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Photodissociation Dynamics of 2-Iodotoluene Investigated by Femtosecond Time-Resolved Mass Spectrometry[†]

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The photodissociation dynamics of 2-iodotoluene following excitation at 266 nm have been investigated employing femtosecond time-resolved mass spectrometry. The photofragments are detected by multiphoton ionization using an intense laser field centered at 800 nm. A dissociation time of 380±50 fs was measured from the rising time of the co-fragments of toluene radical (C_7H_7) and iodine atom (I), which is attributed to the averaged time needed for the C−I bond breaking for the simultaneously excited $n\sigma^*$ and $\pi\pi^*$ states by 266 nm pump light. In addition, a probe light centered at 298.23 nm corresponding to resonance wavelength of ground-state iodine atom is used to selectively ionize ground-state iodine atoms generated from the dissociation of initially populated $n\sigma^*$ and $\pi\pi^*$ states. And a rise time of 400±50 fs is extracted from the fitting of time-dependent I^+ transient, which is in agreement with the dissociation time obtained by multiphoton ionization with 800 nm, suggesting that the main dissociative products are ground-state iodine atoms.

Key words: 2-Iodotoluene, Photodissociation, Dissociation time, Femtosecond time-resolved mass spectrometry

I. INTRODUCTION

The photodissociation dynamics of halogenated organic compounds has attracted historically great attention, not only due to its crucial role in highly detailed fundamental studies but also its harmfulness to environment [1−17]. The principal goal of photodissociation studies is to obtain the clearest picture of the molecular dynamics in the excited state as the molecule leaves the Franck-Condon region such as what transient states to traverse, where the fragments are formed, what the lifetime of the upper state is and which bonds break and so on. Many experimental techniques have been developed to investigate photodissociation reaction process, for instance photofragment translation spectroscopy [4−6], velocity map imaging [7, 8] and ultrafast time-resolved time-of-flight mass spectrometry [9−15], which are coupled with high level *ab initio* calculations [15−17] to provide a clear picture of the fragmentation mechanisms of molecules.

The UV absorption spectra of aryl iodine are dominated by two contributions: one is the $n\sigma^*$ states resulting from the promotion of a nonbonding electron from

the iodine atom valence shell to an antibonding σ^* localized along the C−I bond, which leads to a rapid direct dissociation, and the other is due to the absorption to the bound $\pi\pi^*$ states of the benzene ring which has predissociation character for the coupling with repulsive $n\sigma^*$ states. As a result of the overlap of these two different type states in the same energy region, the dynamics cannot be directly obtained from the absorption spectrum. Femtosecond time-resolved mass spectrometry coupled with state-selective resonance enhanced multiphoton ionization has been emerging as a powerful tool for investigating photodissciation dynamics process. It has two major advantages: the first one is mass selectivity, which allows for the separate study of the reactant and fragment dynamics, the second one is the ability of selectively monitoring all fragments of different masses or same masses in different final state as well as the parent ion simultaneously.

2-Iodotoluene, which is formed by substitution of an iodine atom and a methyl group for two neighboring hydrogen atoms of the benzene, is a very interesting system for study. Using state-selective onedimensional photofragment translational spectroscopy, El-Sayed *et al.* investigated the photodissociation dynamics of 2-iodotoluene upon excitation at 266 nm [6]. The spatial and velocity distributions of ground-state iodine atom I and excited state iodine atom I* were determined. Two distinct ground-state iodine atoms velocity distributions were observed. One is a high velocity, narrow distribution with high anisotropy, which

is attributed to direct dissociation from the repulsive $n\sigma^*$ state. The other one is a low velocity, broader distribution appearing lower anisotropy, which is due to the predissociation from the bound $\pi\pi^*$ state. The dissociation times for these two channels were estimated by calculating time-dependence of anisotropy parameter β. Fang *et al.* have calculated the potential energy curves for the ground and low-lying excited states of 2-iodotoluene along the assumed photolysis reaction coordinates and elucidated the dissociation mechanism and channels following excitation at 266 nm [17].

