X-ray Induced Ultrafast Nonadiabatic Dynamics of Tropone Probed at the O(1s) pre-edge

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Abstract

Nonradiative decay (NRD) governs the performance of many x-ray functional materials. To clarify the x-ray induced NRD dynamics, we performed nonadiabatic reaction dynamics simulations on electronically excited tropone (Tr) dications created by the carbon $KLL$ normal Auger decay. The Tr$^{2+}$ undergoes the NRD cascade via $10^{-10^2}$ states with time constants of 100 fs. We also found that this NRD dynamics shall be extracted from C(1s) edge pump O(1s) pre-edge probe femtosecond transient x-ray absorption spectra (TR-XAS) measured by the O(1s) Auger electron yield method. Our coupled ionization rate model also demonstrates selective and saturable core-ionization from the C(1s) edge of Tr can increase the signal-to-noise ratio up to $\sim 10$, which is mainly determined by the pump absorption edge and independent of the probe peak intensity. Such two-color TR-XAS measurement can be widely applicable to general organic molecules in the gas phase and surfaces of condensed phases.

Graphical TOC Entry

Keywords

Nonadiabatic reaction dynamics theory, X-ray free electron laser, Organic dication, Two-color femtosecond transient x-ray absorption spectroscopy, Radiation damage, Saturable ionization, Auger decay
Ultrafast charge and energy migration following x-ray irradiation to polyatomic molecules and other nano-/bio-materials and subsequent are general phenomena encountered in nature and industry. In biology, high-energy radiation triggers strand break of DNA double helix which results in cancer. In nanomedicine, the high energy radiation/particle deposited in nano-sized structures can be used to enhance cancer treatments. In material science, organic scintillators composed of aromatic molecules detect the energetic radiations by converting high-energy radiation into low-energy light emission.

Recent developments of ultrafast transient x-ray absorption spectra (TR-XAS) measurement using x-ray free electron lasers and high-harmonic generation realize the real-time tracking of the nuclear and valence electron dynamics of the energetic irradiation (e.g. UV/Vis, intense IR etc.) induced processes with femtosecond or attosecond temporal resolutions in any form of matter. Extending the scope of the TR-XAS measurement and the associated theoretical analysis to the x-ray induced nonadiabatic reaction dynamics of polyatomic organic molecules should resolve its complex mechanism — the Auger decay to electronically excited dicationic states after core-ionization and subsequent nonradiative decays (NRDs) — and should give us the basis to develop efficient x-ray functional materials. Namely, this NRD dynamics of dication determines the efficiency of the x-ray functional materials.

In this study, we theoretically explore the NRD dynamics of aromatic molecules by the x-ray irradiation at the C(1s) edge and the capabilities of femtosecond two-color TR-XAS to monitor the NRD dynamics. Aromatic molecules are commonly used for a building block of biomolecules (DNA, proteins) and x-ray functional molecules such as organic x-ray scintillators. The stability and reactivity of electronically excited aromatic molecules are very sensitive to their molecular charges and electron configurations according to Hückel’s and Baird’s laws of aromaticity. We used a typical non-benzenoid aromatic molecule tropone (C_7H_6O, Tr) in gas phase as an example. We simulated the nonadiabatic reaction dynamics and associated C(1s) edge pump O(1s) pre-edge probe femtosecond TR-XAS using
a full-dimensional surface hopping nonadiabatic reaction dynamics technique. We explicitly considered the all valance two-hole states of Tr$^{2+}$ (210 singlet and 190 triplet) states via configuration interaction theory including all valance two-hole electron configurations. We also analytically investigated a possible measurement scheme for the TR-XAS measurement via coupled ionization rate equation model.

We found that soft x-ray irradiated Tr undergoes an cascade of NRD (NRD cascade) passing through 10-10$^2$ two-hole states in the timescale of 100 fs. The resultant signal of the two-color femtosecond TR-XAS clearly reflects the population dynamics of the NRD cascade.

We also demonstrated that the Auger electron yield method is a suitable method for performing the two-color TR-XAS experiment on the NRD cascades of general organic molecules in the gas phase, and surfaces of solid, liquid, and solutions. The Auger electron yield method selectively counts the number of resonance Auger electron emitted by the probe irradiation as a function of probe photon energy and pump-probe delay by using electron spectrometers. The measured Auger electron yield is proportional to the photoabsorption cross section and absorbance. To maximize the signal intensity and signal to noise ratio (S/N), monochromatic pump pulse whose photon energy is set to induce ionization only one inner-shell absorption edge of the parent neutral molecule and whose peak intensity is adjusted large enough to promote the saturable ionization of the neutral. The photon energy of probe pulse should be higher than that of the pump pulse. The S/N is mostly determined by the ratio between the photo-ionization cross section of the core-level molecular orbitals (MOs) which removed an electron by pump pulse and that of valence MOs. This feature makes the S/N independent of the peak intensity of probe pulse and system size.

Let us consider the population dynamics among the N dicationic states $\{|Ψ_ν⟩\}$ ($ν = 1, 2, \ldots, N$) of an organic molecule created by the one-photon core-level photoemission with an x-ray pulse and the subsequent normal Auger decay. The population of $\{|Ψ_ν⟩\}$ in inco-
herent limit $\mathbf{P}(t) = [P_1(t), P_2(t), \ldots, P_\nu(t), \ldots, P_N(t)]^T$ is generally written as,$^{72,73}$

$$
\mathbf{P}(t) = g(t, s_{pu}) \ast \Theta(t)[1 - \exp(-\tau_{\text{Auger}}^{-1} t)] \tilde{\mathbf{P}}(t),
$$

(1)

where $g(t, s_{pu})$ is the envelope function of the Gaussian pump pulse with the full width half maximum (FWHM) of $s_{pu}$, "\ast" represents convolution, $\Theta(t)$ is the Heaviside step function, $\tau_{\text{Auger}}$ is the overall Auger rate constant for the parent molecule, and $\tilde{\mathbf{P}}(t) = [\tilde{P}_1(t), \tilde{P}_2(t), \ldots, \tilde{P}_\nu(t), \ldots, \tilde{P}_N(t)]^T$ is the population of the $\{ |\Psi_\nu\rangle \}$ in sudden ionization limit. The $\tilde{\mathbf{P}}(t)$ can be directly evaluated via nonadiabatic reaction dynamics simulations by setting the initial populations of the dicationic states of the neutral molecule $\{\tilde{P}_\nu(t = 0)\}$ to be proportional to the relative Auger intensity.$^{58}$

For $\text{Tr}^{2+}$, we considered all $\{ |\Psi_\nu\rangle \}$ ($N = 400$: 210 singlet and 190 triplet states) with two holes within 20 valence MOs generated by the carbon $KLL$ normal Auger decay. The relative Auger intensity was evaluated by the two-hole population analysis technique.$^{74,75}$ We adopted $\tau_{\text{Auger}} = 6.1$ fs according to an experimental value on benzene$^{76}$ and set $s_{pu} = 10$ fs.

To evaluate the time evolution of $\tilde{\mathbf{P}}(t)$, we performed full-dimensional surface hopping nonadiabatic reaction dynamics simulations using an Tully’s fewest switching algorithm$^{77–80}$ combined with the linear-vibronic coupling (LVC) model Hamiltonian$^{73,80,81}$ (LVC-MD). We included both internal conversion and intersystem crossing.

The C(1$s$) edge pump O(1$s$) pre-edge probe femtosecond TR-XAS $\Delta A(\hbar \omega_{pr}, \Delta t)$ can be calculated as a function of probe photon energy $\hbar \omega_{pr}$ and pump-probe delay time $\Delta t$ defined by the time interval between the intensity peaks of the pump and probe pulse,

$$
\Delta A(\hbar \omega_{pr}, \Delta t) \\
\propto \sum_{\nu, \mu} g_{\nu \mu}(\hbar \omega_{pr}, \Delta t) \\
\ast \epsilon_{\nu \mu}(\mathbf{R}(\Delta t)) P_\nu(\Delta t) \delta(\hbar \omega_{pr} - \Delta E_{\nu \mu}(\mathbf{R}(\Delta t)), \Delta t),
$$

(2)
where $R(\Delta t)$ is the molecular structure of the dication at $\Delta t$, $\epsilon_{\nu\mu}(R(\Delta t))$ and $\Delta E_{\nu\mu}(R(\Delta t))$ is the molar absorption coefficient and transition energy between the valence two-hole state $|\Psi_{\nu}(R(\Delta t))\rangle$ and O(1s) core-excited state $|\Psi_{\mu}(R(\Delta t))\rangle$, respectively. The $\delta(h\omega_{pr} - \Delta E_{\nu\mu}(R(\Delta t)), \Delta t)$ is the two dimensional delta function located at $h\omega_{pr} = \Delta E_{\nu\mu}(R(\Delta t))$ and $\Delta t$, and $g_{pr}(h\omega_{pr}, \Delta t)$ is the Gaussian instrumental function which determine the energy and temporal resolutions of the TR-XAS.

