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著者	Fanis A. De, Saito N., Pavlychev A. A., Ladonin D. Yu., Machida M., Kubozuka K., Koyano I., Okada K., Ikejiri K., Cassimi A., Czasch A., Dorner R., Chiba H., Sato Y., Ueda K.
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## Symmetry-Dependent Multielectron Excitations near the C 1s Ionization Threshold and Distortion of the Shape Resonance in CO<sub>2</sub>

A. De Fanis,<sup>1</sup> N. Saito,<sup>2</sup> A. A. Pavlychev,<sup>1,3</sup> D. Yu. Ladonin,<sup>3</sup> M. Machida,<sup>4</sup> K. Kubozuka,<sup>4</sup> I. Koyano,<sup>4</sup> K. Okada,<sup>5</sup> K. Ikejiri,<sup>5</sup> A. Cassimi,<sup>6</sup> A. Czasch,<sup>7</sup> R. Dörner,<sup>7</sup> H. Chiba,<sup>1</sup> Y. Sato,<sup>1</sup> and K. Ueda<sup>1,\*</sup>

<sup>1</sup>*Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai 980-8577, Japan*

<sup>2</sup>*National Metrology Institute of Japan, AIST, Tsukuba 305-8568, Japan*

<sup>3</sup>*Institute of Physics, St. Petersburg State University, 198094, St. Petersburg, Russia*

<sup>4</sup>*Department of Material Science, Himeji Institute of Technology, Kamigori, Hyogo 678-1297, Japan*

<sup>5</sup>*Department of Chemistry, Hiroshima University, Higashi-Hiroshima 739-8526, Japan*

<sup>6</sup>*CIRIL/CEA/CNRS/ISMRA, University de Caen, Box 5133, F-14070 Caen Cedex 5, France*

<sup>7</sup>*Institut für Kernphysik, University Frankfurt, D-60486 Frankfurt, Germany*

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Satellite bands accompanying the C 1s photoline for the CO<sub>2</sub> molecule parallel to the electric vector of the incident radiation  $\mathcal{E}$  are found to be more intense than those for CO<sub>2</sub> perpendicular to  $\mathcal{E}$  in the shape resonance region. This indicates that multielectron excitations are caused in part by the interaction of the outgoing C 1s photoelectron with the valence electrons. The photoelectron-impact valence excitations couple with the C 1s single-hole ionization and distort the shape resonance significantly. We assign the broad resonance at  $\sim 312$  eV to a distorted  $\Sigma_u$  shape resonance.

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Photoabsorption spectra of small molecules exhibit resonant features both below and above the inner-shell thresholds. The resonances above the thresholds, assigned to shape resonances, are conventionally described as one-electron phenomena associated either with temporary trapping of the photoelectron by the molecular potential [1,2] or with the promotion of a core electron to an unoccupied molecular orbital [3]. Recent core-level photoemission studies have, however, revealed that multielectron excitations play important roles in the shape resonance regions, raising questions about the validity of one-electron descriptions [4–7].

Such multielectron transitions in molecules induced by a single photon have so far mostly been interpreted as results of a shake-up mechanism. Here a core electron absorbs the photon angular momentum. In a dipole transition it is either emitted to the continuum or to an excited state. The valence electrons are now no longer in an eigenstate of the altered potential and relax in a monopole transition either to a bound state or to the continuum. The electron emitted to the continuum is then observed either as a normal or conjugate satellite of the main photoline.

From atomic double ionization and ionization with excitation, it is known however that, in addition to shakeup/shakeoff, two electron processes can also be induced by an electron-electron scattering (see [8] and references therein). Pavlychev [9] has argued that a similar inelastic scattering of the photoelectron with the valence electrons (i.e., PEVE interaction) could also play a crucial role in multielectron transitions in molecules.

In the present Letter we provide experimental evidence for the existence of the PEVE interaction within a CO<sub>2</sub> molecule. Our experiment is based on the simple idea that (i) the probability of normal shakeup/shakeoff

drops when the photon frequency approaches the ionization threshold [10], (ii) the conjugate transitions regarded as monopole valence ionization accompanying the  $2\sigma_g \rightarrow 2\pi_u^*$  dipole allowed excitation occur mainly in molecules oriented perpendicular to the direction of polarization of the incident radiation  $\mathcal{E}$ , and (iii) the photoelectron impact mechanism caused by the PEVE interaction, in contrast, can be expected to have a higher probability for the parallel molecular orientation for which the photoelectron is driven mainly along the molecular axis.

