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Complete dissociation branching fractions and Coulomb explosion dynamics of SO₂ induced by excitation of O 1s pre-edge resonances

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Fragmentation processes of SO₂ following excitation of the six main O 1s pre-edge resonances, as well as above the ionization threshold and below the resonances, are studied using a position-sensitive

time-of-flight ion imaging detector, and the associated dissociation branching ratios and break-up dynamics are determined. In order to distinguish between the O⁺ and S²⁺ fragments of equal mass-to-charge ratio, the measurements have been performed with the isotopically enriched S¹⁸O₂ sample. By analysis of the complete set of the fragment momentum vectors, the β values for the fragments originating from the SO⁺ + O⁺ break-up and the kinetic energy release for fragmentation channels of both SO²⁺₂ and SO³⁺₂ parent ions are determined. We also present results on the three-body break-up dynamics. © 2015 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4931645]

I. INTRODUCTION

Near-Edge X-ray Absorption Fine-Structure (NEXAFS) spectroscopy is a powerful technique, being both chemical element- and local site-sensitive in molecular cases, because it involves excitation of a core electron from a particular atomic species located on a specific molecular site to unoccupied molecular orbitals (UMOs). When core electrons are excited by soft X-rays, the excess energy is typically removed by rapid autoionization, namely, resonant Auger decay, forming singly or multiply charged molecular species, respectively. Because of the repulsive forces between nuclei, the latter are unstable with respect to dissociation and the molecule undergoes Coulomb explosion. Although upon Auger decay, the corehole is filled, i.e., information about the core-excitation can be lost, correlation between the fragmentation patterns and core-electron excitation transitions has been reported.^{1–8} This can be explained by the nature of the spectator Auger decay, where the electron promoted from the core-shell to the valence orbital is not involved in the deexcitation process and localized valence holes are formed near the core-excited atom.

SO₂ in the neutral ground state belongs to the C_{2v} symmetry group with an intra-molecular bond angle of 119.5° and a S–O bond length of 1.43 Å. The associated electron configuration in terms of frontier MOs can be denoted as $\dots (1a_2)^2 (8a_1)^2 (3b_1)^0 (9a_1)^0 (6b_2)^0 \dots$ SO₂ has been the subject of numerous photoabsorption and photodissociation studies,^{9–20} including experimental and theoretical NEXAFS studies at the S 1*s*, S 2*s*, S 2*p*, and O 1*s* edges.^{21–32} The NEXAFS spectra reported show many different features, the most prominent of which are associated with core-electron

excitations to the lowest UMO(LUMO) (3*b*₁), LUMO+1 (9*a*₁), LUMO+2 (6*b*₂), and higher-energy UMOs of Rydberg characters. In particular, the S 1*s* and O 1*s* NEXAFS spectra show a strong peak assigned to the $1s \rightarrow 3b_1$ transition. Theoretically predicted assignments of the NEXAFS peaks were experimentally verified by investigating asymmetries of the angular distribution of the photoion fragments with respect to the polarization of the X-ray beam.^{30,31}

Partial photoion yields were reported in the region of the S 2*s* and S 2*p* edges as well as above the O 1*s* ionization threshold, and O⁺ was observed to be the most abundant ion fragment.^{21,22,26} However, in those measurements, it was not possible to distinguish between O⁺ and S²⁺ because of their same mass-to-charge ratio.

Lavollée and Brems investigated the Coulomb explosion dynamics of the $SO_2^{3+} \rightarrow S^+ + O^+ + O^+$ channel by exciting the S 2p electrons and collecting the ion fragments on an imaging detector very similar to the one used in the present study.²⁸ They observed that upon S 2p electron excitation to the 9a₁ and 6b₂ orbitals, the molecule has sufficient time to change the geometry significantly with respect to the ground state, before the Auger decay takes place. Furthermore, the break-up dynamics of this three-body channel initiated by the S 2p ionization was observed to be very similar to that when SO_2^{3+} is produced by direct single-photon triple valence electron ionization.

Lindgren *et al.*²⁹ investigated with a time-of-flight (TOF) mass spectrometer the fragmentation dynamics of SO₂ upon O 1*s* core-valence excitations. For the $1s \rightarrow 9a_1$ and $1s \rightarrow 6b_2$ transitions, they observed fast sequential break-up into the S⁺ + O⁺ + O channel. Furthermore, by analyzing SO⁺–O⁺ pairs at some core excitation energies, they found intra-molecular angles of the SO₂²⁺ states to be close to the ground state geometry.

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In this paper, we present a new experimental study of sulfur dioxide break-up dynamics upon resonant excitation of the six main core-valence electron transitions in the vicinity of the O 1*s* edge. More specifically, we report complete dissociation branching fractions for single, double, and triple ion coincidence events. We also present results of investigations into the dynamics of the SO⁺ + O⁺ channel as well as the three-body break-up for the S⁺ + O⁺ + O⁺ and S⁺ + O⁺ + O channels.