To reduce the computational costs of the TR-XAS calculation, we evaluated the $|\Psi_{\nu}(R(\Delta t))\rangle$ in a diabatic representation characterized by the electron configurations at the Franck-Condon geometry $R_0$.\textsuperscript{78,80} We then applied the Condon approximation $\epsilon_{\nu\mu}(R(\Delta t)) = \epsilon_{\nu\mu}(R_0)$. We also set $\Delta E_{\nu\mu}(R(\Delta t)) = \Delta E_{\nu\mu}(R_0)$ since our diabatic LVC potential energy surfaces are parallel and independent of $R$.\textsuperscript{73}

The relative Auger intensity, the potential energy, vibronic\textsuperscript{81} and spin-orbit couplings\textsuperscript{82,83} among $\{ |\Psi_{\nu}\rangle\}$ appeared in the LVC model Hamiltonian were evaluated by the state-averaged complete active space multi-configuration self-consistent field (SA-CASSCF) theory\textsuperscript{84,85} combined with the ANO-RCC-VTZP basis set.\textsuperscript{86} Twenty valence MOs and two holes (= 38 electrons) were included in the RAS2 active space (the [2h,20o] RAS2 space). All two-hole states were included in the state-average procedure. We performed geometry optimization and normal mode analysis at the density fitted localized Möller-Plesset second-order perturbation theory (DF-LMP2)\textsuperscript{87} combined with the Def2-TZVP basis set\textsuperscript{88} as implemented in the MOLPRO 2019.2 quantum chemistry package.\textsuperscript{87} The $\epsilon_{\nu\mu}(R_0)$ were calculated by the SA-2h-CASSCF/ANO-RCC-VTZP method by extending RAS2 space to 20 valence MO and O(1s) MO, and by the restricted active space state interaction (RAS-SI) method.\textsuperscript{89}

To optimize the $h\omega_{pu}$ and $h\omega_{pr}$, we calculated the x-ray photoelectron spectra (XPS) of the lowest energy low spin states of Tr$q^+$ ($q = 0, 1, 2$) at C(1s) and edge O(1s) including low-lying shake-up states. We used multi-state restricted active space second-order perturbation theory (MS-RASPT2)\textsuperscript{85,90} combined with the Supporo-2012-TZP basis set for C and O atoms, and with the Supporo-2012-DZP basis set for H atoms.\textsuperscript{91} The relative intensity of
the XPS was evaluated using the norm of Dyson orbitals.

The OpenMolcas 18.09 and 21.10 quantum chemistry packages\textsuperscript{85} were used for all SA-
CASSCF and MS-RASPT2 calculations, respectively. We used SHARC 2.1 program for
the LVC-MD.\textsuperscript{79} Further computational details were described in section 1 of Supporting
information (SI).

Let us look at the calculated NRD dynamics of Tr$^{2+}$. Hereafter, the $S_n$ ($n = 0, 1, \ldots, 209$)
and $T_{n'}$ ($n' = 1, 2, \ldots, 190$) denote the singlet and triplet diabatic states at the Franck-
Condon geometry $R_0$ of Tr, respectively. $S_n$ and $T_{n'}$ denotes the singlet and triplet adiabatic
states at a given geometry $R(t)$ at a given delay time $t$, respectively.

The calculated Carbon $KLL$ normal Auger spectrum as a function of two-electron binding
energy $E_\nu$ is displayed in Figure 1a. For the convenience of the later discussions, we divide
the spectrum into three bands. Band I: $E_\nu < 30$ eV, Band II: $E_\nu = 30-40$ eV, and Band III:
$E_\nu \geq 40$ eV. The ratio integrated intensity of singlet and triplet states is singlet:triplet = 81:19 and Auger decay to singlet dicaticonic states is dominant. The two most intense bands
located at bands II and III consist of the two-hole states with one hole on the MO originated
from $2p$ orbitals and the others on the $\sigma$ MOs of $2s$ atomic orbitals ($2p^{-1}\sigma(2s)^{-1}$ states).
The most intense transition at the band II is assigned to be the $S_{36}$ state at $E_\nu = 32.95$ eV,
whose normalized intensity is $I_\nu = 0.026$, and that of the band III is assigned to be the $S_{111}$
state) with $E_\nu = 43.95$ eV and $I_\nu = 0.019$, respectively. The major electronic configurations
of both $S_{36}$ and $S_{111}$ states are $\pi^{-1}\sigma(2s)^{-1}$ according to the occupation numbers \{\textit{N}_\text{occ}\} of the natural orbitals of calculated at the [2h,20o]-SA-CASSCF/ANO-RCC-VTZP//DF-
LMP2/Def2-TZVP level of theory as shown in Figures 1b and 1c, respectively.

The NRD cascade proceeds mostly via internal conversion. The intersystem crossing is
observed in only 16.5 % of trajectories. The NRD cascade completes on the time scale of
100 fs and the efficiency of NRD cascade is different in each bands. Figure 2a represents a
representative trajectory of the NRD cascade. This trajectory started from the $S_{117}$ state in
the band III and relaxed into $S_4$ in band I within 461 fs. It took 240 fs to reach the $S_{102}$ state.
Figure 1: (a) The calculated normal Auger spectrum of tropone at carbon C(1s) edge as a function of two-electron binding energy $E_\nu$. Peak position and normalized intensity ($\sum_\nu I_\nu = 1$) for each two hole states described with bar graph were calculated by the two-hole population analysis. The full curve represents the Gaussian convolution of FWHM = 2.5 eV. Band I: $E_\nu < 30$ eV, Band II: $E_\nu = 30$-40 eV, Band III: $E_\nu \geq 40$ eV. (b) and (c) The most intense transition for band II and III, respectively, and the natural orbitals which has the two largest hole populations for each transition. The all results were calculated at the [2h,20o]-SA-CASSCF/ANO-RCC-VTZP/DF-LMP2/Def2-TZVP level of theory.

since energy intervals of the dicationic states are so small that Tr$^{2+}$ can nonadiabatically return back to the higher-lying states as shown in Figure 2b—the mean interval of the singlet states in terms of $E_\nu$ was 0.15 eV in band III. A large in-plane ring distortion observed at $t = 240$ fs (Figure 2a) accelerated the internal conversion within $\sigma$ and $\pi$ orbitals, respectively, and the Tr$^{2+}$ slide down to the S$_1$ state until by $t = 461$ fs and S$_2$ state by $t = 476$ fs (the lowest lying adiabatic state in the present trajectory). The resultant vibrationally hot dications with 2$p^{-2}$ electron configurations have a significant out-of-plane distortion around the C=O double bonds (Figure 2a, $t = 461$ fs), which promotes the hole transfer between $\sigma$ and $\pi$ orbitals as in the $^1\pi \pi^* \rightarrow ^1\Pi \pi$ internal conversion in UV excited nucleobases and their derivatives.$^{92}$ The dihedral angle between the C=O group and the two carbon atoms next to them reached 158°.

The $P(t, E_\nu$) clearly reflects the NRD cascade. Figure 3a represents the $P(t, E_\nu$) for Tr$^{2+}$ calculated by eq. 1, which is broaden along the $E_\nu$ axis with a Gaussian function of FWHM = 2.5 eV. Tr molecules were mainly ionized to bands II and III after the C(1s) core-ionization and subsequent Auger decay in 20 fs. The electronically excited Tr$^{2+}$ in band
Figure 2: A representative trajectory of the NRD cascade of Tr$^{2+}$ starting from the band III calculated by the LVC-MD. (a) Selective snapshots of the trajectory and the adiabatic state $S_n$ is written in parenthesis. (b) Potential energy (black, left axis), kinetic energy (blue, left axis), and adiabatic state $S_n$ (orange, right axis) as a function of time $t$. The origin of potential energy is set to be the $E_\nu$ of the ground ($S_0$) state of the dication (21.91 eV).
III relaxed into band II within 200-400 fs. They further undergone NRD to band I in 200 fs and completed the NRD cascade into the vibrationally hot lower-lying dicationic states in band I (band I*) in 100 fs.

Figure 3: Population dynamics for the NRD cascade of Tr$^{2+}$ calculated by LVC-MD. (a) The Diabatic population as a function of two-electron binding energy $E_\nu$ and time $t$ associated with the bands I-III. We assumed the FWHM of the Gaussian pump pulse is 10 fs and energy resolution in FWHM is 2.5 eV. (b) Calculated C(1s) pump O(1s) pre-edge probe TR-XAS within the dipole and Condon approximation associated with the main contribution (band I, II, or III) for each absorption peak. We assumed that the FWHM of the Gaussian pump and probe pulses is 10 fs and energy resolution in FWHM is 1.0 eV. (c) Cumulative diabatic populations as a function of time and (d) Normalized absorption as a function of Pump-probe delay for the band I (Black), II (aqua), and III (orange) in sudden ionization limit. Solid lines represents the results from the LVC-MD, and dotted line represents fitting ones.

