Electronic Supplementary Information for:

A time-, angle- and kinetic-energy-resolved photoelectron spectroscopic study of tetrakis(dimethylamino)ethylene

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1. Analysis of the pump-probe signals: the kinetic model associated with all excited states

To achieve the corresponding fit to the experimental time-resolved photoelectron spectroscopy (TRPES) data of tetrakis(dimethylamino)ethylene (TDMAE), the excited-state decay process can be simply described using multi-exponential decay function along with an oscillatory component as the following expression for $t \geq 0$:

$$\mathrm{I}(t, eBE) = \sum_{i=1}^{4} DAS_i(eBE) \times \exp\left(-\frac{t}{\tau_i}\right) \times (1+\mathrm{A}_{\mathrm{osc}})$$

Here, $\mathrm{A}_{\mathrm{osc}}$ is described by $A_i \times \cos\left(\frac{2\pi t}{T} + \varphi_0\right) \times \exp\left(-\frac{t}{\tau_d}\right)$ for ith time constants, τ_i. According to the final result of the 2D global least-squares fit, τ_1, τ_2, τ_3 and τ_4 are determined to be 50±10 fs, 240±30 fs, 550±50 fs and >100 ps, while τ_d is 3.0±0.5 ps. The decay associated spectra (DAS) associated with $\tau_{1\text{-}4}$ are also obtained, as presented in Fig. 3(a). In order to better understand the information provided by the DAS, the relationship between the DAS and the energy-resolved photoionization cross sections of each electronic state should be discussed in detail. Here, the decay mechanism of the initially prepared valence ππ* state is proposed to be the following kinetic model: ππ* → π3p → Z → CT → S_0 and ππ* → Z → CT → S_0, while the time constans of τ_1(50 ±10 fs), τ_3(550±50 fs) and τ_4(>100 ps) are assigned to the lifetimes of the ππ*, π3p and zwitterionic states, respectively. The populations of the ππ*, π3p and zwitterionic states can be described by the following expressions:

$$P_{\pi\pi^*}(t) = P_{\pi\pi^*}(0) \times \exp\left(-\frac{t}{\tau_1}\right)$$

$$P_{\pi 3p}(t) = P_{\pi\pi^*}(0) \times R \times \frac{\tau_3}{\tau_3-\tau_1} \times \left\{\exp\left(-\frac{t}{\tau_3}\right) - \exp\left(-\frac{t}{\tau_1}\right)\right\}$$

Here, R is the branching ratio of ππ* → π3p.

$$P_Z(t) = P_{\pi\pi^*}(0) \times \left\{A \times \exp\left(-\frac{t}{\tau_1}\right) + B \times \exp\left(-\frac{t}{\tau_3}\right) + C \times \exp\left(-\frac{t}{\tau_4}\right)\right\}$$

While $A = (1-R) \times \frac{\tau_4}{\tau_1-\tau_4} + R \times \frac{\tau_1\tau_4}{(\tau_1-\tau_3)(\tau_1-\tau_4)}$

$$B = R \times \frac{-\tau_3\tau_4}{(\tau_1-\tau_3)(\tau_3-\tau_4)}$$

$$C = (R-1) \times \frac{\tau_4}{\tau_1-\tau_4} + R \times \frac{\tau_4^{2}}{(\tau_1-\tau_4)(\tau_3-\tau_4)}$$

Note that when R=1, the above expressions are same as those in the previous similar study of TDMAE.[1]

Then $DAS_1(eBE) = \sigma_{\pi\pi^*}(eBE) - R \times \frac{\tau_3}{\tau_3-\tau_1} \times \sigma_{\pi 3p}(eBE) + A \times \sigma_Z(eBE)$

$$DAS_3(eBE) = R \times \frac{\tau_3}{\tau_3-\tau_1} \times \sigma_{\pi 3p}(eBE) + B \times \sigma_Z(eBE)$$

$$DAS_4(eBE) = C \times \sigma_Z(eBE)$$

Here σ is the energy-resolved photoionization cross sections of each electronic excited state.