This PEVE interaction calls for a reevaluation of the concept of shape resonances. They are conventionally regarded as one-electron phenomena, i.e., interference of the photoelectron wave described as occurring in the rigid molecule (valence electrons and nuclear motions are independent of the photoelectron motion). The importance of the PEVE coupling suggests that one describe this interference as occurring in the *soft* molecule: due to the PEVE coupling the valence-excited molecular configurations assist in the intramolecular interference. We will show that this coupling shifts upward the position of the shape resonance considerably.

In the preset experiment, we have investigated the dependence of the satellite excitations accompanying C 1s photoionization in CO<sub>2</sub> on the symmetry of the transitions in the vicinity of the shape resonance. We recorded C 1s photoelectron spectra for CO<sub>2</sub> whose molecular axis is parallel or perpendicular to  $\mathcal{E}$ . To probe the direction of the molecular axis for each photoelectron emission, we use coincidence detection between the photoelectron and the fragment ions [11–15]. In this way, we selectively probe the satellite excitations for either the  $\Sigma \rightarrow \Sigma$  or  $\Sigma \rightarrow \Pi$  transition, labeled as  $\Sigma$  and  $\Pi$ , respectively.

The experiment has been carried out on beam line 27SU at SPring-8 [16]. The photon energy bandpass is set to  $\sim 30$  meV. A supersonic beam of  $\text{CO}_2$  is introduced in the ionization region, where it crosses perpendicularly the photon beam. Electrons and ions are extracted by static electric and magnetic fields. Ions are detected by a position sensitive detector at one side of the acceleration region. At the opposite side, electrons enter a time of flight (TOF) tube, at which end they are detected by a second detector. 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 direction and  $\mathcal{E}$ . To extract the photoelectron spectra for the  $\Sigma$  and  $\Pi$  transitions from the coincidence data, we define the reaction plane perpendicular to the TOF axis. The  $\Sigma$  and  $\Pi$  transitions are selected in such a way that the directions of the molecular axis determined by the linear momenta of the  $\text{O}^+$  and  $\text{CO}^+$  ions measured in coincidence are parallel and perpendicular, respectively, to  $\mathcal{E}$ , and in the reaction plane.

We first present in Fig. 1 the C  $1s$  photoelectron angular distribution (PAD) for the  $\Sigma$  and  $\Pi$  transitions recorded at photon energy 319.4 eV. The C  $1s$  PAD from fixed-in-space  $\text{CO}_2$  molecules varies with the photon energy near the core ionization threshold [15], but far from it (say, for  $E > 20$  eV) it is directed preferentially along  $\mathcal{E}$ , as seen in Fig. 1, and thus along (perpendicular to) the molecular axis for the  $\Sigma$  ( $\Pi$ ) transition. Further discussion on PAD and its photon energy dependence is presented in a separate paper [15].

The photoelectron satellite spectra for the  $\Sigma$  and  $\Pi$  transitions, recorded at  $h\nu = 307.1$ , 311.9, and 319.4 eV, are presented in Fig. 2. The spectra are plotted as a function of the satellite state energy,  $\epsilon$ , relative to the C  $1s^{-1}$  ionized state. The uncertainty of this relative energy scale is  $\sim 1$  eV. The intensities of the spectra are normalized to make each integrated intensity equal to unity. The spectrum measured at  $h\nu = 319.4$  eV, with no selection made for the molecular axis direction, is also shown in Fig. 2(d) for comparison. The relative intensity distribu-

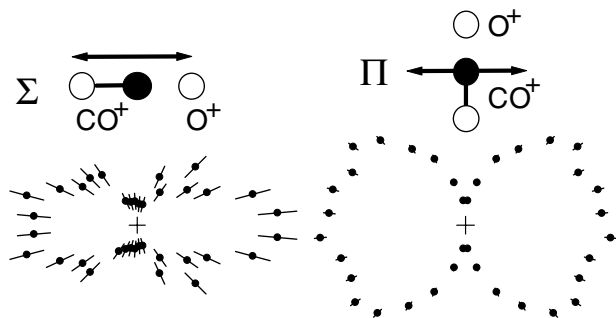


FIG. 1. Polar plots for C  $1s$  photoelectron angular distribution of  $\text{CO}_2$  for the  $\Sigma$  and  $\Pi$  transitions, recorded at the photon energy of 319.4 eV. The  $\mathcal{E}$  vector is horizontal in the figure, as shown by arrows. The crosses in the center represent the origin of the polar plots.

