Disentangling the Resonant Auger Spectra of Ozone: Overlapping Core-Hole States and Core-Excited State Dynamics. Supplementary Information

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For the computation of Auger decay rates according to Equation 11 (main text), one can utilize tabulated atomic two-electron integrals available in the literature,[1–3] or calculate them numerically. We use the values from Ref. 1. They are of the type

$$\langle \chi_{Elm} \chi_{\kappa l_\kappa m_\kappa} | \chi_{\iota l_\iota m_\iota} \chi_{\rho l_\rho m_\rho} \rangle$$

which reduce to a sum of radial integrals (R^k) and analytical angular coefficients (C^k)

$$\langle \chi_\alpha \chi_\beta | \chi_\eta \chi_\delta \rangle = \delta(m_\alpha + m_\beta, m_\eta + m_\delta) \sum_k R^k(\alpha\beta;\eta\delta)\, C^k(l_\alpha m_\alpha; l_\eta m_\eta)\, C^k(l_\delta m_\delta; l_\beta m_\beta)$$

$$R^k(\alpha\beta;\eta\delta) = \int R_{n_\alpha l_\alpha}(1) R_{n_\beta l_\beta}(2) \frac{r_<^k}{r_>^{k+1}} R_{n_\eta l_\eta}(1) R_{n_\delta l_\delta}(2) r_1^2 dr_1 r_2^2 dr_2$$

$$C^k(l_\alpha m_\alpha; l_\beta m_\beta) = \sqrt{\frac{4\pi}{2k+1}} \int Y^*_{l_\alpha m_\alpha} Y_{l_\beta m_\beta} Y_{k m_\alpha - m_\beta} \sin\theta d\theta d\phi =$$

$$(-1)^{m_\alpha} \sqrt{(2l_\alpha+1)(2l_\beta+1)} \begin{pmatrix} l_\alpha & l_\beta & k \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_\alpha & l_\beta & k \\ -m_\alpha & m_\beta & m_\alpha - m_\beta \end{pmatrix}$$

with

$$|l_\alpha - l_\beta| \leq k \leq l_\alpha + l_\beta \qquad l_\alpha + l_\beta + k \ \text{ even.}$$

They can be easily evaluated on the fly, but also calculated once, then tabulated and stored. Here, we use R^k from Ref. 1, whereas C^k are generated analytically on the fly.