To quantify the population dynamics in the NRD cascade, we calculated the time-dependent diabatic population of Tr$^{2+}$ in sudden ionization limit in each bands $\bar{p}_\chi(t) \equiv \sum_{E_\nu \in \chi} \bar{P}_\nu(t)$ ($\chi =$ III, II, I) from the LVC-MD results appearing as solid lines in Figure 3c. To extract the time constants $\{\tau\}$ for the NRD cascades constructed a kinetic model includ-
ing the sequential NRD process of III $\tau_{\text{III} \rightarrow \text{II}}$ II $\tau_{\text{II} \rightarrow \text{I}}$ I $\tau_{\text{I} \rightarrow \text{I}^*}$: The coupled rate equations for this kinetic model can be written as

$$\frac{d}{dt} \tilde{p}(t) = k\tilde{p}(t), \quad (3)$$

where $\tilde{p}(t) \equiv [\tilde{p}_{\text{III}}(t), \tilde{p}_{\text{II}}(t), \tilde{p}_{\text{I}}(t)]^T$. The rate constant matrix $k$ contains three time constants,

$$k = \begin{bmatrix}
-\tau_{\text{III} \rightarrow \text{II}}^{-1} & 0 & 0 \\
\tau_{\text{II} \rightarrow \text{I}}^{-1} & -\tau_{\text{II} \rightarrow \text{I}}^{-1} & 0 \\
0 & \tau_{\text{II} \rightarrow \text{I}}^{-1} & -\tau_{\text{I} \rightarrow \text{I}^*}^{-1}
\end{bmatrix}. \quad (4)$$

We evaluated the $\{\tau\}$ by a lease square fitting into the $\tilde{p}(t)$ calculated by the LVC-MD results. The initial value of the population $\tilde{p}(t = 0)$ were fixed to the LVC-MD values.

Fitted population transients are presented in Figure 3c as the dotted lines. This panel shows the temporal evolution of the three population transients evaluated from the LVC-MD (solid lines) with the fitting functions (dotted lines); the kinetic model reasonably fits the data. The obtained time constants are shown in Table 1 together with their fitting error.

The time constants of inter-band NRD are 100-400 fs. The rate-limiting step is the NRD from band III to II ($\tau_{\text{III} \rightarrow \text{II}} = 362$ fs) due to the inverse internal conversion indicated in Figure 2b. After the NRD from II to I, the exited $\text{Tr}^{2+}$ in band I rapidly relax to $\text{I}^*$ ($\tau_{\text{I} \rightarrow \text{I}^*} = 41$ fs).

Table 1: The optimized time constants $\{\tau\}$ associated with their standard fitting errors extracted for the NRD cascade using eqs 3 and 4. Comparison between the normalized TR-XAS signal $\Delta \tilde{A}(h\omega_{pr}, \Delta t)$ and diabatic population $\tilde{P}(t)$.

| Process     | Population (fs) | TR-XAS (fs) |
|-------------|----------------|-------------|
| $\text{III} \rightarrow \text{II}$ | $362 \pm 1$ | $291 \pm 2$ |
| $\text{II} \rightarrow \text{I}$ | $211 \pm 1$ | $274 \pm 1$ |
| $\text{I} \rightarrow \text{I}^*$ | $41 \pm 1$ | $84 \pm 1$ |

The the time constants for the NRD cascade can be extracted from TR-XAS. Figure 4 shows the pre-edge peaks of C(1s) edge pump O(1s) pre-edge probe femtosecond TR-XAS. According our MS-RASPT2 calculations, the vertical O(1s) core ionization energy of $\text{Tr}^{2+}$,
Tr$^+$, and Tr at $R_0$ are calculated to be 549.41, 542.58, and 536.06 eV, respectively. The corresponding experimental value is 535.04 ± 0.2 eV for Tr.$^{93}$ For Tr$^{2+}$ (Figure 3(b)), there are three peaks at the probe photon energies of $\hbar\omega_{pr} = 548, 542, \text{ and } 538 \text{ eV. Each peak consists of } \sim 10^{-2} \text{ core-to-valence transitions } \{\nu \rightarrow \mu\} \text{ from various valence two-hole states } \{|\Psi_\nu\rangle\}. \text{ However, the peak at } \hbar\omega_{pr} = 548, 542, \text{ and } 538 \text{ eV have the largest contributions from the transitions to bands III, I, and II, respectively.}

To extract the $\{\tau\}$ from the TR-XAS of the O(1s)-pre-edge region ($\hbar\omega_{pr} \leq 550 \text{ eV}$), we first calculated the normalized absorption intensities of bands I-III in the sudden ionization and impulsive excitation limit defined as $\Delta \tilde{A}_\chi(\Delta t) \equiv \sum_{E_{\nu} \in \chi, \mu} \epsilon_{\nu\mu}(R(\Delta t)) \tilde{P}_{\nu}(\Delta t) / \sum_{\nu, \mu} \epsilon_{\nu\mu}(R(\Delta t)) \tilde{P}_{\nu}(\Delta t)$ from the LVC-MD results. The resultant $\{\Delta \tilde{A}_\chi(\Delta t)\}$ is shown in Figure 3d as the solid lines. The $\{\tau\}$ were extracted by using the same sequential NRD kinetic model as the analysis of $\tilde{A}_\chi(\Delta t)$. The calculated normalized absorption intensities $\Delta \tilde{A}(\Delta t) \equiv [\Delta \tilde{A}_{\text{III}}(\Delta t), \Delta \tilde{A}_{\text{II}}(\Delta t), \Delta \tilde{A}_{\text{I}}(\Delta t)]^T$ were fitted by the analytical solution of the coupled differential equation $d\Delta \tilde{A}(\Delta t)/d\Delta t = k\Delta \tilde{A}(\Delta t)$. The initial value $\Delta \tilde{A}(t = 0)$ were fixed to the LVC-MD values.

The fitting results on the TR-XAS transients are presented in Figures 3d. The kinetic model (dotted lines) reasonably fits the LVC-MD results (solid lines). The extracted time constants $\{\tau\}$ are summarized in Table 1 together with their fitting errors. The $\{\tau\}$ extracted from $\Delta \tilde{A}(\hbar\omega_{pr}, \Delta t)$ agree with the reference $\{\tau\}$ obtained from $\tilde{P}(t)$: (i) the rate limiting step is the NRD from III to II; (ii) The intraband NRD from I to I* has the timescales of sub 100 fs.

Let us discuss how Auger electron yield method$^{4-8,70,71}$ is efficient for measuring the two-color TR-XAS for the NRD cascades of dication of a given organic molecule, M. We firstly derive analytical expressions of signal and noise intensities and S/N using coupled ionization rate equation model.$^{69}$ Then, we apply the resultant equations to Tr.

We found that the pump pulse should be monochromatic and it also should satisfy the conditions as described in Figure 4a to obtain large signal intensity and high S/N:
1. The photon energy of the monochromatic pump pulse $\hbar \omega_{pu}$ should be adjusted to selectively ionize one core-level $X$ of the M to avoid sequential core ionization of daughter cations $M^{q+}$, which decreases the signal intensity and increases the background. Setting $\hbar \omega_{pu}$ in between the $X$-edge of M and $M^{+}$ can satisfy this condition. $^{94-96}$

2. The pump pulse has a large enough peak intensity $I_{pu}$ to trigger the saturated one-photon $X$-edge core ionization from M to $M^{2+}$. This maximizes the signal intensity.

For the probe pulse, its photon energy $\hbar \omega_{pr}$ should be set to the pre-edge region of the other core-level $Y$ of neutral $M^{2+}$ as shown in Figure 4a: $\hbar \omega_{pu} < E_{Y}(q = 0) < \hbar \omega_{pr} < E_{Y}(q = 2)$, where $E_{Y}(q)$ is the core ionization energy of $M^{q+}$ at $Y$-edge and its peak intensity $I_{pr}$ should be in the linear absorption regime.

We first consider the TR-XAS signal by including one- and two-photon sequential ionization processes by the pump pulse and one-photon ones by the probe pulse.