II. EXPERIMENTAL DESCRIPTION AND DATA ANALYSIS PROCEDURE

The experimental studies have been carried out at the GasPhase beam line of the synchrotron radiation facility Elettra³⁵ in Trieste, Italy. The storage ring was operated at 2.0 GeV electron energy. In order to record high resolution NEXAFS spectra, the beam line monochromator was set to provide a narrow bandpass (≈50 meV). For the energy scan of the X-rays, the undulator gap was tuned to select the most appropriate harmonic. Mass spectra and complete momenta of the charged fragments were measured with a TOF position-sensitive imaging detector.^{36,37} The detection axis of the spectrometer was set perpendicular to the Xray light polarization axis. The detection efficiency of the detector was estimated to be 32.5%. The sulfur dioxide gas sample was introduced to the interaction region of the spectrometer by an effusive molecular beam source. The sample gas density was adjusted to minimize contributions from accidental coincidences. To set the correct photon energy and to avoid the effect of possible drifts in the experimental settings, a NEXAFS scan was run every time before acquiring data for a certain resonance. As an example, Fig. 1 shows one of the measured NEXAFS spectra (total ion yield spectrum) which is in excellent agreement with the previous data.³¹ The NEXAFS peaks labeled as A-F can be assigned to O 1s electron excitation to the LUMO $(3b_1)$, LUMO+1 $(9a_1)$, LUMO+2 $(6b_2)$, and higher-energy peaks from Rydberg excitations. To be able to distinguish contributions between O⁺ and S²⁺ fragments, which have the same mass-to-charge ratio, we used an ¹⁸O enriched SO₂ gas sample. This is demonstrated by Fig. 2 which shows all-ions TOF mass spectra for the different excitations, revealing distinct S²⁺ and O⁺ peaks at masses of 16 amu and 18 amu, respectively. The contributions



FIG. 1. SO₂ NEXAFS spectrum measured at the O 1s edge.



FIG. 2. All-ions TOF mass spectra of $S^{18}O_2$ measured at the O 1s pre-edge resonances A-F, BR (518 eV), and AIT (560 eV). The BR contributions are subtracted from the A-F and AIT spectra. The spectra are binned at 0.1 amu and normalized to an integrated intensity of 1.

from the $S^{18}O^{16}O$ and $S^{16}O_2$ isotopologues were taken into account by comparing the peak intensities at 64, 66, and 68 amu and were then subtracted from the data. In this way, branching fractions for pure $S^{18}O_2$ were obtained.

With the present detection system, it is not possible to measure neutral fragments. However, in three-body channels with one neutral fragment, the momentum of the latter can be restored from the conservation law of momentum. For instance, for the $S^+ + O^+ + O$ channel, the momentum of the O product can be found as

$$\vec{p}_{\rm O} = -\left(\vec{p}_{\rm S^+} + \vec{p}_{\rm O^+}\right). \tag{1}$$

To determine momenta for the ionic fragments, the position of the center-of-mass was assumed to coincide with the center of the molecular beam in the interaction region projected onto the imaging detector's plane. Uncertainties in the derived \vec{p}_{S^+} and \vec{p}_{O^+} momenta are related to the width of the molecular beam; in order to reduce such uncertainties, we utilized a 0.5 mm diameter capillary to bring the sulfur dioxide gas into the interaction region. To evaluate the capability of this procedure for restoring an undetected fragment, we tested it for the S⁺ + O⁺ + O⁺ channel, in which all fragments were detected. Figures 3(a) and 3(b) compare the fragment kinetic energies,



FIG. 3. Comparison of the restored (see Eq. (1)) (green) and the measured (black) (a) E_{kin} of the S⁺ and one of the O⁺ ions and (b) Θ for the S⁺ +O⁺+O⁺+O⁺ channel (in addition, the measured events were selected by momentum matching of the three ions). The sample was excited at resonance A. A broadening effect can be observed in the restored distributions.

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 E_{kin} , and the angle between the O⁺ momenta, $\Theta = \angle \left(\vec{p}_{O_a^+}, \vec{p}_{O_b^+}\right)$, respectively, obtained from the three detected ions (black curves) and from two detected ions with one O⁺ being restored (green curves). For the former case, only the ions with matched momenta were considered to eliminate possible accidental coincidence contributions. As can be seen, the restoration procedure is not very accurate, as it leads to an artificial broadening of the distribution. However, it does not produce false peaks.

