Electronic Supplementary Information (ESI)

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

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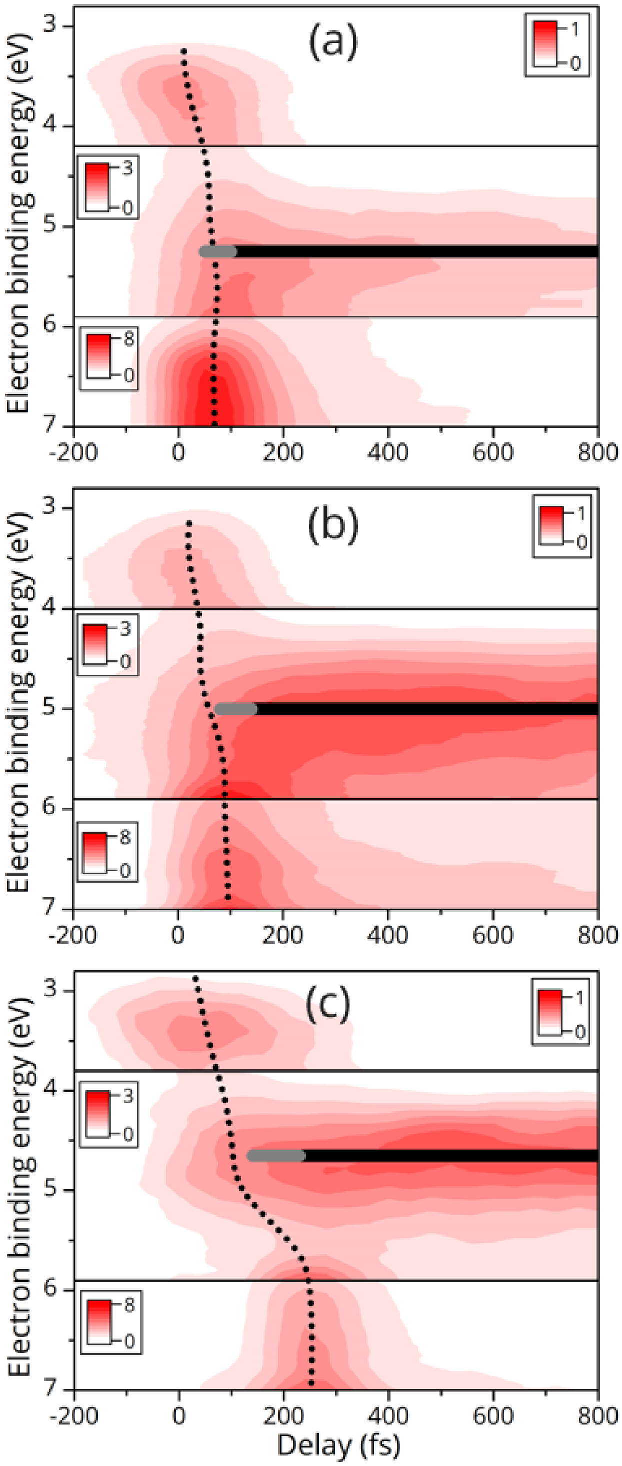

Figure S1. TRPES spectra of (a) benzene, (b) toluene, and (c) o-xylene. Dotted curves show ridge lines of the contours of the fast components [$I_{\text{fast}}(t;E)$] determined from by the fitting. Bold lines indicate spectral peaks of $A_{\text{slow}}(E)$. The regions painted by grey represent rise times of the slow components ($[T_0, T_0 + T_{\text{rise}}]$).