Based on the previous studies on aryl halides, in this work, we identify the photodissociation dynamics of 2-iodotoluene and the processes that participate in the relaxation of the molecule after being initiated by excitation at 266 nm. Especially, the determination of time scales for the dissociation channels is the focus on. Although previous experiment has estimated the dissociation times through measurements of the anisotropy [6], the accuracy is low especially when reaction time is more or comparable to the average rotation time of the parent molecule. Femtosecond time-resolved mass spectrometry enables one to directly measure the dissociation time. To the best of our knowledge, this is the first time-resolved study on the photoinduced C−I bond breaking of 2-iodotoluene at 266 nm.

II. EXPERIMENTAL SETUP

The details of the experimental setup are described elsewhere [18]. Briefly, it consists of a molecular beam machine coupled to a linear time of flight mass spectrometer and a 1 kHz-4 mJ/pulse Ti:Sapphire regenerative-amplified laser system (Coherent Inc.), delivering pulses with a central wavelength of ∼800 nm and a Fourier-transform-limited full width at half-maximum (FWHM) duration of ∼100 fs. One part of the output light was used to produce the pump pulse at 266 nm by mixing the fundamental (800 nm) and the second harmonic beam (400 nm) in a 0.2 mm thick BBO crystal. One part was applied to pump an optical parametric amplifier (OPA, Coherent Inc. TOPAS-C) to generate probe wavelength centered at 298.23 nm, which is used for the resonance-enhanced multiphoton ionization (REMPI) probing of ground-state I atoms. Another part was used as probe light to track the relaxation processes of 2-iodotoluene. The energy intensity for pump light is 0.5 μJ/pulse which keeps no ion signal occurring with it alone. For the probe light, the typical energy is 10 and 60 μJ/pulse for the 298.23 and 800 nm respectively. The probe beam was temporally delayed relative to the pump beam by a computer-controlled linear translation stage (PI, M-126.CG1). The two laser beams were focused with fused silica lens of f=400 mm respectively and introduced into the vacuum chamber collinearly through a dichroic mirror.

The employed apparatus [19] is similar to that de-signed by Eppink and Parker [20]. It consists of a molecular-beam source chamber and an ionization-flight detection chamber. The detection chamber was kept below 0.5 μPa with the molecular beam on. 2-Iodotoluene (99.9% purity) seeded in He was expanded into the source chamber with a stagnation pressure of 2 atm through a pulsed nozzle (General Valve, with a 0.5 mm orifice) with the repetition rate of 10 Hz. The supersonic molecular beam is collimated by a conical skimmer and intersects perpendicularly with the two laser beams in a two-stage ion lens region. Photoion is extracted into a 36 cm field-free region, which is doubly shielded against stray magnetic fields by μ-metal tube. At the end of the time-of-flight tube, the ions strike a two-stage microchannel plate detector backed by a phosphor screen. The emission from the phosphor screen is monitored by a photomultiplier connected to a 1 GS/s digital oscilloscope (Tektronix Inc., TDS2012B) USB interfaced with a computer. The LabView software was used to track the parent ion and fragments signal as function of pump-probe delay time simultaneously.

III. RESULTS AND DISCUSSION

With the help of detailed theoretical calculation [17] and experimental investigation [6] on 2-iodotoluene, it is easy to determine that upon excitation at 266 nm, the dominant excited states are the $\pi\pi^*$ state with a bound character and the $n\sigma^*$ state with a repulsive character along the C−I stretching coordinate, which leads to the production of ground-state iodine atoms. So, the parallel relaxation processes for those two excited states are monitored by probe pulse which ionized the excited molecules.

