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Methyl substitution effects on the non-adiabatic dynamics of benzene: lifting three-state quasi-degeneracy at conical intersections;

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Previously, theoretical calculations on the non-adiabatic dynamics of benzene from the S_2 state have indicated that the S_2/S_1 and S_1/S_0 conical intersections (CIs) facilitate ballistic nuclear wavepacket motion from S_2 to S_0 (fast channel) and branching to S_1 (slow channel). In this paper, we present time-resolved photoelectron spectra of benzene and its methyl-derivatives (toluene and *o*-xylene) measured with a vacuum-UV laser, which clearly reveal both the fast and slow channels. The extremely short propagation time of the wavepacket between the two CIs of benzene indicates that the two are in close proximity to each other, while methyl substitution extends the propagation time and decreases the branching ratio into the fast channel. The results suggest that the quasi-degeneracy of the three states in benzene is lifted by the geometrical shifts of the CIs by methyl substitution.

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Introduction

Ultrafast reactions of polyatomic molecules generally involve non-adiabatic dynamics *via* conical intersections (CIs) of potential energy surfaces. A CI occurs between two electronic states, while three-state CIs have also been identified.^{1–3} A single three-state CI or multiple two-state CIs that are in close proximity⁴ can open a passage for rapid electronic relaxation down to the electronic ground state.

Benzene is the paradigmatic aromatic molecule and its photophysics and photochemistry have been extensively studied theoretically and experimentally. Time-resolved photoelectron spectroscopy (TRPES) has shown that the ultrafast internal conversion from the $S_2(\pi, \pi^*)$ to the $S_1(\pi, \pi^*)$ state occurs within *ca.* 50 fs *via* CIs of the potential energy surfaces.^{5–7} On the other hand, theoretical calculations indicate that the S_1/S_0 CI also exists in proximity to the S_2/S_1 CI,⁸ which facilitates ultrafast internal conversion from S_2 to S_0 ; however, as far as we know, ultrafast internal conversion to S_0 is yet to be identified experimentally. In this paper, we employ TRPES using a vacuum-UV laser to study cascade internal conversion to S_0 in benzene and its methyl substituted compounds. The results clearly show the influence of methyl substitution on the dynamics. Fig. 1(a) shows a schematic diagram of the relaxation channels from the S₂ state of benzene.⁸ The vibrational wavepacket immediately departs the Franck–Condon (FC) region in a planar geometry to propagate toward the non-planar minimumenergy structure in S₂,⁹ which also brings the system to the S₂/S₁ CI (called CI₁ hereafter) located in the non-planar geometry. The non-adiabatic transition *via* CI₁ funnels the wavepacket to the S₁ surface, where the S₁/S₀ CI (hereafter called CI₂) located in the vicinity of CI₁^{8,10} facilitates consecutive non-adiabatic transition channel A \rightarrow B \rightarrow C \rightarrow D (called the "fast channel" hereafter). On the other hand, CI₁ also directs the wavepacket into other directions on the S₁ surface, and a part of the wavepacket that



Fig. 1 (a) Relaxation from the S₂ state of benzene. Bifurcation occurs at the S₂/S₁ CI (Cl₁). (b) TRPES spectra of benzene. The dotted and solid lines indicate the fast (A \rightarrow B \rightarrow C \rightarrow D) and slow (B \rightarrow C' \rightarrow D) channels, respectively. Molecular geometries are adapted from ref. 8 with permission from The Royal Society of Chemistry.

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[†] Electronic supplementary information (ESI) available: TRPES spectra of benzene, toluene, and *o*-xylene, examples of the least squares fitting, comparison of ridge lines of the contours, and TRPES spectra of toluene in the even higher eBE region. See DOI: 10.1039/c9cp06164a

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misses CI_2 is temporarily trapped in the planar S_1 minimum prior to its decay (B \rightarrow C' \rightarrow D, called the "slow channel" hereafter).

Experimental

The experimental apparatus used in this study has been described in detail previously.^{11–13} A pump pulse ($h\nu_{pump} = 6.0 \text{ eV}$) creates a vibrational wavepacket in the FC region of the S₂ state of benzene (or its methyl derivatives), and the subsequent dynamics are interrogated through photoionization by a time-delayed probe pulse in the vacuum-UV ($h\nu_{probe} = 14 \text{ eV}$). The photoelectron kinetic energy (PKE) distribution is measured as a function of the delay time between the pump and probe pulses, and the electron binding energy (eBE) is given by the difference between the probe photon energy and the measured PKE.

