Negative-Fragment-Ion Formation by Photon Excitation of Molecules in the Vicinity of Their Core-Ionization and Direct-Double-Ionization Thresholds

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By using SO_2 as a prototype molecule, negative fragment ions are produced by photon excitation in the vicinity of its sulfur $2p$ core-ionization ($\simeq 175$ eV) and direct-double-ionization ($\simeq 34.1$ eV) thresholds. This new class of processes is shown to be at least partly related to the existence of superexcited electronic states of the singly charged parent cation lying above the double-ionization-threshold energy. The use of these mechanisms as a specific tool for probing the nature and the relaxation of core-excited states of molecules is also illustrated.

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Processes induced by photon impact on a molecule in the energy region of core excitation and of direct double photoionization are receiving considerable attention.[1-5] The spectroscopic and dynamic properties of core-excited molecules in which a core electron has been promoted to a valence or Rydberg unoccupied molecular orbital are of special interest since the recent advent of the so-called site-specific fragmentation studies of molecules.[1-5] Although a complete understanding of the involved mechanisms is far from being achieved, it was shown[3,4] that doubly charged molecular parent cations could play an important role as intermediate species in these fragmentation processes. The fragment ions observed in these previous studies are exclusively positive ions since it was implicitly assumed that only singly or multiply charged cations or neutral fragments could be produced by soft-x-ray photoabsorption.

The aim of this paper is to demonstrate that negative fragment ions can also be produced by core photoexcitation as well as that in the vicinity of the direct-double-photoionization threshold. These results will be shown to imply the existence of superexcited states of molecular cations which have never been observed so far. As an important consequence, we will also point out the specific interest of negative-ion mass spectrometry for studying core-excited states of molecules.

The SO_2 molecule is chosen as an example because of experimental convenience. It is indeed possible to explore the energy region of sulfur $2p$ core ionization ($\simeq 175$ eV)[6] and that of double photoionization ($\simeq 34$ eV)[7] by using the same synchrotron-radiation beam line of ACO (Orsay's storage ring) equipped with two interchangeable gratings of 450 and 1200 lines/mm, respectively, and working at grazing angles. The photon intensity at 70 Å is $\simeq 10^{12}$ photons $Å^{-1}$ s^{-1} and the excitation bandpass is $\simeq 0.2$ Å. Positive or negative ions are mass selected through a Riber SQ X 156 quadrupole filter and counted as a function of the photon energy. The pressure of SO_2 can be varied from 10^{-6} up to 10^{-3} Torr. The number of detected negative ions is always very small as compared to that of positive ions. As an example, for mass 16 the relative number of negative to positive ions is at the maximum about 10^{-5} in the energy region of the sulfur $2p$ ionization of SO_2.

Similar experiments performed with other compounds, i.e., SiF_4 (in the vicinity of the silicon $2p$ ionization) and XeF_2 (in the vicinity of the xenon $4d$ ionization)[8] yield similar or smaller relative abundances of negative ions. Such small relative numbers of negative ions prevented their detection in previous experiments. In order to ensure that negative ions are produced through unimolecular processes, the negative-ion spectra are recorded at various gas pressures. It is thus checked that the current of negative ions is a linear function of the pressure and not a quadratic function as it would be the case if negative ions were produced by dissociative attachment on a molecule of electrons produced by photoionization of other molecules. Also the possible influence of negative-ion resonances[9] due to energetic electrons issued from photon impact on surfaces is ruled out by the fact that the observed resonances have exactly the same energies and widths in both negative- and positive-ion spectra. We are thus quite confident that, although with a very small intensity, the detected negative ions arise from unimolecular processes directly induced by photon impact on molecules.

Positive-ion (mass to charge ratio $m/q = 16$ and 32) and negative-ion ($m/q = -16$) spectra recorded under the same experimental excitation conditions in the energy region of the sulfur $2p$ ionization of SO_2 are shown in Fig. 1. These spectra are corrected for the variation of the photon excitation intensity as recorded from the pho-

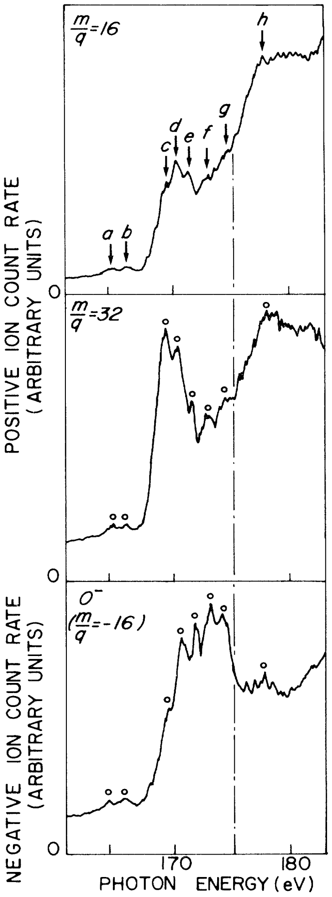

FIG. 1. Positive ($m/q=16$ and 32) and negative ($m/q=-16$) ion spectra of SO_2 (pressure $\simeq 10^{-4}$ Torr) in the vicinity of the sulfur $2p$ threshold energy (indicated by the dotted line).

toemission of a gold mesh. Negative ions with $m/q=-16$ are O^- ions, whereas positive ions with $m/q=16$ and 32 represent the contributions of (O^+,S^{++}, O_2^{++}) and (S^+,O_2^+) ions, respectively.