III. RESULTS AND DISCUSSION

Data were obtained at six resonant energies corresponding to features A-F of Fig. 1, and for one photon energy above the O 1s ionization threshold (AIT, 560 eV) as well as for one photon energy below all resonances (BR, 518 eV) to account for nonresonant contributions to the data. The BR measurements are presumably dominated by S 2p ionization. To support such an assertion, we assess the relative contributions from valence, S 2s, and S 2p ionizations at 518 eV by estimating their oscillator strength. A fit of the absolute values of the valence ionization oscillator strength, df/dE, of Ref. 27 in the range of E = 80-160 eV to the expression

$$\frac{df}{dE} = aE^{-2} + bE^{-3} + cE^{-4} \tag{2}$$

yields the constants a = 323 eV, $b = 6585 \text{ eV}^2$, $c = -54094 \text{ eV}^3$, which results in a valence oscillator strength of 1.25×10^{-3} eV⁻¹ at 518 eV. Considering the calculated oscillator strengths of the resonances A-F²⁴ and the relative intensities of the resonances with respect to the S 2*s*, S 2*p*, and valence ionizations (Fig. 1), we estimated the added S 2*s* and S 2*p* ionization oscillator strength to be in the range of 1- $2 \times 10^{-2} \text{ eV}^{-1}$, i.e., 8-16 times higher than that of the valence ionization. The S 2*s* contribution is approximately a factor of 3-4 smaller than that of S 2*p*, ³⁸ and consequently, we conclude that the S 2*p* ionization dominates at 518 eV.

A. Branching ratios

Upon resonant core-valence excitation and subsequent Auger decays, sulfur dioxide will end up in various charge states. Table I lists relative abundances of singly, doubly, and triply charged cations of SO_2 after excitation at the six resonances marked in Fig. 1 as well as BR and AIT. The

TABLE I. Estimated abundances of parent sulfur dioxide cations, dications, and trications, for the different excitations of SO₂. The error margins are calculated based on the uncertainty of the detection efficiency of $\pm 0.5\%$.

Resonance	SO ₂ ⁺ (%)	$SO_2^{2+}(\%)$	SO ₂ ³⁺ (%)
BR	5.5 ± 2.3	75.5 ± 1.7	19.0 ± 0.7
А	70.1 ± 0.4	26.7 ± 0.3	3.2 ± 0.1
В	68.3 ± 0.4	28.3 ± 0.3	3.4 ± 0.1
С	61.1 ± 0.6	34.1 ± 0.5	4.8 ± 0.2
D	66.4 ± 0.5	30.0 ± 0.4	3.6 ± 0.1
Е	55.4 ± 0.7	38.7 ± 0.6	5.9 ± 0.2
F	55.1 ± 0.7	38.9 ± 0.6	6.0 ± 0.2
AIT	1.6 ± 2.8	89.0 ± 2.5	9.4 ± 0.4

amounts of SO_2^+ , SO_2^{2+} , and SO_2^{3+} were defined as numbers of detected events when fragments had a total charge of one, two, and three, respectively. Here we have assumed an equivalent probability to trigger the ion TOF detector by an electron irrespectively whether a single- or multi-ionization event occurred. These data, as well as all ion yields presented below, were corrected for the finite detector detection efficiency, and BR contributions were removed from the A-F and AIT data. As one would expect from a resonant excitation followed by Auger decay, the total ion yield is dominated by the singly charged cations. The minor non-zero abundance of the SO_2^+ parent ion at BR is mainly due to single-valence ionization reactions. A similar abundance at the AIT photon energy cannot be inferred unambiguously because of the large uncertainty in the result.

Table I also shows that upon O 1*s* core-valence excitation, a significant fraction of the SO₂ molecules decays by double and triple Auger emissions to produce dications and trications. High probabilities of double Auger decay after resonant molecular excitation has been reported previously in, e.g., CO.³⁹ For this molecule, it was also demonstrated that the cascade double Auger process is dominant over the direct double Auger decay.⁴⁰ Also, we note that resonant multiple Auger decay was recently studied in Ar⁴¹ which shows similar branching ratios as found in Table I for resonances A and B.

Table I generally reveals a trend of increasing yield of multiple charge states for higher lying resonances. Such a tendency can be explained by the fact that upon excitation to higher lying UMOs, the core electrons excited to these UMOs are loosely bound. For example, core electron excitations occurring above the C resonance are associated with excitation to Rydberg orbitals. Therefore, single-electron Auger emission of the molecule with such a loosely bound electron might not be sufficient to stabilize the system and an additional electron is involved in the Auger process producing, thus, SO₂ dicationic states.