The pump pulse can trigger the core ionization and subsequent normal Auger decay for M at the $X$-edge ($X^{-1}$), valence ionization ($V^{-1}$) for $M^{q+}(q = 0, 1, 2)$, and core excitation from $X$-edge to valence holes and subsequent resonance Auger decay ($X \rightarrow V$) for $M^{+}$ and $M^{q+}$. The possible two ionization pathways by the pump pulse are $M \xrightarrow{X^{-1}} M^{2+}$, $V^{-1}$ or $X \rightarrow V$, $M^{3+}$ and $M \xrightarrow{V^{-1}} M^{+}$, $V^{-1}$ or $X \rightarrow V$, $M^{2+}$. The $X^{-1}$ process from M to $M^{2+}$ contributes to the signal and the others do to background noise. As the photo-ionization and absorption cross sections are almost independent of $q$, $^{69}$ the yield of $M^{2+}$ after pump irradiation can be written as functions of $I_{pu}$ and $\hbar \omega_{pu}$ as

$$[M^{2+}](I_{pu}, \hbar \omega_{pu}) = \left[ \exp \left( -\lambda_{V}(I_{pu}, \hbar \omega_{pu}) \right) - \exp \left( -\lambda_{V}(I_{pu}, \hbar \omega_{pu}) - \lambda_{X}(I_{pu}, \hbar \omega_{pu}) \right) \right],$$  \hspace{1cm} (5)

$$\lambda_{A}(I_{pu}, \hbar \omega_{pu}) = \sigma_{A}(\hbar \omega_{pu}) \frac{I_{pu}}{\hbar \omega_{pu}} \sqrt{\frac{\pi}{4 \ln 2}} s_{pu} (A = V^{-1}, X^{-1}, X \rightarrow V),$$  \hspace{1cm} (6)
Figure 4: (a) Schematic figure on relation among binding energies of $M^q+$ ($q = 0, 1, 2$) at X- and Y-edges, $\hbar\omega_{pu}$, and $\hbar\omega_{pr}$. (b) The calculated XPS spectra of $\text{Tr}^{q+}$ ($q = 0, 1, 2$) at the C(1s) edge. Results at the MS-RASPT2/Sapporo-2012 (C,O: TZP, H: DZP) level of theory. The calculated spectra were broadened by a Gaussian function of FWHM = 1.0 eV. The position of $\hbar\omega_{pu}$ is shown in orange. (c) The $S^2/N$ ratio $\Upsilon(I_{pu}, I_{pr})$ at $\hbar\omega_{pu} = 292.3$ eV and $\hbar\omega_{pr} = 542.0$ eV. (d) The ion yields $[\text{Tr}^{q+}](I_{pu})$ ($q = 0, 1, 2, 2', 3$) at $\hbar\omega_{pu} = 292.3$ eV. (e) The resonance Auger electron yield for $\text{Tr}^{2+} N_e(q = 2, I_{pu}, I_{pr})$ at $\hbar\omega_{pu} = 292.3$ eV and $\omega_{pr} = 542.0$ eV. (f) The $S/N$ ratio $\eta(I_{pu}, I_{pr})$ at $\hbar\omega_{pu} = 292.3$ eV and $\omega_{pr} = 542.0$ eV. We set $\theta(q = 0, \hbar\omega_{pr}) = 1.0$ and $\theta(q = 1, 2, 2', \hbar\omega_{pr}) = 0.10$. 
where $\sigma_A(\hbar \omega_{pu})$ represents the photoionization cross section of the ionization processes of $A$ ($A = V^{-1}, X^{-1}, X \rightarrow V$) as functions of $\hbar \omega_{pu}$, respectively. $\lambda_{V/X}(I_{pu}, \hbar \omega_{pu})$ means the number of absorbed photons during the pump irradiation for the ionization process $V^{-1}$ and $X^{-1}$. The analytical expressions for $[M^{q+}](I_{pu}, \hbar \omega_{pu})$ ($q = 0, 1, 2'$) can be found in section 2.1 of SI. For the Gaussian pump pulse with a peak intensity of $I_{pu}$ and full width at half maximum (FWHM) of $s_{pu}$, $\lambda_{V/X}(I_{pu}, \hbar \omega_{pu})$ is written as $\lambda_{tot}(I_{pu}, \hbar \omega_{pu})$ can obviously be expressed as the sum of $\lambda_{V}(I_{pu}, \hbar \omega_{pu})$ and $\lambda_{X}(I_{pu}, \hbar \omega_{pu})$.

One photon absorption from the probe pulse at the $Y$-pre-edge of $M^{2+}$ excites core electron at $Y$-edge to the valence hole. The core-excited $M^{2+}$ which is rapidly ionized into $M^{3+}$ via resonance Auger relaxation emits one fast Auger electron $e^{-}_{Auger}$, $M^{2+} \xrightarrow{Y \rightarrow V} M^{3+} + e^{-}_{Auger}$.

The TR-XAS measurement using the Auger electron yield method selectively count up the number of $e^{-}_{Auger}$ as a function of $\hbar \omega_{pr}$ and $\Delta t$ by using electron spectrometers. This scheme can eliminate photoelectrons from core ionization and $V^{-1}$ processes, and Auger electrons from the $X^{-1}$ process of $M^{q+}(q = 0 - 3)$ by the pump and probe pulses. The background sources can come from the resonance Auger electrons from the $Y \rightarrow V$ excitation process of $M^{+}$ and $M^{2+}$, and normal Auger electron from $Y^{-1}$ core ionization of M and $M^{+}$, which can overlap with the signal from $Tr^{2+}$.

When the temporal overlap between the pump and probe pulse is negligibly small, the Auger electron yield $N_{e}$ originated from $M^{q+}(q = 0, 1, 2, 2')$ can be written as,

$$N_{e}(q, I_{pu}, \hbar \omega_{pu}, I_{pr}, \hbar \omega_{pr})$$

$$= \theta(q, \hbar \omega_{pr})[M^{q+}](I_{pu}, \hbar \omega_{pu}) \frac{\sigma_{Y \rightarrow V/V}(q, \hbar \omega_{pr})}{\sigma_{tot}(q, \hbar \omega_{pr})}$$

$$\times [1 - \exp(-\lambda_{tot}(q, I_{pr}, \hbar \omega_{pr}))].$$  (7)

Here, $\theta(q, \hbar \omega_{pr})$ describes the fraction of bright states for $M^{q+}$ at $\hbar \omega_{pr}$ ($\theta(q = 0, \hbar \omega_{pr}) = 1$ and $0 \leq \theta(0 < q, \hbar \omega_{pr}) \leq 1$). $\sigma_{Y \rightarrow V/V}(q, \hbar \omega_{pr})$ represents the mean photoionization cross sections
for the $Y \to V$ excitation and subsequent resonance Auger decay, and the $Y^{-1}$ core ionization and subsequent Auger decay in $M^{q+}$, respectively, and $\sigma_{Y \to V/V}(q = 2, \hbar \omega_{pr}) = \sigma_{Y \to V}(\hbar \omega_{pr})$ (See section 2.2 of SI for $q = 0, 1, 2'$). $\sigma_{tot}(q, \hbar \omega_{pr}) \equiv \sigma_{Y \to V/V}(q, \hbar \omega_{pr}) + \sigma_{V}(\hbar \omega_{pr}) + \sigma_{X}(\hbar \omega_{pr})$ is the total photoionization cross section for $M^{q+}$ as a function of $\hbar \omega_{pr}$, and $\lambda_{tot}(q, I_{pr}, \hbar \omega_{pr})$ is the total number of absorbed photon in the probe irradiation. For the Gaussian probe pulse with a peak intensity of $I_{pr}$ and FWHM of $s_{pr}$, $\lambda_{tot}(q, I_{pr}, \hbar \omega_{pr})$ is written as $\lambda_{tot}(q, I_{pr}, \hbar \omega_{pr}) = \sigma_{tot}(q, \hbar \omega_{pr})(I_{pr}/\hbar \omega_{pr})(\pi/4 \ln 2)^{1/2}s_{pr}$. In the liner probe regime, eq (7) is finally simplified to

$$N_e(q, I_{pu}, \hbar \omega_{pu}, I_{pr}, \hbar \omega_{pr}) \approx \frac{\theta(q, \hbar \omega_{pr})[M^{q+}](I_{pu}, \hbar \omega_{pu})}{\sigma_{Y \to V/V}(q, \hbar \omega_{pr}) \times \sum_{q = 1, 2'} [M^{q+}](I_{pu}, \hbar \omega_{pu}) \sigma_{Y \to V/V}(q, \hbar \omega_{pr}) \leq \frac{\sigma_{X}(\hbar \omega_{pu})}{\sigma_{V}(\hbar \omega_{pu})} \sim 10. \quad (10)$$

This indicates that the S/N does not depend on $I_{pr}$. The $\eta(\hbar \omega_{pu}, \hbar \omega_{pr})$ is almost independent
of systems size and is determined by the edge X since $\sigma_X(h\omega_{pu}, h\omega_{pr})$ and $\sigma_V(h\omega_{pu}, h\omega_{pr})$ are nearly proportional to the system size if X-edge is the dominant absorption edge in the system (e.g. C(1s) edge of organic molecules, O(1s) edge of liquid water etc.). These behaviors of $\eta(h\omega_{pu}, h\omega_{pr})$ allow us to efficiently apply the proposed TR-XAS protocol to nano-/bio-molecules and other extended system. Auger electron yield method has surface sensitivity,\textsuperscript{97,98} and the proposed protocol for the TR-XAS measurement shall also be a powerful tool to analyze the x-ray induced dynamics in the surface regions of solids, liquids, and solutions.

Such extensions cannot be achieved by using conventional transmission/reflection measurement or ion-yield methods since they cannot distinguish the signal from the $Y \rightarrow V$ process of M$^{2+}$ and the dominant background from the $X^{-1}$ process in the proposed absorption edge selective saturation pump scheme. The S/N for conventional methods can be approximated as $\eta'(h\omega_{pr}) \approx \sigma_{Y \rightarrow V}(h\omega_{pr})/\sigma_X(h\omega_{pr})$. The $\eta'(h\omega_{pr})$ obviously asymptotes to zero as the system size grows. This clearly indicates that the conventional methods are only applicable to small molecules\textsuperscript{62,99} and not suitable for the extended systems.

