Population Trap in X-ray-induced Ultrafast Nonadiabatic Dynamics of Tropone Probed at the O(1s) pre-edge

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Nonadiabatic transition (NAT) drives a variety of x-ray-induced photochemistry and photophysics used in nature and various fields. To clarify the x-ray-induced NAT dynamics, we performed nonadiabatic molecular dynamics simulations on electronically excited tropone (Tr) dications created by the carbon $KLL$ normal Auger decay. The $Tr^{2+}$ undergoes the NAT cascade via $10-10^{2}$ states with time constants of $200-400$ fs. We observed population traps in the highly excited states in $100$ fs during the NAT cascade. The fingerprint of this population trap can be extracted from $C(1s)$ edge pump $O(1s)$ pre-edge probe femtosecond transient x-ray absorption spectra measured by the $O(1s)$ Auger electron yield method (TR-AEYS) using intense narrow band femtosecond x-ray free electron laser pulses. Our coupled ionization rate equation model demonstrates that selective and saturable $C(1s)$ core-ionization of $Tr$ realizes background-free measurement. These results indicate that the importance of NAT in x-ray photochemistry and photophysics in large molecules. The real-time tracking of the NAT dynamics using TR-AEYS shall be a powerful approach for deeper insight.

1 Introduction

X-ray-induced photochemistry and photophysics are widely involved in nature and various fields. In biology, x-ray radiation triggers strand break of DNA double helix, resulting in cancer. In nanomedicine, x-ray deposited in nano-structures can be used for cancer treatments. Material science, organic scintillators convert x-ray radiation into low-energy light emission.

Such x-ray-induced processes are initiated by creating multiply charged cations populated in more than $10^{2}$ or $10^{3}$ electronically excited dicaticonic states via core ionization and subsequent Auger decay. The excited dications undergo nonadiabatic transitions (NATs) to the lower-lying states via many intermediate states. The NATs after the Auger decay promote the ultrafast processes in x-ray photochemistry and photo-physics in small molecular systems such as sub $10$ fs proton migration between the water dimer dication ($H_{2}O_{2}^{2+}$) in liquid water, femtosecond C–C bond breaking in acetylene dication ($C_{2}H_{2}^{2+}$), and femtosecond vibronic charge migration in glycine dication ($NH_{2}CH_{2}COOH^{2+}$). Understanding the NAT dynamics after the Auger decay is key to clarifying the x-ray response of various molecular systems both in gas and condensed phases.

However, there is a debate on the contribution of the NATs in the electronically excited dications in the gas phase created by x-ray irradiation for larger molecules. Inhaster et al. performed an x-ray photofragmentation experiment at the $C(1s)$ edge of ethyltrifluoroacetate ($CF_{3}COOC_{2}H_{5}$) using synchrotron-based photoelectron–photoion–photoion coincidence measurements and charge distribution analysis of the electronically excited $CF_{3}COOC_{2}H_{5}^{2+}$ created by the carbon $KLL$ normal Auger decay using ab-initio electronic structure calculations. They suggested that the fragmentation pattern is mostly determined by the initial hole distribution of dications just after the Auger decay and the contribution of NAT is negligibly small. Kukk et al. conducted the static and time-resolved Auger electron photo-ion coincidence measurements using synchrotron and soft x-ray free electron laser (XFEL) facilities, respectively, and tight-binding reaction dynamics simulations, which are dedicated to the fragmentation dynamics of thiophene dication ($C_{4}H_{4}S^{2+}$) created by the S(2p) inner-shell ionization and subsequent Auger decay. They argued that the NAT from highly excited dicationic states to lower ones converts electronic energy to vibrational energy in the timescale $10^{2}$ fs and that the fragmentation occurs in the lower-lying states. This NAT could make the fragmentation statistical.

To obtain a complete picture of the x-ray-induced NATs of large polyatomic molecules and deeper insights on the question above, ultrafast transient x-ray absorption spectra (TR-XAS) measurement using x-ray free electron lasers (XFELs) or high-harmonic generation light sources is a prominent approach since they have realized the real-time tracking of the UV/Vis and intense IR induced nuclear and valence electron dynamics with femto- to atto-second temporal resolutions in any form of mat-

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† Electronic Supplementary Information (ESI) available: The details of computational methods, supplemental discussions, and parameters for DVC potentials. See DOI: 00.0000/00000000.
ter 42–58. Namely, TR-XAS measured by the Auger electron yield method (TR-AEYS), which uses the fact that the Auger electron yield at the probe process is proportional to the photoabsorption cross section, is becoming a useful tool with XFEL to investigate the x-ray-induced dynamics. 21,29,59–63.

To interpret the measured TR-XAS and TR-AEYS, the detailed theoretical investigations of the NAT dynamics and its associated TR-XAS/TR-AEYS are essential. 21,27,37. The combination of the ab-initio simulation of the Auger spectrum, which determines the initial states of NATs and nonadiabatic molecular dynamics method including the all two-hole dicaticionic states 17,20 is a straight forward approach to simulate the NAT dynamics and associated associated TR-XAS/TR-AEYS. This approach has successfully applied to small molecules such as acetylene 40 and glycine 17 but not yet to the larger ones since the computational costs exponentially increase as a function of molecular size.

In this study, we theoretically investigated the NAT dynamics of an aromatic molecule tropone (C\(_7\)H\(_6\)O, Tr) 54,65 before fragmentation triggered by the x-ray irradiation at the C(1s) edge in the gas phase. We simulated the associated femtosecond C(1s) edge pump O(1s) pre-edge probe femtosecond TR-AEYS. Tr is a good showcase of the x-ray-induced NAT dynamics since it contains a C=O group in its aromatic skeleton like the nucleobases and the other aromatic molecules used in organic x-ray scintillators 11,13–16. The pre-edge absorption bands originated from the electronic transition from the 1s core orbitals to valence holes are sensitive to the electronic structure of cationic systems 27,29,37. The final states of the carbon KLL Auger decay were determined by the two-hole population analysis technique, which calculates the relative intensity of the normal Auger spectra as a function of the electron population on the core-hole atoms 22,66. To simulate the subsequent NAT dynamics, we used a computationally efficient full-dimensional surface hopping nonadiabatic reaction dynamics technique on the pre-computed linear vibronic coupling model potential energy surface (IVC-MD) 67–69. We explicitly considered all valence two-hole states of Tr\(^{2+}\) (210 singlet and 190 triplet states) via configuration interaction theory including all valence two-hole electron configurations. We also investigated a possible measurement scheme for the TR-XAS measurement via coupled ionization rate equation model 70.

