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Kinetic-energy release and intercharge distance of the sulfur dioxide dication (SO_2^{2+})

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Abstract

The kinetic-energy release distributions (KERDs) of the fragment ion pairs ($O^+ + SO^+$ and $O^+ + S^+$) produced in dissociative double photoionization of sulfur dioxide have been determined by analyzing the photoion-photoion coincidence spectra measured in the energy region of 37–130 eV by use of a time-of-flight mass spectrometer and synchrotron radiation. It should be noted that the KERDs obtained for the $O^+ + S^+$ channel represent lower limits because the kinetic energy of the neutral O atom is not involved. The kinetic-energy releases (KERs) in the $O^+ + SO^+$ dissociation channel do not vary but remain almost constant across this broad range of excitation energies. This means that low-lying electronic states of SO_2^{2+} below 37 eV are mainly responsible for this channel. However, the average KERs in the $O^+ + S^+$ dissociation channel depend strongly on the excitation energies in the 40–60-eV region and weakly above 60 eV. This indicates that high-lying electronic states of SO_2^{2+} as well as low-lying ones, contribute to this channel. From the observed KERDs in the $O^+ + SO^+$ and $O^+ + S^+$ channels of SO_2^{2+}, the range of the intercharge distances is estimated by assuming that the KERs are simply given by Coulomb repulsion. The estimated intercharge distances for the $O^+ + S^+$ channel are wide and deviate largely from the equilibrium internuclear distance, which is not possible by direct double ionization only and which indicates a significant role of indirect processes. (Int J Mass Spectrom 209 (2001) 125–131) © 2001 Elsevier Science B.V.

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1. Introduction

Many doubly charged molecular ions dissociate into ionic fragments with concomitant kinetic-energy releases (KERs) because of Coulomb repulsion between two positive charges. To elucidate the production and dissociation dynamics of doubly charged molecular cations, it is necessary to determine the KERs experimentally. In the framework of direct double photoionization of molecules and their subsequent dissociation, the KERs are related both to the potential energies of the parent-ion states and to the energy partitioning among the internal degrees of freedom of the ionic fragments.

Therefore, kinetic energies released in the charge separations of doubly charged molecular ions have been studied for many years for diatomic and triatomic molecules by electron impact experiments [1–3] with the use of conventional mass spectrometers. Among these studies, Cooks et al. [3] reported the average KER for SO_2^{2+}, observing metastable

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peak shapes formed with ionizing electron energy of 130 eV. Assuming a single-valued KER, they deduced a value of 3.98 eV for the $O^+ + SO^+$ dissociation channel and the corresponding intercharge distance of 3.62 Å because of the Coulomb repulsion between two positive charges. The doubly charged SO_2^{2+} ion has received much attention recently by photoion-photoion coincidence (PIPICO) [4–6], photoelectron-photoion-photoion coincidence (PEPIPICO) [7–10], and the combination of a position-sensitive detector with the (PSD-PEPIPICO) [11,12] methods, one of which has realized the estimation of the KERs in the main dissociation channels of SO_2^{2+}, by analyzing these coincidence peak shapes. However, most of the studies, except for this Reference [12] have reported only the average or maximum KERs. Furthermore, the energy range of these photon impact experiments on the dissociative double photoionization of SO_2 has been limited to up to 54 eV in almost all cases. The KERDs have also been reported for other dications [13–18] by photoionization and electron impact experiments, one of which has realized vibrational resolution.

Hsieh and Eland [19] have reported continuous KERDs released in the dissociation of N_2^{2+}, CO^{2+}, O_2^{2+}, and NO^{2+}, using both the PIPICO and PEPIPICO techniques combined with a position-sensitive detector at excitation energies of 40.8 and 48.4 eV. The use of position-sensitive detection allowed the direct measurement of differential spectra of energy release. For CO^{2+}, for example, some structures have been observed in their KERD at 48.4 eV, in agreement with our previous observation [14] as far as the broad features of the KERD are concerned. Furthermore, for NO^{2+}, their KERD at 48.4 eV shows a broad structure similar to our previous observation [15]. The agreement mentioned above encouraged us to continue our effort to obtain KERDs by analyzing conventional PIPICO spectra. Eland's group [12] has also reported KERDs for the dissociation channels $O^+ + SO^+$, $S^+ + O_2^+$, and $O^+ + S^+ + O$ from SO_2^{2+} using the same method at two excitation energies, 40.8 and 48.4 eV, which should be compared with the present results. Here it should be noted that there exist no data of KERDs in this wide range (37–130 eV) of excitation energies. Energies of low-lying electronic states of SO_2^{2+} have been studied both experimentally with double-charge transfer (DCT) spectroscopy [20] and Auger electron spectroscopy (AES) [21] and theoretically [4,19,22].