Before discussing the assignment of the resonances in Fig. 1 and the meaning of the dramatic changes of their relative intensities from positive- to negative-ion spectra, we will concentrate on the mechanisms for production of negative fragment ions. Until now, the only known process for negative-fragment-ion formation by photon impact on a molecule is the ion pair formation[10-12] in which highly excited Rydberg states AB^* of a neutral molecule AB are predissociated by ion pair states leading to the fragmentation into A^+ and B^-. Such neutral-molecule processes could account for the observation of resonances in the O^- spectrum of Fig. 1(c) if we assumed that the core-hole relaxation by x-ray fluorescence or the ion pair fragmentation occurs before the core-excited molecule is ionized by Auger relaxation mechanisms. However, this could not explain in any way the negative-ion continuum of Fig. 1(c) which behaves as a function of the photon energy like the positive-ion continua of Figs. 1(a) and 1(b). In order to account for the existence of this negative-ion continuum, we have to consider that some ionization channel(s) of SO_2 can also produce negative fragment ions. As a consequence, there must exist some highly excited states $(SO_2^+)^*$ of the parent ion that are predissociated by ion pair states (or directly dissociate) into $SO^{++}+O^-$. This is clearly evidenced by looking at the SO^{++} and O^- spectra recorded in the double-photoionization energy region of SO_2. A threshold energy at 35.6 ± 0.3 eV for formation of both SO^{++} and O^- is seen in the curves of Fig. 2. The formation of O^- is then most probably correlated with the formation of SO^{++} through the following process:

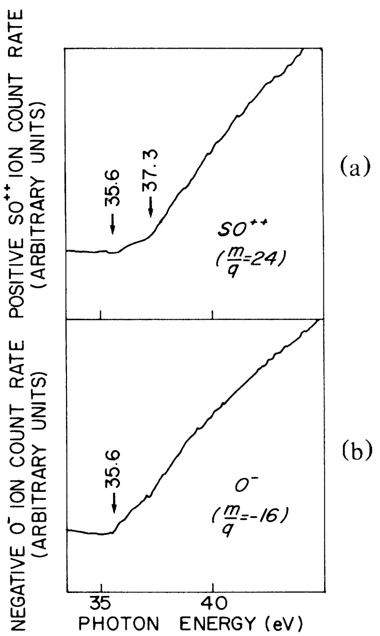

FIG. 2. SO^{++} ($m/q=24$) and O^- ($m/q=-16$) spectra of SO_2 (pressure $\simeq 10^{-4}$ Torr) in the vicinity of the double-photoionization threshold energy (34.1 eV).

$$SO_2+h\nu \rightarrow (SO_2^+)^* \rightarrow SO^{++}(^1\Sigma^+)+O^-(^2P)\,,$$

of which the thermodynamic threshold energy can be estimated to be about 33.0 eV on the basis of the previous estimation of the $SO^{++}(^1\Sigma^+)+O(^3P_g)$ threshold formation energy[7] and of the known electron affinity of $O(^3P_g)$.[13] Also, a second break appears in the SO^{++} curve of Fig. 2(a) at 37.3 ± 0.3 eV which seems to be absent in the O^- curve of Fig. 2(b). It may be related to the

$$SO_2+h\nu \rightarrow SO_2^{++} \rightarrow SO^{++}(^1\Sigma^+)+O(^3P_g)$$

reaction of which the thermodynamic threshold is estimated to be at 34.5 eV.[7] The nonzero underlying

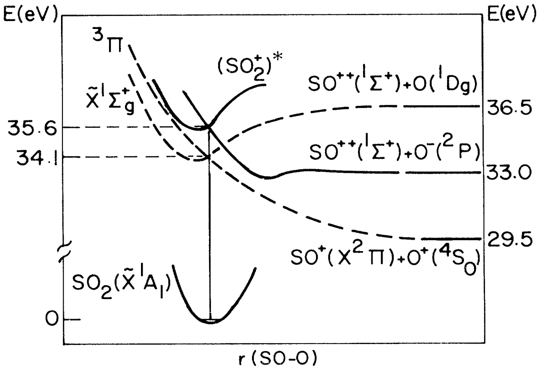

FIG. 3. Electronic-state correlation diagram for dissociation of SO_2^{++} (dotted lines) as taken from Ref. 7 and for negative-fragment-ion formation from superexcited states of SO_2^+ (full lines).

background observed in the curves of Fig. 2 is most probably due to second-order effects of the monochromator. The schematic diagram of Fig. 3 represents the mechanisms for formation of negative ions in the double-photoionization energy region via the predissociation or direct dissociation of superexcited states $(SO_2^+)^*$ of the singly charged ion. Furthermore, these mechanisms can also account for the occurrence of the resonances in the O^- spectrum of Fig. 1(c) if we consider that the resonances can decay by Auger processes to the superexcited $(SO_2^+)^*$ states. We note that the position of the crossing point of the $X^1\Sigma_g^+$ and $^3\Pi$ SO_2^{++} potential-energy curves in Fig. 3 has been confirmed by recent *ab initio* calculations and is discussed in more detail in Ref. 14.