Results and discussion

Fast and slow channels in TRPES spectra

Fig. 1(b) shows the TRPES spectra of benzene measured in the present study, which clearly reveal both channels described above. For example, one can find a path with rapidly increasing eBE from 3.5 eV in the FC region to 9.2 eV¹⁴ of S₀ within 100 fs. This feature is attributed to the fast channel. On the other hand, the signal at an eBE of 5–6 eV with a several-ps lifetime is attributable to the slow channel.

We performed similar measurements for toluene^{6,15} and *o*-xylene¹⁶ as shown in Fig. S1 in the ESI.[†] Similarly to benzene, internal conversion to S₀ occurs predominantly within a fraction of a picosecond *via* the fast and slow channels. For further investigation of the dynamics, we have separated the spectral features of the fast and slow channels by least squares fitting using a kinetics model. The total signal I(t;E) and its components $I_{\text{fast}}(t;E)$ and $I_{\text{slow}}(t;E)$ are expressed as follows:

$$I(t;E) = I_{\text{fast}}(t;E) + I_{\text{slow}}(t;E)$$
(1)

Arrival times of the wavepacket to S1 and S0 via the fast channel

Fig. 2 shows contour maps of the fast components $[I_{fast}(t;E)]$ extracted by the numerical fitting for (a) benzene, (b) toluene, and (c) o-xylene. The dotted lines shown on the contours are the ridge lines, which highlight the rapid increase of eBE due to the $S_2 \rightarrow S_1 \rightarrow S_0$ wavepacket propagation in the fast channel. A comparison of the three systems clearly reveals that methyl substitution delays internal conversion to S₀ (see Fig. S3 in the ESI \dagger). As most evident in Fig. 2(c), each map consists of three bands that are located at around 3.5, 5, and >7 eV. Fig. 2(d)–(f) (solid) show slices of the contour maps along the ridge lines. These distributions are reasonably well expressed with three Gaussians (dotted) corresponding to S_2 (blue), S_1 (red), and S_0 (black). (Within the displaced harmonic oscillator approximation, a photoelectron spectrum without discernible individual vibrational lines is often expressed by a Gaussian function which is centered at the FC vertical transition.¹⁷) Taking these results, the arrival times of the wavepacket to S_1 and S_0 were evaluated respectively as the averaged appearance time of the ridge over the S_1 and S_0 eBE region (Table 1). The obtained arrival times for benzene (64 fs at S1 and 68 fs at S0) broadly agree with an *ab initio* multiple spawning study (40 fs at S_1 and 50 fs at S_0).⁸ The extremely short propagation time on the S_1 surface (4 fs) proves that CI₁ and CI₂ are in close proximity to each other. It is interesting that the propagation time increases $(4 \rightarrow 30 \rightarrow 140 \text{ fs})$ with the methyl substitution.

It is noteworthy that the signals in Fig. 1(b) and 2 are mainly due to ionization to the cationic ground state D_0 . In the nonadiabatic dynamics of benzene, a transition to $D_0(e_{1g}^{-1})$ is always allowed within the frozen core approximation $[cf. S_2(e_{1g}^{-1}e_{2u})]$, $S_1(e_{1g}^{-1}e_{2u})]$. Since the bands due to ionization to the cationic excited states D_x ($x \ge 1$) are separated from the D_0 band by > 2 eV,¹⁸ $D_x \leftarrow S_2$ transitions may appear at eBE $\ge 6 \text{ eV}$. (The small bump around the time origin in Fig. S4 in the ESI† may be attributed to $D_x \leftarrow S_2$ ionization. As discussed later,

$$I_{\text{fast}}(t;E) = \begin{cases} 0 & [t \le \tau_0(E)] \\ A_{\text{fast}}(E) \left[\exp\left(-\frac{t - \tau_0(E)}{\tau_{\text{rise}}(E)}\right) - \exp\left(-\frac{t - \tau_0(E)}{\tau_{\text{decay}}(E)}\right) \right] & [\tau_0(E) < t] \end{cases}$$
(2)

$$I_{\text{slow}}(t;E) = \begin{cases} 0 & (t \le T_0) \\ A_{\text{slow}}(E) \left[\exp\left(-\frac{t-T_0}{T_{\text{rise}}}\right) - \exp\left(-\frac{t-T_0}{T_{\text{decay}}}\right) \right] & (T_0 < t) \end{cases}$$
(3)