Since $\tau_1 = 50$ fs, $\tau_3 = 550$ fs, $\tau_4 > 100$ ps, so $\tau_4 >> \tau_1$ and $\tau_4 >> \tau_3$

Then $A \cong 1.1\times R-1$, $B \cong -1.1\times R$, $C \cong 1$

Therefore,

$\mathrm{DAS}_1(\mathrm{eBE}) = \sigma_{\pi\pi^*}(\mathrm{eBE}) - 1.1\times R\times\sigma_{\pi 3\mathrm{p}}(\mathrm{eBE}) + (1.1\times R-1)\times\sigma_{\mathrm{Z}}(\mathrm{eBE})$

$\mathrm{DAS}_3(\mathrm{eBE}) = 1.1\times R\times\sigma_{\pi 3\mathrm{p}}(\mathrm{eBE}) - 1.1\times R\times\sigma_{\mathrm{Z}}(\mathrm{eBE})$

$\mathrm{DAS}_4(\mathrm{eBE}) = \sigma_{\mathrm{Z}}(\mathrm{eBE})$

$\sigma_{\pi\pi^*}(\mathrm{eBE}) = \mathrm{DAS}_1(\mathrm{eBE}) + \mathrm{DAS}_3(\mathrm{eBE}) + \mathrm{DAS}_4(\mathrm{eBE})$

$\sigma_{\pi 3\mathrm{p}}(\mathrm{eBE}) = \frac{\mathrm{DAS}_3(\mathrm{eBE})}{1.1\times R} + \mathrm{DAS}_4(\mathrm{eBE})$

$\sigma_{\mathrm{Z}}(\mathrm{eBE}) = \mathrm{DAS}_4(\mathrm{eBE})$

If the photoionization cross-sections of the ππ* state and the π3p state are assumed to be identical, then $\sum\sigma_{\pi\pi^*}(\mathrm{eBE}) = \sum\sigma_{\pi 3\mathrm{p}}(\mathrm{eBE})$,

$R = \sum DAS_3(\mathrm{eBE}) / \{1.1\times\sum DAS_1(\mathrm{eBE}) + 1.1\times\sum DAS_3(\mathrm{eBE})\}$

It should be noted that the π3d state is also partly excited at 266.9 nm, and its deactivation pathway is suggested to be internal conversion of π3d → ππ*, followed by the decay dynamics of the ππ* state. The time constant of τ_2 (240±30 fs) is assigned to the lifetime of the π3d state. Therefore,

$P_{\pi 3\mathrm{d}}(t) = P_{\pi 3\mathrm{d}}(0) \times \exp\left(-\frac{t}{\tau_2}\right)$

$P_{\pi\pi^*}(t) = P_{\pi 3\mathrm{d}}(0) \times \frac{\tau_1}{\tau_2-\tau_1} \times \{\exp\left(-\frac{t}{\tau_2}\right) - \exp\left(-\frac{t}{\tau_1}\right)\} + P_{\pi\pi^*}(0) \times \exp\left(-\frac{t}{\tau_1}\right)$

For low eBE region, for example, eBE ≤ 1.8 eV, $\sigma_{\pi 3\mathrm{p}}(\mathrm{eBE}) \cong 0$, $\sigma_{\mathrm{Z}}(\mathrm{eBE}) = 0$, then,

$\mathrm{DAS}_2(\mathrm{eBE}) = \frac{\tau_2}{\tau_2-\tau_1} \times \sigma_{\pi 3\mathrm{d}}(\mathrm{eBE})$

$\mathrm{DAS}_1(\mathrm{eBE}) = \{\frac{-\tau_1}{\tau_2-\tau_1} + P_{\pi\pi^*}(0)/P_{\pi 3\mathrm{d}}(0)\} \times \sigma_{\pi\pi^*}(\mathrm{eBE})$

If we assume that $\sum\sigma_{\pi\pi^*}(\mathrm{eBE}) = \sum\sigma_{\pi 3\mathrm{d}}(\mathrm{eBE})$,

$P_{\pi\pi^*}(0)/P_{\pi 3\mathrm{d}}(0) = \frac{\tau_2}{\tau_2-\tau_1} \times \sum DAS_1(\mathrm{eBE}) / \sum DAS_2(\mathrm{eBE}) + \frac{\tau_1}{\tau_2-\tau_1}$