Figure 1(a) displays the time-of-flight mass spectra obtained with the pump pulse at 266 nm alone, the probe pulse at 800 nm alone and in pump-probe configuration at Δt=0 (time-overlap). The power of the probe light is ∼26 μJ/pulse. As observed in the mass spectra, there are many fragment ions generated other than parent ion $C_7H_7I^+$, especially for toluene ion $C_7H_7^+$ which is the dominant signal in the mass spectra, indicating that the parent ion will to a large extent undergo photo-induced fragmentation [21, 22], which is similar to the femtosecond pump-probe investigation on iodobenzene [10]. Figure 1(b) shows the measured time transients of the total signals of $C_7H_7I^+$ and $C_7H_7^+$, following excitation at 266 nm and probe with 800 nm (26 μJ/pulse). The polarizations of pump and probe beam are parallel with each other. The decay time profile for parent ion $C_7H_7I^+$ and $C_7H_7^+$ can be best fitted by one exponential with decay time constant τ_d of 92±10 and 129±15 fs respectively convoluted with a Gaussian that describes the pump-probe cross correlation.

It is not likely that those fragment ions shown in Fig.1(a) are produced from the ionization of the corresponding neutral radicals, which is generated from
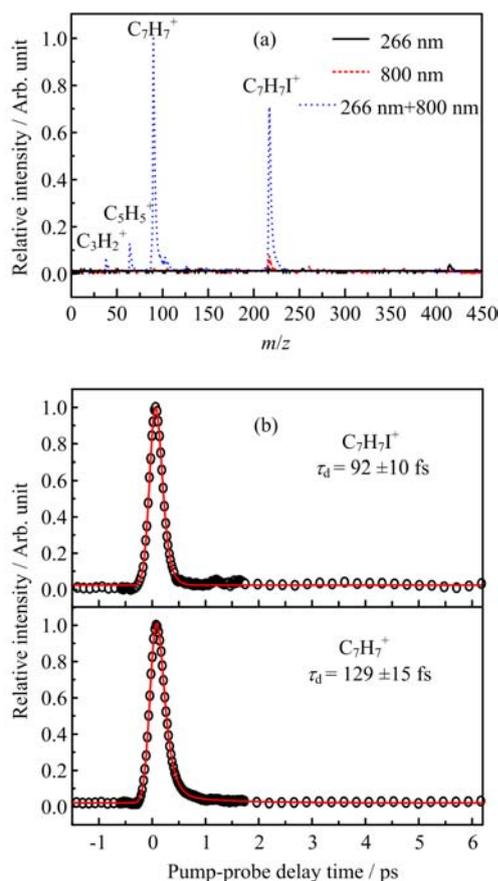
FIG. 1 (a) One color and two color (at time overlap) mass spectra of 2-iodotoluene at 266 and 800 nm. The typical energy was 0.5 and 26 μJ/pulse for the 266 nm pump and 800 nm probe pulse respectively. (b) Time-resolved $C_7H_7I^+$ and $C_7H_7^+$ transients recorded under the same conditions as (a), the circles represent experimental data and the solid lines are fitting results.

dissociation of neutral molecules or fragmentation of molecular ion, due to their high ionization potential under our low probe light intensity. For instance, ionization of neutral toluene radical would require absorption at least six probe photons (800 nm) since the ionization potential of the toluene radical is expected to be only slightly lower than the ionization potential of the phenyl radical, which is 9.13 eV [23, 24]. If the neutral radicals can be detected, the time-profile of $C_7H_7^+$ should have a stable channel at longer pump-probe delay time, which is not observed on the fragment ion in Fig.1(b), indicating that the neutral radical C_7H_7 generated from dissociation in electronically excited states induced by the pump pulse is not ionized by the probe pulse 800 nm with intensity of 26 μJ/pulse. So, it is expected that all fragment ions observed here are originated from dissociative ionization of parent molecules. Since no ion signals were generated with pump pulse alone, the time-dependent fragment ions signal should also reflect the neutral excited states dynamics of 2-iodotoluene.