We next applied the derived equations above to Tr. The calculated C(1s) and O(1s) XPS spectra at the MS-RASPT2 level of theory are shown in Figures 4b and S2, respectively. Both C(1s) and O(1s) edge blue-shifts by 6-7 eV for each valence ionization of $q \rightarrow q + 1$. We have searched for the condition that the $N_e(q, I_{pu}, h\omega_{pu}, I_{pr}, h\omega_{pr})$ in eq. (7) and $\eta(I_{pu}, h\omega_{pu}, I_{pr}, h\omega_{pr})$ in eq. (11) should be simultaneously maximized upon scanning $I_{pu}$ and $I_{pr}$ at fixed $q$, $h\omega_{pu}$, and $h\omega_{pr}$. In the searching process, we have chosen $h\omega_{pu} = 292.3$ eV to avoid sequential C(1s) core ionization process in Tr$^+$ and Tr$^{2+}$ cations, and $h\omega_{pr} = 542.0$ eV in the strongest O(1s)→V$^{-1}$ absorption band of Tr$^{2+}$ as shown in Figure 3b. The charge number $q$ is set to 2. We defined a merit function $\Upsilon(I_{pu}, I_{pr}) \equiv N_e(I_{pu}, I_{pr})\eta(I_{pu}, I_{pr})$ to be maximized, where we omit the variables other than scanning variables for simplicity. The scanning range of $I_{pu}$ is determined to be $I_{pu} \geq 1.0 \times 10^{15}$ W/cm$^2$ to saturate the absorption of the pump pulse, while that of $I_{pr}$ is determined to be $I_{pr} \leq 1.0 \times 10^{14}$ W/cm$^2$ to avoid
nonlinear absorption of the probe pulse. The values of cross sections\textsuperscript{100} are summarized in Table S2 in the SI.

We found that $\Upsilon(I_{pu}, I_{pr})$ becomes maximized to 0.032 at $I_{pu} = I_{opt,pu} = 3.7 \times 10^{15}$ \text{W/cm$^2$} and $I_{pr} = I_{opt,pr} = 1.0 \times 10^{14}$ \text{W/cm$^2$} as shown in Figure 4c. This optimized $I_{opt,pu}$ is a bit larger than to the saturable intensity $I_{max} = 2.0 \times 10^{15}$ \text{W/cm$^2$} which maximizes $[\text{Tr}^{2+}](I_{max})$ to 0.76 (Figure 4d) and $N_e(q = 2, I_{max}, I_{pu})$ to $N_{max} = 0.0042$ to minimize the major background from Tr$^{2+}$. At the optimized $I_{opt,pu}$ and $I_{opt,pr}$, $\eta(I_{opt, pu}, I_{opt, pr})$ reaches 8.52, which is not sensitive to the value of $I_{pu}$ in the saturable regime ($\eta \sim 7 – 9$ for $I_{pu} = 3.0 – 7.0 \times 10^{15}$ \text{W/cm$^2$}) and constant for the hole range of the investigated $I_{pr}$ as suggested in eq. (10). The optimal $\eta = 8.52$ and $N_e(q = 2) = 0.0037$ are also close to $\eta_{max} = \sigma_{C(1s)}/\sigma_V = 13.3$ and $N_{max}$, respectively. These clearly show that the $\eta$ is surely governed by the choice of the absorption edge at which pump pulse induces the core ionization, and that the maximization of $[\text{M}^{2+}]$ by the neutral selective core-ionization with a narrow band pump pulse (ideally a seeded x-ray free electron laser pulse\textsuperscript{101}) is the key to realize the precise TR-XAS measurement. The $N_e(q = 2) = 0.0037$ also indicates that a repetition rate of $\sim 0.1 – 1.0$ MHz is essential for the data acquisition in a reasonable machine time. The suggested laser parameters for the pump and probe pulses and detection scheme have already been available at the NAMASTE end station of LCLS-II.\textsuperscript{102}

In conclusion, we simulated the carbon $KLL$ Auger induced nonadiabatic reaction dynamics of Tr that were revealed with C(1s) edge pump and O(1s) pre-edge probe femtosecond TR-XAS using surface hopping nonadiabatic reaction dynamics technique and the coupled rate equation model. We found that soft x-ray irradiated Tr undergoes NRD cascade passing through $10^{-10^2}$ of two-hole dicationic states in the timescale of 100 fs. The C(1s) edge pump O(1s) pre-edge probe femtosecond TR-XAS clearly reflects the population dynamics of the NRD cascade. We also demonstrated that the Auger electron yield method is suitable for measuring the two-color TR-XAS for the NRD cascades of general organic molecules in the gas phase, and surfaces of solid, liquid, and solutions. To maximize the signal intensity and
S/N, an monochromatic pump pulse whose photon energy is set to ionize only one core-level of the parent neutral molecule and whose peak intensity is adjusted large enough to saturate the ionization of the neutral. The selective collection of the resonance Auger electrons from a deeper inner-shell absorption edge emitted by the probe pulse irradiation also increases the S/N (eg. S/N = 8.52 for Tr). The S/N is mostly determined by the ratio between the photo-ionization cross section of the core-level MOs, which an electron is removed by pump pulse, and that of valence MOs. This feature makes the S/N ratio independent of the peak intensity of probe pulse, and system size. We hope that the propose two-color TR-XAS scheme will widely used for investigating the various x-ray induced photochemical reactions in near the future.

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Supporting Information Available

The details of computational methods, supplemental discussions, and parameters for LVC potentials.

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Supporting Information:

X-ray Induced Ultrafast Nonadiabatic Dynamics of Tropone Probed at the O(1s) pre-edge

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1 Details of computational methods

1.1 Auger decay probability from two-population analysis

Given that an core ionization creates an core-hole state $|\Psi_{1s}^i\rangle$ whose core-hole is located at the $i$-th 1s molecular orbital (MO) located on the atoms A and it rapidly undergoes Auger decay. In the single-electron configuration limit, the $|\Psi_{1s}^i\rangle$ can be calculated by a $\Delta$SCF procedure and the relative Auger amplitude $t_{ab}$ can be written as a function of the Löwdin electron populations of MOs $a$ and $b$ on the core-hole atoms A, $Q_a(A)$ and $Q_a(A)$ with assuming that the contribution from the continuum photoelectron and Auger electron is constant for all decay channels.\textsuperscript{S1} The representations of $t_{ab}$ for singlet configuration are\textsuperscript{S1}

$$t_{ab}(A) \approx \sqrt{\frac{1}{2}} (Q_a(A) + Q_b(A)), \quad (a \neq b) \quad (1)$$
$$t_{aa} \approx Q_a(A), \quad (a = b) \quad (2)$$

and that for triplet one is\textsuperscript{S1}

$$t_{ab}(A) \approx \sqrt{\frac{3}{2}} (Q_a(A) - Q_b(A)). \quad (a \neq b) \quad (3)$$

In general, the electronic wave function of the dicationic state $|\Psi^{q=2}\rangle$ can be represented as the linear combination of the all possible two hole-electron configurations.\textsuperscript{S1} The wave function within the two-hole configuration interaction theory on the top of $|\Psi_{1s}^i\rangle$ is written using the second quantization notation as

$$|\Psi_{1s}^{q=2}\rangle = \sum_{a \leq b} c_a c_b c_{1s}^\dagger |\Psi_{1s}^i\rangle, \quad (4)$$

where $c_a$, $c_b$, $c_{1s}^\dagger$ are the annihilation operator for an electron in the MO $a$ and $b$, and the creation operator for that in the core-hole 1s MO. We further included the MO relaxation
effect by taking the overlap between the $|\Psi_q^{q=2}\rangle$ and the $\nu$-th dication wave function calculated by the state-averaged complete active space self consistent active field methods averaged over all two-hole electronic state (SA-2h-CASSCF) for given spin-multiplicity $|\Psi_{\nu}^{q=2}\rangle$. The final expression for the relative Auger transition intensity from $|\Psi_i\rangle$ to $|\Psi_{\nu}^{q=2}\rangle$ is written as:

$$I_{i\rightarrow\nu} = 2\pi \left| \sum_{a\leq b} \langle \Psi_{\nu}^{q=2} | c_a c_b c_{1s}^\dagger | \Psi_i^{1s} \rangle t_{ab} \right|^2,$$

(5)

The normalized cumulative relative intensity (Auger spectrum) for the $|\Psi_{\nu}^{q=2}\rangle$ as a function of its two-hole electron binding energy $E_{\nu}$ represents the initial population for the subsequent nonadiabatic reaction dynamics simulations:

$$I_{\nu}(E_{\nu}) = \frac{\sum_i I_{i\rightarrow\nu}}{\sum_{i,\nu} I_{i\rightarrow\nu}},$$

(6)

$$\tilde{P}_{\nu}(t = 0) = I_{\nu}.$$

(7)

1.2 Nonadiabatic reaction dynamics

We performed surface hopping molecular dynamics simulations on the NRD dynamics of tropone dications using an Tully’s fewest switching algorithm combined with a linear vibronic coupling (LVC) model potential energy surfaces (PESs)$^{33-35}$ (LVC-MD). We included 210 singlet and 190 triplet two-hole states, and the all 36 vibrational degrees of freedom. The details of the evaluations of the LVC parameters are described in section 1.3. Trajectories were set up using 1000 initial coordinates and momenta from the Wigner distribution of the ground-state potential energy surface at the temperature of 108 °C according to an gas phase electron diffraction experiment by Ogasawara et al.$^{36}$ The initial dication states for 200 trajectories were selected according to the relative normal Auger probability$^{37}$ initiated by the core ionization at the Carbon 1s edge (See Figure 1 in the main text).