According to the eBE-resolved DAS shown in Fig. 3(a),

ΣDAS_1(eBE) / ΣDAS_2(eBE) ≤ ΣDAS_1(eBE1≤1.8 eV) / ΣDAS_2(eBE≤1.8 eV) $\cong$ 4.3

Then, $P_{\pi\pi^*}(0)/P_{\pi 3d}(0) \leq \frac{\tau_2}{\tau_2-\tau_1} \times 4.3 + \frac{\tau_1}{\tau_2-\tau_1} \cong 5.7$

$P_{\pi 3d}(0)/\{P_{\pi\pi^*}(0)+P_{\pi 3d}(0)\} \leq \frac{1}{6.7} \cong 15\%$

Therefore, when $P_{\pi\pi^*}(0)/P_{\pi 3d}(0) = 5.7$

$P_{\pi\pi^*}(t) = P_{\pi\pi^*}(0) \times \{0.954 \times \exp\left(-\frac{t}{\tau_1}\right) + 0.046 \times \exp\left(-\frac{t}{\tau_2}\right)\}$

Compared with $P_{\pi\pi^*}(t) = P_{\pi\pi^*}(0) \times \exp\left(-\frac{t}{\tau_1}\right)$, i.e., the excitation of π3d is not considered, when both ππ* and π3d states are excited here, we still have

$R \cong \Sigma DAS_3(\text{eBE}) / \{1.1 \times \Sigma DAS_1(\text{eBE}) + 1.1 \times \Sigma DAS_3(\text{eBE})\}$

When the DAS_1 and DAS_3 in the higher eBE region (eBE >2.2 eV) is not used,

$R \cong \Sigma DAS_3(\text{eBE} \leq 2.2\ \text{eV}) / \{1.1 \times \Sigma DAS_1(\text{eBE} \leq 2.2\ \text{eV}) + 1.1 \times \Sigma DAS_3(\text{eBE} \leq 2.2\ \text{eV})\} \cong 0.7$

Both qualitative and quantitative analyses of the decay associated spectra at electron binding energies higher than 2.5 eV are beyond our ability.

2. Analysis of the damping of the oscillations

The population of each electronic excited state, $P_j(t)$, should be multiplied by 1+ A'_{osc}, where A'_{osc} is described by $A'_j \times \cos\left(\frac{2\pi t}{T_j} + \varphi_j\right) \times \exp\left(-\frac{t}{\tau_d}\right)$ for jth electronic excited state (ππ*, π3d, π3p, Z). Then,

$$I(t \geq 0, eBE) = \Sigma_j\, \sigma_j(\text{eBE}) \times P_j(t) \times \{1 + A'_j \times \cos\left(\frac{2\pi t}{T_j} + \varphi_j\right) \times \exp\left(-\frac{t}{\tau_d}\right)\}$$

$$I(t < 0, eBE) = 0$$

The experimental TRPES signal should be a numerical convolution of the instrumental response function (IRF) and the multi-exponential decay function of excited state populations, I(t, eBE). As illustrated in Fig. S1, the photoelectron transients in different electron binding energy regions contain the oscillations with a very regular period (T) of ~500 fs and an invariant initial phase (φ_0) of zero. Then,

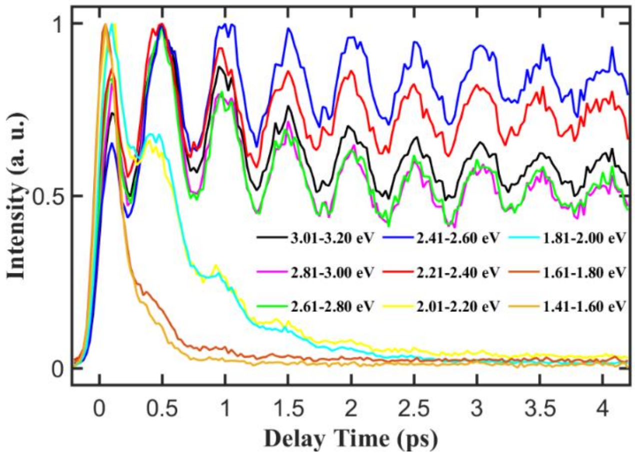

Fig. S1 Normalized photoelectron transients integrated over different electron binding energy ranges.