Relative yields for the formation of the different fragment ions of SO₂ are presented in Tables II–V. The results of Table II were obtained from measurements on the S¹⁶O₂ pure sample with excitation energies above, at and below the O 1*s* ionization threshold, and with all fragmentation channels (single-, double-, and triple-ion channels) included. This provides a direct comparison with the data reported by Fisher *et al.*²² where the photon energy was tuned to the O 1*s* edge at about 540 eV and with Cooper *et al.*,²¹ who excited at 206 eV, just above the S 2*p* edge. Our measurements at

TABLE II. Relative yields (%) for the formation of different ion fragments of $S^{16}O_2$ below (518 eV), at (540 eV), and just above (560 eV) the O 1s ionization threshold. All fragmentation channels are included. The statistical uncertainties are less than 1%.

	518 eV	206 eV ²¹	540 eV	560 eV	540 eV ²²
O ⁺ /S ²⁺	63.9	58.7	55.9	57.8	59.8
SO^{2+}	2.7	2.7	2.5	4.2	4.9
S^{+}/O_{2}^{+}	26.5	26.0	32.0	28.3	22.4
SO ⁺	6.5	9.2	9.3	9.5	12.9
SO_2^+	0.4	3.5	0.3	0.2	0.0

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TABLE III. Relative yields (%) for the formation of charged fragments originating from the reaction channels containing only one ion. The data are presented for different core electron excitations of $S^{18}O_2$ below the O 1*s* ionization threshold. The above resonance excitation is not included because of the large uncertainty related to the low SO₂⁺ yield. The error margins are calculated based on an uncertainty of the detection efficiency of ±0.5%.

	BR	А	В	С	D	Е	F
O ⁺	0 ± 7.8	13.0 ± 0.7	15.6 ± 0.6	26.4 ± 0.8	24.9 ± 0.6	36.2 ± 0.4	37.6 ± 0.6
S^{2+}	43.6 ± 3.9	2.9 ± 0.1	3.7 ± 0.2	6.1 ± 0.1	4.4 ± 0.1	6.4 ± 0.1	6.9 ± 0.1
SO^{2+}	23.5 ± 4.3	2.0 ± 0.2	1.9 ± 0.1	2.4 ± 0.2	1.8 ± 0.2	2.6 ± 0.1	2.9 ± 0.2
S^+	20.2 ± 0.9	42.5 ± 0.2	60.1 ± 0.7	58.2 ± 0.5	61.4 ± 0.5	53.0 ± 0.6	51.0 ± 0.6
SO^+	9.9 ± 0.2	37.5 ± 0.5	17.3 ± 0.1	5.8 ± 0.1	6.4 ± 0.1	1.5 ± 0.2	1.2 ± 0.3
SO_2^+	$2.8\ \pm 0.4$	2.1 ± 0.1	1.4 ± 0.1	1.1 ± 0.1	1.1 ± 0.1	0.3 ± 0.1	0.4 ± 0.1

518 eV can be compared with the data of Cooper *et al.*, since contributions at 518 eV are dominated by S 2p ionization, as discussed above. The sets of relative yields above the O 1s edge are in reasonable agreement with those of Fisher *et al.*, though their values seem to match better with our results for 560 eV excitation. Our data below the O 1s edge (518 eV) also compare quite well with those of Cooper *et al.* with excitation just above the S 2p edge. The similarities between the relative ion yields after excitation above and below the O 1s edge indicate that this quantity does not strongly depend on the initial core ionization and that similar molecular states might be populated after the decays of the S 2p or O 1s holes.

Tables III and IV show the relative yields for the different channels which produce only single ions (i.e., channels producing only one ion with other fragments being neutral) and ion-pairs, respectively. These measurements were carried out with the isotopically enriched $S^{18}O_2$ sample in order to distinguish between the S^{2+} and O^{+} fragments. In Table III, we do not present data for AIT due to the large uncertainties in the results (Table I). Table III shows a tendency that production of single-ion channels with the O^+ and S^{2+} fragments increases with the core electron excitation energy, while the opposite occurs for the channels producing SO⁺ and SO⁺₂. Lindgren et al. reported ion TOF mass spectra of ordinary sulfur dioxide at the photon energies corresponding to the BR contributions (500 eV) and to the A-D resonances.²⁹ Although they did not derive branching fractions, their mass spectra imply a significant enhancement of the SO⁺ fragments at the A resonance that is similar to our findings. The data in Table III also indicate that the relative yields of the channels containing a dication, either S²⁺ or SO²⁺, and neutral fragments are significantly reduced upon O 1s core electron excitation compared with S 2p ionization.

TABLE IV. Relative yields (%) for the formation of different ion-pairs at various excitations of S¹⁸O₂ around the O 1*s* ionization threshold. The statistical uncertainties are less than 1%. The last row presents the β values (Eq. (3)) obtained for the SO⁺ + O⁺ break-up channel.