The trajectories were then propagated on the LVC potential energy surfaces until they encountered to a surface hop at a dissociative crossing point of the LVC potential energy.
surfaces or trajectory lengths reached 1000 fs. Each trajectory was stopped if it reaches the dissociative states where any bond-length elongates to the threshold bond-length $R_{th} = 3.4 \, \text{Å}$, which corresponds to the double of the Van der Waals radius of carbon atom, and thereafter regarded as *vibrationally hot* molecule.

The settings for the LVC-MD are as follows: We used a nuclear time step of 0.1 fs and an electronic time step of 0.004 fs An energy-based decoherence correction with a constant of 0.1 Hartree$^{58}$ was used. The kinetic energy was adjusted by rescaling the velocity vectors. The time derivative couplings to evaluate the surface hopping probabilities were approximated using the wave function overlaps. A local diabatization method$^{59}$ was applied to evaluate the $\{ \tilde{P}_\nu(t) \}$ for the LVC-MD.

### 1.2.1 Linear vibronic coupling (LVC) model

In an LVC model,$^{53}$ the PESs are approximated via the ground-state PES $V_0$ and the first-order (linear) vibronic coupling term $W$ on the basis of the mass-frequency scaled normal mode coordinate $\mathbf{x} = [x_1, x_2, \ldots, x_l, \ldots, x_{3N' - 6}]$,

$$V(\mathbf{x}) = V_0(\mathbf{x}) \mathbf{1} + W(\mathbf{x}). \quad (8)$$

The ground-state PESs for $N'$-atom molecules are approximated as harmonic oscillators with frequencies $\omega_l$ as

$$V_0(\mathbf{x}) = \sum_{l=1}^{3N' - 6} \frac{\hbar \omega_l}{2} x_l^2. \quad (9)$$

The coupling matrix $W(\mathbf{x})$ serves to create the individual potential energy surfaces from the reference potential, and consists of constant and linear terms

$$W_{nn}(\mathbf{x}) = E^{(n)}_\nu + \sum_{l=1}^{3N' - 6} \kappa^{(n)}_l x_l, \quad (10)$$
and

\[
W_{mn}(x) = \sum_{l=1}^{3N'-6} L_{i}^{(n,m)} x_l
\]

where \(E_{n}^{(n)}\) are the two-hole binding energies at \(x_0 = R_0\), while \(\kappa_{i}^{(n)} x_l\) and \(L_{i}^{(n,m)}\) are the intrastate and interstate coupling elements for the normal mode coordinate \(x_l\). The coupling elements were obtained numerically from SA-2h-CASSCF calculations (see below) on geometries displaced by \(\pm 0.05\) units from \(x_0\) for each normal mode. The intrastate coupling \(\kappa_{i}^{(n)} x_l\) values were obtained as numerical gradients and the interstate couplings \(L_{i}^{(n,m)}\) were obtained from the change in the wavefunction overlaps. The spin–orbit couplings (SOCs) in the LVC model potential were approximated by constant SOCs obtained at \(x_0\).

### 1.3 Quantum chemistry methods

In this study, we consequently used the optimized geometry in the neutral grand state of tropone at the density fitted localized Möller–Plesset second order perturbation (DF-LMP2) theory \(^{S10}\) combined with the Def2-TZVP basis set. \(^{S11}\) The convergence of geometry optimization was confirmed by the normal mode analysis at the same level of theory.

For the Auger spectrum calculation and LVC-parameter evaluation, we used the SA-2h-CASSCF method including all two-hole states represented by 20 valence active MO (the [2h, 20o] RAS2 space) combined with ANO-RCC-VTZP basis set. 210 singlet and 190 triplet states were included, respectively. The SOCs were evaluated by the Breit-Pauli SOC operator with the mean-field approximation combined with the restricted active space state interaction (RAS-SI) method. \(^{S12,S13}\)

The \(\epsilon_{\nu\mu}(R_0)\) were calculated by the SA-2h-CASSCF/ANO-RCC-VTZP method with extending the RAS2 space to 20 valence MO and O(1s) MO, and by RAS-SI method. The photoabsorption cross sections for the C(1s) \(\rightarrow V^{-1}\) transitions of the doublet monocations at the Franck-Condon geometry were also calculated at the SA-1h-CASSCF/ANO-RCC-VTZP method which includes 20 valence MO and 7 C(1s) MO to the RAS2 space combined
with the RAS-SI method. We included all 27 monocationic states to this calculation. We did not use point group symmetry for the SA-1h/2h-CASSCF calculations above.

For the x-ray photoelectron spectra (XPS) of the lowest energy low spin state of \( \text{Tr}^{q+} \) \((q = 0, 1, 2)\) at the C(1s) and O(1s) edges including low-lying shape-up states. We used non-relativistic multi-state restricted active space second order perturbation theory (MS-RASPT2)\(^{14}\) with use of \( C_{2v} \) point group symmetry. We used the Supporo-2012-TZP basis set for C and O atoms, and the Supporo-2012-DZP basis set for H atoms.\(^{15}\) We created reference wave functions for initial and final states by single-state and state-average restricted active space self-consistent field (RASSCF) method, respectively. We included four \( \pi \), four \( \pi^* \), and one \( n \) orbitals, and the all \( 10 - q \) electrons in the RAS2 space \( \{[10 - q]e, 9o\} \) RAS2 space) as shown in Figure S1. We added all C(1s) or O(1s) orbitals to RAS1 space for C(1s) and O(1s) XPS calculation, respectively. We created one core-hole by the HEXS keyword and super-symmetry for final core-hole state calculations.\(^{16}\) The number of core-hole states included in the final state calculations were summarized in Table S1. The SA-RASSCF calculations and subsequent MS-RASPT2 calculations were performed for each irreducible representation group. We used the IPEA shift of 0.25 Hartree and imaginary shift of 0.20 Hartree to reduce intruder problems on MS-RASPT2 calculations. The relative intensity of the XPS was evaluated by using the norm of Dyson orbitals \textit{via} the RAS-SI method.

We used Molpro 2019.2 quantum chemistry package for the geometry optimization and normal mode analysis.\(^{10}\) The OpenMolcas 18.09 and 21.10 quantum chemistry packages\(^{16}\) were used for all SA-2h/1h-CASSCF and MS-RASPT2 calculations, respectively. Nonadiabatic reaction dynamics simulations were performed with the SHARC 2.1 program.\(^{17}\)
Figure S1: The natural orbitals included in the RAS2 space for the XPS calculations for Tr at the MS-RASPT2/Sapporo-2012 (C, O: TZP, H: DZP) level of theory. The occupation numbers of the natural orbitals are indicated in the parenthesis.

Table S1: The number of core-hole states in each irreducible representation for the XPS calculations on Tr_{q^+}(q = 0, 1, 2) at the C(1s) and O(1s) edges by means of the MS-RASPT2 level of theory.

| Absorption edge | q | Spin multiplicity | A_1 | B_1 | A_2 | B_2 | Total |
|-----------------|---|-------------------|-----|-----|-----|-----|-------|
| C(1s)           | 0 | Doublet           | 60  | 14  | 14  | 59  | 147   |
| C(1s)           | 1 | Singlet           | 22  | 68  | 65  | 20  | 175   |
| C(1s)           | 1 | Triplet           | 22  | 68  | 65  | 20  | 175   |
| C(1s)           | 2 | Doublet           | 57  | 17  | 18  | 57  | 149   |
| O(1s)           | 0 | Doublet           | 9   | 2   | 2   | 8   | 21    |
| O(1s)           | 1 | Singlet           | 2   | 11  | 8   | 4   | 25    |
| O(1s)           | 1 | Triplet           | 2   | 11  | 8   | 4   | 25    |
| O(1s)           | 2 | Doublet           | 9   | 2   | 3   | 7   | 21    |
2 Ionization kinetics including sequential double ionization process of organic molecule M

2.1 Photo-ions yields for the pump pulse irradiation in saturable regime

We first consider the TR-XAS signal including one- and two-photon sequential ionization processes by the pump pulse and one-photon ones by the probe pulse.