We found the population traps in highly excited dicaticionic states in 100 fs as experimentally observed in C\(_4\)H\(_4\)S\(^{2+}\) 24 during the cascade of NATs (NATs cascade) passing through 10–10\(^2\) two-hole states. The time constants of NATs extracted from the calculated TR-AEYS clearly reflects the population trap. Such x-ray induce NAT dynamics shall be extracted from the TR-AEYS. The TR-AEYS can be measured ideally in a background-free mode with an intense narrow band femtosecond XFEL light source.

## 2 Computational methods

### 2.1 Population dynamics of electronically excited Tr\(^{2+}\)

We consider the population dynamics on the N dicaticionic states \(\{|\Psi_v\rangle\}, v = 1,2,\ldots,N\) of organic molecules created by the one-photon C(1s) photoemission with an x-ray pulse and the subsequent normal Auger decay. The population of \(\{|\Psi_v\rangle\}\) in incoherent limit \(P(t) = [P_1(t), P_2(t), \ldots, P_N(t)]\) is written as 68,71,

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

where \(g(t, s_{pu})\) is the envelope function of the Gaussian pump pulse with the full width half maximum (FWHM) of \(s_{pu}\), \(\Theta(t)\) represents convolution, \(\Theta(t)\) is the Heaviside step function, \(\tau_{Auger}\) is the overall Auger rate constant for the parent molecule, and \(\tilde{P}(t) = [\tilde{P}_1(t), \tilde{P}_2(t), \ldots, \tilde{P}_N(t)]\) is the population of \(\{|\Psi_v\rangle\}\) during the NAT dynamics in sudden ionization limit. The \(\tilde{P}(t)\) can be directly evaluated via nonadiabatic reaction dynamics simulations by setting the initial populations of dicaticionic states of the neutral molecule \(\{\tilde{P}_v(t = 0)\}\) to be proportional to the relative Auger intensity \(I_v\) \(\tilde{P}_v(t = 0) = I_v / \sum_v I_v\) 17.

For Tr\(^{2+}\), we considered all \(\{|\Psi_v\rangle\}\) \((N = 400: 210\) singlet and 190 triplet states\) that has two holes in the 20 valence MOs generated by the carbon KLL normal Auger decay. The relative Auger intensity was evaluated by the two-hole population analysis technique 22,66. We calculated the relative Auger transition amplitude from the C(1s) core-hole MOs to valence two-hole electron configuration as a function of the electron population on the core-hole atoms according to Mitani et al 66. The relative Auger intensity were evaluated by including the configuration interactions among the two-hole electron configurations and orbital relaxation effect 22. The detailed formation can be found in Electronic Supplementary Information (ESI). We adopted \(\tau_{Auger} = 6.1\) fs according to an experimental value on benzene 72 and set \(s_{pu} = 10\) fs.

To evaluate the time evolution of \(P(t)\), we performed full-dimensional surface hopping nonadiabatic reaction dynamics simulations using an Tully’s fewest switching algorithm 69,73–75 combined with the linear-vibronic coupling (IVC) model Hamiltonian 67–69 (IVC-MD). We included both internal conversion and intersystem crossing. The IVC-MD initially constructs full dimensional harmonic oscillator potential energy surfaces for all electronic states of interest including vibronic and spin-orbit couplings 67. Surface hopping simulations on the pre-computed IVC potential energy surfaces allow us to treat larger molecules with reasonable computational cost and statics 58,63 than conventional on-the-fly nonadiabatic molecular dynamics methods 17,20. Our approach cannot treat dissociation. Thus, each trajectory was stopped if it reaches the electronic states where any bond-length elongates to the threshold bond-length \(R_{th} = 3.4\) Å, which corresponds to the double of the Van der Waals radius of carbon atom. After satifying the stop criteria, we thereafter regarded the Tr\(^{2+}\) as “vibrationally hot” molecule and excluded it from the statistics.

### 2.2 TR-AEYS

In this study, we focus on the O(1s)→valence hole transitions of Tr\(^{2+}\) at O(1s) pre-edge. Such "core to valence hole" transition is sensitive to the energy level of cationic states and the NAT dynamics among them 27,37. Tr\(^{2+}\) ejects an Auger electron via the resonant Auger decay after the core excitation. We then measure the yield of the Auger electron \(N_{Auger}(q = 2)\) as a function of probe photon energy \(\hbar \omega_{probe}\) and pump-probe delay time \(\Delta\). We neglect the O(1s)→virtual orbital transitions, which will appear in the O(1s) near-edge region. These transitions surely reflect the elec-
troncic structure of cations but their interpretation is difficult due to the spectral overlap among many transitions. Furthermore, the simultaneous calculation of O(1s)→valence hole and O(1s)→virtual orbitals transitions for Tr$^{2+}$ in various electronically excited states is computationally very expensive.

The C(1s) edge pump O(1s) pre-edge probe femtosecond TR-AEYS of Tr$^{2+}$ $N_0(q = 2, \hbar \omega_{pr}, \Delta \tau)$ can be calculated as a function of probe photon energy $\hbar \omega_{pr}$ and peak intensity of probe pulse $I_{pr}$ and pump-probe delay time $\Delta \tau$ defined by the time interval between the intensity peaks of the pump and probe pulse,

$$N_0(q, \hbar \omega_{pr}, \Delta \tau) \propto \sum_{\nu \mu} g_{\nu \mu} (\hbar \omega_{pr}, \Delta \tau) \left( 0 \nu_{\mu} \sigma \nu_{\mu} (R(\Delta \tau)) - \Delta E_{\nu_{\mu}} (R(\Delta \tau)), \Delta \tau \right) \frac{I_{pr}}{\hbar \omega_{pr}}$$