$$\mathrm{I}(t \geq 0, eBE) = \sum\nolimits_{\mathrm{j}} \sigma_{\mathrm{j}}(\mathrm{eBE}) \times \mathrm{P}_{\mathrm{j}}(\mathrm{t}) \times \{1 + A'_j \times \cos\left(\frac{2\pi t}{T} + \varphi_0\right) \times \exp\left(-\frac{t}{\tau_d}\right)\}$$

$$= \sum\nolimits_{\mathrm{j}} \sigma_{\mathrm{j}}(\mathrm{eBE}) \times \mathrm{P}_{\mathrm{j}}(\mathrm{t}) + \sum\nolimits_{\mathrm{j}} \sigma_{\mathrm{j}}(\mathrm{eBE}) \times \mathrm{P}_{\mathrm{j}}(\mathrm{t}) \times \{A'_j \times \cos\left(\frac{2\pi t}{T} + \varphi_0\right) \times \exp\left(-\frac{t}{\tau_d}\right)\}$$

$$= \sum\nolimits_{\mathrm{j}} \sigma_{\mathrm{j}}(\mathrm{eBE}) \times \mathrm{P}_{\mathrm{j}}(\mathrm{t}) + \{\cos\left(\frac{2\pi t}{T} + \varphi_0\right) \times \exp\left(-\frac{t}{\tau_d}\right)\} \times \sum\nolimits_{\mathrm{j}} A'_j \times \sigma_{\mathrm{j}}(\mathrm{eBE}) \times \mathrm{P}_{\mathrm{j}}(\mathrm{t})$$

According to the above specific kinetic model,

$$\mathrm{I}(t \geq 0, eBE) = \sum_{i=1}^{4} DAS_i(eBE) \times \exp\left(-\frac{t}{\tau_i}\right) + \{\cos\left(\frac{2\pi t}{T} + \varphi_0\right) \times \exp\left(-\frac{t}{\tau_d}\right)\} \times \sum_{i=1}^{4} A_i \times DAS'_i(eBE) \times \exp\left(-\frac{t}{\tau_i}\right)\}$$

Note that here the decay associated spectra ($\mathrm{DAS'_i}$) of the oscillatory components are not identical to those ($\mathrm{DAS_i}$) of the components without the oscillations.

Since τ_1(50 fs) << T(500 fs), the oscillation associated with τ_1 can be neglected, so $1+\mathrm{A}_{\mathrm{osc(i=1)}} \cong 1$, moreover, τ_2(240 fs) < T(500 fs) and its amplitude ($\mathrm{DAS_2}$) is relatively weak, then we assume that $1+\mathrm{A}_{\mathrm{osc(i=2)}} \cong 1$ in the fit, therefore,

$$\mathrm{I}(t \geq 0, eBE) = \sum_{i=1}^{4} DAS_i(eBE) \times \exp\left(-\frac{t}{\tau_i}\right) + \{\cos\left(\frac{2\pi t}{T} + \varphi_0\right) \times \exp\left(-\frac{t}{\tau_d}\right)\} \times \sum_{i=3}^{4} A_i \times DAS'_i(eBE) \times \exp\left(-\frac{t}{\tau_i}\right)\}$$

Only if A'_j is invariant for the involved π3p and Z states, i.e., $A'_{j=3} = A'_{j=4} = \mathrm{A'}$,

$$\mathrm{I}(t \geq 0, eBE) = \sum_{i=1}^{4} DAS_i(eBE) \times \exp\left(-\frac{t}{\tau_i}\right)$$

$$+ \{\mathrm{A'} \times \cos\left(\frac{2\pi t}{T} + \varphi_0\right) \times \exp\left(-\frac{t}{\tau_d}\right)\} \times \sum_{i=3}^{4} DAS_i(eBE) \times \exp\left(-\frac{t}{\tau_i}\right)$$

i.e., $$\mathrm{I}(t \geq 0, eBE) = \sum_{i=1}^{2} DAS_i(eBE) \times \exp\left(-\frac{t}{\tau_i}\right)$$

$$+ \left\{1 + \mathrm{A}' \times \cos\left(\frac{2\pi t}{T} + \varphi_0\right) \times \exp\left(-\frac{t}{\tau_d}\right)\right\} \times \sum_{i=3}^{4} DAS_i(eBE) \times \exp\left(-\frac{t}{\tau_i}\right)$$