The pump pulse can trigger the core ionization and subsequent normal Auger decay for M at the X-edge ($X^{-1}$), valence ionization ($V^{-1}$) for $M^{q+}$ ($q = 0, 1, 2$), and core excitation from X-edge to valence holes and subsequent resonance Auger decay ($X \to V$) for $M^+$ and $M^{q+}$. The possible two ionization pathways by the pump pulse are

\[ M \xrightarrow{X^{-1}} M^{2+} \quad \text{or} \quad X \xrightarrow{\cdot \cdot \cdot \cdot \cdot \cdot \cdot} M^{3+}, \quad (12) \]

and

\[ M \xrightarrow{V^{-1}} M^+ \quad \text{or} \quad X \xrightarrow{\cdot \cdot \cdot \cdot \cdot \cdot \cdot} M^{2'+}. \quad (13) \]

The $X^{-1}$ process from M to $M^{2+}$ contributes to the signal and the others do to background noise. As the photo-ionization and absorption cross section are almost independent from $q$, the yield of $M^{q+}$ ($q = 0, 1, 2, 2'$) after pump irradiation can be written as functions of
$I_{pu}$ and $h\omega_{pu}$ as

$$[M](I_{pu}, h\omega_{pu}) = \exp(-\lambda_V(I_{pu}, h\omega_{pu}) - \lambda_X(I_{pu}, h\omega_{pu})), \quad (14)$$

$$[M^+](I_{pu}, h\omega_{pu}) = \frac{\sigma_V(h\omega_{pu})}{\sigma_X(h\omega_{pu}) - \sigma_{X\rightarrow V}(h\omega_{pu})} \times \left[ \exp(-\lambda_V(I_{pu}, h\omega_{pu}) - \lambda_X(I_{pu}, h\omega_{pu})) - \exp(-\lambda_V(I_{pu}, h\omega_{pu}) - \lambda_X(I_{pu}, h\omega_{pu})) \right], \quad (15)$$

$$[M^{2+}](I_{pu}, h\omega_{pu}) = \exp(-\lambda_V(I_{pu}, h\omega_{pu})) - \exp(-\lambda_V(I_{pu}, h\omega_{pu}) - \lambda_X(I_{pu}, h\omega_{pu})), \quad (16)$$

$$[M^{3+}](I_{pu}, h\omega_{pu}) = \frac{\sigma_V(h\omega_{pu})}{\sigma_V(h\omega_{pu}) + \sigma_X(h\omega_{pu})} \times \left[ 1 + \frac{1}{\sigma_X(h\omega_{pu}) - \sigma_{X\rightarrow V}(h\omega_{pu})} \times \{(\sigma_V(h\omega_{pu}) + \sigma_{X\rightarrow V}(h\omega_{pu})) \exp(-\lambda_V(I_{pu}, h\omega_{pu}) - \lambda_X(I_{pu}, h\omega_{pu})) - (\sigma_V(h\omega_{pu}) + \sigma_X(h\omega_{pu})) \exp(-\lambda_V(I_{pu}, h\omega_{pu}) - \lambda_X(I_{pu}, h\omega_{pu})) \} \right], \quad (17)$$

$$[M^{3+}](I_{pu}, h\omega_{pu}) = \frac{\sigma_X(h\omega_{pu})}{\sigma_V(h\omega_{pu}) + \sigma_X(h\omega_{pu})} \times \left[ 1 + \frac{1}{\sigma_X(h\omega_{pu})} \times \{\sigma_V(h\omega_{pu}) \exp(-\lambda_V(I_{pu}, h\omega_{pu}) - \lambda_X(I_{pu}, h\omega_{pu})) - (\sigma_V(h\omega_{pu}) + \sigma_X(h\omega_{pu})) \exp(-\lambda_V(I_{pu}, h\omega_{pu})) \} \right], \quad (18)$$

where $\sigma_V(h\omega_{pu})$, $\sigma_X(h\omega_{pu})$, and $\sigma_{X\rightarrow V}(h\omega_{pu})$ represent the photoionization cross sections of the $V^{-1}$, $X^{-1}$, and $X \rightarrow V$ ionization processes as functions of $h\omega_{pu}$, respectively. The $\lambda_{V/X}(I_{pu}, h\omega_{pu})$ means the number absorbed photons during the pump irradiation for the ionization processes $V^{-1}$ and $X^{-1}$, respectively. For the Gaussian pump pulse with a peak intensity of $I_{pu}$ and full width at half maximum (FWHM) of $s_{pu}$, $\lambda_{V/X}(I_{pu}, h\omega_{pu})$ is written...
\[ \lambda_{V/X}(I_{pu}, \hbar\omega_{pu}) = \sigma_{V/X}(\hbar\omega_{pu}) \frac{I_{pu}}{\hbar\omega_{pu}} \sqrt{\frac{\pi}{4 \ln 2}} s_{pu}. \] (19)

\[ \lambda_{tot}(I_{pu}, \hbar\omega_{pu}) \] can obviously be expressed as the sum of \( \lambda_V(I_{pu}, \hbar\omega_{pu}) \) and \( \lambda_X(I_{pu}, \hbar\omega_{pu}) \).

### 2.2 Yield of Auger electron generated by the probe pulse in linear regime

One photon absorption from the probe pulse at the Y-pre-edge of \( M^{2+} \) excites core electron at Y-edge to the valence hole. The core-excited \( M^{2+} \) which is rapidly ionized into \( M^{3+} \) via resonance Auger relaxation emits one fast Auger electron \( e_{Auger}^- \).

\[ M^{2+} \xrightarrow{Y \rightarrow V} M^{3+} + e_{Auger}^- \] (20)

The TR-XAS measurement using the Auger electron yield method selectivily counts the number of \( e_{Auger}^- \) as a function of \( \hbar\omega_{pr} \) and \( \Delta t \) by using electron spectrometers as described in Figure 4b. This scheme can eliminate the photoelectrons from core ionization and \( V^{-1} \) processes, and the Auger electrons from the \( X^{-1} \) process of \( M^{q+}(q = 0, 1, 2, 3) \) by the pump and probe pulses. The background sources can come from the resonance Auger electrons from the \( Y \rightarrow V \) excitation process of \( M^+ \) and \( M^{2+} \), and normal Auger electron from \( Y^{-1} \) core ionization of \( M \) and \( M^+ \). The contribution of \( M^{2+'} \) is negligibly small since \( \sigma_{V}(\hbar\omega_{pu}) \) is smaller than \( \sigma_X(\hbar\omega_{pu}) \) by a magnitude nearby the \( X \)-edges of \( M \) and \( M^+ \).

When the temporal overlap between the pump and probe pulse is negligibly small, the Auger electron yield \( N_e(q) \) originated from \( M^{q+}(q = 0, 1, 2, 2') \) can be written as,

\[ N_e(q, I_{pu}, \hbar\omega_{pu}, I_{pr}, \hbar\omega_{pr}) = \theta(q, \hbar\omega_{pr}) [M^{q+}](I_{pu}, \hbar\omega_{pu}) \frac{\sigma_{Y \rightarrow V/V}(q, \hbar\omega_{pr})}{\sigma_{tot}(q, \hbar\omega_{pr})} \left[ 1 - \exp(-\lambda_{tot}(q, I_{pr}, \hbar\omega_{pr})) \right]. \] (21)

Here, \( \theta(q, \hbar\omega_{pr}) \) describes the fraction of the bright states for \( M^{q+} \) (\( \theta(q = 0, \hbar\omega_{pr}) = 1 \) and \( 0 \leq \theta(q > 0, \hbar\omega_{pr}) \leq 1 \)). \( \sigma_{Y \rightarrow V/V}(q, \hbar\omega_{pr}) \) represents and photoionization cross sections for
the \( Y \to V \) excitation and subsequent resonance Auger decay, and the \( Y^{-1} \) core ionization and subsequent Auger decay in \( M^{q^+} \), respectively. \[ \sigma_{\text{tot}}(q, \hbar \omega_{\text{pr}}) \equiv \sigma_{Y \to V/V}(q, \hbar \omega_{\text{pr}}) + \sigma_{V}(\hbar \omega_{\text{pr}}) + \sigma_{X}(\hbar \omega_{\text{pr}}) \] is the total photoionization cross section for \( M^{q^+} \) as a function of \( \hbar \omega_{\text{pr}} \), and \( \lambda_{\text{tot}}(q, I_{\text{pr}}, \hbar \omega_{\text{pr}}) \) is the total number absorbed photon during the probe irradiation for all ionization processes. Because the \( Y \to V \) core excitation and the \( Y^{-1} \) core ionization processes are the dominant \( Y \)-edge related processes for \( \hbar \omega_{\text{pr}} \leq E_{Y}(q) \) and \( \hbar \omega_{\text{pr}} < E_{Y}(q) \), respectively in \( M^{q^+} \), the \( \sigma_{Y \to V/V}(q, \hbar \omega_{\text{pr}}) \) should be read as

\[ \sigma_{Y \to V/V}(q = 0, \hbar \omega_{\text{pr}}) = \sigma_{Y}(\hbar \omega_{\text{pr}}), \quad (22a) \]
\[ \sigma_{Y \to V/V}(q = 1, \hbar \omega_{\text{pr}} < E_{Y}(q = 1)) = \sigma_{Y \to V}(\hbar \omega_{\text{pr}}), \quad (22b) \]
\[ \sigma_{Y \to V/V}(q = 1, \hbar \omega_{\text{pr}} \geq E_{Y}(q = 1)) = \sigma_{Y}(\hbar \omega_{\text{pr}}), \quad (22c) \]
\[ \sigma_{Y \to V/V}(q = 2, 2', \hbar \omega_{\text{pr}}) = \sigma_{Y \to V}(\hbar \omega_{\text{pr}}). \quad (22d) \]

