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ARTICLE

Wavelength-dependent Photodissociation Dynamics of Benzaldehyde[†]

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The ultrafast dynamics of benzaldehyde upon 260, 271, 284, and 287 nm excitations have been studied by femtosecond pump-probe time-of-flight mass spectrometry. A bi-exponential decay component model was applied to fit the transient profiles of benzaldehyde ions and fragment ions. At the S_2 origin, the first decay of the component was attributed to the internal conversion to the high vibrational levels of S_1 state. Lifetimes of the first component decreased with increasing vibrational energy, due to the influence of high density of the vibrational levels. The second decay was assigned to the vibrational relaxation of the S_1 whose lifetime was about 600 fs. Upon 287 nm excitation, the first decay became ultrashort ($\sim$56 fs) which was taken for the intersystem cross from S_1 to T_2, while the second decay component was attributed to the vibrational relaxation. The pump-probe transient of fragment was also studied with the different probe intensity at 284 nm pump.

Key words: Benzaldehyde, Ultrafast process, Femtosecond pump-probe

I. INTRODUCTION

Nonadiabatic dynamics plays key roles in photochemistry of polyatomic molecules. There had been many experimental and theoretical studies of S_1 electronic relaxations in gaseous aromatic molecules. Both internal conversion (IC) between the S_1 and S_0 states and intersystem crossing (ISC) between the S_1 and T_1 states were involved in the electronic relaxation. ISC between S_1 and T_1 had been supposed to be the predominant electronic relaxation channel at small excitation energies where it was favored by Franck-Condon factors [1–3]. However, increased excitation energy changed the electronic relaxation dynamics. For example, a rapidly increasing electronic relaxation rate at larger excitation energy, the "channel-three" decay, was attributed to S_1–S_0 IC [1–6]. The fast IC process started from the S_1 minimum geometry and tunneled through the transition state to prefulvene, after which it entered the S_0 surface via S_1–S_0 IC. Strong repulsion between S_1 and S_0 surfaces along the coupling coordinate contributed to the lack of a potential barrier from prefulvene to S_0 benzene. Substituents of benzene might modify the electronic states, couplings and the rigidity of the molecular frame. Substituent effects in molecular electronic relaxation dynamics using a series of monosubstituted benzenes, such as styrene, benzaldehyde, and phenylacetylene, had been studied by using femtosecond time-resolved photoelectron spectroscopy [7] and velocity mapping methods [8]. Laser induced fluorescence experiment on the photodissociation of nitrosobenzene at 266 nm implied the excited S_2 sate might predissociate via vibrational redistribution or intersystem crossing to T_1 or intersystem conversion to S_1 [9].

Photoprocess studies of benzaldehyde have been of theoretical and experimental interest of decades for the compound with close-lying $n\pi^*$ and $\pi\pi^*$ excited states in both singlet and triplet states. This was ideally suited for the study of the physical processes of intersystem crossing and phosphorescence, as well as photochemical reactions of valence isomerization, bond breakage, and atom transfer [10]. The lifetime of the S_2 state of benzaldehyde was determined as 440 fs at the origin and showed a monotonic lifetime decrease with increasing vibrational energy [7]. While benzaldehyde in the S_2 state had a short lifetime, similar to other derivatives, the relaxation in its S_1 state was orders of magnitude faster than that of the noncarbonyl compounds, due to the well-known presence of a lower lying $n\pi^*$ state. The ultrafast electron diffraction with the resolution in space and time was also used to observe the intermediate structures formed through radiationless transitions, which were termed "dark" state because their existence was inferred indirectly from radiative transitions [10–12]. In addition, the structures of the electronic states of benzaldehyde had been performed by a few theoretical studies [13–15].

The spectroscopy of benzaldehyde has been extensively studied experimentally, recently reported in

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Refs.[16,17]. According to the absorption spectrum of vapor-phase benzaldehyde with wavelengths longer than 260 nm (see the Fig.1 in Ref.[9]), electronic excitation to the first singlet excited state (S_1) was a weak absorption band with resolved structures. Meanwhile, the band in short wavelength range (260–290 nm), assigned as transition to the S_2 ($\pi\pi^*$) state, was much more intense and showed less structured.