Finally, a satisfactory 2D global least-squares fit to the TRPES spectrum (Fig. 2 (a)) can be achieved, as shown in Fig. 3 and Fig. 4. In Fig. 4(b) and (c), the dashed line represents the fit without the oscillatory component (i.e., $\mathrm{A_i} = \mathrm{A}' = 0$ in the above equation). The damping time constant (τ_d) of 3.0 ± 0.5 ps must be needed to represent the dephasing of the specific vibrational motion which causes the periodic modulation, while $\tau_d = \infty$ (i.e., $\exp\left(-\frac{t}{\tau_d}\right) \cong 1$) corresponds to a complete decoupling of this vibrational motion. The comparison of these different fits is shown in Fig. S2.

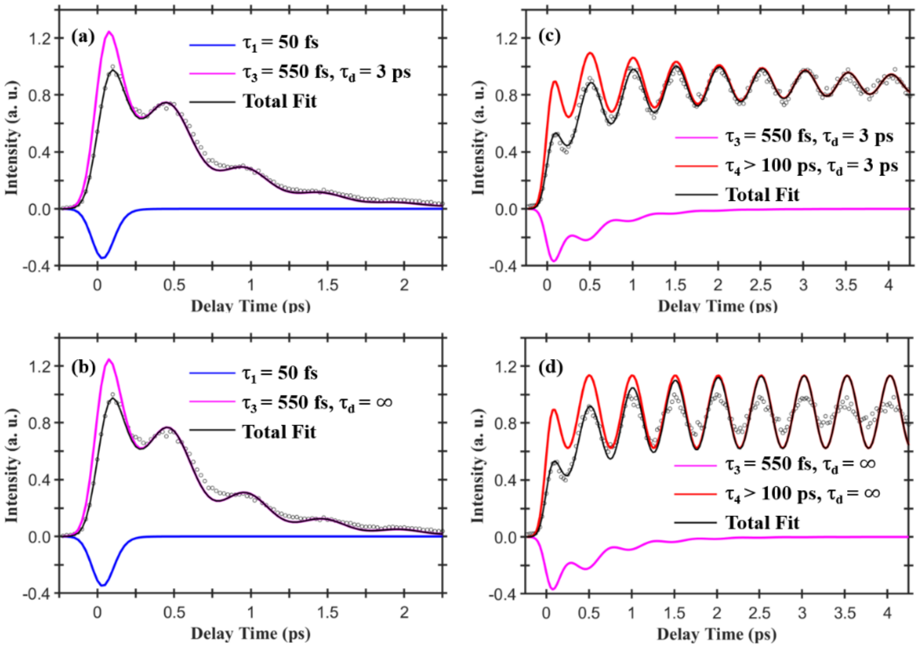

Fig. S2 (a) and (c) Normalized photoelectron transients integrated over electron binding energy ranges of 1.88-2.02 and 2.35-2.45 eV, respectively. The cycles show the experimental data, while the solid lines show the corresponding fits. (b) and (d) Same as (a) and (c), but the value of τ_d is ∞, instead of 3 ps.

3. TRPES spectrum at large delays

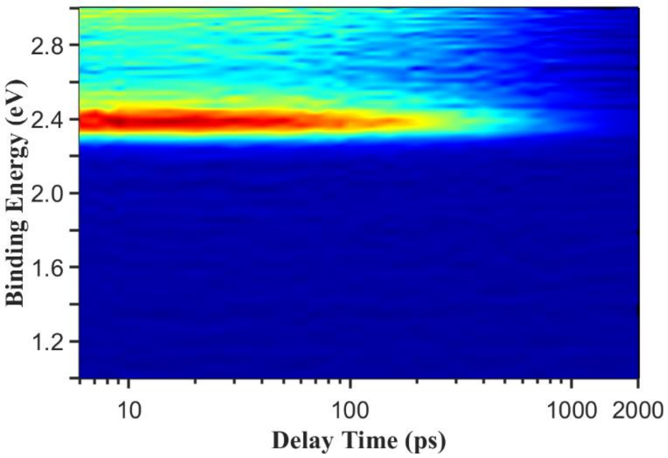

Fig. S3 TRPES spectrum of TDMAE excited at 266.9 nm after subtracting the background photoelectrons generated from single-color multiphoton ionization. Note that a logarithmic scale is used for the delays larger than 6 ps.

