Satellite excitations due to internal inelastic scattering in the K-shell photoemission from CO_2

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Abstract

The O and C 1s photoelectron satellites for the CO_2 molecule fixed in space parallel to the electric vector of the incident radiation E are found to be more intense, in general, than those perpendicular to E and are enhanced at the photon energy in the vicinity of the shape resonance for the single-hole ionization cross section. This suggests that the excitation of the valence electron may be caused by the internal inelastic scattering of a primary 1s photoelectron with a valence electron.
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1. Introduction

K-shell absorption spectra of small molecules often exhibit resonances above the ionization threshold, described as the transitions of the 1s electron to an unoccupied molecular valence-like orbital [1]. These resonances are often called shape resonances, and can also be viewed as a temporary trap of a photoelectron by the molecular potential [2,3]. The general description of the shape resonance phenomena is based on the independent particle approximation [1–4].

Recent K-shell photoemission studies [4–7] have revealed that the satellite excitations are significant in the near-threshold regions where the shape resonances are often located. Two-electron transitions responsible for the satellite excitations have so far been interpreted as results of shake-up: the core-hole creation changes the potential for valence electrons and thus they are no longer in an eigenstate and relax via a monopole transition [8–10]. The shake-up

processes are generally classified into direct shake-up and conjugate shake-up [9,10]. In the direct shake-up process, the dipole ionization of the core electron is accompanied by the monopole excitation of the valence electron. In the conjugate shake-up process, the dipole excitation of the core electron to an unoccupied molecular orbital is accompanied by the monopole ionization of the valence electron. Though the direct shake-up excitations dominate in the satellite spectra when the photon energy is much higher than the ionization threshold, their intensity drops when the photon energy approaches the threshold energy [8–10]. In contrast to the direct shake-up process, the conjugate shake-up process is minor for high-energy photoemission and becomes important in the threshold region [9,10].

In the case of atomic two-electron excitation and ionization, however, the contribution from internal inelastic scattering of the primary photoelectron by the valence electron (see, for example, [11]), often called two-step process (see, for example, [12]), is as significant as shake-up in the threshold region. A well-known example may be the 4d photoionization of the Xe atom [11,13]. It is well known that

both internal elastic and inelastic scattering of a 4d primary photoelectron with an outer valence electron play an essential role in the description of the atomic shape resonance in the 4d photoionization. The shape resonance in this class is called the giant resonance because the independent-particle description of the resonance does not hold any more (see, for example, [11,13].) Thus, it seems reasonable to consider that internal inelastic scattering of a primary photoelectron with a valence electron may play an important role in the two-electron transitions in the molecular shape resonance region [14,15].

In the present paper, we report experimental evidence that the internal inelastic scattering plays an essential role in the satellite excitations in the molecular shape resonance regions of the single-hole ionization (SHI) cross-sections, using a specific example, O and C 1s photoemission of CO_2. We discuss also assignments of the satellite bands referring to the internal inelastic scattering mechanism. A part of the experimental results can be seen in reference [15].

2. Experimental

The electronic configuration of the CO_2 molecules is

$$1\sigma_g^2\, 1\sigma_u^2\, 2\sigma_g^2\, 3\sigma_g^2\, 2\sigma_u^2\, 4\sigma_g^2\, 3\sigma_u^2\, 1\sigma_u^4\, 1\sigma_g^4(^1\Sigma_g);\; 2\pi_u^0\, 5\sigma_g^0\, 4\sigma_u^0,$$

where $1\sigma_g$ and $1\sigma_u$ are the symmetry-adopted O 1s orbitals and $2\sigma_g$ is the C 1s orbital. The lowest unoccupied orbital is $2\pi_u$.