	BR	А	В	С	D	Е	F	AIT
$\frac{1}{0^{+}+0^{+}}$	17.4	14.7	14.9	16.4	15.4	17.5	17.2	13.9
$S^{2+}+O^{+}$	11.7	2.5	3.1	4.4	3.2	3.9	4.4	2.6
$S^+ + O^+$	60.0	71.1	70.8	68.0	70.9	66.5	66.4	61.3
$\mathrm{SO}^+\mathrm{+O}^+$	10.9	11.7	11.2	11.2	10.5	12.1	12.0	22.2
$\beta(\mathrm{SO^+}\!+\!\mathrm{O^+})$	0.06	-0.78	0.62	0.53	0.45	0.71	0.33	0.20

The branching fractions between created ion-pairs are listed in Table IV and, as an example, Fig. 4 demonstrates a coincidence map composed of ion-pairs detected at the A resonance. The clearly dominant fragmentation path for the creation of ion-pairs is that of $S^+ + O^+ + O$, with over 65% relative yield for all resonances. The O⁺ + O⁺ + S and $SO^+ + O^+$ channels are of about equal significance with about 16% and 12% contribution, respectively. The changes of the ion-pair branching fractions with the excitation of different pre-edge resonances are smaller compared with single ions. This can be understood by considering that the spectator type Auger decay, in which the electron excited from the core level does not participate in the Auger process, will be more likely when one Auger electron is ejected leading to production of singly charged ion. The partial ion-pair yields above the ionization threshold of SO₂ reported by Fisher et al. disagree significantly with our data;²² their findings imply similar probabilities for the $S^+ + O^+$ and $SO^+ + O^+$ channels, while our results suggest the $S^+ + O^+$ channel to be almost three times stronger than $SO^+ + O^+$ (Table IV). We note that Fisher et al. used a threshold photoelectron-ion-ion coincidence technique which is different from ours. Basically with the threshold photoelectron technique, ions are filtered on electrons that have nearly zero kinetic energies, while in our case, such a filtering does not take place. Furthermore, the ion mass spectrometer used by Fisher et al. allowed only detecting ions with kinetic energies below 3 eV. Since the average kinetic energy release (KER) of the ions in the $S^+ + O^+ + O$ channel is $\approx 10 \text{ eV}$ (Fig. 5(c)) and it is larger than for SO⁺ + O⁺ (Fig. 5(a)), the importance of the $S^+ + O^+ + O$ channel might potentially be underestimated in the work by Fisher et al.

Table V shows the relative yields of the channels corresponding to fragmentation of the $S^{18}O_2^{3+}$ parent ions.

TABLE V. Relative yields (%) of the fragmentation channels generated from dissociation of $S^{18}O_2^{3+}$ at the different excitations around the O 1*s* edge. The statistical uncertainties are less than 5%.

	BR	А	В	С	D	Е	F	AIT
$S^{+} + O^{+} + O^{+}$	47.4	60.9	59.9	58.5	61.1	61.0	60.8	59.5
$S^{2+} + O^+$	44.2	32.4	31.9	32.7	30.8	30.6	31.1	31.5
$SO^{2+} + O^{+}$	1.7	1.2	1.4	1.5	1.2	1.3	1.2	2.1
$O^{2+} + S^+$	2.4	2.2	2.6	3.2	2.8	3.0	2.9	2.6
$O^{2+} + O^+$	4.3	3.3	4.2	4.1	4.1	4.1	4.0	4.3

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FIG. 4. Ion pairs from $S^{18}O_2$ fragmentation detected in coincidence for the A resonance.

It is dominated by the 3-ion break-up, and among the 2ion channels, the $S^{2+} + O^+$ fragmentation is clearly the most probable. The dominance of the $S^{2+} + O^+$ channel over the $O^{2+} + S^+$ channel can intuitively be explained by higher



FIG. 5. Total KER distributions of the (a) $SO^+ + O^+$ and (b) $S^+ + O^+ + O^+$ channels for the different excitations. (c) The ion KER distributions for the $S^+ + O^+ + O$ channel. (d) The individual ion fragment energy distributions for the $S^+ + O^+ + O^+$ channel. The data are presented for the different excitations compared with those of the BR (green dashed line) and the A-resonance (red dashed-dotted line).

electronegativity of oxygen compared with sulfur, i.e., the channel with the least positive charge on oxygen should be more abundant. Similar to the dissociation of the dications, SO_2^{3+} fragmentation branching ratios show a weak dependence on the core-valence excitation energy which is contrary to dissociation of SO_2^+ .