4. Single-color two-photon photoelectron spectrum at 266.9 nm

The single-color photoelectron spectrum of TDMAE at 266.9 nm are shown in Fig. S4. The pulse duration of 266.9 nm femtosecond laser pulses was estimated to be 110-120 fs (FWHM), which strongly affect the relative detection efficiency of electronic excited states with different lifetimes. Therefore, the peak positions of the electron binding energy should be invariant compared with those in Fig. 2(a) and (b), while the relative intensity of these peaks is different in single-color and time-resolved two-color 1+1' photoelectron spectra.

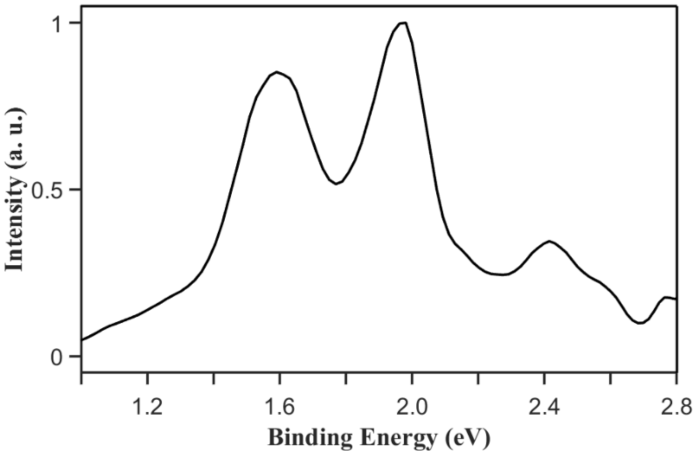

Fig. S4 Normalized electron binding energy distribution of TDMAE generated from single-color two-photon ionization at 266.9 nm.

5. The measurement of the time-zero and cross-correlation

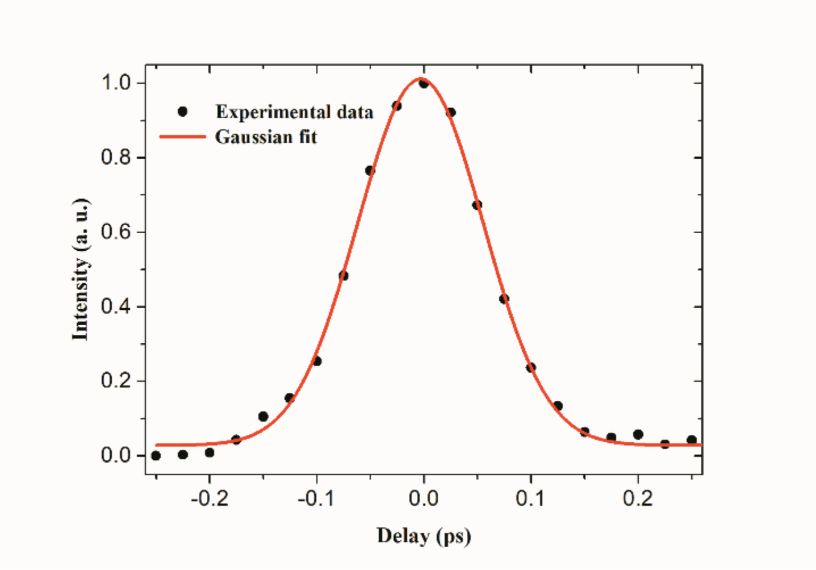

Fig. S5 Normalized photoelectron transient generated from two-color 1+3' multiphoton ionization process of Xe.

1. E. Gloaguen, J. M. Mestdagh, L. Poisson, F. Lepetit, J. P. Visticot, B. Soep, M. Coroiu, A. Eppink and D. H. Parker, *J. Am. Chem. Soc.*, 2005, **127**, 16529-16534.