(2)

where $\rho_{\nu_{\mu}} (R(\Delta \tau))$ is the molecular structure of the dication at $\Delta \tau$, $\sigma_{\nu_{\mu}} (R(\Delta \tau))$ and $\Delta E_{\nu_{\mu}} (R(\Delta \tau), \Delta \tau)$ is the photoabsorption cross section and transition energy between the valence two-hole state $|\Psi_{\nu}(R(\Delta \tau))\rangle$ and O(1s) core-excited state $|\Psi_{\mu}(R(\Delta \tau))\rangle$, respectively. The $\delta (\hbar \omega_{pr} - \Delta E_{\nu_{\mu}} (R(\Delta \tau), \Delta \tau))$ is the two dimensional delta function located at $\hbar \omega_{pr} = \Delta E_{\nu_{\mu}} (R(\Delta \mu))$ and $\Delta \tau$, and $g_{\nu \mu} (\hbar \omega_{pr}, \Delta \tau)$ is the Gaussian instrumental function which determines the energy and temporal resolutions of the TR-AEYS. To reduce the computational costs of the TR-AEYS calculation, we evaluated the $|\Psi_{\nu}(R(\Delta \tau))\rangle$ and $\Delta E_{\nu_{\mu}} (R(\Delta \tau), \Delta \tau)$ in a diabatic representation characterized by the electron configurations at the Franck-Condon geometry $R_0$. We then applied the Condon approximation $\sigma_{\nu_{\mu}} (R(\Delta \tau)) = \sigma_{\nu_{\mu}} (R_0)$.

2.3 Quantum chemistry calculations

The relative Auger intensity, the potential energy, vibronic and spin-orbit couplings among $|\Psi_{\nu}(R(\Delta \tau))\rangle$ appeared in the IVC model Hamiltonian were evaluated by the state-averaged complete active space multi-configurational self-consistent field (SA-CASSCF) theory combined with the ANO-RCC-VTZP basis set. All twenty valence MOs and two holes (= 38 electrons) were included in the RAS2 active space (the [2h,20o] RAS2 space). All two-hole states resulting from the RAS2 space 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) combined with the Def2-TZVP basis set as implemented in the MOLPRO 2019.2 quantum chemistry package. The $\sigma_{\nu_{\mu}} (R_0)$ were calculated by the SA-2h-CASSCF/ANO-RCC-VTZP method by extending RAS2 space to 20 valence MOs and O(1s) MO, and by the restricted active space state interaction (RAS-SI) method. To optimize the $\hbar \omega_{	ext{ps}}$ and $\hbar \omega_{\text{pr}}$, we calculated the x-ray photoelectron spectra (XPS) of the lowest energy low spin states of Tr$^{2+}$ (q = 0, 1, 2) at the C(1s) and O(1s) edges with low-laying shake-up states. We used multi-state restricted active space second-order perturbation theory (MS-RASPT2) combined with the Supporo-2012-TZP basis set for C and O atoms, and with the Supporo-2012-DZP basis set for H atoms. The relative intensity of the XPS was evaluated using the norm of Dyson orbitals. The OpenMolcas 18.09 and 21.10 quantum chemistry packages were used for all SA-CASSCF and MS-RASPT2 calculations, respectively. We used SHARC 2.1 program for the IVC-MD. Further details were described in ESI.

3 Results and discussions

3.1 Structural and population dynamics during the NATs

Let us look at the calculated NAT 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 $T_n$ denote the singlet and triplet adiabatic states at a given geometry $R(t)$ at time $t$, respectively.

3.1.1 Carbon KLL Auger spectrum

The calculated Carbon KLL normal Auger spectrum as a function of two-electron binding energy $E_v$ is displayed in Figure 1a. The integrated intensity ratio of singlet and triplet states is singlet:triplet = 81:19 and Auger decay to singlet dicaticionic states is dominant. For the convenience of the later discussions, we divide the spectrum into three bands based on the peaks in the Auger spectrum and the character of each peaks. Band I: $E_v < 30$ eV, Band II: $E_v = 30-40$ eV, and Band III: $E_v \geq 40$ eV. According to the occupation numbers of the natural orbitals $\{\Lambda_{\text{occ}} \}$ calculated at the [2h,20o]-SA-CASSCF/ANO-RCC-VTZP/DF-LMP2/Def2-TZVP level of theory, band I is predominantly generated by the low-lying two-hole dicaticionic states whose holes are located in the MOs originated form the 2p atomic orbitals ($2p^-2$ states). The band II is the mixture of the high-lying $2p^-2$ and low-lying $2p^-12s^-1$ states. For band III, the strongest peak in $E_v = 40 - 50$ eV originates from the high-lying $2p^-12s^-1$ and low-lying $2s^-2$ states. The peaks above $E_v = 60$ eV are predominantly created by the high-lying $2s^-2$ states.

The most intense transition at band II is assigned to the $S_{38}$ state at $E_v = 32.95$ eV, whose normalized intensity is $I_v = 0.026$, and that of the III is assigned to the $S_{1111}$ state with $E_v = 43.95$ eV and $I_v = 0.019$, respectively. The major electronic configurations of both $S_38$ and $S_{1111}$ states are $\pi^-12s^-2$ according to the $\{\Lambda_{\text{occ}} \}$ as shown in Figures 1b and 1c, respectively.

3.1.2 Population trap during the nonadiabatic transitions

The NAT cascade proceeds mostly via internal conversion. The intersystem crossing is observed in only 16.5 % of trajectories. We observed population trap in bands III in 100-200 fs. Figure 2a represents a representative trajectory of the NAT cascade. This trajectory started from the $S_{1111}$ state in band III relaxes into $S_4$ in band I within 461 fs. Tr$^{2+}$ is trapped in band III until $t = 240$ fs since energy intervals of the dicaticionic 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 $E_v$ was 0.15 eV in band III. A large in-plane ring distortion observed at $t = 240$ fs (Figure 2a) drives the internal conversion between $\sigma$ and $\pi$ orbitals, respectively. Tr$^{2+}$ slides down to the $S_4$ 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 $2p^2$ electron configurations ($I^*$) 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 $1\pi\pi \rightarrow 1\pi\sigma$ internal conversion in UV excited nucleobases and their derivatives. 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 population trap. Figure 3a represents the $P(t, E_\nu)$ for $Tr^{2+}$ calculated by eq. 1, which is broadened 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 carbon $KLL$ Auger decay in 20 fs. The population of the most prominent band III ($E_\nu = 44$ eV) is almost constant until $t = 100$ fs. The electronically excited $Tr^{2+}$ in band III relaxed into band II within 200-400 fs. This refills the population in band II whose initial population relaxes to band I within 140 fs and makes the population of band II quasi-stational until $t = 200$ fs. $Tr^{2+}$ in band II further undergoes NAT to band I in 200 fs and completed the NAT cascade into the vibrationally hot lower-lying dicaticionic states in band I (band $I^*$) in 100 fs.