B. $SO_2^{2+} \rightarrow SO^+ + O^+$ break-up dynamics

The complete set of momentum vectors of the ions were measured with an imaging detector. The distributions of the product KER in the $SO_2^{2+} \rightarrow SO^+ + O^+$ fragmentation channel for the different resonant excitations, BR, and AIT are shown in Fig. 5(a). The obtained KER distributions are very similar in shape and most of them have a peak at \approx 4.9 eV apart from the A resonance distribution which has a slight shift towards larger values. A similar tendency that the KER is larger upon excitation of the A resonance compared with BR and the B-D resonances was observed by Lindgren et al.,²⁹ though the absolute KER values reported by them are larger than our results. For example, their KER values for BR and the A resonance are 5.5 eV and 8.0 eV, respectively. The discrepancy might be related to a different approach that was used by Lindgren et al. to obtain the KER values. These authors used a TOF mass spectrometer to detect ions and the KER in the $SO^+ + O^+$ channel was obtained by analyzing the spreads in the TOF values of SO⁺ and O⁺ fragments detected in coincidence. Such derived KER values are based on the direct measurement of only one component of the ion momentum vectors, the one along the TOF axis. In contrast, in the present study, the ion imaging detector enabled us to measure the KER for individual ion pairs by directly measuring all three momentum vector components and thus to obtain the KER distribution rather than a specific KER value. For example, the KER distribution measured by us for the A resonance extends up to 15 eV with a maximum at 5.1 eV.

By measuring the complete set of momentum vectors of the charged products, we can also investigate the spacial product distributions. As an example, the blue dots in Figs. 6(a)-6(d) depict the ϕ distributions measured for BR, the A and B resonances, and AIT, respectively, where ϕ is the angle between the product momentum and the light polarization vector. In the general case, such distributions can be described by^{42,43}



FIG. 6. Experimental ϕ distributions obtained for BR, the A and B resonances, and AIT shown as blue dots in (a)-(d), respectively. The distributions obtained by resonantly exciting O 1s electrons (b)-(d) were corrected for the non-resonant contributions (a). The solid red lines are Eq. (3) with beta equal to 0.06 (a), -0.78 (b), 0.62 (c), and 0.20 (d).

$$P(\phi)/\sin\phi \propto 1 + \frac{\beta}{2} \left(3\cos^2\phi - 1\right),\tag{3}$$

where β is the asymmetry parameter which can vary between -1 and 2. The β values obtained with the least-square fitting of Eq. (3) to the experimental ϕ distributions, which for the A-F resonances and AIT were corrected for non-resonant contributions, are listed in Table IV for all the photon energies considered. The experimental ϕ distributions have a drop in intensity for $\phi \approx 90^{\circ}$ (Figs. 6(a)–6(d)), which is due to a reduced sensitivity in the center of the detector, and this region of the ϕ values was disregarded in the fitting.

The β values for the A-F resonances and AIT were previously determined by angle-resolved photoion-yield spectroscopy (ARPIS) in the work of Gejo et al.³¹ Similar to our results, the ARPIS measurements showed a large negative β value for the A resonance as well as similar relative β values for the B-F resonances and AIT; the only exception is the E resonance for which we obtained a larger value compared with other excitation energies. However, our results seem to be systematically larger by ≈ 0.3 compared with the results reported by Gejo et al. The source of the discrepancy is not clear to us but it might partly be due to the fact that we subtracted non-resonant contributions for the ϕ distributions that should affect the beta values making them larger. The background subtraction, in particular, might explain the higher discrepancy for the E resonance, as for this resonance, the non-resonant contributions are larger compared with other excitation energies. In order to assess the accuracy of the β values obtained, we also performed β measurements on CO₂ by exciting the C 1s pre-edge resonances at 291 eV and 312 eV. The values obtained are -0.5 and 0.6, respectively, which are in decent agreement with values known in the literature, -0.3 and 0.8, ^{33,34} although smaller by ≈ 0.2 . We note that even if the β values measured by us are systematically lower by ≈ 0.2 , it cannot explain the discrepancy with the ARPIS results as the difference with the ARPIS β values has the opposite sign.

The absolute value of the β parameter relates to the symmetry of the molecular state that is resonantly excited with X-ray photons and the time span between the fragmentation and X-ray absorption. For example, excitation of the A resonance (O $1s \rightarrow 3b_1$) is governed by a molecular dipole transition momenta perpendicular to the molecular plane and, if the fragmentation process occurs almost instantaneously upon absorption of the X-ray photon, i.e., is significantly shorter compared with a molecular rotation period, the $P(\phi)$ distribution can be described by Eq. (3) with $\beta = -1$. Indeed, the measured β value for the A resonance, which is -0.78, is quite close to -1 and the difference between the two values can be explained by a finite lifetime of SO₂²⁺ formed upon A resonance excitation and subsequent Auger decay.