The direct shake-up transition consists of the dipole ionization of a core electron ($1\sigma_g$, $2\sigma_g \rightarrow \varepsilon\sigma_u$, $\varepsilon\pi_u$, or $1\sigma_u \rightarrow \varepsilon\sigma_g$, $\varepsilon\pi_g$) and the monopole excitation of a valence electron ($1\pi_u \rightarrow 2\pi_u$; note that $3\sigma_u \rightarrow 2\pi_u$ and $1\pi_g \rightarrow 2\pi_u$ are monopole forbidden). Thus the direct shake-up can be both parallel ($\Sigma_g \rightarrow \Sigma_u$) and perpendicular ($\Sigma_g \rightarrow \Pi_u$) transitions in which the dipole moment is parallel and perpendicular, respectively, to the polarization vector of incident radiation E. Here Σ_g is the symmetry of the ground state and Σ_u and Π_u are the symmetry of the continuum state consisting of the core-ionized molecule and the satellite photoelectron. The direct shake-up satellite exhibits the shape resonance at about the same kinetic energy as that of the mainline [10].

The conjugate shake-up, on the other hand, predominantly consists of the dipole excitation of a core electron ($1\sigma_g$, $2\sigma_g \rightarrow 2\pi_u$) and the monopole ionization of a valence electron ($4\sigma_g \rightarrow \varepsilon\sigma_g$, $3\sigma_u \rightarrow \varepsilon\sigma_u$, $1\pi_u \rightarrow \varepsilon\pi_u$, $1\pi_g \rightarrow \varepsilon\pi_g$). The conjugate shake-up is therefore predominantly a perpendicular transition ($\Sigma_g \rightarrow \Pi_u$). As a result, the transition occurs mainly for the molecules perpendicular to the direction of polarization.

In contrast, the internal inelastic scattering mechanism causes the satellite excitations whose strength are roughly proportional to the SHI cross section and thus the satellite excitations are enhanced by the shape resonance of the SHI cross-section, the enhancement of the satellites and the mainline occurs at about the same photon energy. In addition, the satellite excitations due to internal inelastic scattering are expected to be stronger for the parallel transition in which the primary photoelectron is driven mainly along the molecular axis [16,17].

In consequence, one should be able to identify the excitation mechanisms of the satellites by resolving the transition symmetry ($\Sigma_g \rightarrow \Sigma_u$ or $\Sigma_g \rightarrow \Pi_u$) of the satellite excitations and by observing them as functions of photon energy.

We have investigated satellite spectra accompanying the O and C 1s mainline of CO_2 at photon energies across the $4\sigma_u$ shape resonances, centred at $\approx$559 and $\approx$310 eV in the O 1s and C 1s absorption spectra, respectively. To record photoelectron spectra of CO_2 whose molecular axis is parallel or perpendicular to E, we use the coincidence detection between the photoelectron and the fragment ions [15–20]. With this technique, we selectively probe the satellite excitations for either the parallel or perpendicular transition, respectively.

The experiments are performed on the undulator beamline 27SU at SPring-8 [21,22]. A supersonic beam of CO_2 is introduced in the source point, where it crosses perpendicularly the photon beam. Electrons and ions are extracted by a static electric field. Ions are detected by a micro-channel-plate (MCP) detector fitted to a two-dimensional (2D) multi-hit readout delay-line anode (Roentdek RD-80 [23]) at one end of the acceleration region. At the opposite side, electrons enter a time of flight (TOF) tube and at its end reach the second MCP detector fitted to another 2D multi-hit readout delay-line anode (Roentdek HEX-80 [23]). A magnetic field parallel to the TOF axis is applied, in order to confine the electrons within the spectrometer. The particles detected are registered in coincidence. From the measured TOF and position of detection, the momentum vector of each particle is extracted. The TOF axis is perpendicular to the photon beam and the molecular beam.

To extract the photoelectron spectra for the parallel and perpendicular transitions from the coincidence data, we count electrons emitted in the "reaction plane" perpendicular to the TOF axis, with an acceptance of $\pm40°$. The parallel transition is selected in such a way that the angle between the direction between E and the molecular axis determined by the linear momenta of the O^+ and CO^+ ions, measured in coincidence, is smaller than $20°$. The perpendicular transition is selected in such a way that the direction of the molecular axis and E make an angle 70 and $110°$.