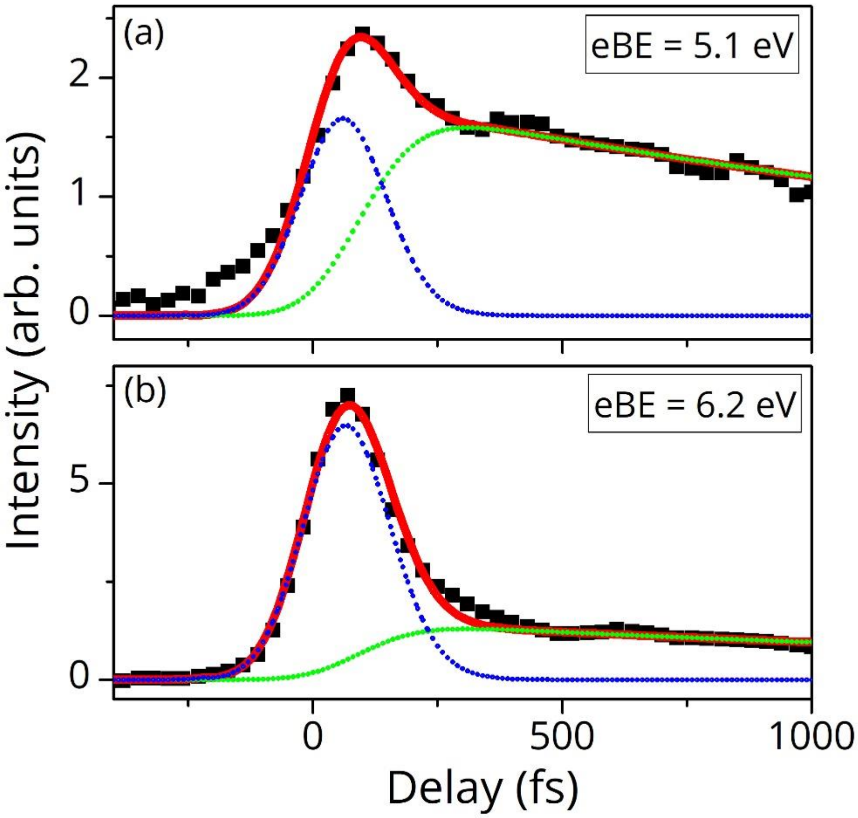

Figure S2. (a) Results of least squares fitting for benzene at the eBEs of (a) 5.1 eV and (b) 6.2 eV. Symbols, experimental; solid, fitting; dotted, individual fast and slow components.

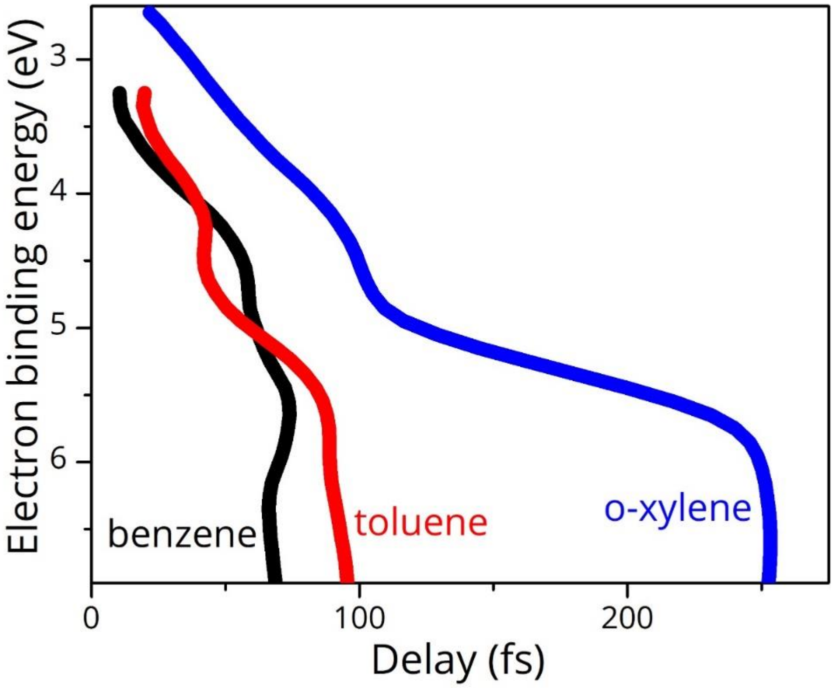

Figure S3. Comparison of ridge lines of the contours in Fig. 2.

Photoelectron signals due to ionization to the cationic excited states:

Figure S4 shows the result of least squares fitting for o-xylene at eBE = 6.0 eV (Symbols, experimental; solid, fitting; dotted, individual fast and slow components). Both fast (blue) and slow (green) components are due to ionization to the cationic ground state D_0; they are respectively assignable to $D_0 \leftarrow S_0$ and $D_0 \leftarrow S_1$ transitions. Meanwhile, there exists a small bump around the time origin in the experimental time profile. This may be attributed to $D_x \leftarrow S_2$ ionization.

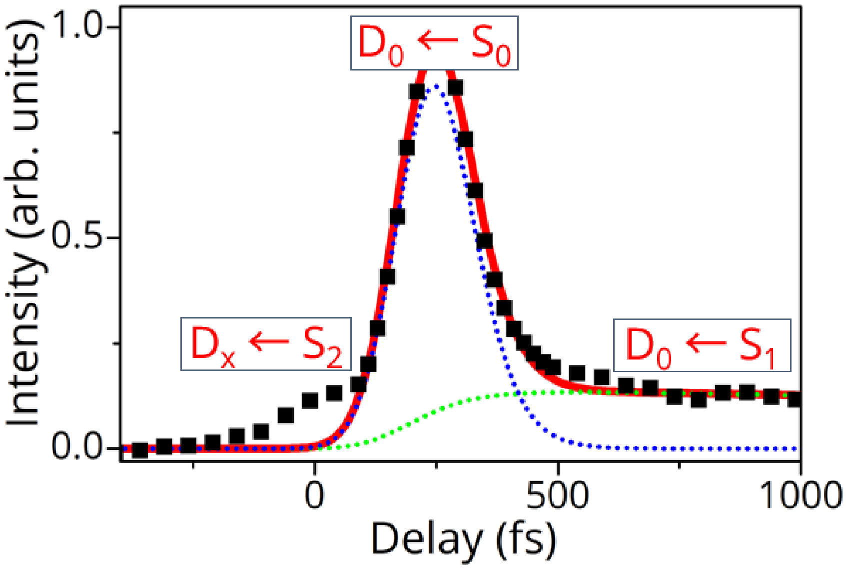

Figure S4. Result of least squares fitting for o-xylene at eBE = 6.0 eV. Symbols, experimental; solid, fitting; dotted, individual fast and slow components.