This study reports the KERDs of the ion pairs, $O^+ + SO^+$ and $O^+ + S^+$, produced on dissociative double ionization of sulfur dioxide by 37–130-eV photons. Computer simulations have been carried out for the PIPICO peak shapes resulting from the dissociation of SO_2^{2+} with given values of KER. These values are optimized to reproduce the measured peak shapes with an appropriate number of KER components.

2. Experimental

PIPICO spectra were measured in the region of 37–130 eV by the use of a time-of-flight (TOF) mass spectrometer and a constant-deviation grazing incident monochromator together with synchrotron radiation at the Ultraviolet Synchrotron Orbital Radiation (UVSOR) facility of the Institute for Molecular Science (IMS) in Okazaki. The details of the TOF mass spectrometer and of the associated electronic apparatus used in the present experiments have been described elsewhere [23–25]. The photoion signals detected by a microchannel plate were fed into both the start and stop inputs of a time-to-amplitude converter (TAC).

The monochromatized photon beam was focused to the ionization region by means of a toroidal mirror. Aluminum optical filters were used to eliminate higher-order radiation. The PIPICO spectra were measured at an angle of ~55° with respect to the polarization vector of incident light where the second-order Legendre polynomial is close to zero, thus minimizing any effects of anisotropic angular distribution of fragment ions. The TOF mass spectrometer employs a drift tube of adjustable length. In this study, two experimental conditions were used: (a) a high electric field (2250 V/cm) applied to the ionization region and a 20-cm drift tube to provide efficient detection of energetic ion pairs; and (b) a 1000 V/cm field and a 60-cm drift tube to differentiate energetic ion pairs. In the first case, all KER components contribute almost equally to the PIPICO spectrum over the entire spectral region, whereas in the second, low-energy components contribute only to the central part of the spectrum and high-energy components to the outer parts of the spectrum [17]. A comparison of the KERDs obtained under these two different conditions showed that low-energy components were overemphasized in the second case. This is because the central part of the spectrum is simulated only by low-energy components, as mentioned above. For this reason, the results obtained in the first case are believed to be more reliable and will be presented in section 4.

3. Data analysis

The method for data analysis has been described previously [14–17] and is briefly summarized here. For a single value of energy release K_0 the width of a PIPICO spectrum (w) is given by

$$w = 2\sqrt{2\mu K_0}/(qE), \qquad (1)$$

where μ is the reduced mass, E is the electric field, and q is the ionic charge. In previous papers [14,15,17] a factor of 2 in Eq. (1) was replaced with 4 by mistake. Because all experimental conditions that affect the shapes of the PIPICO spectra are well defined, the KERDs are obtained by analyzing the PIPICO spectra measured at the pseudomagic angle, which is approximately equal to 55°, under the assumption that the degree of polarization of the photon beam is equal to 0.9 [16].

The analysis of the spectral profiles of the PIPICO peaks makes use of a least-squares fit of simulated profiles obtained by an ion-trajectory calculation to those measured. The program uses an initial estimate for the KER components, then runs automatically and requires few input parameters such as the measured peak profiles, the masses of ionic fragments, and the experimental conditions (the electric fields across the ionization and acceleration regions, the geometry of the TOF mass spectrometer, the effective size of the ion detector, and the size of the photon beam). A typical example of our fitting to a PIPICO peak is shown in Fig. 1. To obtain a smooth KERD, the four sets of kinetic energies were used in the simulation with one set in each simulation [14,15]. Because the energy resolution attained by this analysis is rather broad, only the broad features of the KERD can be elucidated.