3. Results

The O 1s photoelectron satellite spectra for the parallel and perpendicular transitions, recorded at $h\nu \approx$552.5, 557.5, 561.8 and 569.9 eV, are presented in Fig. 1. The spectra are plotted as functions of the satellite state binding energy ϵ, relative to the O 1s ionized state. The uncertainty of this relative energy scale is $\approx$1 eV. The spectra are normalized to
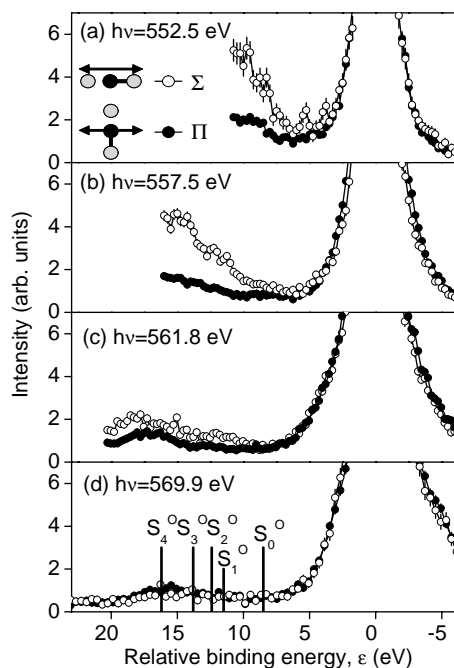
Fig. 1. O 1s photoelectron satellite spectra of CO_2 for the molecular axis fixed in space parallel ($\Sigma_g \to \Sigma_u$) and perpendicular ($\Sigma_g \to \Pi_u$) to the direction of polarization of the radiation, excited by (a) 552.5 eV, (b) 557.5 eV, (c) 561.8 eV and (d) 569.9 eV photons. The binding energy (satellite state energy) is relative to the O 1s ionized state. The integrated intensity for each spectrum is normalized to unity. The vertical bars and the labels S^O_0–S^O_4 refer to the labelling of the satellite bands taken from reference [6].

Fig. 2. C 1s photoelectron satellite spectra of CO_2 for the molecular axis fixed in space parallel ($\Sigma_g \to \Sigma_u$) and perpendicular ($\Sigma_g \to \Pi_u$) to the direction of polarization of the radiation excited by (a) 307.1 eV, (b) 311.9 eV, (c) 319.4 eV, and (d) 329.3 eV photons. The vertical bars and the labels S^C_0–S^C_4 refer to the labelling of the satellite bands taken from reference [5].

make each integrated intensity equal to unity. The O 1s satellite spectra were investigated by Maier et al. [6], at higher resolution, without taking the coincidence with ions and thus without resolving the transition symmetry. The present symmetry-resolved spectra show reasonable general agreement in the spectral behaviour with those observed by Maier et al. at similar energies. Maier et al. resolved five satellite bands S^O_0–S^O_4 at $\varepsilon \approx 8.5$, 11.5, 12.4, 13.8 and 16.8 eV, as indicated by bars in Fig. 1.