To quantify the population dynamics associated with the population trap, we calculated the time-dependent diabatic population of $Tr^{2+}$ in sudden ionization limit in each bands $\rho_x(t) \equiv \sum_{E_\nu \chi} P_x(t)$ ($\chi = II, I, III$) from the LVC-MD results appearing as solid lines in Figure 3c. To extract the time constants $\{\tau\}$ for the NAT cascades which has sequential nature as discussed above, we constructed a kinetic model including the sequential NAT process of $III \rightarrow II \rightarrow I$, $I \rightarrow II \rightarrow III$. The coupled rate equations for this kinetic model can be written as

$$\frac{d}{dt} \mathbf{P}(t) = \mathbf{k} \mathbf{P}(t),$$

where $\mathbf{P}(t) \equiv [\rho_{III}(t), \rho_{II}(t), \rho_{I}(t)]^T$. The rate constant matrix $\mathbf{k}$ contains three time constants,

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

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

Fitted population transients are presented in Figure 3c. 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 errors. The resultant time constant of the NAT from band III to II $\tau_{III-II}$ was 362 fs, which is longer than that of band III to II ($\tau_{III-II} = 211$ fs) due to the 100 fs population trap originating from the internal conversion indicated in Figure 2b. After the NAT from II to I, the exited $Tr^{2+}$ in band I
rapidly relaxes into \( \text{I}^* \) (\( \tau_{\text{rel}} = 41 \text{ fs} \)).

### 3.2 Fingerprints of the population trap in the TR-AEYS

The time constants for the NAT dynamics can be extracted from TR-AEYS. Figure 3b shows the pre-edge peaks of C(1s) edge pump O(1s) pre-edge probe TR-AEYS 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 represent the results from the LVC-MD, and dotted line represents fitting ones. We excluded vibrationally hot Tr\( ^2\) and the integrated population becomes smaller than unity for panels (a) and (c).

![Fig. 3 Population dynamics for the NAT cascade of Tr\( ^2\)+ except vibrationally hot ones calculated by LVC-MD. (a) The Diabatic population as a function of two-electron binding energy \( E_s \) 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-AEYS 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.](image)

### Table 1

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

 Contributions from the transitions to bands III, I, and II, respectively. The intensity of the peak at \( \hbar \omega_{\text{pr}} = 548 \text{ eV} \) is almost constant until \( \Delta t = 100 \text{ fs} \) as observed in the population of the most prominent peak of band III (\( E_s = 44 \text{ eV} \), Figure 3a) reflecting the population trap. One electron picture conserves in the intense transitions from bands I and II. On the other hand, the weak transitions from band III have multi-electron nature and we observed not only the "core to valence hole" transitions but also associated shake-up and shake-off processes among the valence orbitals: another electron in valence MOs moves to the remaining vacancy which is not filled by the excited electron from the O(1s) orbital. This makes the transition energy of the band III transition higher than those of bands I and II.

To extract the \( \{ \tau \} \) from the TR-AEYS of the O(1s)-pre-edge region (\( \hbar \omega_{\text{pr}} \leq 550 \text{ eV} \)) of Tr\( ^2\)+, we first calculated the integrated absorption intensities originated from the transition from bands I-III in the sudden ionization and impulsive excitation limit defined as \( \tilde{N}_\text{c} (\Delta \nu) \equiv \sum_{E_s, \chi, \mu} \sigma_{\chi \mu} (\mathbf{R}(\Delta \nu)) \tilde{P}_\chi (\Delta \nu) / \sum_{E_s, \chi, \mu} \sigma_{\chi \mu} (\mathbf{R}(\Delta \nu)) \tilde{P}_\chi (\Delta \nu) \) from the LVC-MD results. We omit \( q = 2 \) for clarity in this subsection. The resultant \( \tilde{N}_\text{c} (\Delta \nu) \) is shown in Figure 3d as the solid lines. The \( \{ \tau \} \) were extracted by using the same sequential NAT kinetic model as the analysis of \( P_\chi (\Delta \nu) \). The calculated integrated absorption intensities \( \tilde{N}_\text{c} (\Delta \nu) \equiv [\tilde{N}_\text{c} (\Delta \nu), \tilde{N}_\text{c} (\Delta \nu), \tilde{N}_\text{c} (\Delta \nu)]^\top \) were fitted by the analytical solution of the coupled differential equation \( d\tilde{N}_\text{c} (\Delta \nu) / d\Delta \nu = k\tilde{N}_\text{c} (\Delta \nu) \). The initial value \( \tilde{N}_\text{c} (t = 0) \) was fixed to the LVC-MD values.

The fitting results on the TR-AEYS 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 \( \Delta \tilde{N}_\text{c} (\hbar \omega_{\text{pr}}, \Delta \nu) \) agree with the reference \( \{ \tau \} \) obtained from \( P_\chi (\Delta \nu) \): (i) the rate limiting step is the NAT from band III to II due to the population trap; (ii) the intraband NAT from band I to I* has the timescales of sub 100 fs. TR-AEYS emphasizes the decay profiles between specific diaticonic states which have optically allowed core-to-valence transitions, especially if one evaluated the averaged time constants using the integrated intensity over each band as in this study. This slightly deviates the TR-AEYS based \( \{ \tau \} \) to the population-based ones.

### 3.3 Proposed experimental setup

Let us discuss how to efficiently measure the TR-AEYS using coupled ionization rate equation model\(^70\). We found that a narrow band pump pulse whose photon energy \( \hbar \omega_{\text{pr}} \) is set to be 292.3 eV to ionize only the C(1s) orbitals of the neutral Tr and whose peak intensity \( I_{\text{pr}} \) should be larger than the value of \( 10^{15} \text{ W/cm}^2 \) to saturate the ionization of the neutral. For the probe pulse, its photon energy \( \hbar \omega_{\text{pr}} \) should be set to the O(1s) pre-edge region of Tr\( ^2\)+ and \( I_{\text{pr}} \) should be in the linear absorption regime (\( \sim 10^{14} \text{ W/cm}^2 \)). Here, we first explain the analytical formula for the ion yields \( \{ \text{Tr}^{\text{I}+} \} (q = 0, 1, 2, 3) \) and the Auger electron yield \( N_\text{c} \) in the pump-probe processes. We included one- and two-photon sequential ionization processes by the pump pulse and one-photon ones by the probe pulse. Then, we discuss the optimal laser parameters for the proposed experiment.