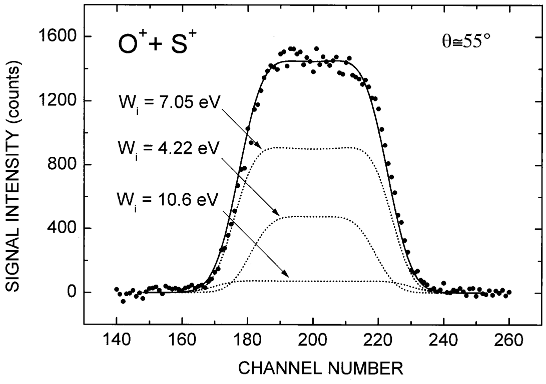

Fig. 1. Observed (dots) and simulated (solid line) PIPICO spectral profiles of $O^+ + S^+$ produced from SO_2^{2+} at 60 eV. The simulated profiles are shown with dotted lines for the set of kinetic energies, 4.22, 7.05, 10.6 eV (set A). The 200 channel has been set at the center of the peak.

The meaning of the KERDs determined in the present analysis depends on the dissociation mechanism, which can be clarified by PEPIPICO [7–10] and PSD-PEPIPICO [11,12] experiments. The KER determined in the present analysis (K_{exp}) for the two-body dissociation ($O^+ + SO^+$) represents the total KER. For the three-body dissociation ($O^+ + S^+ + O$), the dissociation mechanism has been assigned to concerted explosion. Concerted reactions have been defined as those in which two bonds break within one vibrational period of each other, that is, very fast reactions occurring in the zone of charge exchange [26]. However, recent studies by PSD-PEPIPICO method [11,12] showed that the dissociation dynamics are more complicated than assumed in the prototype mechanism of concerted explosion. This issue will be discussed in section 4.2.

4. Results and Discussion

Two dissociation channels of SO_2^{2+}, $O^+ + SO^+$ and $O^+ + S^+ + O$, are observed in the PIPICO spectra. The former is dominant below 50 eV, whereas the latter is more intense above 50 eV in the PIPICO branching ratios [6].

4.1. $O^+ + SO^+$ channel

The double photoionization energy of SO_2 is at 34.0 ± 0.2 eV as measured by the TPEsCO technique [27]. The threshold for the $O^+ + SO^+$ formation has been reported to be 34.0 ± 0.5 [10] or 34.1 ± 0.4 eV [4]. Hsieh and Eland [12] have measured the KERDs at 40.8 and 48.4 eV. The present KERDs close to these energies (41 and 48 eV) are qualitatively in good agreement with their observation, particularly if one considers that the present minimum and maximum KERs were obtained by linear extrapolation of the intensities at the innermost and outermost two energy points, respectively.

The average KER in this channel at 39 eV is 4.7 eV (with 2.8 eV FWHM), which is in good agreement with the 4.7 eV at 38 eV reported by Dujardin et al. [4] and 4.7 eV (with 1.6 eV FWHM) at 40.8 eV reported by Curtis and Eland [5]. At the lowest excitation energy, 37 eV, the minimum (2.4 eV), average (4.8 eV), and maximum (7.6 eV) KERs were observed. The maximum KER corresponds to hν (37 eV) minus the lowest dissociation limit (LDL) of SO_2^{2+} at 29.52 eV. The results show that the KERDs and the minimum, average, and maximum KERs do not change appreciably but remain almost constant across this broad range of excitation energies (37–130 eV). It is concluded from the results that this dissociation process mainly proceeds from low-lying states of SO_2^{2+} below 37 eV. The mean energy of dications that fragment to $O^+ + SO^+$ have been obtained as 35.1 ± 0.3 eV from the coincident photoelectron spectrum at an excitation energy of 40.8 eV by Field and Eland [10]. From the small gap between this mean energy and the threshold for double ionization (~1 eV), they concluded that formation of $O^+ + SO^+$ is mostly because of dication states within 2 eV of the double ionization threshold, in agreement with the present conclusion. Estimating a mean internal energy of the ionic fragments, they also concluded that dication states below 36 eV dissociate to ground state products and that only a fraction of fragmentations can be formed in electronically excited states.