tion within each spectrum may be only semiquantitative, since we have selected a specific fragmentation channel resulting in two-body dissociation  $\text{O}^+ + \text{CO}^+$ . Even so, the *symmetry-unresolved* spectrum in Fig. 2(d) shows reasonable agreement with the spectrum observed by Schmidbauer *et al.* [5], at similar photon energy, at higher resolution, without taking the coincidence with ions, and without selecting the transition symmetry. Schmidbauer *et al.* observed five satellite bands  $S_0 - S_4$  at energies  $\epsilon$  ranging from 10.9 to 18.0 eV. All these satellite bands are observed also in the spectra recorded at  $h\nu = 319.4$  eV [Figs. 2(c) and 2(d)]. Only  $S_1$  and  $S_4$  can exist at the lower photon energy of 311.9 eV [Fig. 2(b)], and none of the  $S_0 - S_4$  bands are energetically accessible at 307.1 eV [Fig. 2(a)]. An additional structure, labeled  $I$  in Fig. 2, can also be noticed at  $\epsilon \sim 6-8$  eV. This  $I$  band corresponds to the bands at 5.8 and 7.3 eV observed before [5].

The relative intensity and profile in the symmetry-resolved spectra show significant differences. It is evident that satellites are excited more effectively for the  $\Sigma$  transition. The satellite intensity in the symmetry-unresolved spectrum is intermediate between the  $\Sigma$  and  $\Pi$  spectra. Our observation rules out the assignment of the  $S_3$ ,  $S_4$ , and  $I$  bands to the conjugate satellites [5]. According to this

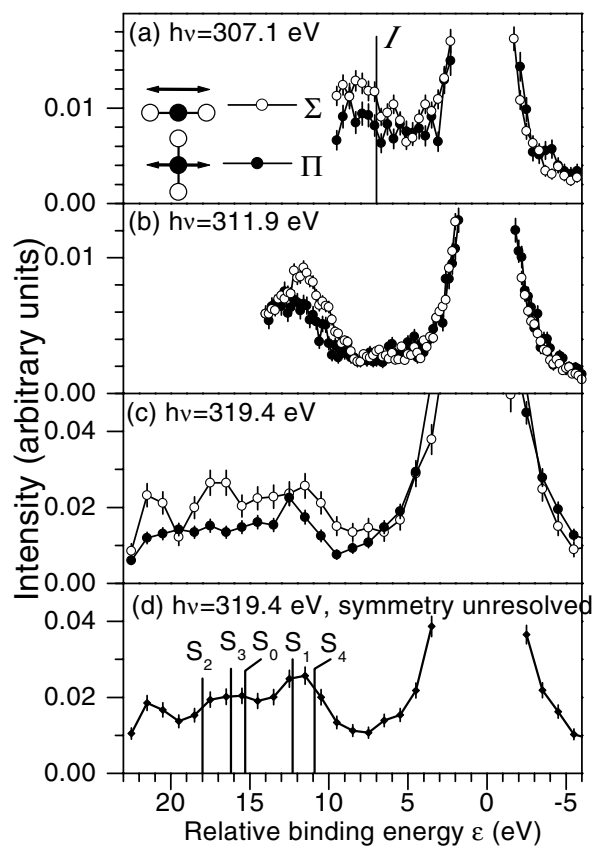
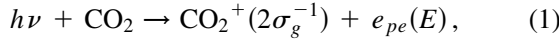


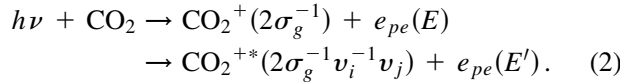
FIG. 2. Photoelectron spectra of  $\text{CO}_2$  for the molecular axis fixed in space parallel ( $\Sigma$ ) and perpendicular ( $\Pi$ ) to the direction of polarization of the radiation, (a)–(c), and without selection of the molecular axis (d).

assignment they are expected to be more intense for the  $\Pi$  transitions, which is in contrast to the results in Fig. 2. The strong enhancement of the satellites for parallel orientation of the molecule provides direct evidence for the photoelectron-impact mechanism: photoelectrons emitted originally along the molecular axis (the  $\Sigma$  transition as seen in Fig. 1) are much more likely to interact with a valence electron than those which escape perpendicular to the molecule (the  $\Pi$  transition).

The photoelectron-impact mechanism can be described as follows. The transmission of the primary photoelectron  $e_{pe}$  through the valence shells can be expressed by the sum of the elastic channel:



and the inelastic channel:



Channel (2) represents the photoelectron transmission accompanying the excitation of valence electrons; ionization can also be included. A fraction of the initial photoelectron kinetic energy  $E$  is transferred to the residual ion:  $E - E'$ . The energy difference  $E - E'$  is accumulated in the residual ion resulting in valence excitations  $\text{CO}_2^+ \rightarrow \text{CO}_2^{+*}$ . The photoelectron  $e_{pe}(E')$  with kinetic energy  $E'$  contributes to the satellite structure. In contrast to channel (1), where the  $e_{pe}(E)$  electron carries the angular momentum away, in channel (2) the angular momentum can be transferred to the residual ion. Thus, in addition to monopole transitions, the photoelectron-impact excitations give rise to nonmonopole valence transitions. In particular, valence excitations such as  $1\pi_g^{-1}2\pi_u^1$  and  $4\sigma_g^{-1}2\pi_u^1$  appear in the satellite spectra. These photoelectron-impact excitations are dependent on the kinetic energy  $E$  and the direction of the photoelectron emission with respect to the molecular axis.