Maier et al. investigated the photon energy-dependence of the satellite bands and found that the overlapping bands S^O_1 and S^O_2 are strongly enhanced at kinetic energy of ≈ 7 eV, but the changes in the intensities of S^O_3 and S^O_4 are much weaker. Thus, they identified S^O_1 and S^O_2 as the conjugate shake-up and S^O_3 and S^O_4 as direct shake-up. According to our symmetry-resolved spectra, however, the satellite bands S^O_1 and S^O_2 at ≈ 12 eV seems to be excited more effectively for the parallel transition (see Fig. 1a), casting doubts on the identification of these bands as due to the conjugate shake-up process, because the conjugate shake-up satellites are expected to be more intense for the perpendicular transition. Furthermore, the present symmetry-resolved spectra indicate that the observed satellite bands in the parallel transition are enhanced by the $4\sigma_u$ shape resonance of the SHI cross section (see Fig. 1b). This resonant behaviour rules out the general identification of the observed bands to the
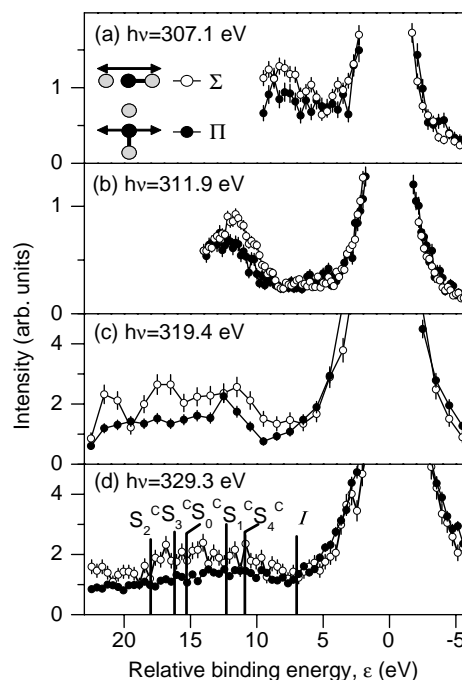
direct shake-up satellites, because the shape resonances of the direct shake-up satellites are expected to be at photon energy higher by more than ≈ 10 eV than that of the SHI cross-section. The observed symmetry dependence and resonant behaviour strongly support that the observed bands are excited predominantly by the internal inelastic scattering mechanism.
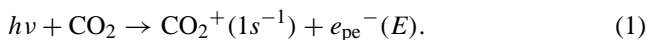
The photoelectron satellite spectra for the parallel and perpendicular transitions, recorded at $h\nu \approx 307.1$, 311.9, 319.4 and 329.3 eV, are presented in Fig. 2. The satellite spectra accompanying the C 1s mainline were investigated by Schmidbauer et al. [5], at higher resolution, without taking the coincidence with ions and thus without selecting the transition symmetry. The present symmetry-resolved spectra show reasonable general agreement with the spectra observed by Schmidbauer et al. at similar energies. Schmidbauer et al. observed five satellite bands S^C_0–S^C_4 at energies ϵ between 10.9 and 18.0 eV. These bands are only partly resolved in the symmetry-resolved spectra recorded at $h\nu \approx 319.4$ eV (Fig. 2c) and hardly resolved in the spectra recorded at $h\nu \approx 329.3$ eV (Fig. 2d). Only S^C_1 and S^C_4 can exist at $h\nu \approx 311.9$ eV (Fig. 2b), and none of the S^C_0–S^C_4 bands are energetically accessible at $h\nu \approx 307.1$ eV (Fig. 2a). The satellite band I at $\varepsilon \approx 7$ eV observed at $h\nu \approx 307.1$ eV (Fig. 2a) was observed also previously [5].

Schmidbauer et al. [5] observed the bands S^C_1, S^C_0 and S^C_2 at $\varepsilon \approx 12.3$, 15.3 and 18.0 eV, in the photoelectron spectra at high photon energies, and the bands S^C_3 and S^C_4 at
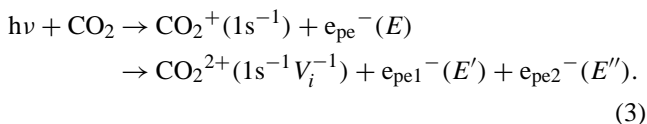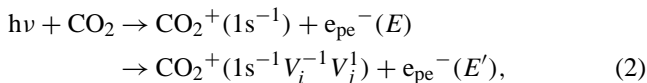
$\varepsilon \approx 16.2$ and 10.9 eV, when the $h\nu$ was close to the threshold: the intensities of S^C_3 and S^C_4 quickly decreased with an increase in $h\nu$. Thus, they identified S^C_1, S^C_0 and S^C_2 to the direct shake-up satellites and S^C_3 and S^C_4 to the conjugate shake-up satellites [5]. According to our symmetry-resolved spectra, however, both S^C_3 and S^C_4 seems to be more intense in the parallel transition than in the perpendicular one, casting doubts on the identification of these bands as due to conjugate shake-up process. These bands, as well as the other bands S^C_1, S^C_0, S^C_2 and I, are very likely excited by the internal inelastic scattering mechanism. Note also that we can expect the enhancement of the direct shake-up in the parallel transition by the shape resonance in the range $319 \le h\nu \le 329$ eV.

