Ionic photofragmentation of SO_2 in the sulfur 2p and 2s regions

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Available online 17 February 2005

Abstract

Ionic photofragmentation of SO_2 in the sulfur 2p and 2s regions has been investigated using monochromatic synchrotron radiation. Multi-stop time-of-flight mass spectrometry was used to collect photoelectron–photoion coincidence (PEPICO), photoion–photoion coincidence (PIPICO) and photoelectron–photoion–photoion coincidence (PEPIPICO) spectra simultaneously. Partial ion yields and partial ion-pair yields have been determined. Dissociation mechanisms of the productions of ion-pairs O^+-S^+ and O^+-SO^+ have been discussed briefly.
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Keywords: Photofragmentation; Coincidence; Time-of-flight; Ion yield; Ion-pair yield

1. Introduction

Molecular photofragmentations have been widely studied by many of experimental techniques because of their importance in fundamental sciences, as well as environmental and astronomical sciences [1]. In recent years, many photoionization and photofragmentation studies have been carried out on molecule SO_2 in the vacuum ultraviolet (VUV) region (i.e., the valence-shell region) using coincidence spectroscopies, such as photoelectron–photoion coincidence (PEPICO) [2,3], photoion–photoion coincidence (PIPICO) [4–8], and photoelectron–photoion–photoion coincidence (PEPIPICO) [9–12]. However, relatively little photofragmentation work has been performed in the higher energy (soft X-ray) inner-shell regions.

Around the S 2p edge, a study of the three-body dissociation of SO_2^{3+} has been reported by Lavollée and Brems [13]. A near-edge threshold PEPIPICO study of SO_2 has been published by Fisher et al. [14] around both S 2p and O 1s edges. In addition, ion yield measurements have been reported at limited energies in the S 2p and 2s regions [15] and near the S 1s edge [16].

In the present work, we report an ionic photofragmentation study of SO_2 throughout the whole region of the S 2p and 2s L-shells using monochromatic synchrotron radiation. Multi-stop time-of-flight mass spectrometry was used to collect PEPICO, PIPICO and PEPIPICO spectra simultaneously. Partial ion yields and partial ion-pair yields have been determined. Dissociation mechanisms of the productions of ion-pairs O^+-S^+ and O^+-SO^+ have been discussed briefly.

2. Experimental

The experiments were conducted at the Canadian Synchrotron Radiation Facility (CSRF) at the Synchrotron Radiation Centre (SRC) in Stoughton, Wisconsin. All the measurements in the present work were performed using the CSRF Grasshopper beamline. Photon energies from 152 to 244 eV were selected by an 1800 line/mm plane grating providing 0.07 Å resolution with slits set at 25 μm [17,18]. The energy scale has been calibrated using the SO_2 $2p \rightarrow 3b_1$ and $2s \rightarrow 6b_2$ resonance lines at 164.57 and 233.65 eV, respectively [19].

The detailed description of the multi-coincidence time-of-flight (TOF) apparatus employed in this work can be found elsewhere [20]. Briefly, it consists of a time-of-flight mass spectrometer and an electron detector mounted opposite one

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another and perpendicular to the incident photon beam. An effusive gas jet is mounted mutually perpendicular to the photon beam and the TOF. A static electric field was used to extract electrons and ions from the ionization region and direct the charged particles towards the appropriate detectors. The remainder of the TOF voltages were chosen to meet Wiley-McLaren space-focusing condition [21], so that ions of identical mass/charge ratio will have approximately the same flight time regardless of where they are produced in the ionization region. The flight time is determined with a multi-stop time-to-digital converter (TDC) for each ion associated with start photoelectron signal. The use of multi-coincidence techniques enables the produce of PEPICO, PEPIPICO and PIPICO spectra easily and simultaneously.

The sample of SO_2 was obtained commercially and used without further purification.