The repulsive $n\sigma^*$ and the bound $\pi\pi^*$ states can be excited simultaneously. So, it is expected that two decay components should be observed on the time profile of parent ion or fragment ions. Such kinetics is observed on iodobenzene molecule [10]. Unfortunately, only one decay component is observed for $C_7H_7I^+$ and $C_7H_7^+$ transients shown in Fig.1(b) and we tend to attribute this component to the decay dynamics of the initially populated $n\sigma^*$ state. There are two possible reasons for not observing the contribution from $\pi\pi^*$ state: one is that the absorption cross-section of the $\pi\pi^*$ state is much lower than the $n\sigma^*$ state and indeed the absorption coefficient of the $n\sigma^*$ state is an order larger than that of the $\pi\pi^*$ state according to the theoretical calculation [7]; another one is that the ionization cross-section for the $\pi\pi^*$ state is probable low with 800 nm as probe light. Thus, the ionization signal from the $\pi\pi^*$ state would be faint, which is likely to be suppressed by strong ionization signal from the $n\sigma^*$ state.

Now we turn to discuss the observed lifetime τ_d, which is assigned to the decay dynamics of the initial populated $n\sigma^*$ state as mentioned above. Indeed, a very fast relaxation will occur when excited to this state due to its repulsive character. Using state-selective photofragment translational spectroscopy Freitas and coworkers [6] studied the photodissociation dynamics of 2-iodotoluene upon excitation by 266 nm and observed a sharp high velocity distribution of ground-state iodine atoms, which was assigned to a direct dissociation occurring on the $n\sigma^*$ state. And they estimated the dissociation time (0.51 ps) of C−I bond on this state by calculating β variation as a function of time. According to the calculations [17], it has big possibility for the molecules to stay on this state during decay processes. Therefore, the observed lifetime for the decay of $n\sigma^*$ state should be shorter than the dissociation time which is associated with the time needed from the Franck-Condon region to the production of freedom iodine atoms. Thus, the fitted τ_d is reasonable and not contradicted with the estimated dissociation time of 0.51 ps in Freitas' work. It is persuasive to assign the lifetime constant τ_d to the decay dynamics on the initially excited $n\sigma^*$ state.

In order to get more insight to the dissociation dynamics of the excited states induced by 266 nm, we increase the power of probe pulse to try to detect the dissociative products. It is an ideal tool to detect molecular species with easily achieved multiphoton ionization using femtosecond lasers [25]. By increasing the power of the probe beam from 26 μJ/pulse to 60 μJ/pulse, a time-of-flight mass spectrum recorded at pump-probe delay time zero is shown in Fig.2. More visible fragment ions signal intensity is observed compared with the mass spectrum obtained with probe intensity 26 μJ/pulse. To follow the transient dynamics for these fragment ions, the signal intensities against the pump-probe delay time for these peaks were acquired, which is shown in Fig.3. The temporal behavior of all fragment ions
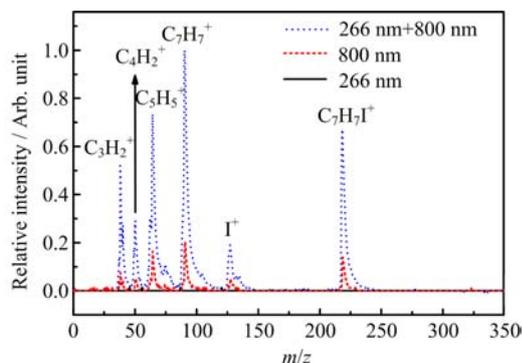
FIG. 2 The mass spectra of 2-iodotoluene obtained with 266 nm pump light alone and 800 nm probe light alone and at time overlap between pump and probe light. The typical energy was 0.5 and 60 μJ/pulse for the 266 nm pump and 800 nm probe pulse respectively.

