Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Investigating charge-up and fragmentation dynamics of oxygen molecules after interaction with strong X-ray free-electron laser pulses

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Electronic Supplementary Information (ESI)

Procedures for fitting the backward-forward ratio shown in Fig. 3

Here, we describe how the fitting of the experimental data, shown in Fig. 3 using Eq. (3) was performed. We first converted the ratio of the backward to forward intensities $\eta_k(R)$ to $\eta_k(E_{KER})$ using Eq. (1). The averaged values of the photoelectron kinetic energies ε for each channel were converted to photoelectron momenta $k = (2<\varepsilon>)^{1/2}$ in atomic units (a.u.). The input parameters are summarized in Table S1.

Table S1: The input parameters used in the fittings for Fig. 3.

ε (eV)	Channel	$<\varepsilon>$ (eV)	k (a.u.)	R_{eq} (a.u.)	(z_l, z_r)	(z_l', z_r')
55-80	$O^{1+} + O^{1+} \rightarrow O^{2+} + O^{3+}$	67.5	2.23	2.28	(1, 1)	(2, 3)
80-110	$O^{2+} + O^{1+} \rightarrow O^{2+} + O^{3+}$	95.0	2.64	2.28	(2, 1)	(2, 3)

For the fitting procedure using $\eta_k(E_{KER})$, we assumed the coefficients $a_k(E_{KER})$, $b_k(E_{KER})$, and the back-scattering phases $\varphi_k^{Or}(\pi)$ as constant fitting parameters, as described in the main text. For the main channel with electron energies ε = 80-110 eV, we fully optimized these three parameters by least-square fitting with equal weight for all data points provided by the experiment. We used a KER fitting range of E_{KER} = 45-62 eV.

For the satellite channel with electron energies ε = 55-80 eV, we optimized $\eta_k(E_{KER})$ and $\varphi_k^{Or}(\pi)$ by least-square fitting with equal weight for all experimental data points. Parameter $a_k(E_{KER})$ was manually optimized due to its too strong correlations with $\eta_k(E_{KER})$ and $\varphi_k^{Or}(\pi)$. We used a KER fitting range of E_{KER} = 40-60 eV.

The optimized values of the fitting parameters are displayed in Table S2.

Table S2: The optimal fitting parameters for Fig. 3 with the fitting ranges of E_{KER} = 40-60 eV for ε = 55-80 eV and E_{KER} = 45-62 eV for ε = 80-110 eV.

ε (eV)	Channel	$a_k(E_{KER})$	$b_k(E_{KER})$	$\varphi_k^{Or}(\pi)$
55-80	$O^{1+} + O^{1+} \rightarrow O^{2+} + O^{3+}$	−0.80	0.85 ± 0.04	−7.80 ± 0.24
80-110	$O^{2+} + O^{1+} \rightarrow O^{2+} + O^{3+}$	−0.62 ± 0.22	0.84 ± 0.04	4.65 ± 0.32

In order to check the sensitivity of the fitting results on the fitting range, we also performed the

same fitting procedures extending the fitting range to E_{KER} = 40-65 eV for both, ε = 55-80 eV and ε = 80-110 eV. The resulting ratio of the backward to forward intensities $\eta_k(E_{KER})$ and optimal parameters are displayed in Fig. S1 and Table S3, respectively.

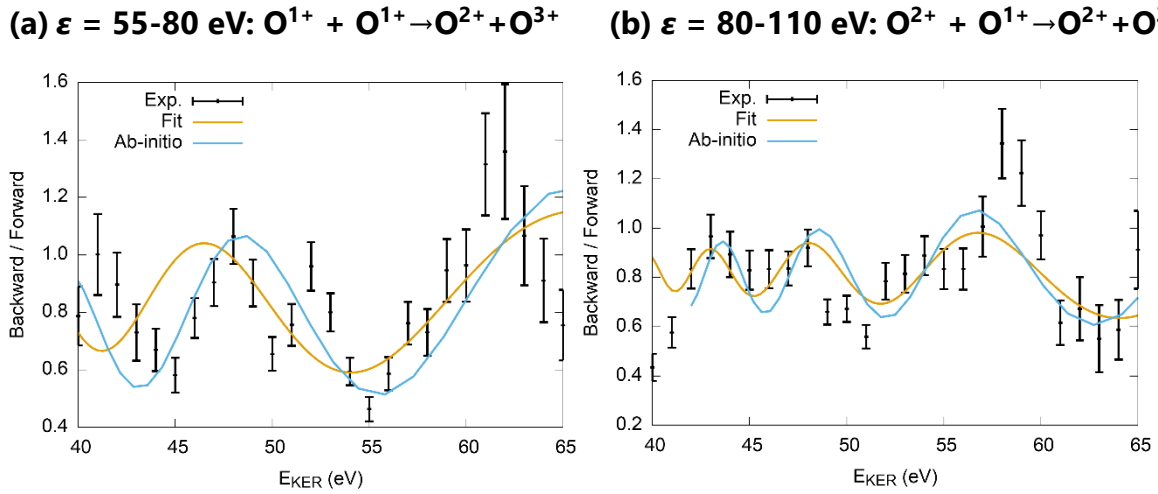

Fig. S1: Comparison between the experimental backward-forward ratios (symbols with error bars), measured for the $O^{3+} + O^{2+}$ final charge state and the photoelectron kinetic-energy ranges of: (a) ε = 55−80 eV and (b) ε = 80−110 eV. We used the extended fitting range of E_{KER} = 40-65 eV for both, ε = 55-80 eV and ε = 80-110 eV. The fitted ratios (orange) and the *ab initio* theoretical results (blue) represent individual contributions from the main channel $O^{1+} + O^{2+} \rightarrow O^{3+} + O^{2+}$ in panel (b) and from the satellite channel $O^{1+} + O^{1+} \rightarrow O^{3+} + O^{2+}$ in panel (a). To facilitate comparison with the experiment, the *ab initio* ratios include a constant background of +0.5.

Table S3: The optimal fitting parameters for Fig. S1 with the extended fitting range of E_{KER} = 40-65 eV.

ε (eV)	Channel	$a_k(E_{KER})$	$b_k(E_{KER})$	$\varphi_k^{Or}(\pi)$
55-80	$O^{1+} + O^{1+} \rightarrow O^{2+} + O^{3+}$	−0.80	0.84 ± 0.04	−8.17 ± 0.26
80-110	$O^{2+} + O^{1+} \rightarrow O^{2+} + O^{3+}$	−0.52 ± 0.18	0.83 ± 0.04	4.46 ± 0.39

Comparing Figs. 3 and S1 as well as Tables S2 and S3 shows that $\eta_k(E_{KER})$ is not very sensitive to the fitting range. In both cases, $\eta_k(E_{KER})$ well reproduces the overall trend of the experimental and theoretical *ab initio* ratios in the given fitting range. Any discrepancies likely stem from our oversimplified fitting model: Our straightforward approach is based on the analytic expression derived in the single-scattering wave approximation (multiple-scattering contributions are omitted), and it assumes that all free parameters of the fitting are fixed

numbers and not energy-dependent. However, this simple approximation is sufficiently powerful to distinguish the main and satellite channels unambiguously, and it can capture the main effects as the *ab initio* calculation, as we emphasized in the main text.