Few direct measurements of the electronic relaxation of the S_2 states in benzene derivatives, such as benzene [18], benzene dimmer [19], benzene-ammonia clusters [20], phenol [21], etc, had been reported. These aromats typically showed subpicosecond lifetimes for the S_2 state with much longer lifetimes for the S_1 state. In general, the S_2 states might be expected to exhibit greater sensitivity to the electronic structure of the substituent than the S_1 states, which decayed predominantly as did benzene.

In this work, we presented the experimental study of wavelength effects on electronic relaxation dynamics in benzaldehyde around its S_2 states using the pump-probe technique and time-of-flight mass spectroscopy. The dynamical principle was the nonadiabatic coupling of electronic and vibrational motions. We noticed the lifetimes of excited states heavily depended on the excitation energy. Different from benzene, vibrational excitation above the S_1 and below the S_2 origin in benzaldehyde lead much faster relaxation.

II. EXPERIMENTS

The laser system used for pump-probe experiments with femotosecond laser pulses has been described previously [22,23]. Briefly, our homemade solid-state femtosecond laser system output 814 nm fundamental pulses at 20 Hz repetition rate. The width of the laser pulses was about 67 fs, measured by single-shot intensity autocorrelation method. The fundamental light was divided into 40% and 60% by a 40/60 beam splitter mirror. The probe light, 407 nm, was the frequency doubling result of the 40% residual fundamental light by a β-BaB_2O_4 crystal (BBO, type I). The pump light was the frequency doubling result of the output of an optical parametric amplifiers (Quantronix/Light Conversion, TOPAS), excited by the 60% fundamental light. Intensities of both the pump and the probe pulses were controlled independently by two continuously variable neutral density attenuators. The two laser beams were collinearly combined by a dichroic mirror and focused independently in the interaction region by two 450 mm fused silica lens, whose positions were kept unchanged in our experiments. Both the pump and probe laser pulses were kept weak enough to avoid one colour background signal. A computer controlled delay stage line was used to scan the delay time between the pump and probe pulses.

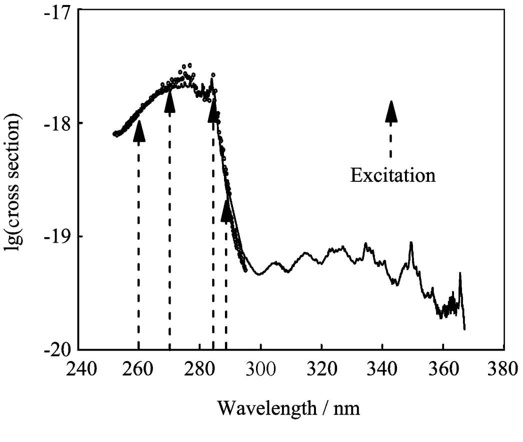

FIG. 1 UV-Vis spectrum of benzaldehyde and excitation positions in current experiments [8].

The sample gas, vapor pressure of benzaldehyde in 0.06 MPa helium, was expanded through a pulsed valve (General Valve, with a 0.5 mm orifice) into the ionization region. After flying in a 40 cm field-free region, ions were detected by a two-stage microchannel plate (MCP) detector. With molecular beam on, the source chamber and flight chamber were maintained at 450 and 8 μPa to avoid the space-charge effect. At a repetition rate of 20 Hz, time-of-flight mass spectra were averaged over 512 laser shots. Typically, each datum point was the averaged result over more than 20 scans to yield a pump-probe transient with good signal-to-noise ratio.

The selected pump wavelengths were shown in Fig.1. Excitations at 260, 271, and 284 nm populated the parent molecules into different vibrational levels of the S_2 electronic state. 287 nm, which was longer than the origin of S_2 from its ground state (~284 nm) [24,25], projected the molecules into high vibrational excited states of the S_1 state.

III. RESULTS AND DISSCUSSION

A. Transients of the parent ions

Figure 2 showed the pump-probe transients of the benzaldehyde ion signals, excited at 260 nm and probed by 407 nm. Figure 2(b) showed Xe^+ transient profile. Cross-correlation function between the pump and probe light was determined by fitting the Xe^+ transient profile using a Gaussian function. The full width at half maximum (FWHM) of this function was about 82 fs, as indicated in Fig.2(b).