can be well fitted to one fast decay component and one rise component, convoluted with a Gaussian describing the pump-probe cross correlation. All decay and rise times measured for all cation transients are summarized in Table I. Those two components correspond to two different channels for the production of the fragment ions. For the fast decay time constant τ_d, it is reasonable to attribute this component to the dissociation of the parent ions after the pump-probe ionization, since it has similar trend to the parent $C_7H_7I^+$ ion time profile shown in Fig.3. For the second rising component τ_r, it is a constant component without decay. Furthermore, this component depends greatly on the power of the probe beam. Thus this component is attributed to the ionization of the neutral fragments generated by the pump pulse. As mentioned above, the dissociative products are toluene radical C_7H_7 and iodine atom I induced by the pump light. So, it is easy to assign the rise component for $C_7H_7^+$ and I^+ transients to the ionization of neutral C_7H_7 and I. It is very interesting to observe that the $C_5H_5^+$, $C_4H_2^+$, $C_3H_2^+$ transients also show the rise component. By closely inspecting the time profile of these transients, it is discovered that the time constants τ_r are in agreement with that for $C_7H_7^+$. Thus, it is likely that the rise components in $C_5H_5^+$, $C_4H_2^+$, $C_3H_2^+$ transients are from the dissociative ionization of neutral radical C_7H_7. Indeed, there are no dissociative channels from the parent molecules to product neutral radical C_5H_4, C_4H_2 and C_3H_2 after being excited by 266 nm, which further evidence our conclusion. So, the τ_r components in these fragment ions transients reflect the same dynamics as in $C_7H_7^+$. It is worth noting that the rise time constant τ_r reflects the averaged time needed for all dissociative channels initialed by 266 nm, leading to generation of neutral radical C_7H_7 and iodine atom I.

It is interesting that the decay times increase as the mass of the fragment ions decreases. As mentioned above, the decay components in all fragment ions tran-
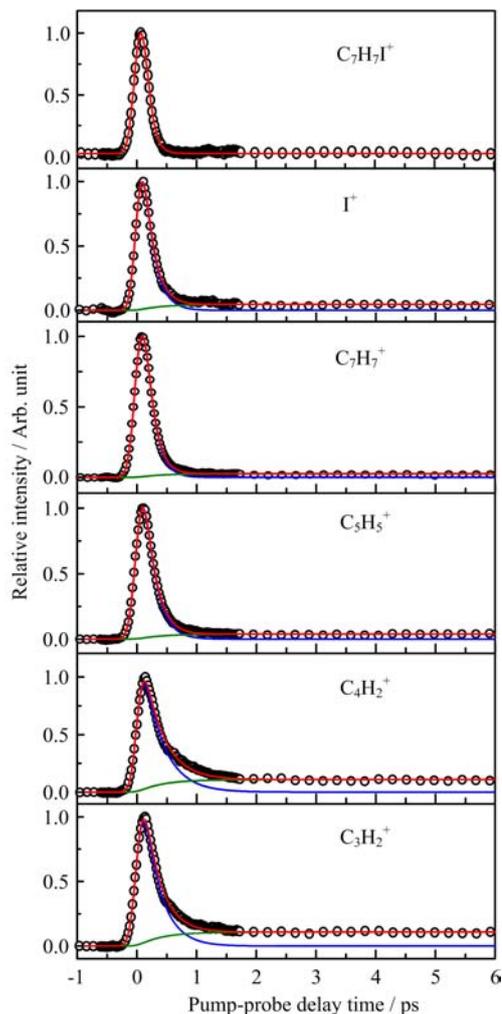

FIG. 3 Time-resolved cation transients recorded under the same conditions as Fig.2. The circles represent experimental data and the solid lines are fitting results. All transients are normalized to their maxima value.

TABLE I The time constants extracted from the fits of all cation transients shown in Fig.3.

	τ_d/fs	τ_r/fs
$C_7H_7I^+$	105±10	–
I^+	170±30	380±50
$C_7H_7^+$	146±20	395±80
$C_5H_5^+$	185±15	392±40
$C_4H_2^+$	220±20	400±80
$C_3H_2^+$	245±30	405±40

sients are from the fragmentation after pump-probe ionization of parent molecule. These observations are similar to the ones obtained, for instance, on tetrathiafulvalene and $Cr(CO)_6$ probed with an intense probe pulse [26, 27]. Here as well, the degree of fragmentation is weaker at small pump-probe delays and becomes stronger at long pump-probe delays. As explained,

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when the molecule relaxes, the electronic energy is converted into vibrational energy, which remains in the ion upon ionization. Dissociative ionization is sensitive to vibrational relaxation since the bonds in the ion are generally weaker than those of the neutral molecules. Therefore, upon ionization, the internal energy of the ion will be more and more important and fragmentation to the smaller species will take place once intramolecular vibrational relaxation becomes effective [26].