For the Gaussian probe pulse with a peak intensity of \( I_{\text{pr}} \) and FWHM of \( s_{\text{pr}} \), \( \lambda_{\text{tot}}(q, I_{\text{pr}}, \hbar \omega_{\text{pr}}) \) is written as

\[ \lambda_{\text{tot}}(q, I_{\text{pr}}, \hbar \omega_{\text{pr}}) = \sigma_{\text{tot}}(q, \hbar \omega_{\text{pr}}) \frac{I_{\text{pr}}}{\hbar \omega_{\text{pr}}} \sqrt{\frac{\pi}{4 \ln 2}} s_{\text{pr}}. \quad (23) \]

In the linear probe regime, eq (21) is finally simplified to

\[ N_{e}(q, I_{\text{pu}}, \hbar \omega_{\text{pu}}, I_{\text{pr}}, \hbar \omega_{\text{pr}}) \approx \theta(q, \hbar \omega_{\text{pu}})[M^{q^+}](I_{\text{pu}}, \hbar \omega_{\text{pu}}) \sigma_{Y \to V/V}(q, \hbar \omega_{\text{pr}}) \frac{I_{\text{pr}}}{\hbar \omega_{\text{pr}}} \sqrt{\frac{\pi}{4 \ln 2}} s_{\text{pr}}. \quad (24) \]

### 2.3 Upper limit of S/N ratio

We next discuss the S/N. We found that the S/N mainly depends on \( I_{\text{pu}} \) but not \( I_{\text{pr}} \) in the linear probe regime. Furthermore, the S/N have an upper bound mostly determined by \( \sigma_{X}(\hbar \omega_{\text{pu}})/\sigma_{V}(\hbar \omega_{\text{pu}}) \) in the saturable pump regime.

The S/N \( \eta \) can be defined as the ratio of \( N_{e}(q = 2, I_{\text{pu}}, \hbar \omega_{\text{pu}}, I_{\text{pr}}, \hbar \omega_{\text{pr}}) \) and the sum of
the electron yields originated from the other $Y$-edge Auger processes

$$\eta(I_{pu}, \hbar \omega_{pu}, I_{pr}, \hbar \omega_{pr}) \equiv \frac{N_e(q = 2, I_{pu}, \hbar \omega_{pu}, I_{pr}, \hbar \omega_{pr})}{\sum_{q=0,1,2'} N_e(q, I_{pu}, \hbar \omega_{pu}, I_{pr}, \hbar \omega_{pr})} \quad (25)$$

In the linear probe regime, eq. (25) can be rewritten by using eq. (24),

$$\eta(I_{pu}, \hbar \omega_{pu}, \hbar \omega_{pr}) \approx \frac{\theta(q = 2, \hbar \omega_{pr}) [M^{2+}](I_{pu}, \hbar \omega_{pu}) \sigma_{Y \rightarrow V/V}(q = 2, \hbar \omega_{pr})}{\sum_{q=0,1,2'} \theta(q, \hbar \omega_{pr}) [M^{q+}](I_{pu}, \hbar \omega_{pu}) \sigma_{Y \rightarrow V/V}(q, \hbar \omega_{pr})} \quad (26)$$

This indicates that the S/N does not depend on $I_{pr}$ but $[M^{2+}](I_{pu}, \hbar \omega_{pu})$.

When $I_{pu}$ is set to be an intensity $I_{max}$ which is large enough to saturate the ionization of M, $[M](I_{max}, \hbar \omega_{pu})$ is almost zero,

$$\eta(I_{max}, \hbar \omega_{pu}, \hbar \omega_{pr}) \approx \frac{[M^{2+}](I_{max}, \hbar \omega_{pu}) \sigma_{Y \rightarrow V/V}(q = 2, \hbar \omega_{pr})}{\sum_{q=1,2'} [M^{q+}](I_{max}, \hbar \omega_{pu}) \sigma_{Y \rightarrow V/V}(q, \hbar \omega_{pr})} \quad (27)$$

We can further simplify the eq. (27) since $\sigma_{Y \rightarrow V/V}(q, \hbar \omega_{pr})$ is almost constant except $Y \rightarrow V$ resonances,

$$\eta(I_{pu}, \hbar \omega_{pu}) \approx \frac{[M^{2+}](I_{pu}, \hbar \omega_{pu})}{\sum_{q=1,2'} [M^{q+}](I_{pu}, \hbar \omega_{pu})} \quad (28)$$

One can find a maximum value of S/N $\eta_{max}(I_{max}, \hbar \omega_{pu})$,

$$\eta_{max}(I_{max}, \hbar \omega_{pu}) \leq \frac{\sigma_X(\hbar \omega_{pu})}{\sigma_V(\hbar \omega_{pu})} \sim 10, \quad (29)$$

by using the facts

$$[M^{q+}](I_{pu}, \hbar \omega_{pu}) \leq \frac{\sigma_X(\hbar \omega_{pu})}{\sigma_V(\hbar \omega_{pu}) + \sigma_X(\hbar \omega_{pu})}[1 - \exp(-\lambda_V(I_{pu}, \hbar \omega_{pu}) - \lambda_X(I_{pu}, \hbar \omega_{pu})))] \quad (30)$$
and

\[
\sum_{q=1,2'} [M^q](I_{pu}, \hbar \omega_{pu}) = \frac{\sigma_V(\hbar \omega_{pu})}{\sigma_V(\hbar \omega_{pu}) + \sigma_X(\hbar \omega_{pu})} [1 - \exp (-\lambda_V(I_{pu}, \hbar \omega_{pu}) - \lambda_X(I_{pu}, \hbar \omega_{pu}))].
\]

(31)

2.4 Photoionization cross sections

Core and valance photoionization cross section \(\{\sigma_A|A = C(1s), O(1s), V\}\) of \(\text{Tr}^{q+} (q = 0, 1, 2)\) were calculated from the atomistic calculations by Yeh. et al.\textsuperscript{S26} We used the values of \(\hbar \omega = 300\) eV for the representative values of \(\{\sigma_A\}\) above the \(C(1s)\) edge and \(\hbar \omega = 542\) eV for \(O(1s)\) (pre-) edge. The photoabsorption cross sections of \(C(1s) \rightarrow V^{-1}\) of \(\text{Tr}^{q+}\) and \(O(1s) \rightarrow V^{-1}\) of \(\text{Tr}^{2+}\) were calculated by averaging over the photoabsorption cross sections of the corresponding optically allowed core-to-valence transitions whose oscillator strengths are larger than 0.01.\textsuperscript{S27,S28} We assumed that all core-to-valence excited states rapidly undergoes the resonance Auger process and \(\text{Tr}^{q+}\) is ionized to \(\text{Tr}^{(q+1)+}\). We also given that these cross sections do not depend on \(q.\textsuperscript{S18}\)

Table S2: The photo-ionization cross sections \(\{\sigma_A(\hbar \omega_{pu/pr})\}\) used in the calculation in \(10^{-18}\) cm\(^2\).

| \(A\) | \(\sigma_A(\hbar \omega_{pu})\) | \(\sigma_A(\hbar \omega_{pr})\) |
|------|----------------|----------------|
| \(V\) | 0.45\textsuperscript{a}\ | 0.18\textsuperscript{a}\ |
| \(C(1s)\) | 6.01\textsuperscript{a}\ | 1.55\textsuperscript{a}\ |
| \(C(1s) \rightarrow V\) | 1.69\textsuperscript{b}\ | — |
| \(O(1s)\) | — | 0.51\textsuperscript{a}\ |
| \(O(1s) \rightarrow V\) | — | 2.35\textsuperscript{c}\ |

\(\textsuperscript{a}\)Yeh et al.;\textsuperscript{S26}\n
\(\textsuperscript{b}\)SA-1h-CASSCF/ANO-RCC-VTZP//DF-LMP2/Def2-TZVP;\n
\(\textsuperscript{c}\)SA-2h-CASSCF/ANO-RCC-VTZP//DF-LMP2/Def2-TZVP.
3  X-ray photoelectron spectra of $\text{Tr}^{q+}(q = 0, 1, 2)$ at the $\text{O}(1s)$ edge

Figure S2: The calculated XPS spectra of $\text{Tr}^{q+}(q = 0, 1, 2)$ at the $\text{O}(1s)$ edge. Results at the MS-RASPT2/Sapporo-2012 (C,O: TZP, H: DZP)//DF-LMP2/Def2-TZVP level of theory. The calculated spectra were broaden by a Gaussian function of FWHM = 1.0 eV.
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