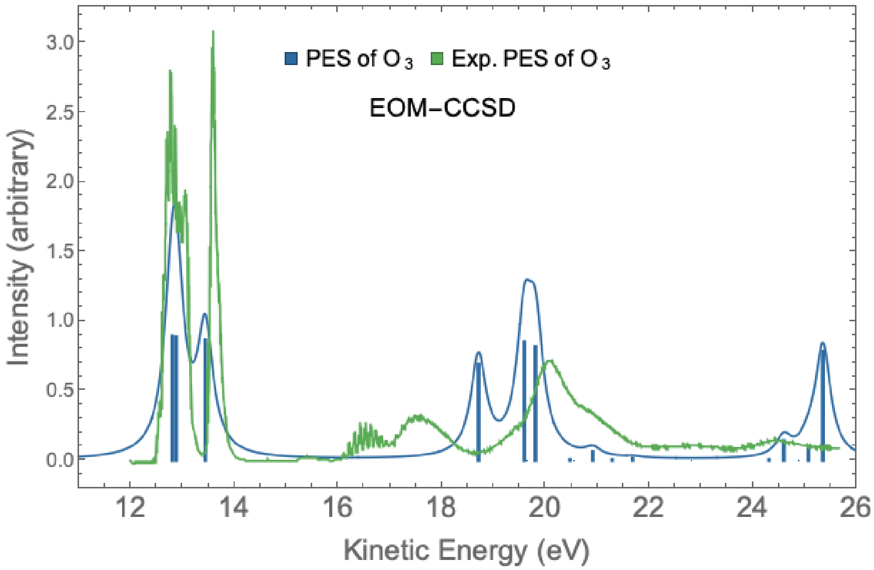
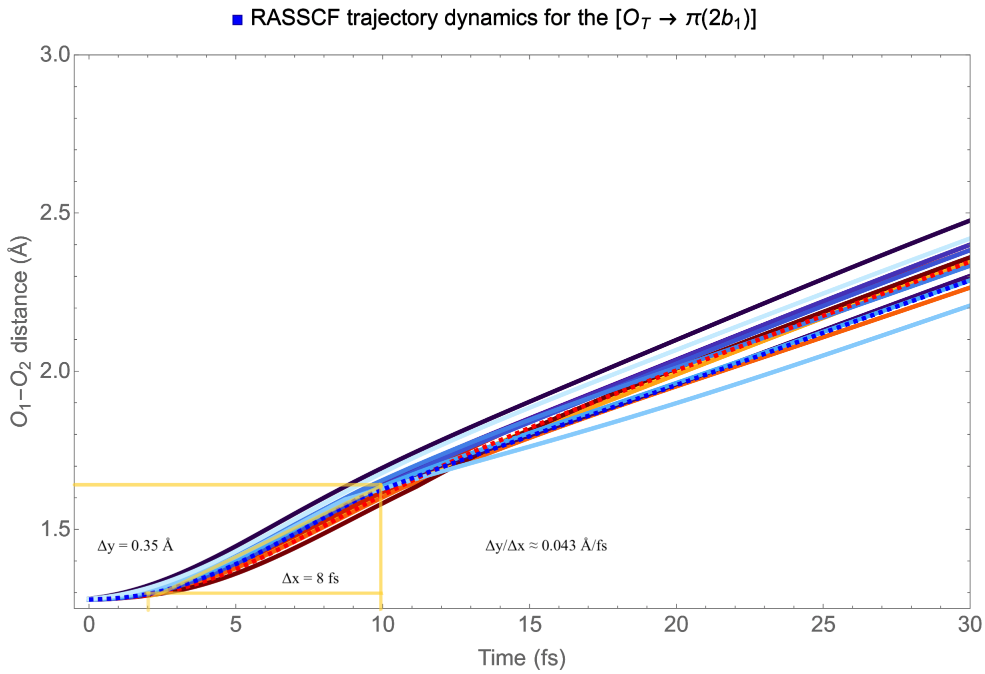


Figure S1: Ozone. PES computed at the EOM-CCSD/cc-pVTZ level of theory at the ground state geometry. The spectrum was broadened with Lorentzian functions with hwhm = 0.10 eV.