3. Results and discussion

3.1. PEPICO and PIPICO spectra

The time-of-flight spectra have been measured at a series of photon energies from 152 to 244 eV. Fig. 1 shows the typical TOF spectra measured at 197 eV using 400 V/cm extraction field. Seven peaks exist clearly in the spectra (see bottom panel in Fig. 1) and they are assigned as O^{2+}, S^{3+},

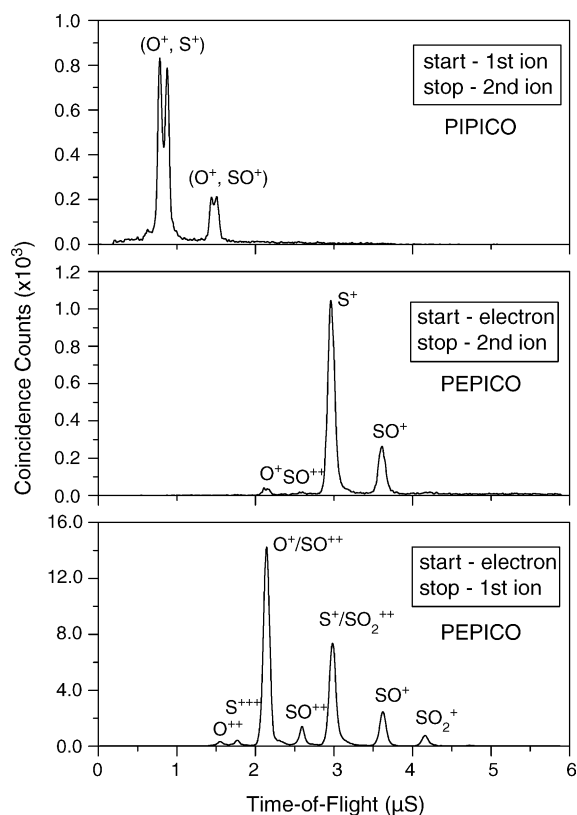O^+/S^{2+}, SO^{2+}, S^+/SO_2^{2+}, SO^+ and SO_2^+, respectively. The time correlation between the first and second ion stops gives PIPICO spectra, which are shown in top panel of Fig. 1. Two groups of ion-pairs, O^+–S^+ and O^+–SO^+, are observed. The peak split is obviously seen in the PIPICO spectra, and this is due to the different initial directions of motion of the ionic fragments. It provides the kinetic energy information about the ionic fragments.

3.2. Partial ion yield spectra

Fig. 2 gives the partial ion yield spectra using high extraction field (400 V/cm) obtained by measuring a series of TOF spectra while scanning the photon energy. The molecular ion SO_2^+ shows, generally, a very flat ion yield distribution. Below the S 2p edges, the ion yield curve of SO_2^+ decreases slightly as the photon energy increases. This is because the contribution in this region is only due to the valence shell. The ion yield curves of all other ion fragments (SO^+, S^+/SO_2^{2+}, SO^{2+}, O^+/S^{2+}, S^{3+} and O^{2+}) show generally similar features. Some below-edge discrete features contribute more to the ion yields in the case where singly charged ion fragments (SO^+, S^+ and O^+) are involved. It appears that the $3b_1$ and $3\underline{b}_1$ contributions (around ~165 eV) to the ion yields of multiply charged ion fragments (SO^{2+}, S^{3+} and O^{2+}) are negligible.

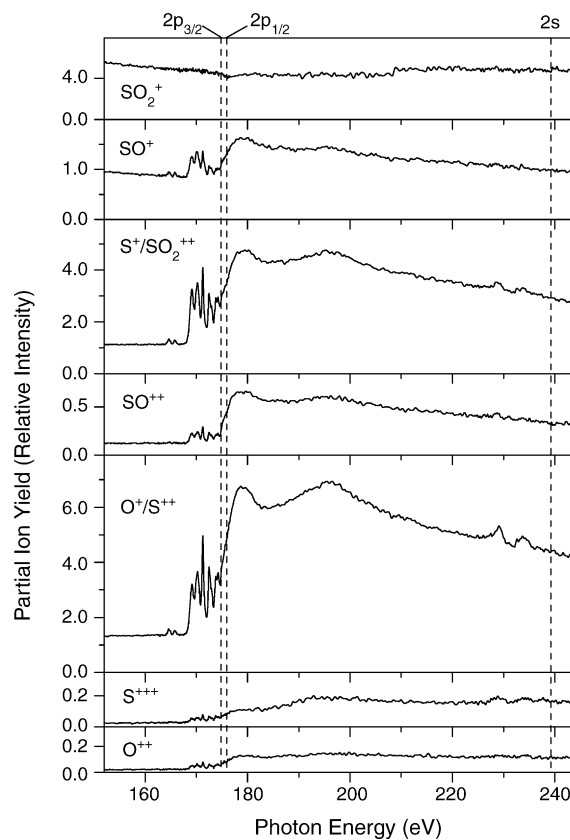Fig. 1. TOF spectra measured at 197 eV using an extraction field of 400 V/cm.