C. Three-body break-up dynamics of SO_2^{2+} and SO_2^{3+}

1. Distributions of the fragment kinetic energies and angles between fragment momenta

KER distributions of the charged products in the S^+ + O^+ + O^+ and S^+ + O^+ + O channels for the different exci-

tations are shown in Figs. 5(b) and 5(c), respectively. It can be seen that the KER distributions for both channels do not strongly depend on the core electron excitation and, e.g., for the $S^+ + O^+ + O^+$ channel, similar to the $SO^+ + O^+$ case, only for the A resonance there is a slight shift towards higher KER (Figs. 5(a) and 5(b)). For the $S^+ + O^+ + O$ channel, the KER distribution at the BR photon energy appears to be broader when compared with other KER distributions (Fig. 5(c)) which might be due to the comparatively strong accidental coincidence contributions originating from the $S^+ + O^+ + O^+$ channel at this particular photon energy (see Tables I and IV). We note that for the full mass detected channels, such as $S^+ + O^+ + O^+$ and $SO^+ + O^+$, accidental coincidence contributions can readily be eliminated based on momenta matching while it is not the case for the channels with neutral fragments.

Fig. 5(d) shows the kinetic energy, E_{kin} , distributions of individual ions in the $S^+ + O^+ + O^+$ channel. Since the two O^+ ions are indistinguishable, the average of their E_{kin} is presented. The E_{kin} distributions (Fig. 5(d)) reveal that the small increase of KER at the A resonance is mostly associated with the increase of the S^+ kinetic energy, while the two oxygen ion energies stay almost the same. If the momentum of the S⁺ fragment is increased with the O⁺ momenta being unchanged, then the total momentum conservation implies a reduction of the angle between the oxygen momenta. Indeed, such a tendency is seen from Fig. 7(a) which compares the distributions of Θ angle between the momenta of the oxygen ions for all excitations; i.e., the A resonance Θ distribution has a peak at $\approx 114^\circ$, while for other excitations, it is at $\approx 116^\circ$. A similar tendency that the molecular break-up geometries is slightly different upon excitation of the A resonance is also seen for the $S^+ + O^+ + O$ channel from Fig. 7(b) which presents the distribution of angle Ψ between S⁺ and O⁺ momenta, $\Psi = \angle(\vec{p}_{S^+}, \vec{p}_{O^+})$. The peaks of the Ψ distributions are significantly broader compared to the Θ distributions, which partly can be explained by inaccuracies in the neutral oxygen restoration procedure (see, e.g., Fig. 3).



FIG. 7. (a) The distributions of the angle between oxygen ion momenta for the $S^++O^++O^+$ channel. (b) The distributions of the angle between the O^+ and S^+ momenta for the S^++O^++O channel. The data are presented for the different excitations compared with those of the BR (green dashed line) and the A-resonance (red dashed-dotted line).



FIG. 8. The charge-exchange model predictions for the angle between O⁺ momenta (Θ) versus intra-molecular angle of SO₂³⁺ upon Coulomb explosion. \angle (O–S–O) \approx 120° corresponds to the ground state geometry (red lines) and $\Theta \approx$ 116° is the most likely angle measured between the O⁺ moment (blue lines).

To identify SO_2^{3+} intra-molecular angles upon fragmentation from the measured angle between fragment momenta, we employ the charge-exchange Coulomb explosion model.44,45 Although this model is over-simplified as it does not simulate the molecular break-up dynamics considering actual potential energy surfaces, the model was demonstrated to be valid to describe three-body fragmentation dynamics of molecular dications created with Vacuum Ultraviolet (VUV) photoionization and, in particular, for SO₂^{2+.11} Assuming synchronous concerted break-up mechanism and S–O bond lengths of SO₂³⁺ upon fragmentation to be unchanged from their ground state values, the relation between intra-molecular angles in SO_2^{3+} and Θ , obtained with the charge-exchange Coulomb explosion model, is presented in Fig. 8. The results obtained imply that SO_2^{3+} molecular break-up geometries (blue line, Fig. 8) upon fragmentation differ from those of the ground state (red line, Fig. 8).

2. Molecular break-up geometries

To further illustrate the break-up dynamics, we visualize our data in form of Newton diagrams. In our Newton diagrams, the momenta of the O^+ (and O) fragments are shown in the polar coordinates with respect to the S⁺ momentum and the absolute values of the momenta are normalized to $|\vec{p}_{S^+}|$. We plot the Newton diagrams for the $S^+ + O^+ + O^+$ channel for the A resonance at different ranges of the KER values in Figs. 9(a)-9(d). The Newton diagrams for other O 1s pre-edge resonances as well as BR and AIT are not shown since they are very similar to those presented in Figs. 9(a)-9(d). It follows from the figure that upon the SO_2^{3+} break-up, the O⁺ fragments have similar momenta which points towards a synchronous concerted break-up mechanism in which the two S-O bonds break synchronously. Furthermore, the Newton diagrams reveal a minor dependence of Θ on the KER range selected. Such a tendency might indicate the importance of S–O bond stretching motion, i.e., the smaller the distances between the S and O nuclei are, the larger the KER value becomes.