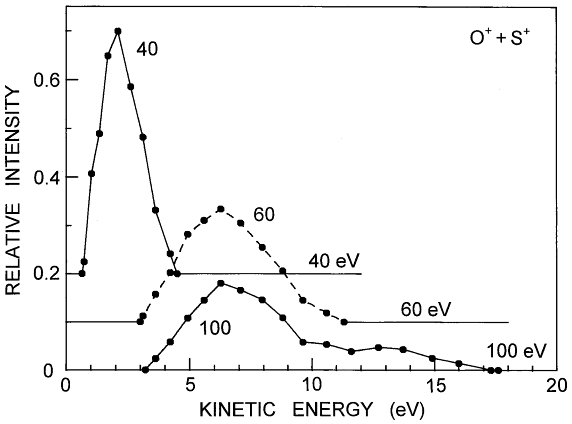

Fig. 2. Kinetic-energy release distribution in the $O^+ + S^+$ channel of SO_2^{2+} at excitation energies of 40, 60 and 100eV. Note that the distributions indicate lower limits for this channel because the kinetic energy of the neutral O atom is not involved.

If it is assumed that the observed KERs for two-body dissociation are simply because of Coulomb repulsion between two positive charges, it is possible to estimate the intercharge distances necessary to produce the observed KERs [3]. Here the intercharge distance is the distance between the centers of density of the charge distribution on the two separating product ions. The intercharge distances for the minimum, average, and maximum KERs at 37 eV are 6.0, 3.0, and 1.9 Å, respectively.

4.2. $O^+ + S^+ + O$ channel (three-body dissociation)

The threshold for this channel is at 37.7 ± 0.5 eV [6], and the KERDs for this channel are shown in Fig. 2. The results shown in the figure represent the KERs of the two ionic fragments projected on the TOF axis. The kinetic energy of the neutral O is unknown. In contrast to the $O^+ + SO^+$ channel, the KERD in this channel changes drastically between 40 and 60 eV. At 60 eV, the distribution shifts toward the higher-energy side and becomes much wider compared with the one at 40 eV. At 100 eV, although the main broad peak is

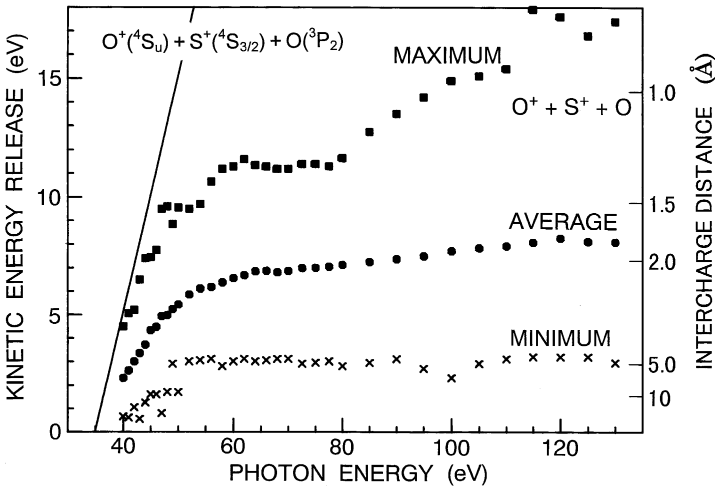

Fig. 3. Minimum, average, and maximum kinetic energy releases in the O^+ + S^+ channel of SO_2^{2+} as a function of excitation energy.

similar to the one at 60 eV, a long tail extends to the higher-energy side.