To gain more information on the photodissociation dynamics of 2-iodotoluene upon excitation by 266 nm, the probe light at 298.23 nm, corresponding to the ground-state iodine atom resonance wavelength [28], is used to track the appearance of ground state iodine atoms product generated by cleavage of C−I bond in this molecule. There are no excited state I atom resonance wavelengths within the bandwidth of the probe light (450 cm^{-1}), which enables us to probe the ground state iodine atoms only. Figure 4 displays the I$^+$ transient obtained following excitation at 266 nm and probe with 298.23 nm. It can be fitted with a single rising exponential convoluted with the Gaussian pump-probe cross correlation, yielding a rising time constant of 400±50 fs, which reflects the average time for all dissociative channels leading to ground state I atoms. Two distinct ground-state I atom spatial and velocity distributions were observed by El-Sayed's group [6] using nanosecond lasers. One is a high velocity, narrow distribution that exhibits a high anisotropy, which is assigned to the direct dissociation from nσ^* state. The other one is a low velocity, broader distribution accompanied by a lower averaged anisotropy, which is attributed to the predissociation dynamics of $\pi\pi^*$ state. And they speculated that the dominant products of ground-state I atoms resulted from direct dissociation process. The dissociation time of this process is estimated to be 0.51 ps. The value 400±50 fs extracted from the time transients of ground-state I atom in our experiment is in agreement with the estimated value 0.51 ps [6]. Therefore, it is reasonable to conclude that the measured rise time 400±50 fs dominantly reflects the dissociation time needed for C−I fission on the nσ^* state populated by 266 nm, though we cannot rule out the contribution from the predissociation dynamics of initially excited $\pi\pi^*$ state.

IV. CONCLUSION

The ultrafast relaxation of 2-iodotoluene has been studied after excitation at 266 nm with the goal of determining the time scales of the dissociation channels. In this excitation wavelength, a repulsive nσ^* state and a bound $\pi\pi^*$ state are populated simultaneously. The obtained time-profile of parent ion (C$_7$H$_7$I$^+$) with 800 nm as probe light (26 or 60 µJ/pulse) can be best fitted by one decay exponential convoluted with a Gaussian describing the pump-probe cross correlation. However,
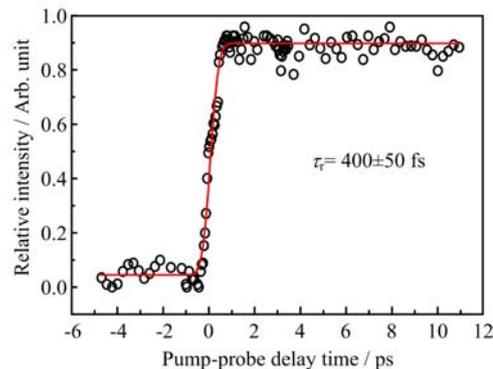

FIG. 4 The I$^+$ transient obtained following excitation at 266 nm and probing at 298.23 nm corresponding to the resonance wavelength of ground state iodine atom. The circles are experimental data and the solid line is the fitting result.

a decay component and a rise component are needed to fit the temporal behavior of all fragment ions (C$_3$H$_2^+$, C$_4$H$_2^+$, C$_5$H$_5^+$, C$_7$H$_7^+$, I$^+$) obtained with strong intensity of 800 nm probe light (60 µJ/pulse). The decay time constant τ_d (105−245 fs) for all ions reflects the decay dynamics of the initially populated repulsive nσ^* state. While the rise time constant τ_r (380−405 fs) is attributed to the averaged dissociation time for all the dissociation channels induced by pump light 266 nm. In addition, we selectively tracked the dissociation channels leading to ground-state iodine atoms using ground-state iodine atom resonance wavelength of 298.23 nm as probe light. The measured appearance time 400±50 fs for I$^+$ transient is in agreement with the dissociation time obtained with multiphoton ionization with 800 nm as probe light, which indicates that the main products of dissociation induced by 266 nm are ground-state iodine atoms.

V. ACKNOWLEDGMENTS

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