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The pump pulse can trigger the carbon KLL normal Auger decay for Tr (C), valence ionization (V−1) for Trq+(q = 0, 1, 2), and core excitation from C(1s) edge to valence holes and subsequent resonant Auger decay (C(1s) → V) for Tr+. The possible two ionization pathways by the pump pulse are Tr C → Tr2+ V− or C(1s) → V → Tr3+ and Tr C → V− or C(1s) → Tr2+ , where Tr2+ is theication of Tr which has two holes in valence MOs created by the C process as discussed above and Tr2+ represents those created by the two-photon sequential double ionization process. The C process from Tr to Tr2+ contributes to the signal and the others do to the background. As the photo-ionization and absorption cross sections are almost independent of q21,29,59–63, the yield of Tr2+ after the Gaussian pump pulse irradiation whose peak intensity is Ip and full width at half maximum (FWHM) is spu can be written as functions of Ip and hωpu as

\[
[\text{Tr}^2\text{+}](I_{pu}, h\omega_{pu}) = [\exp(-\lambda_{V}(I_{pu}, h\omega_{pu})) - \exp(-\lambda_{C}(I_{pu}, h\omega_{pu}))],
\]

\[
\lambda_{pu}(I_{pu}, h\omega_{pu}) = \sigma_{pu}(h\omega_{pu}) I_{pu} h\omega_{pu} \sqrt{\frac{e}{4\ln^2 spu}}.
\]

where \(\sigma_{pu}(h\omega_{pu})\) represents the photoionization cross section of the ionization processes of \(A_{pu} = V−1, C,C(1s) \rightarrow V\) as functions of \(h\omega_{pu}\), respectively. \(\lambda_{V}(I_{pu}, h\omega_{pu})\) and \(\lambda_{C}(I_{pu}, h\omega_{pu})\) mean the number of absorbed photons during the pump irradiation for the ionization processes V−1 and C, respectively. The analytical expressions for \([\text{Tr}^2\text{+}](I_{pu}, h\omega_{pu})\) (q = 0, 1, 2) can be found in ESI.

One photon absorption from the probe pulse at the O(1s)-edge of Tr2+ excites core electron at O(1s)-edge to the valence hole. The core-excited Tr2+ which is rapidly ionized into Tr3+ via resonant Auger relaxation emits one fast Auger electron \(e_{\text{Auger}}\).

\[\text{Tr}^2\text{+} \rightarrow \text{O(1s)−V} \rightarrow \text{Tr}^3\text{+} + e_{\text{Auger}}\].

The TR-AEYS measurement selectively counts up the number of \(e_{\text{Auger}}\) as a function of \(h\omega_{pr}\) and \(\Delta\) by using electron spectrometers.11,29,59–63 This scheme can eliminate photoelectrons from core-ionization processes and \(V^{-1}\) processes, and Auger electrons from the C process of Tr2+ (q = 0 − 3) by the pump and probe pulses. The major background sources can come from the resonant Auger electrons from the O(1s) → V excitation process of Tr+ and Tr2+, and normal Auger electron from O(1s)−1 core ionization of Tr, which can overlap with the signal from Tr2+.

When the temporal overlap between the pump and probe pulse is negligibly small, the Auger electron yield \(N_{e}\) originated from Tr2+ (q = 0, 1, 2) can be written as,

\[
N_{e}(q, I_{pu}, h\omega_{pu}, I_{pr}, h\omega_{pr}) = \theta(q, h\omega_{pr})[\text{Tr}^{2+}](I_{pu}, h\omega_{pu}) \frac{\sigma_{pu}(q, h\omega_{pr})}{\sigma_{tot}(q, h\omega_{pr})} \times [1 - \exp(-\lambda_{tot}(q, I_{pr}, h\omega_{pr}))].
\]

Here, \(\theta(q, h\omega_{pr})\) describes the fraction of bright states for Tr2+ at \(h\omega_{pr}\) (\(\theta(q = 0, h\omega_{pr}) = 1\) and \(|0 < q < h\omega_{pr} \leq 1\)). \(\sigma_{pu}(q, h\omega_{pr})\) represents the mean photoabsorption cross section for the O(1s) → V excitation and subsequent resonant Auger decay for \(q = 1, 2, 3\) and the O(1s)−1 core ionization and subsequent oxygen KLL Auger decay (O) for \(q = 0\), respectively. \(\sigma_{tot}(q, h\omega_{pr}) \equiv \sigma_{pu}(q, h\omega_{pr}) + \sigma_{V}(h\omega_{pr}) + \sigma_{C}(h\omega_{pr})\) is the total photoionization cross section for Tr2+ as a function of \(h\omega_{pr}\), and \(\lambda_{tot}(q, I_{pr}, h\omega_{pr}) = \sigma_{tot}(q, h\omega_{pr})(I_{pr}/h\omega_{pr})(\pi/4n^2)^{1/2}I_{pu}\). In the linear probe regime, eq (7) is finally simplified to

\[
N_{e}(q, I_{pu}, h\omega_{pu}, I_{pr}, h\omega_{pr}) \approx \theta(q, h\omega_{pr})[\text{Tr}^{2+}](I_{pu}, h\omega_{pu}) \times \frac{\sigma_{pu}(q, h\omega_{pr}) I_{pr} h\omega_{pr}}{\sigma_{tot}(q, h\omega_{pr})} \sqrt{\frac{e}{4\ln^2 spu}}.
\]

The S/B \(\eta\) can be defined as the ratio of \(N_{e}(q = 2, I_{pu}, h\omega_{pu}, I_{pr}, h\omega_{pr})\) and the sum of the electron yields originated from the other O(1s)-edge (resonant) Auger processes,

\[
\eta(I_{pu}, h\omega_{pu}, I_{pr}, h\omega_{pr}) = \frac{N_{e}(q = 2, I_{pu}, h\omega_{pu}, I_{pr}, h\omega_{pr})}{\sum_{q=0.1}^{1.6} N_{e}(q, I_{pu}, h\omega_{pu}, I_{pr}, h\omega_{pr})}.
\]

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 \(h\omega_{pr}\). To optimize \(h\omega_{pu}\), we calculated C(1s) XPS spectra for Tr2+ (q = 0, 1, 2) at the MS-RASPT2 level of theory are shown in Figures 4 and S2, respectively. Both C(1s) and O(1s) edges blue-shift by 6–7 eV for each valence ionization of \(q → q+1\). We have chosen \(h\omega_{pu} = 292.3 eV\) to avoid sequential C(1s) core ionization processes in Tr2+ and Tr2+. We set \(h\omega_{pr} = 542.0 eV\) since the strongest O(1s)−V absorption band of Tr2+ appears here as shown in Figure 3b. The charge number \(q\) is set to 2. We defined a merit function \(\Upsilon(I_{pu}, I_{pr}) \equiv N_{e}(I_{pu}, h\omega_{pr})\eta(I_{pu}, I_{pr})\) 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 are summarized in Table S2 in ESI.