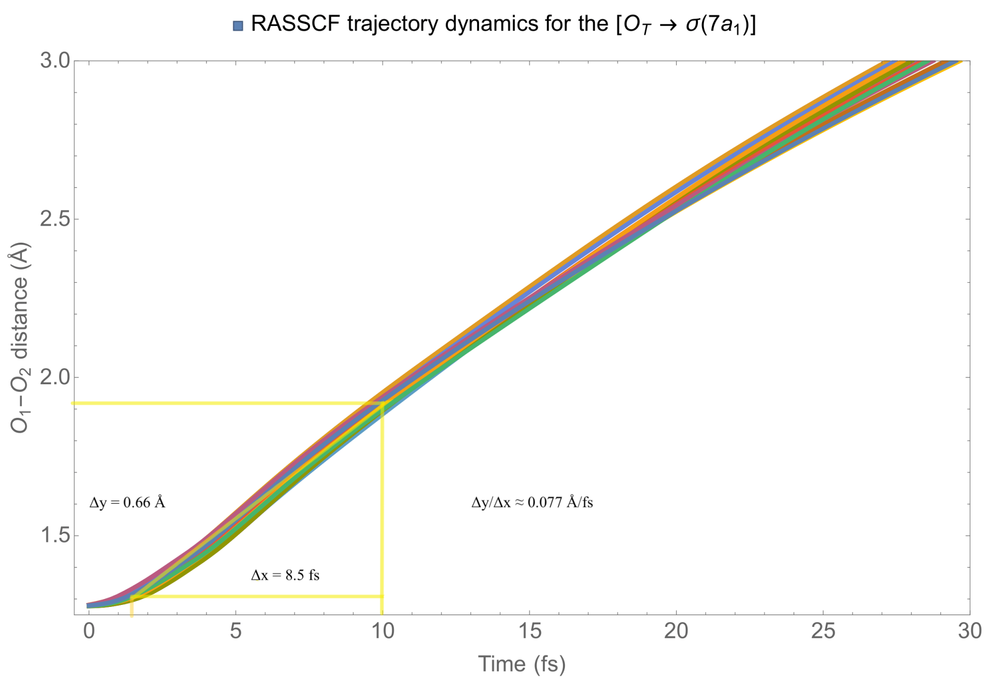


Figure S2: Ozone. Trajectory molecular dynamics at the core-excited states $1s_{\mathrm{O_T}} \rightarrow \pi(2b_1)$ (top) and $1s_{\mathrm{O_T}} \rightarrow \sigma^*(7a_1)$ (bottom) using sixteen initial conditions from a Maxwell–Boltzmann distribution at 300 K.

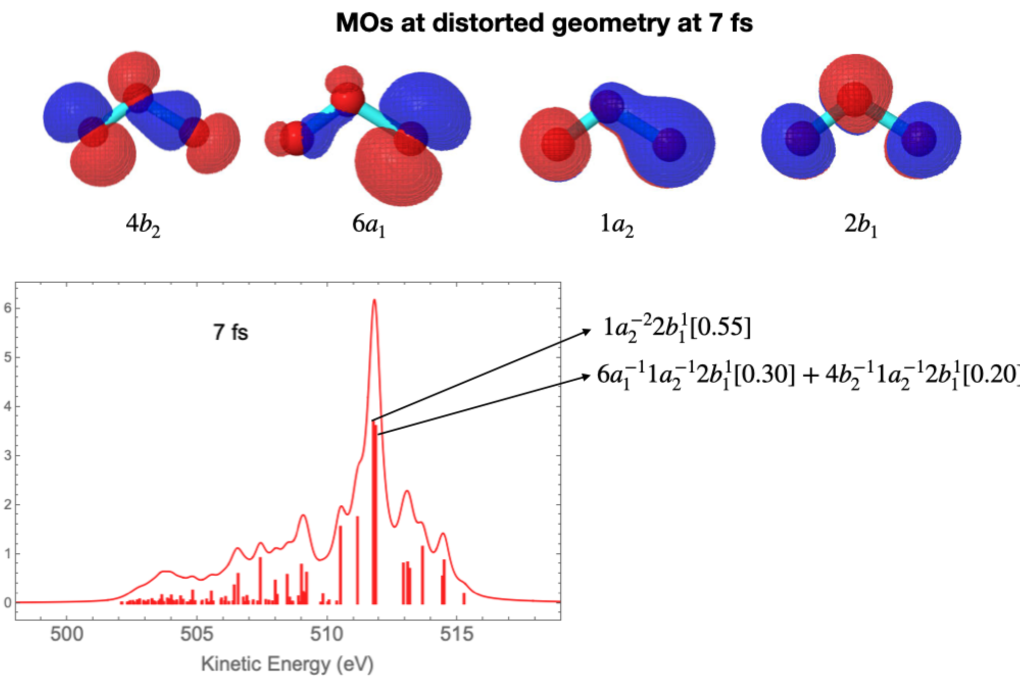


Figure S3: RAES of O_3 at the $1s_{O_T} \rightarrow \pi^*(2b_1)$ resonance computed with the geometry at 7 fs.

References

(1) McGuire, E. J. K-Shell Auger Transition Rates and Fluorescence Yields for Elements Be-Ar. *Phys. Rev.* **1969**, *185*, 1–6.

(2) Walters, D. L.; Bhalla, C. P. Nonrelativistic K-shell Auger rates and matrix elements for $4 \leq Z \leq 54$. *Atomic Data* **1971**, *3*, 301–315.

(3) Chen, M. H.; Larkins, F. P.; Crasemann, B. Auger and Coster-Kronig radial matrix elements for atomic numbers $6 \leq Z \leq 92$. *Atomic Data and Nuclear Data Tables* **1990**, *45*, 1–205.