Fig. 2. Partial ion yield spectra obtained using an extraction field of 400 V/cm. The dashed vertical lines indicate the ionization limits of S 2p and 2s.
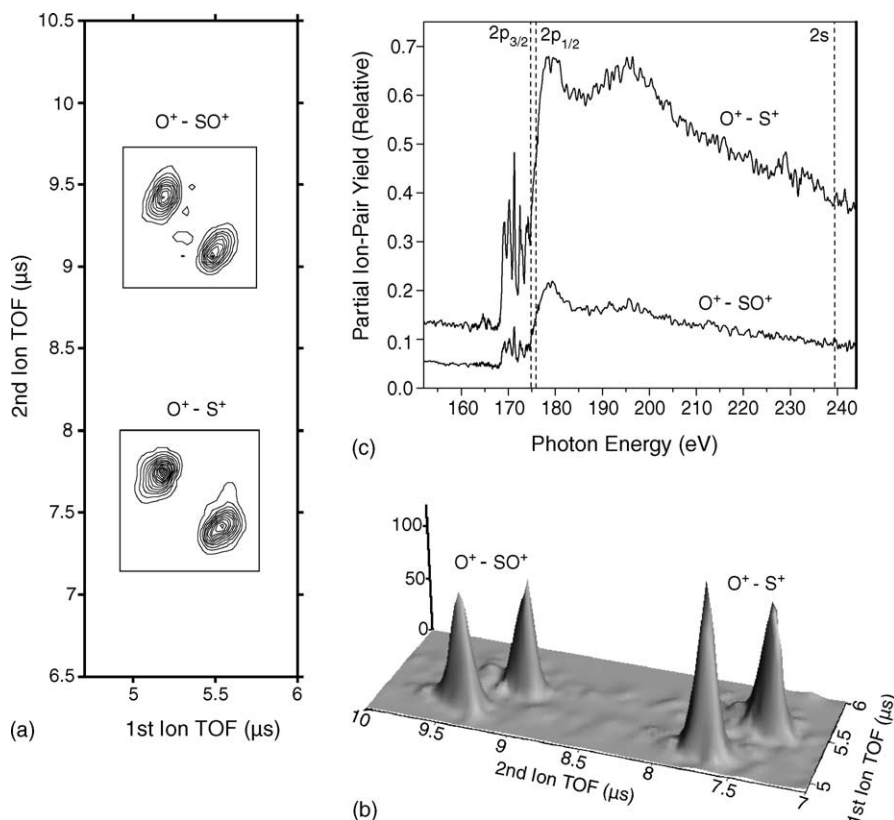
Fig. 3. PEPIPICO coincidence maps and partial ion-pair yield spectra: (a) two-dimensional contour plot, and (b) three-dimensional TOF image, at 178.5 eV obtained using a lower extraction field of 50 V/cm; (c) partial ion-pair yield spectra obtained using an extraction field of 400 V/cm. The dashed vertical lines in (c) indicate the ionization limits of S 2p and 2s. The peaks and their positions in (a) and (b) show the existence of two groups of ion-pairs O^+-SO^+ and O^+-S^+.

This may suggest that the neutrally excited SO_2 molecule dissociates mainly to singly charged ion fragments.

In addition to the partial ion yields given above, absolute partial cross-sections (oscillator strengths) for all the ion fragments could be determined by normalizing the present work to the absolute total absorption oscillator strengths reported earlier [1].

3.3. PEPIPICO spectra

The multi-coincidence technique used in the present work provides easy and simultaneous production of PEPICO, PEPIPICO and PIPICO spectra. Fig. 3(a) and (b) illustrate the typical PEPIPICO coincidence maps at 178.5 eV using the lower extraction field of 50 V/cm. Fig. 3(a) is presented as a two-dimensional contour plot (left panel), which shows the ion-pair productions of O^+-S^+ and O^+-SO^+ and the orientation of two peaks from each ion-pair. The peak at the upper left of each ion-pair in this contour plot arises from events in which the lighter ion (O^+) flies directly towards the TOF tube and the heavier ion (S^+ or SO^+) flies directly away, while the peak at the lower right corresponds to the opposite process. It can also be seen that the O^+-SO^+ ion-pair signal is aligned along the −1 slope line as is required for a two-body dissociation. The orientation (slope close to −1) and line shape of the O^+-S^+ ion-pair signal suggest that these

ion-pairs are produced in concerted dissociative processes, with most of the kinetic energy taken by these two ions.