We found that \(\Upsilon(I_{pu}, I_{pr})\) becomes maximized to \(3.5 \times 10^{-2}\) at \(I_{pu} = 80\mu W/cm^2\) and \(I_{pr} = 1.0 \times 10^{14} W/cm^2\) as shown in Figure 5a. This optimized \(I_{pu}\) is a bit larger than to the saturable intensity \(I_{max} = 2.0 \times 10^{15} W/cm^2\) which maximizes \([\text{Tr}^{2+}](I_{max})\) to 0.76 (Figure 5b) and \(N_{e}(q = 2, I_{pu}, h\omega_{pu})\) to \(N_{max} = 4.2 \times 10^{-3}\) to minimize the background from Tr2+. At the optimized \(I_{opt,pu}\) and \(I_{opt,pr}\), \(\eta(I_{opt,pu}, I_{opt,pr})\) reaches 9.3 (Figure 5c), which is not sensitive to the value of \(I_{pu}\) in the saturable regime \((q \geq 8.0\) for \(I_{pu} = 3.0 – 6.5 \times 10^{15} W/cm^2)\) and constant for the whole range of the investigated \(I_{pr}\). The maximization of \([\text{Tr}^{2+}\) by the neutral selective core-ionization with a narrow band pump pulse (ideally a seeded x-ray free electron laser pulse) is the key to realizing the precise TR-AEYS mea-
measurement. The $N_{q}(q=2) = 3.7 \times 10^{-3}$ (Figure 5d) indicates that a repetition rate of ~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.

4 Conclusions

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-AEYS using IVC-MD and the coupled rate equation model. We found population traps in highly excited dicationic states in 100 fs as experimentally observed in $\text{C}_4\text{H}_4\text{S}^{2+}$ during the NAT cascade passing through 10-10^2 two-hole states. The time constants of NATs extracted from the calculated TR-AEYS reflect the population trap. Such x-ray induce NAT dynamics shall be detected by the TR-AEYS. The TR-AEYS can be measured ideally in a background-free mode with an intense narrow band femtosecond XFEL light source. For this background-free TR-ARES measurement, a narrowband pump pulse whose photon energy is set to ionize only the C(1s) MO of Tr and whose peak intensity is adjusted to be large enough to saturate the C(1s) core ionization. Our theoretical study demonstrates that it is essential to seriously consider the effect of NAT on the x-ray photochemistry and photophysics of large molecules. We also hope that the proposed two-color TR-AEYS scheme will by widely used for investigating the nonadiabatic nature of x-ray photochemistry and photophysics.

Author Contributions
K. Y.: Conceptualization, Methodology, Resources, Investigation, Formal analysis, Writing - Original Draft, and Funding acquisition.

K. M.: Resources, Writing - Review & Editing, Funding acquisition, and Supervision.

Conflicts of interest
There are no conflicts to declare.

Acknowledgements
K.Y. acknowledges to JST-PRESTO (JPMJPR210A) for financial support. K. Y. and K. M. are grateful to the financial support from JSPS KAKENHI Grant Number 19H05628. We also thank Drs. Tomoya Okino and Yasuo Nabekawa at RIKEN for their fruitful comments and discussions. A part of calculations was performed using Research Center for Computational Science, Okazaki, Japan (Project numbers: 20-IMS-C505, 21-IMS-C502, and 22-IMS-C508).

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TOC figure: Tropone\(^{2+}\) created by the carbon KLL Auger decay are trapped in the highly excited electronic states in 100 fs during the nonadiabatic transitions. This can be traced by measuring transient Auger electron yield spectra (TR-AEYS) at the O(1s) pre-edge.
1 Details of computational methods

1.1 Auger decay probability from two-population analysis

Given that an core ionization creates an core-hole state $|\Psi_i^{1}\rangle$ 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 $|\Psi_i^{1}\rangle$ 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 $Q_b(A)$ with assuming that the contribution from the continuum photoelectron and Auger electron is constant for all decay channels.\(^1\) The representations of $t_{ab}$ for singlet configuration are\(^1\)

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

(1)

$$t_{aa} \approx Q_a(A), \quad (a = b)$$

(2)

and that for triplet one is\(^1\)

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

(3)

In general, the electronic wave function of the dicaticon state $|\Psi_i^{d=2}\rangle$ can be represented as the linear combination of the all possible two-hole-electron configurations.\(^1\) The wave function within the two-hole configuration interaction theory on the top of $|\Psi_i^{1}\rangle$ is written using the second quantization notation as

$$|\Psi_i^{d=2}\rangle = \sum_{a \leq b} c_a c_b \tilde{c}_{1s}^\dagger |\Psi_i^{1}\rangle,$$

(4)

where $c_a$, $c_b$, $\tilde{c}_{1s}$ 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 $|\Psi_i^{d=2}\rangle$ 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 $|\Psi_i^{d=2}\rangle$. The final expression for the relative Auger transition intensity from $|\Psi_i^{d=2}\rangle$ to $|\Psi_i^{d=2}\rangle$ is written as\(^2\)

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

(5)

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

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

(6)

$$P_{\nu}(t = 0) = I_{\nu},$$

(7)

1.2 Nonadiabatic reaction dynamics

We performed surface hopping molecular dynamics simulations on the NRD dynamics of tropone dications using a Tully’s fewest switching algorithm combined with a linear vibronic coupling (LVC) model potential energy surfaces (PES)\(^3\)–\(^5\) (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.\(^6\). The initial dication states for 200 trajectories were selected according to the relative normal Auger probability\(^7\) initiated by the core ionization at the
Carbon 1s edge (See Figure 1 in the main text).