TRPES spectra of toluene in the even higher eBE region:

Figure S5(a) and (b) show two different eBE regions of the same TRPES spectra of toluene. In Fig. 5(b), toluene molecules unexcited by the pump pulses give rise to a one-color background signal. The one-color signal was evaluated by averaging the photoelectron spectra over negative delays and subtracted it to obtain Fig. S5(b). Figure S5(c) shows expected band positions due to ionization from S_0 (blue) and S_1 (red). The former is a static photoelectron spectrum of toluene digitized from ref. 18. To yield the latter, the former is shifted by 4.0 eV so that expected band position via $D_0 \leftarrow S_1$ transition matches observed one. It is notable that the latter is only as a guide. Under the frozen-orbital approximation, the selection rules for $D_x \leftarrow S_0$ and $D_x \leftarrow S_1$ transitions are different from each other.

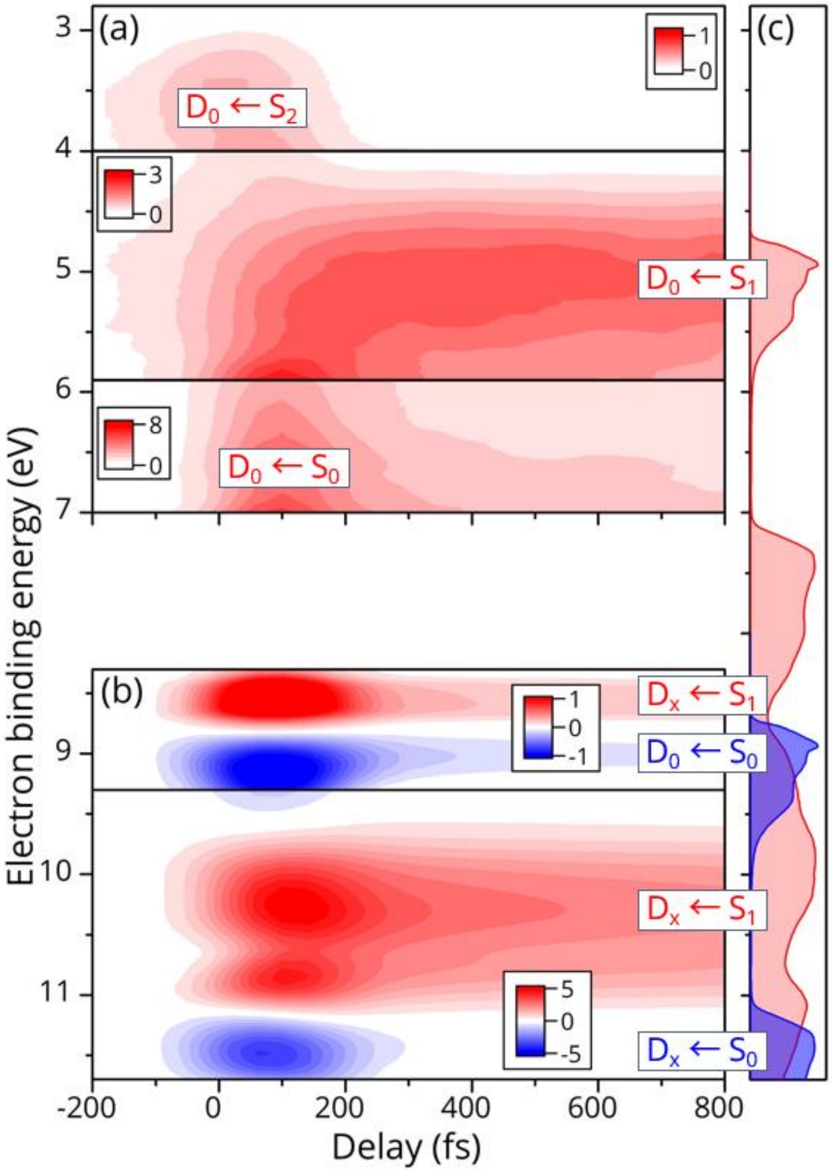

Figure S5. (a) and (b) Two different eBE regions of the same TRPES spectra of toluene. (c) Expected band positions due to ionization from S_0 (blue) and S_1 (red).