We have also investigated the three-body break-up dynamics of the channels containing one neutral fragment, $S^+ + O^+ + O$, and $O^+ + O^+ + S$. Here, we focus on the former channel because the latter has a non-negligible contribution of false detections from the 3-ions channel. These contributions are smaller for the $S^+ + O^+ + O$ channel due to its considerably higher relative yield as can be verified by Table IV. The



FIG. 9. Newton diagrams for the S⁺ + O⁺ + O⁺ (a)-(d) and S⁺ + O⁺ + O (e)-(h) channels measured for the A resonance selected by the KER values in different regions. For the S⁺ + O⁺ + O⁺ channel, the KER regions are 10–17.5 eV (a), 17.5–22.5 eV (b), 22.5–27.5 eV (c), and 27.5–40 eV (d), and for S⁺ + O⁺ + O, they are 0–7.5 eV (e), 7.5–12.5 eV (f), 12.5–17.5 eV (g), and 17.5–25 eV (h).

 $S^+ + O^+ + O$ Newton diagrams for the different KER ranges are shown in Figs. 9(e)-9(h) for the A resonance and, similarly to the $S^+ + O^+ + O^+$ channel, for other photon energies considered, the Newton diagram are very similar. Figs. 9(e)-9(h) imply that at small kinetic energies, the neutral O fragment receives a little amount of the kinetic energy and the angle between the S⁺ and O⁺ momenta is nearly 180°. However, when the E_{kin} of the charged products increases, the neutral fragment tends to receive a higher amount of E_{kin} accompanied by a reduction of the angle between the S⁺ and O⁺ momenta. In the ultimate case (Fig. 9(h)), the break-up geometry becomes identical to that in the $S^+ + O^+ + O^+$ channel (Figs. 9(a)-9(d)). We note that a similar tendency of the Ψ reduction with increasing KER was observed for the SO_2^{2+} states prepared by the VUV ionization.¹¹ Using the charge-exchange Coulomb explosion model and assuming synchronous concerted breakup, Hsieh and Eland related such a tendency to asymmetric molecular break-up geometries with one S-O bond being elongated and with the intra-molecular angle being the same as in the ground state. In order to explain the similarities of the $S^+ + O^+ + O^+$ break-up with $S^+ + O^+ + O$, the authors suggested that for higher KER, dication three-body breakup proceeded via three charges fragmentation with a distant optical electron.11

IV. CONCLUSIONS

We have investigated the branching ratios and dissociation dynamics of different fragmentation channels of SO₂ by exiting various O 1*s* pre-edge resonances. Relative abundances of parent SO₂ cations, formed upon O 1*s* core electron excitation and subsequent Auger decay, have been observed to decrease with excitation energy, while the opposite occurs for multiply charged ions. After Auger decay, the molecular ions are unstable towards dissociation and the relative yields of charged fragments measured in this work agree reasonably well with previous measurements.^{21,22} We have also determined the branching fractions between different fragmentation channels of singly, doubly, or triply charged parent ions. By performing measurements on the S¹⁸O₂ isotopologue, the O⁺ and S²⁺ fragments of equal mass to charge ratio could be distinguished. A stronger dependence of the branching fractions on the O 1s core electron excitation energy have been revealed for fragmentation of SO_2^+ compared with the cases of SO_2^{2+} and SO_2^{3+} . Such a tendency can be explained by a lower probability of spectator type decays for double- and triple-electron Auger emission.

The molecular break-up dynamics has been investigated by measuring the complete set of momentum vectors of the charged fragments with an imaging detector. We have observed similar break-up dynamics in the $SO_2^{3+} \rightarrow S^+ + O^+$ + O^+ channel for BR, AIT, and all the O 1s pre-edge resonances considered. Furthermore, similar break-up dynamics (namely, angle between oxygen ion momenta of $\approx 120^{\circ}$ with nearly equal absolute momenta values) was observed by Lavollée and Brems²⁸ upon direct single-photon triple valence ionization. Since the triple-valence ionization does not involve intermediate Auger decay, we can assert that during the time span between the resonant X-ray photon absorption and Auger decay, the molecule does not perform any significant nuclear motion. However, the fact that molecular break-up geometries differ from the ground state geometry, as can be inferred both from the Newton diagrams and the results of the chargeexchange Coulomb explosion model, suggests that molecular deformations predominantly occur in SO_2^{3+} after the Auger decay has taken place. We hope that the experimental results presented in this paper will stimulate theoretical investigations of the dissociation dynamics of core-excited SO₂ to obtain an even deeper understanding of this kind of reactions.

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