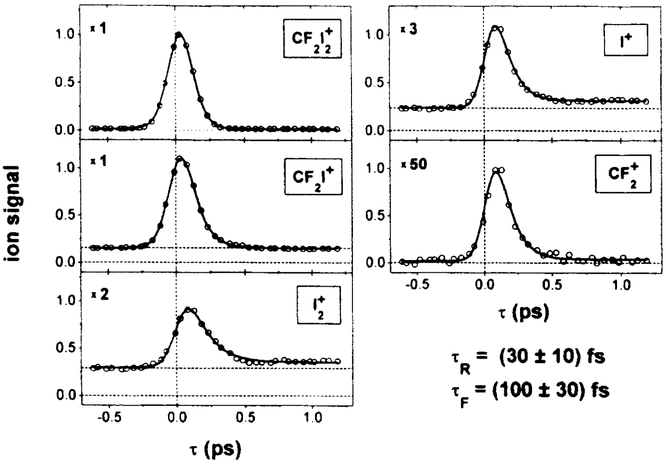

Fig. 1. Ion signals vs. delay time τ between pump (267 nm) and probe (400 nm) pulses. (The signals are magnified by the factors given in the upper left corner.)

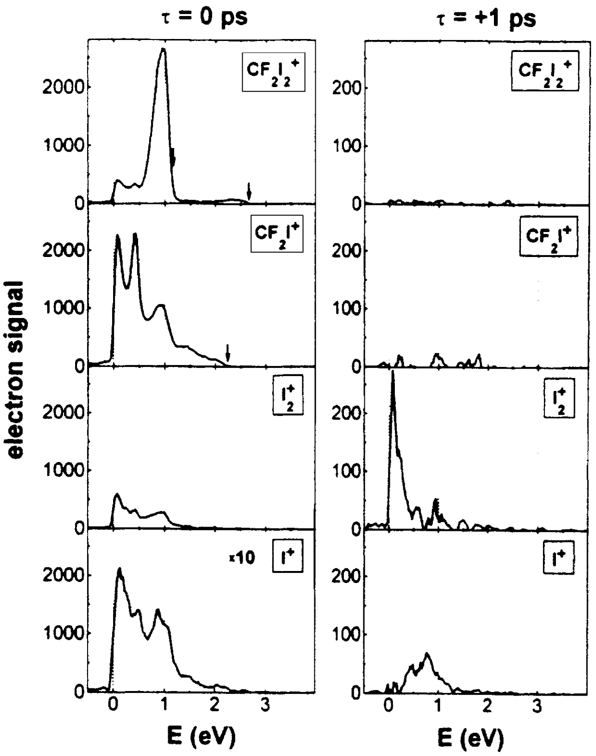

Fig. 2. Photoelectron spectra of $CF_2I_2^+$ and fragment ions for $\tau = 0$ and $\tau = +1$ ps. Note the magnification by the factor 10 for the I^+ signal at $\tau = 0$.

The detailed interpretation of the time dependent ion signals – for the peaks near $\tau = 0$ as well as for the relatively large and nearly constant signals at $\tau \ll 0$ and $\tau \gg 0$ (cf. Fig. 1) – is rather complex due to a superposition of simultaneously active decay channels in the neutral parent molecule and the ionic species created by multiphoton absorption. Therefore we have also applied the fs time resolved photoelectron spectroscopy [4] to obtain further information about these processes in real time.

In Fig. 2 preliminary results of the photoelectron spectroscopy are shown obtained for the pump wavelength $\lambda_1 = 267$ nm and the probe wavelength $\lambda_2 = 400$ nm, i.e., for the same combination as in Fig. 1. On the left hand side the spectra of the parent ion and the fragment ions are compared for $\tau = 0$ while on the right hand side the spectra are shown for $\tau = +1$ ps. The background signals ($\tau < 0$) have been subtracted. The electron spectrum of $CF_2I_2^+$ for $\tau = 0$ is characterized by two thresholds at $E_{\mathrm{el}} = 1.1$ eV and $E_{\mathrm{el}} = 2.65$ eV. Both values are consistent with an ionization threshold of IP = 9.75 eV for the parent molecule which up to now has been unknown: $h\nu_1 + 2h\nu_2 - \mathrm{IP} = 1.1$ eV and $2h\nu_1 + h\nu_2 - \mathrm{IP} = 2.65$ eV, respectively. The upper threshold of the electron spectrum of the fragment ion CF_2I^+ suggests a binding energy $E(CF_2I^+...I)$ of 0.55 eV. Analogously the binding energies of the other fragments in the ion state can be estimated which leads to an improved understanding of the energetics in the ion state.

The maxima in the electron spectra at $\tau = 0$ reflect different electronic states excited by the pump photon in the parent molecule. Their appearance also in the electron spectra of the fragment ions demonstrates that for $\tau = 0$ the fragmentation in the ion state is the dominant channel for product ion formation.

Whereas the electron spectra at $\tau = +1$ ps vanish completely for $CF_2I_2^+$ and CF_2I^+ we observed significant signals for I_2^+ and I^+ in agreement with the results in Fig. 1. The electron spectrum of I_2^+ at $\tau = +1$ ps may be interpreted as due to a concerted fragmentation of the two iodine atoms from the excited neutral parent molecule followed by ionization with the probe pulse. Possibly this signal can also result from complete dissociation of parent molecule ions formed via a longer living excited neutral state. The electron spectrum of I^+ at $\tau = +1$ ps is not yet understood. Here further experiments with a resonant probe wavelength are required.

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