The transient profile of benzaldehyde ion could be fitted by a two-exponential decay model comprising two ultrafast decay component. The faster decay componen with lifetime of about 238 fs was due to the internal conversion of the coherent excitation S_2 ($\pi\pi^*$) to vibrationally excited S_1 ($n\pi^*$). The lifetime constant was consistent with the reported value excited by 266.7 nm [7,10]. The second decay component with lifetime of about 560 fs was contributed to the vibrational relax-

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TABLE I Fitting parameters for transient profiles of $C_6H_5CHO^+$ and $C_6H_5CO^+$ shown in Figs. 3 and 4 by a bi-exponential model: $a\exp(-t/\tau_1)+b\exp(-t/\tau_2)$, where a and b represent the amplitudes of the two components with lifetimes of τ_1 and τ_2, meanwhile, fitting errors were also given, respectively.

Wavelength/nm	a/b		τ_1/fs		τ_2/fs	
	$C_6H_5CHO^+$	$C_6H_5CO^+$	$C_6H_5CHO^+$	$C_6H_5CO^+$	$C_6H_5CHO^+$	$C_6H_5CO^+$
260	2.1	3.0	238±13	100±14	560±10	617±11
271	1.9	2.3	427±11	121±17	625±12	672±11
284	1.6	1.0	892±11	530±10	650±11	672±11
287	3.7	3.3	56±1	70±1	604±11	617±11

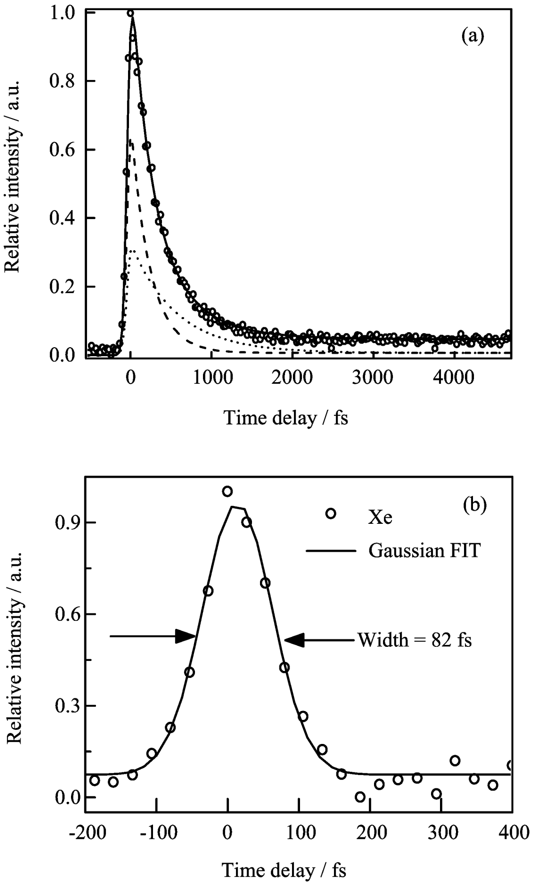

FIG. 2 (a) Transient profiles of $C_6H_5CHO^+$ pump by 260 nm and probed by 407 nm. Lines were fitting results. (b) The cross-correlation functions measured by Xe.

ation of the vibrationally excited S_1 [7,10].

The pump-probe transients of benzaldehyde molecular ions excited by different pump laser wavelengths were presented in Fig.3. The same bi-exponential model: $a\exp(-t/\tau_1)+b\exp(-t/\tau_2)$ was applied to fitting the transient profiles. The second component represented the vibrational relaxation of the S_1 state. As the pump light wavelength increased from 260 nm to 284 nm, the electronic relaxation of the S_2 state slowed down, as illustrated in Fig.3. Fitting results listed in Table I also showed this trend. Lifetimes of the τ_1 components increased with the excitation wavelength while the relative contribution of this component decreased with the excitation wavelength. This observation was consistent with the previous reports [7,10].

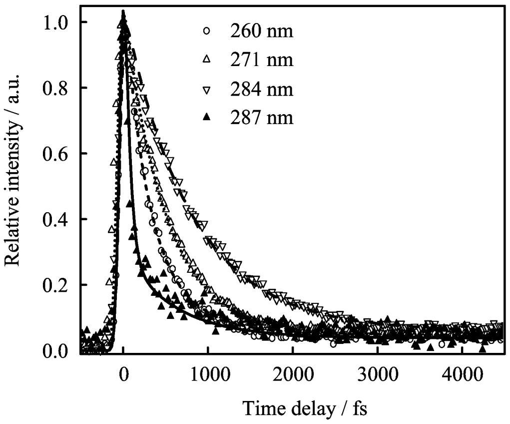

FIG. 3 Transient profiles of $C_6H_5CHO^+$ at different pump wavelengths, probed by 407 nm. Lines were fitting results.