In addition to the above, Fig. 3(b) gives a three-dimensional TOF image (right bottom panel) showing the co-incidence peak shapes and relative intensities of the ion-pair O^+-S^+ and O^+-SO^+. Detailed kinetic energy releases of each of the ion fragments can be derived from these PEPIPICO coincidence maps and will be reported later.

3.4. Partial ion-pair yield spectra

Fig. 3(c) shows the partial ion-pair yield spectra (which can be determined from either PIPICO or PEPIPICO spectra) of O^+-SO^+ and O^+-S^+ (right top panel) using an extraction field of 400 V/cm. The uncertainty in this case was estimated to be ∼10%. It is clear that the yields of ion-pair O^+-S^+ are much higher than those of O^+-SO^+. However, they show generally similar features except for some very small below-edge discrete features around ∼165 eV ($2p \rightarrow 3b_1$ and $3\underline{b}_1$).

Acknowledgements

References

[1] R. Feng, G. Cooper, G.R. Burton, C.E. Brion, L. Avaldi, Chem. Phys. 240 (1999) 371.

[2] T. Masuoka, Y. Chung, E. Lee, J.A.R. Samson, J. Chem. Phys. 109 (1998) 2246.

[3] T.A. Field, J.H.D. Eland, Int. J. Mass Spectrom. 192 (1999) 281.

[4] G. Dujardin, S. Leach, O. Dutuit, P. Guyon, M. Richard-Viard, Chem. Phys. 88 (1984) 339.

[5] D.M. Curtis, J.H.D. Eland, Int. J. Mass Spectrom. Ion Process. 63 (1985) 241.

[6] T. Masuoka, A. Kobatashi, J. Chem. Phys. 113 (2000) 6634.

[7] T. Masuoka, J. Chem. Phys. 115 (2001) 264.

[8] T. Masuoka, Int. J. Mass Spectrom. 209 (2001) 125.

[9] J.H.D. Eland, F.S. Wort, R.N. Royds, J. Electron Spectrosc. Relat. Phenom. 41 (1986) 297.

[10] J.H.D. Eland, Mol. Phys. 61 (1987) 725.

[11] T. Masuoka, J. Chem. Phys. 98 (1993) 6989.

[12] S. Hsieh, J.H.D. Eland, J. Phys. B: At. Mol. Opt. Phys. 30 (1997) 4515.

[13] M. Lavollée, V. Brems, J. Chem. Phys. 110 (1999) 918.

[14] B.O. Fisher, M.K. Thomas, P.A. Hatherly, K. Codling, M. Stankiewicz, A. Karawajczyk, M. Roper, J. Phys. B: At. Mol. Opt. Phys. 32 (1999) 4437.

[15] G. Cooper, E.B. Zarate, R.K. Jones, C.E. Brion, Chem. Phys. 150 (1991) 251.

[16] J. Adachi, Y. Takata, N. Kosugi, E. Shigemasa, A. Yagishiya, Y. Kitajima, Chem. Phys. Lett. 294 (1998) 559.

[17] Z.F. Liu, G.M. Bancroft, J.N. Cutler, D.G. Sutherland, K.H. Tan, J.S. Tse, R.G. Cavell, Phys. Rev. A 46 (1992) 1688.

[18] K.H. Tan, G.M. Bancroft, L.L. Coatsworth, B.W. Yates, Can. J. Phys. 60 (1982) 131.

[19] K.-H. Sze, C.E. Brion, X.-M. Tong, J.-M. Li, Chem. Phys. 115 (1987) 433.

[20] A.P. Hitchcock, J.J. Neville, in: T.K. Sham (Ed.), Chemical Applications of Synchrotron Radiation, World Scientific, 2002, p. 154 (Chapter 4).

[21] W.C. Wiley, I.H. McLaren, Rev. Sci. Instrum. 26 (1955) 1150.