Both $I_{\text{fast}}(t;E)$ and $I_{\text{slow}}(t;E)$ were well approximated by an exponential rise and decay with a time delay (see the examples of the least squares fitting for benzene in Fig. S2 in the ESI†). Time constants $\tau_0(E)$, $\tau_{\text{rise}}(E)$, and $\tau_{\text{decay}}(E)$ are of the fast channel. Due to the rapid increase of eBE *via* the fast channel, there was a general trend towards larger $\tau_0(E)$ and $\tau_{\text{rise}}(E)$ as eBE increases. Meanwhile, time constants T_0 , T_{rise} , and T_{decay} , which are of the slow channel, were treated as global parameters for all the time profiles. In other words, we assumed the spectral shape of the slow channel to be time-independent.

the signals due to ionization to D_x are more evident in an even higher eBE region.) However, these signals have only a marginal effect on the argument of the propagation time on the S_1 surface above.

Branching ratios between the fast and slow channels

Previously, Radloff *et al.* estimated the quantum yield of the long-lived S₁ state (QY_{slow}) to be 0.01 in benzene;¹⁹ however, as Suzuki *et al.* pointed out,⁶ it was a considerable underestimation because the insufficient probe photon energy ($h\nu_{probe} = 4.6 \text{ eV}$)



Fig. 2 (a–c) Fast components $I_{fast}(t; E)$. The dotted curves show the ridge lines of the contours, highlighting the rapid increase of eBE *via* the fast channel. (d–f) Slices of the contour maps along the ridge lines (solid) and fitting results with three Gaussians (dotted). The broken curves show the individual contributions of the three Gaussians that are assigned to S₂ (blue), S₁ (red), and S₀ (black), respectively.

 Table 1
 Methyl substitution effects on the non-adiabatic dynamics of benzene

| | Arrival times (fs) | | |
|----------|--------------------|-----|--------------------|
| | S ₁ | So | QY _{slow} |
| Benzene | 64 | 68 | 0.08 |
| Toluene | 61 | 91 | 0.15 |
| o-Xylene | 107 | 245 | 0.33 |

of their experiment¹⁹ did not enable a reliable estimation of the relative populations in S₁ and S₂. For the same reason, the 30-fold enhancement of QY_{slow} by methylation (benzene: $0.01 \rightarrow$ toluene: 0.3) argued by Farmanara *et al.* is not supported either.¹⁵ Thompson and Martínez predicted approximately equal amounts of population decay *via* the fast and slow channels (*i.e.* QY_{slow} ~ 0.5) in benzene,⁹ although, as they mentioned, precise determination of the branching ratio is still challenging for computational studies.

We evaluated the branching ratio using the ground state bleach signal.²⁰ Fig. 3(a) shows the time profile of the photoelectron



Fig. 3 (a) Time profile of the photoelectron signal of toluene at eBE = 9.0 eV (symbols) and the result of least-squares fitting (broken). (b) Ground state population determined from the fitting.

signal of toluene at eBE = 9.0 eV, corresponding to photoionization from the ground state; the one-color background signal has been subtracted, so that this figure indicates the relative change of the signal induced by the pump pulse (see the ESI† for more details). In Fig. 3(a), it is seen that the signal is depleted by photoexcitation to the S₂ state, while the bleach signal is recovered rapidly with sub-picosecond and picosecond time constants. The former corresponds to the fast channel discussed above. The ground-state population is expressed by the following kinetic equation:

 $I_{\rm GS}(t) =$

$$\begin{cases} -A & (0 \le t \le \tau_0) \\ -A \left[QY_{\text{fast}} \exp\left(-\frac{t - \tau_0}{\tau_{\text{fast}}}\right) + QY_{\text{slow}} \exp\left(-\frac{t - \tau_0}{\tau_{\text{slow}}}\right) \right] & (\tau_0 < t) \end{cases}$$

In this model, the bleach signal is recovered with τ_{fast} and τ_{slow} from $t = \tau_0$. The result of least-squares fitting to this kinetic model convolved with our apparatus function (a Gaussian with 80 fs FWHM) is shown in Fig. 3(a) (dashed curve), and the ground state population determined from the fitting is shown in Fig. 3(b). Thus, if intersystem crossing can be completely neglected, QY_{slow} for toluene is estimated to be 0.15.