The trajectories were then propagated on the IVC potential energy surfaces until they encountered to a surface hop at a dissociative crossing point of the IVC 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 IVC-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\(^8\) 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\(^9\) was applied to evaluated the \(\{P_i(t)\}\) for the IVC-MD.

### 1.2.1 Linear vibronic coupling (IVC) model

In an IVC model\(^3\), 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 \(x = [x_1, x_2, \ldots, x_{l}, \ldots, x_{N''-6}],\)

\[
V(x) = V_0(\mathbf{x}) + W(x).
\]  

(8)

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

\[
V_0(x) = \sum_{l=1}^{3N''-6} \frac{\hbar \omega_l}{2} x_l^2.
\]  

(9)

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

\[
W_{nn}(x) = E_{\nu}^{(n)} + \sum_{l=1}^{3N''-6} \kappa_{l}^{(n)} x_l,
\]  

(10)

and

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

(11)

where \(E_{\nu}^{(n)}\) are the two-hole binding energies at \(x_0 = \mathbf{R}_0\), while \(\kappa_{l}^{(n)}\) and \(L_{l}(n,m)\) 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 elements \(\kappa_{l}^{(n)}\) values were obtained as numerical gradients and the interstate couplings \(L_{l}(n,m)\) were obtained from the change in the wavefunction overlaps. The spin–orbit couplings (SOCs) in the IVC 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 the neutral grand state of tropone at the density fitted localized Möller–Plesset second order perturbation (DF-LMMP2) theory\(^10\) combined with the Def2-TZVP basis set\(^11\). The convergence of geometry optimization was confirmed by the normal mode analysis at the same level of theory.

For the Auger spectrum calculation and IVC-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\(^12,13\).

The \(\epsilon_{v\mu}(\mathbf{R}_0)\) 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 used 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 \(\text{Tr}^{+} (q = 0, 1, 2)\) 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 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\(^16,17\) 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\(^18\).
functions of $I_{pu}$ and $\hbar \omega_{pu}$ as

$$[\text{Tr}](I_{pu}, \hbar \omega_{pu}) = \exp \left( -\lambda_V (I_{pu}, \hbar \omega_{pu}) - \lambda_C (I_{pu}, \hbar \omega_{pu}) \right), \quad (14)$$

$$[\text{Tr}]^+(I_{pu}, \hbar \omega_{pu}) = \frac{\sigma_V (\hbar \omega_{pu})}{\sigma_C (\hbar \omega_{pu}) - \sigma_C^{(1s)} \rightarrow V (\hbar \omega_{pu})} \times \left[ \exp \left( -\lambda_V (I_{pu}, \hbar \omega_{pu}) - \lambda_C^{(1s)} \rightarrow V (I_{pu}, \hbar \omega_{pu}) \right) \right. \right.$

$$- \exp \left. \left. \exp \left( -\lambda_V (I_{pu}, \hbar \omega_{pu}) - \lambda_C (I_{pu}, \hbar \omega_{pu}) \right) \right) \right), \quad (15)$$

$$[\text{Tr}]^{2+}(I_{pu}, \hbar \omega_{pu}) = \exp \left( -\lambda_V (I_{pu}, \hbar \omega_{pu}) \right) - \exp \left( -\lambda_V (I_{pu}, \hbar \omega_{pu}) - \lambda_C (I_{pu}, \hbar \omega_{pu}) \right), \quad (16)$$

$$[\text{Tr}]^{2+}(I_{pu}, \hbar \omega_{pu}) = \frac{\sigma_V (\hbar \omega_{pu})}{\sigma_V (\hbar \omega_{pu}) + \sigma_C (\hbar \omega_{pu})} \times \left[ 1 + \frac{1}{\sigma_C (\hbar \omega_{pu})} \times \{ \sigma_V (\hbar \omega_{pu}) + \sigma_C^{(1s)} \rightarrow V (\hbar \omega_{pu}) \} \right] \times \exp \left( -\lambda_V (I_{pu}, \hbar \omega_{pu}) - \lambda_C^{(1s)} \rightarrow V (I_{pu}, \hbar \omega_{pu}) \right) \right], \quad (17)$$

$$[\text{Tr}]^{2+}(I_{pu}, \hbar \omega_{pu}) = \frac{\sigma_C (\hbar \omega_{pu})}{\sigma_V (\hbar \omega_{pu}) + \sigma_C (\hbar \omega_{pu})} \times \left[ 1 + \frac{1}{\sigma_C (\hbar \omega_{pu})} \times \{ \sigma_V (\hbar \omega_{pu}) + \sigma_C^{(1s)} \rightarrow V (\hbar \omega_{pu}) \} \right] \times \exp \left( -\lambda_V (I_{pu}, \hbar \omega_{pu}) - \lambda_C^{(1s)} \rightarrow V (I_{pu}, \hbar \omega_{pu}) \right) \right], \quad (18)$$

where $\sigma_V (\hbar \omega_{pu})$, $\sigma_C (\hbar \omega_{pu})$, and $\sigma_C^{(1s)} \rightarrow V (\hbar \omega_{pu})$ represent the photoionization cross sections of the $V^{-1}$, $C$, and $C(1s) \rightarrow V$ ionization processes as functions of $\hbar \omega_{pu}$, respectively. $\lambda_V (I_{pu}, \hbar \omega_{pu})$ and $\lambda_C (I_{pu}, \hbar \omega_{pu})$ mean the number of absorbed photons during the pump irradiation for the ionization processes $V^{-1}$ and $C$, respectively. For the Gaussian pump pulse with a peak intensity of $I_{pu}$ and full width at half maximum (FWHM) of $s_{pu}$, $\lambda_{\text{pu}} (I_{pu}, \hbar \omega_{pu}) (A_{pu} = V^{-1}, C, X \rightarrow V)$ is written as

$$\lambda_{\text{pu}} (I_{pu}, \hbar \omega_{pu}) = \sigma_{\text{pu}} (\hbar \omega_{pu}) I_{pu} \sqrt{\frac{\pi}{4 \ln^2 s_{pu}}}. \quad (19)$$
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 Tr$^{2+}$ excites core electron at Y-edge to the valence hole. The core-excited Tr$^{2+}$ which is rapidly ionized into Tr$^{3+}$ via resonance Auger relaxation emits one fast Auger electron $e_{\text{Auger}}^{-}$.

$$\text{Tr}^{2+} \xrightarrow{O(1s) \rightarrow V} \text{Tr}^{3+} + e_{\text{Auger}}^{-} \quad \text{(20)}$$