The minimum, average, and maximum KERs are shown in Fig. 3 as a function of excitation energy. The LDL of this channel, O^+ (^4S_u) + S^+ (^4S_u) + O(^3P_g), is at 34.95 eV [4]. The maximum KER of O^+ + S^+ expected at the threshold is 2.7 eV (=37.7–34.95 eV) and 15 eV at 50 eV, as indicated by a slanted straight line in the figure. The maximum KER observed at the lowest excitation energy (40 eV) lies closely on the straight line, indicating that it is given by $h\nu$ (=40 eV) minus the LDL (34.95 eV). The average KER in this channel increases considerably at the low excitation energies up to ~60 eV and then increases gradually above 60 eV. This behavior exhibits a sharp contrast to the results for the O^+ + SO^+ channel. At the lowest excitation energy, the average, minimum, and maximum KERs are smaller than those in the O^+ + SO^+ channel. As the excitation energy increases, the KERD becomes wider and wider, extending up to ~17.4 eV at a photon energy of 130 eV. The observed features that the KERs increase with increasing excitation energy indicate that high-lying electronic states participate in the excitation and dissociation and that these states dissociate preferentially to O^+ + S^+ + O. However, the increase of the KER is not as large as the increase in the excitation energy. This implies that high-lying dication states dissociating into O^+ + S^+ + O result in O^{+*}, S^{+*}, and/or O* with higher levels of excitation and with larger KER than those resulting from low-lying states. In other words, potential-energy surfaces of high-lying states are steeper and more repulsive than those of low-lying states.

Recently, the KERDs in this channel have been measured by Hsieh and Eland [12], using the PSD-PEPIPICO method at 40.8 and 48.4 eV. Their distributions are considerably broader than the present ones. This is because their KERDs represent the total energy releases of O^+ + S^+ + O, whereas the present ones express the KERs of O^+ + S^+ projected on the TOF axis, and the KERs of the neutral O are not included. Their Newton diagrams show that O^+ and O have a similar velocity–vector distribution in opposite directions in the polar plot, which means that the neutral O has a considerable amount of KER. However, their distributions, KER + E_{products} (Fig. 2 of reference [12]), well exceeds the excitation energies at both 40.8 and 48.4 eV. They assumed that the products are formed in the ground states. It should be pointed out that the maximum of the distribution should not exceed the excitation energy in both cases. I asked the authors [12] of this issue about, and one of their replies was that their data collection and reduction was such that a three-body reaction with a single

KER would appear broadened by as much as 1.6 eV and that, because of the experimental uncertainty (which was not mentioned clearly in the paper), obtaining minimum and maximum KER values from their data was not meaningful. (S. Hsieh, personal communication).

As for the dissociation mechanism, Hsieh and Eland [12] analyzed their results in terms of both sequential and concerted bond-breaking mechanisms from dications that were assumed to be formed by vertical double-ionization processes. Although each mechanism can explain selected parts of the data, none can explain the full set of data unless indirect double ionization is taken into account. Hsieh and Eland [12] arrived at one common feature: the best-fitting model involves asymmetric fast bond extension and bond breaking, all within a period of the order of 100 fs, followed by an explosion dominated by Coulomb forces. "The only satisfactory model for full set of data comes from using the charge-exchange model of synchronous dissociation starting at a range of asymmetric initial geometries outside the normal Franck-Condon region. The model is interpreted as formation of the dications by indirect double ionization via an intermediate molecular species which starts to dissociate asymmetrically before becoming doubly ionized." [12, p. 4533].

The estimated intercharge distances are shown in Fig. 3 by assuming simple Coulomb repulsion. It should be noted that as the average KERs in the $O^+ + S^+ + O$ channel are larger than those in the $O^+ + SO^+$ channel above 50 eV, the intercharge distance for the $O^+ + S^+ + O$ dissociation is smaller than that for the $O^+ + SO^+$ dissociation. This means that the ejection of more inner-valence electrons is related to the $O^+ + S^+ + O$ dissociation above 50 eV. Furthermore, the estimated intercharge distances in the three-body dissociation are large and deviate significantly from the equilibrium internuclear distance ($R_{OS} = 1.43$ Å) of the neutral SO_2, which is not possible by direct vertical double ionization and which inevitably suggests the important contribution of indirect processes, in agreement with the conclusion of reference [12]. Note that indirect double-ionization processes may populate dication states far outside the vertical Franck-Condon region.

As triple photoionization is energetically possible above ~80 eV, as observed for carbon monoxide [28] and carbonyl sulfide [29], the increase in the maximum KER above 80 eV may be attributed to the triple photoionization. In this case, as triple photoionization is a very weak process compared with double photoionization, the average KER is not affected appreciably by triple photoionization.

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