In the UV photolysis of benzene, production of various valence isomers, e.g. benzvalene, fulvene, and Dewar benzene, was reported.²¹ The photoproduct formation is mediated by a prefulvene-like S_1/S_0 CI (*e.g.* CI₂ in this study) upon photoexcitation of both the S1 and S2 states.9 Meanwhile, their quantum yields were very small and extrapolated to zero at zero pressure in the vacuum-UV photolysis of benzene vapor.²² According to dynamical calculations using semi-classical surface-hopping trajectories, most trajectories after passing through a S₁/S₀ CI do not reach the region of the prefulvene intermediate, but return to the original S₀ minimum of benzene.²³ Therefore, we assumed that all of the excited molecules return to their original ground state via either the fast or slow channels. Another caution in the above analysis is that the photoelectron signal in the even higher eBE region [Fig. S5(b) in the ESI[†]] contains ionization from S_1 to the cationic excited states D_x . The expected band positions due to ionization from S₀ (blue) and S₁ (red) are shown in Fig. S5(c) (ESI⁺). (The latter is only as a guide. Under the



Fig. 4 Spectral intensities (a) A_{fast} and (b) A_{slow} for benzene, toluene, and o-xylene.

frozen-orbital approximation, the selection rules for the $D_x \leftarrow S_0$ and $D_x \leftarrow S_1$ transitions are different from each other.) The positive bands in Fig. S5(b) (ESI[†]) (eBE < 8.8 eV and 9.5 eV < eBE < 11.1 eV) are presumably attributed to ejection of an electron from benzene's σ orbitals²⁴ via $D_x \leftarrow S_1$ ionization. We carefully avoided these eBE regions for the above argument.

Similar analyses could not be performed on benzene and *o*-xylene for experimental problems, so we have used an alternative method of estimation for these molecules. Fig. 4(a) shows spectral intensities $A_{\text{fast}}(E)$ of benzene, toluene, and *o*-xylene, obtained from the fitting using eqn (1)–(3). Here the displayed eBE regions correspond to the S₂ state, and each spectrum is normalized to unity using its peak intensity. Meanwhile, Fig. 4(b) compares spectral intensities $A_{\text{slow}}(E)$ of the three molecules, in which each spectrum is normalized by the factor used in Fig. 4(a). Since each spectral intensity in Fig. 4(b) is normalized for the S₂ signal before bifurcation, it is proportional to QY_{slow}. As compared to benzene, the peak intensities increased by factors of 1.9 (toluene) and 4.2 (*o*-xylene). Since QY_{slow} for toluene is 0.15 as we discussed above, those for benzene and *o*-xylene are estimated to be 0.08 and 0.33, respectively (Table 1).

Methyl substitution effects on the dynamics

In the non-adiabatic dynamics of benzene, quasi-three state CIs facilitate ultrafast consecutive relaxation from S_2 to S_0 .⁸ The extended propagation time on the S_1 surface ($<10 \rightarrow 30 \rightarrow 140$ fs) suggests that CI_1 and CI_2 are further separated by methyl substitution. This may also affect the branching ratio; the nuclear wavepacket motion from S_2 to S_0 becomes diffusive rather than ballistic, which leads to the decrease of QY_{fast} (0.92 $\rightarrow 0.85 \rightarrow 0.67$).

Conclusions

TRPES using vacuum-UV probe pulses enabled real-time observation of the non-adiabatic dynamics of benzene and its methyl-derivatives (toluene and *o*-xylene). Ballistic nuclear wavepacket motion from S_2 to S_0 and branching to S_1 were manifested in the measured TRPES spectra. The extremely short propagation time of the wavepacket on the S_1 surface of benzene indicates that the S_2/S_1 and S_1/S_0 CIs are in close proximity to each other. Methyl substitution extended the propagation time and decreased the yield of the ballistic internal conversion pathway. This suggests that the three-state quasi-degeneracy at the two CIs is lifted and that the effective geometric difference between the CIs is greater in methyl substituted compounds.

Conflicts of interest

There are no conflicts to declare.

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