S_2 state of jet-cooled benzaldehyde has its origin at 35191 cm^{-1} (~284 nm) relative to the ground state, determined by laser ionization spectrum [24,25]. 271 and 260 nm should pump the molecules from the ground state to the vibrational levels. Benzaldehyde could be populated into high vibrational levels of S_1 by excitation at 287 nm. The most interesting thing was that when the pump wavelength was 287 nm or even longer, the relaxation showed an ultrafast decay (~56 fs) component, followed by a relative slow decay component with lifetime of about 680 fs. The slower decay component, excited at 287 nm, was attributed to the vibrational relaxation of the S_1. The faster decay here was assigned to the channel of the intersystem crossing from S_1 to T_2. The fitting results were also listed in Table I.

B. Decay of the fragment

The pump-probe transients of $C_6H_5CO^+$ were shown in Fig.4. The detected fragment ion signals might be combination results of both the dissociation-ionization and ionization-dissociation processes. According to the

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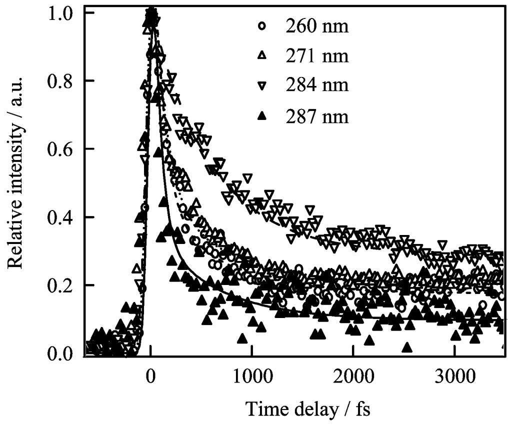

FIG. 4 Transient profiles of $C_6H_5CO^+$ at different pump wavelengths, probed by 407 nm. Lines were fitting results.

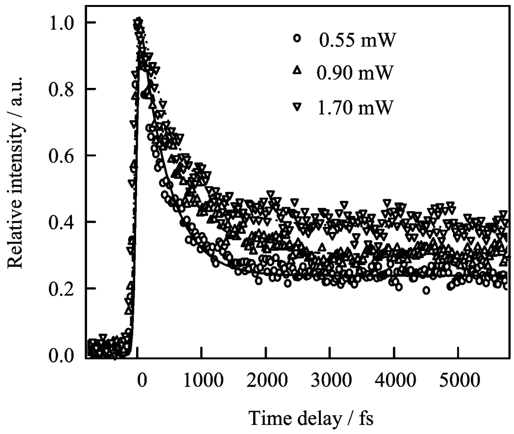

FIG. 5 Transient profiles of $C_6H_5CO^+$ at different probe intensities, pumped by 284 nm. Lines were fitting results.

transient profiles and fitting results, the main contribution should be due to the fragmentation of the parent ion state. Contribution from ionization of the neutral fragments from the vibrationally excited S_1 would be minor, and $C_6H_5CO^+$ signal resulting from ionization of neutral fragment would show growth dynamics. From Fig.4, the transient dynamics of the $C_6H_5CO^+$ could be well fitted by the bi-exponential model, similar to the case of the parent ion. The results were also listed in Table I for comparison. In the S_2 origin, the first fast decay increased with the pump wavelength, and the amplitude ratio of the two components with lifetimes of τ_1 and τ_2, decreased with the vibrational excitation energy. For the 287 nm pump, the $C_6H_5CO^+$ showed similar results with the parent ions.

The transient profiles of $C_6H_5CHO^+$ parent ion and $C_6H_5CO^+$ fragment ion were obtained simultaneously under the same conditions. While the decay profiles of the parents ion kept unchanged with the probe laser intensities increases, transient profiles of $C_6H_5CO^+$ changed a lot, as shown in Fig.5. Fitting results were listed in Table II. As illustrated in Fig.5 and listed in Table II, it was obviously the signal intensity of the fragment ion increased with the probe laser intensity in long delay time region.