Previous photoabsorption spectroscopic work on SO_2 by Vinogradov and Zimkina[6] and Kondratenko, Mazalov, and Neiman[15] enable us to propose in Table I the assignment of the observed resonances. The electronic configuration of SO_2 in its $\tilde{X}^1A_1$ ground state [C_{2v} point-group symmetry; $C_2(z)$ and y axis in plane as defining axes] is considered to be as follows on a single configuration basis[7]: $\ldots 6a_1^2 2b_1^2 7a_1^2 4b_2^2 5b_2^2 1a_2^2 8a_1^2$.

TABLE I. Experimental energies and assignment of the SO_2 resonances observed in the negative-ion spectrum of Fig. 1(c).

Resonance label in Fig. 1	Energy (eV)	Electronic transition
a	164.3 ± 1	$2p_{3/2} \rightarrow 3b_1$
b	165.5 ± 1	$2p_{1/2} \rightarrow 3b_1$
c	169.3 ± 0.4	$2p \rightarrow 9a_1$
d	170.4 ± 0.4	
e	171.8 ± 0.4	
f	172.7 ± 0.4	$2p_{3/2} \rightarrow 6b_2$
g	174.4 ± 0.4	$2p_{1/2} \rightarrow 6b_2$
h	178 ± 2	$2p \rightarrow 11a_1$

The three $3b_1$, $9a_1$, and $6b_2$ orbitals as calculated by Kondratenko, Mazalov, and Neiman[15] have energies below the $2p$ (sulfur) ionization energy and the $11a_1$ orbital is associated with the shape resonance above the ionization threshold. The assignment of the *c*, *d*, and *e* resonances is not yet clear. They partly correspond to the $2p \rightarrow 9a_1$ transition but also probably include some Rydberg contributions which have not been taken into account in the energy calculations of Ref. 15.

As compared to the positive-ion spectra of Figs. 1(a) and 1(b), the negative-ion spectrum of Fig. 1(c) exhibits two main features of special interest, i.e., the huge enhancement of the *f* and *g* resonances and the strong decrease of the shape resonance (*h*) intensity. Assuming that the excited electron of the resonances remains as a spectator during the Auger relaxation processes, the intensities of the resonances in the negative-ion spectrum can be considered to be associated with the ability of the excited electron to be attached to the electronegative oxygen atom. This may be related to the extent of the excited electron wave function in the vicinity of the oxygen atom. By nature the wave function associated with the shape resonance is kept away from the electronegative atom.[16] Consequently, we expect the intensity of the corresponding resonance (*h*) to be reduced in the negative-ion spectrum. This is indeed observed in Fig. 1. Furthermore, from the correlation diagrams[17] of the SO_2 molecule, the $6b_2$ orbital is believed to be mainly built from the $3s$ oxygen orbitals and then to be located around these atoms, whereas the $3b_1$ and $9a_1$ orbitals, built from the $2p$ oxygen and sulfur orbitals and from the $2s$ oxygen and sulfur orbitals, respectively, are considered to be spread over the whole SO_2 molecule. It is then remarkable that there seems to exist a strong relation between the oxygen location of the $6b_2$ orbital and the enhancement of the corresponding resonances in the O^- spectrum of Fig. 1(c). In a simplified picture the process for negative-ion formation by core excitation can be regarded as an electronic transition from a core orbital ($2p$) of sulfur into a molecular unoccupied orbital from which the electron can be attached to the electronegative oxygen atom during the fragmentation of the molecule.

The negative-fragment-ion formation that we described here is believed to be not specific to the SO_2 molecule but of general purpose. Similar studies in progress on other molecules such as SiF_4, XeF_2,[8] and CO[18] have confirmed this statement. These processes may have important consequences for core-excitation as well as for double-photoionization studies. As illustrated in the SO_2 case, negative-ion mass spectrometry appears to be a new tool for core-excitation studies in molecules. Its uses as a specific probe of resonances may be of great help particularly in identifying resonances corresponding to electronic transitions from a core orbital of a given atom into a Rydberg or valence molecular orbital concentrated around a separate electronegative atom. Such resonances, which are expected to be weak in the absorption spectra and consequently in the positive-ion spectra because of the unfavorable overlap of the wave functions, could be favored and appear as relatively strong resonances in negative-ion spectra. Furthermore, this is the first observation of superexcited states of singly charged molecular ions lying above the double-photoionization threshold energy. The existence of these states, which have been ignored until now, may be of crucial interest in double-photoionization studies since they may not only dissociate into negative ions but also autoionize into doubly charged ions giving rise to new indirect double-photoionization processes.

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