4. Discussion

If the internal inelastic scattering is negligible, the photoemission reaction contributing to the 1s mainline is expressed as

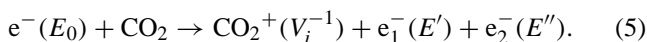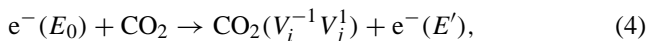$$h\nu + CO_2 \rightarrow CO_2^+(1s^{-1}) + e_{pe}^-(E). \qquad (1)$$

This includes only the elastic channel in transmission of the primary photoelectron with kinetic energy E through the molecular region. However, if the internal inelastic scattering is considered, the inelastic channels will also accompany the transmission of the primary photoelectron:

$$\begin{aligned} h\nu + CO_2 \rightarrow{} & CO_2^+(1s^{-1}) + e_{pe}^-(E) \\ \rightarrow{} & CO_2^+(1s^{-1}V_i^{-1}V_j^1) + e_{pe}^-(E'), \end{aligned} \qquad (2)$$

$$\begin{aligned} h\nu + CO_2 \rightarrow{} & CO_2^+(1s^{-1}) + e_{pe}^-(E) \\ \rightarrow{} & CO_2^{2+}(1s^{-1}V_i^{-1}) + e_{pe1}^-(E') + e_{pe2}^-(E''). \end{aligned} \qquad (3)$$

These channels represent the photoelectron transmission accompanied by excitation and ionization of valence electrons. The initial kinetic energy lost by the primary photoelectron is accumulated in the residual ion and contributes to valence excitations or ionizations. The photoelectrons $e_{pe}^-(E')$, $e_{pe1}^-(E')$ and $e_{pe2}^-(E'')$ with kinetic energies E' and E'' contribute to the satellite formation.

Let us pay attention to the correlation between the internal inelastic scattering in reactions (2) and (3) and low-energy electron-impact excitation/ionization:

$$e^-(E_0) + CO_2 \rightarrow CO_2(V_i^{-1}V_j^1) + e^-(E'), \qquad (4)$$

$$e^-(E_0) + CO_2 \rightarrow CO_2^+(V_i^{-1}) + e_1^-(E') + e_2^-(E''). \qquad (5)$$

The satellite excitations due to the internal inelastic scattering are correlated to the electron-impact excitations of CO_2 when the incident electron of similar kinetic energy collides with the molecule. Within this simple model, the satellite band S^C_4 at $\varepsilon \approx 10.9$ eV, as well as S^O_1 and S^O_2

at $\varepsilon \approx 11.5$ and 12.4 eV, respectively, could be associated with excited electronic states of CO_2 located at 10.98, 11.05, 11.16 and 11.40 eV in the energy-loss spectra [24]. The spectroscopic assignments of these satellite bands are not suggested here because the excited electronic states of CO_2 are only tentatively assigned in [24]. In principle, other satellite bands prominent in the parallel transition can also be correlated to other excited electronic states of CO_2.

The integrated cross-section Q of satellite excitations due to the internal inelastic scattering behaves resonantly when $h\nu$ is scanned through the shape resonance [14]. The $h\nu$ dependence of the satellite cross-section σ_{1+2} for S^O_1 and S^O_2, as measured by Maier et al. [6], peaks at about the same photon energy as the O $1s^{-1}$ $4\sigma_u$ shape resonance in the SHI cross section, supporting our conclusion on the importance of the internal inelastic scattering in the excitation of the S^O_1 and S^O_2 bands.

Recently, Hatherly et al. [7] measured the C 1s satellite structure using threshold photoelectron spectroscopy, and suggested a satellite band labelled S' at $\varepsilon \approx 14$ eV. This band could be attributed to the direct knock-out from the highest occupied molecular orbital of the C 1s ionized state, since the ionization energy of CO_2 is 13.78 eV [25].

5. Conclusion

Satellite excitations accompanying the O and C 1s photoionization in CO_2 differ for the parallel and perpendicular transitions in the vicinity of the $4\sigma_u$ shape resonance. These satellites are generally more intense for the parallel transition and enhanced by the shape resonance. These results provide clear evidence that the internal inelastic scattering plays a significant role in the satellite formation. The importance of the internal inelastic scattering calls for a reconsideration of the independent-particle picture for the molecular shape resonances, in which valence electrons behave as independent spectators. Recall that atomic shape resonances are more generally called the giant resonances because the inidependent particle picture does not hold here. The relation of the satellite excitation due to internal inelastic scattering and the low-energy electron impact excitation was elucidated and the assignments of the satellite structures were discussed.

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