Recent theoretical studies on benzaldehyde [14,15] figured out a minimum energy crossing point among three potential energy surfaces (S_1, T_1, and T_2), which would be common to a wide variety of aromatic carbonyl compounds with a constant structure [14]. The possible mechanisms of the ultrafast process in benzaldehyde were illustrated in Fig.6. Benzaldehyde molecule was excited into the S_2 state (pumped by 284, 271, and 260 nm) and then internally converted into the S_1 state. The molecule in the S_1 state with the high vibrational energy preceded the vibrational relaxation. According to the calculation result [14], the $S_1/T_2/T_1$ structure had barrier energy of 12.54 kJ/mol, relative to the S_1 minimum for benzaldehyde. The molecules had sufficient internal energy to overcome the energy barrier between the S_1 minimum and the $S_1/T_1/T_2$ intersection after internal conversion or direct photoexcitation to the S_1 state. For the 287 nm pump, the bi-exponential fit showed a ~56 fs decay. We took it as the intersystem crossing after the initially excited wave packet started from the fc geometry. For the S_2 state, the lifetimes decaying with increasing vibrational energy could be understood as the correct S_1 surface and S_2 surface. The S_2 minimum was higher than the S_1 minimum in energy, but the S_2 state was energetically lower than the S_1 state at some nuclear configurations.

TABLE II Fitting parameters for transient profiles of $C_6H_5CO^+$ under different probe laser intensities, pumped at 284 nm. Fitting errors were also given.

Intensity/mW	a/b	τ_1/fs	τ_2/fs
0.55	1.44	172±14	672±11
0.90	1.00	530±17	672±11
1.7	0.80	479±10	672±11

Benzaldehyde had been extensively studied by ultrafast electron diffraction method [10–12]. By using ultrafast electron diffraction method, molecular structures in different excited states could be determined directly. For benzaldehyde, a time constant of 42 ps for the triplet formation channel and 61 ps for the molecular dissociation channel were determined by this method. Both ISC and dissociation processes were suggested to start from the vibrational excited S_1 after internal conversion. However, even by using this novel method, the existence of S_1 state, as well as the phosphorescing T_1 state, could not be confirmed due to their structural similarity with ground state benzaldehyde. No depletion of T_2 had been observed, so the population of T_1 was suggested to be negligible [10]. However, recent theoretical predictions [14,15] disagree with this physical picture. Intersection structures of different electronic

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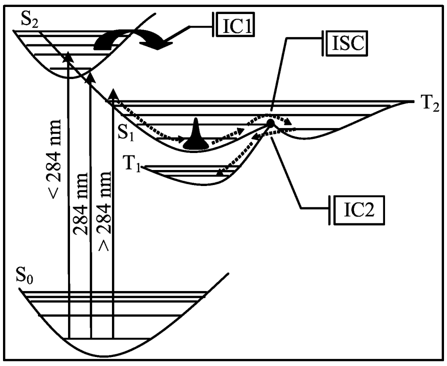

FIG. 6 Possible mechanisms of the ultrafast process in benzaldehyde.

states (S_1, T_1, and T_2) provided an efficient "funnel" for both the IC and ISC processes. The three potential energy surface crossing point played key roles in the radiationless processes after photoexcitation. The S_1–T_2 ISC process happened with high efficiency due to a strong spin-orbit interaction. The timescale for the T_2–T_1 IC via the cross point was expected to be on the order of a vibrational period. Via the T_2 state, the $S_1/T_2/T_1$ intersection leaded to the S_1–T_1 ISC taking place. The T_2 state functioned as a relay and enabled the S_1–T_1 ISC to take place with a high rate. In this sense, the T_2 structure reported in Refs.[10–12] were still in doubt.

IV. CONCLUSION

In this work, we reported the pump-probe experiments on the wavelength dependent photodynamics of benzaldehyde around its S_2 electronics state. The electronic relaxation behaviors in S_1 vibrational excited state exhibited different from those in the S_2 state. To the best of our knowledge, this was the first time directly study of the S_1 state by ultrafast pump-probe method. Comparison between the parent ion transient and H-loss fragment ion profile indicated the fragmentation occurred after ionization of the excited parent molecule. The ultrafast relaxation of the S_1 state was suggested to be due to the three potential energy surface crossing point.

V. ACKNOWLEDGMENT

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