The TR-XAS measurement using the Auger electron yield method\textsuperscript{20–26} selectively counts the number of $e_{\text{Auger}}^{-}$ as a function of $\hbar\omega_{pu}$ and $\Delta t$ by using electron spectrometers. This scheme can eliminate the photoelectrons from core ionization and $V^{-1}$ processes, and the Auger electrons from the $C$ process of Tr$^{q+}$ ($q = 0, 1, 2, 2', 3$) by the pump and probe pulses. The background sources can come from the resonance Auger electrons from the O(1s) $\rightarrow$ V excitation process of Tr$^{+}$ and Tr$^{2+}$, and normal Auger electron from O(1s)$^{-1}$ core ionization of Tr. The contribution of Tr$^{2+}$ is negligibly small since $\sigma_{\text{q}}(\hbar\omega_{pu})$ is smaller than $\sigma_{\text{C}}(\hbar\omega_{pu})$ by a magnitude nearby the C(1s) edges of Tr and Tr$^{+}$.

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

$$N_{e}(q, I_{pu}, \hbar\omega_{pu}, I_{pr}, \hbar\omega_{pr}) = \frac{\theta(q, \hbar\omega_{pr})[\text{Tr}^{q+}]/(I_{pu}, \hbar\omega_{pu})}{\sigma_{\text{q}}(q, \hbar\omega_{pr})} \times \left[1 - \exp\left(-\lambda_{\text{tot}}(q, I_{pr}, \hbar\omega_{pr})\right)\right]. \quad \text{(21)}$$

Here, $\theta(q, \hbar\omega_{pr})$ describes the fraction of bright states for Tr$^{q+}$ at $\hbar\omega_{pr}$ ($\theta(q = 0, \hbar\omega_{pr}) = 1$ and $0 \leq \theta(0 < q, \hbar\omega_{pr}) \leq 1$). $\sigma_{\text{q}}(q, \hbar\omega_{pr})$ represents the mean photoabsorption cross section for the O(1s) $\rightarrow$ V excitation and subsequent resonance Auger decay ($q = 1, 2, 2'$), and the O(1s)$^{-1}$ core ionization and subsequent oxygen KLL Auger decay (O) for $q = 0$, respectively. $\sigma_{\text{q}}(q, \hbar\omega_{pr}) \equiv \sigma_{\text{q}}(q, \hbar\omega_{pr}) + \sigma_{\text{O}}(\hbar\omega_{pr}) + \sigma_{\text{C}}(\hbar\omega_{pr})$ is the total photoionization cross section for Tr$^{q+}$ as a function of $\hbar\omega_{pr}$, and $\lambda_{\text{tot}}(q, I_{pr}, \hbar\omega_{pr})$ 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 $\sigma_{pr}$, $\lambda_{\text{tot}}(q, I_{pr}, \hbar\omega_{pr})$ is written as

$$\lambda_{\text{tot}}(q, I_{pr}, \hbar\omega_{pr}) = \sigma_{\text{tot}}(q, \hbar\omega_{pr}) I_{pr} \frac{\pi}{4 \ln^{2}} \sigma_{pr}. \quad \text{(22)}$$

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

$$N_{e}(q, I_{pu}, \hbar\omega_{pu}, I_{pr}, \hbar\omega_{pr}) \propto \theta(q, \hbar\omega_{pr})[\text{Tr}^{q+}]/(I_{pu}, \hbar\omega_{pu}) \times \sigma_{\text{q}}(q, \hbar\omega_{pr}) I_{pr} \frac{\pi}{4 \ln^{2}} \sigma_{pr}. \quad \text{(23)}$$

The S/B $\eta$ can be defined as the ratio of $N_{e}(q = 2, I_{pu}, \hbar\omega_{pu}, I_{pr}, \hbar\omega_{pr})$ and the sum of the electron yields originated from other O(1s)-edge (resonance) Auger processes,

$$\eta(I_{pu}, \hbar\omega_{pu}, I_{pr}, \hbar\omega_{pr}) \equiv \frac{N_{e}(q = 2, I_{pu}, \hbar\omega_{pu}, I_{pr}, \hbar\omega_{pr})}{\sum_{q = 0, 1, 2'} N_{e}(q = 2, I_{pu}, \hbar\omega_{pu}, I_{pr}, \hbar\omega_{pr})}. \quad \text{(24)}$$

Table S2 The photo-ionization cross sections $\sigma_{\text{q}}(\hbar\omega_{pu})$ and $\sigma_{\text{pr}}(\hbar\omega_{pr})$ used in the calculation in $10^{-18}$ cm$^2$.

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

$^a$Yeh et al.\textsuperscript{27}; $^b$ SA-1h-CASSCF/ANO-RCC-VTZP//DF-LMP2/Def2-TZVP; $^c$SA-2h-CASSCF/ANO-RCC-VTZP//DF-LMP2/Def2-TZVP.

2.3 Photoionization cross sections

Core and valance photoionization cross section $\{\sigma_{\text{A}}(A = C(1s), O(1s), V)\}$ of Tr$^{q+}$ ($q = 0, 1, 2$) were calculated from the atomic calculations by Yeh. et al.\textsuperscript{27} We used the values of $\hbar\omega = 300 \text{ eV}$ for the representative values of $\{\sigma_{\text{q}}\}$ above the C(1s) edge and $\hbar\omega = 542 \text{ eV}$ for O(1s) (pre-) edge. The photoabsorption cross sections of C(1s) $\rightarrow$ V$^{-1}$ of Tr$^{+}$ and O(1s) $\rightarrow$ V$^{-1}$ of 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{28,29} We assumed that the all core-to-valence excited states rapidly undergoes the resonance Auger process and Tr$^{q+}$ is ionized to Tr$^{(q+1)+}$. We also given that these photoionization cross sections do not depend on $q$\textsuperscript{19}.

3 X-ray photoelectron spectra of Tr$^{q+}$ ($q = 0, 1, 2$) at the O(1s) edge

Fig. S2 The calculated XPS spectra of Tr$^{q+}$ ($q = 0, 1, 2$) at the O(1s) edge. Results at the MS-RASPT2/Sapporo-2012 (C.O. TZP, H. DZP)\textsuperscript{27}//DF-LMP2/Def2-TZVP level of theory. The calculated spectra were broadened by a Gaussian function of FWHM = 1.0 eV.

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