We have analyzed the effect of the PEVE coupling on the spectral dependence of the C  $1s$  photoionization within the framework of the quasiatomic model [9,17]. Excitation and direct knockout of valence electrons by the  $1s$  photoelectron lead to dissipation of the primary photoelectron flux  $J(E)$  inside the molecular region. The divergence of  $J(E)$  (see, e.g., [18]) is given by

$$\nabla J = -\Psi^*(\vec{k}_e)\Psi(\vec{k}_e)\text{Im}W^{\text{opt}}, \quad (3)$$

where  $\Psi$  is the photoelectron wave function,  $\vec{k}_e$  is the photoelectron wave vector, and the imaginary part of the molecular optical potential,  $\text{Im}W^{\text{opt}}$ , describes dissipation of the flux  $J(E)$  due to the presence of the inelastic channel (2). The cross section  $Q_{\Sigma(\Pi)}$  for the satellite excitations for parallel (perpendicular) transitions is defined as the difference between the single-hole creation cross section  $\sigma_{\Sigma(\Pi)}^{\oplus}$  and single-hole ionization cross section  $\sigma_{\Sigma(\Pi)}^+$ .  $\sigma_{\Sigma(\Pi)}^+$  is determined by  $J(E)$  transmitted through the molecular region and crossing a sphere with radius larger than the

molecular size and is the cross section of the photoelectron emission in channel (1).  $\sigma_{\Sigma(\Pi)}^{\oplus}$  is determined by  $J(E)$  transmitted through a sphere of small radius surrounding the core-ionized atom and is the total cross section for channels (1) and (2). These cross sections are computed in respect to the intramolecular interference of the photoelectron waves using the equations described in [9]. The amplitudes of the waves take account of coupling of channels (1) and (2) inside the molecular region. In the calculation, the imaginary part of the optical potential  $\text{Im}W^{\text{opt}}$ , which differs from 0 for  $E > 7.5$  eV [19], is extracted from the inelastic electronic cross sections of  $\text{CO}_2$  [20,21].

The computed cross sections  $\sigma_{\Sigma}^{\oplus}$  and  $\sigma_{\Sigma}^+$  are presented in Fig. 3. At energies lower than  $\sim 305$  eV they are degenerate. They exhibit an anomalous spectral feature  $i$  at 305 eV, split ( $\sigma_{\Sigma}^{\oplus} > \sigma_{\Sigma}^+$ ) above it, and then exhibit a resonance with a maximum at  $\sim 312$  eV. If the PEVE interaction is reduced (i.e.,  $\text{Im}W^{\text{opt}}$  approaches zero), then  $\sigma_{\Sigma}^{\oplus}$  and  $\sigma_{\Sigma}^+$  converge to  $\sigma_0^+$ ,  $Q_{\Sigma}(\equiv \sigma_{\Sigma}^{\oplus} - \sigma_{\Sigma}^+)$  approaches zero, and the  $i$  feature disappears.  $\sigma_0^+$  corresponds to the cross section for a pure one-electron (shape resonance) transition and thus the resonance in  $\sigma_0^+$  can be labeled as  $4\sigma_u^*$ , as denoted in Fig. 3. The 312-eV resonance in  $\sigma_{\Sigma}^+$  and  $\sigma_{\Sigma}^{\oplus}$ , on the other hand, can no longer be assigned to a one-electron transition and thus is denoted as  $\Sigma_u$  in Fig. 3, instead of  $4\sigma_u^*$ .

As seen in Fig. 3, it is clear that the PEVE coupling induces (i) the formation of the anomalous feature  $i$  in  $\sigma_{\Sigma}^{\oplus}$  and  $\sigma_{\Sigma}^+$  at the inelastic threshold, (ii) the upward shift of  $\sim 3$  eV of the  $\Sigma_u$  resonance in  $\sigma_{\Sigma}^+$  and  $\sigma_{\Sigma}^{\oplus}$  from the reference position of  $4\sigma_u^*$  in  $\sigma_0^+$ , and (iii) the splitting between  $\sigma_{\Sigma}^{\oplus}$  and  $\sigma_{\Sigma}^+$  above the inelastic threshold. As a consequence of this splitting the photoelectron-impact satellites arise above the inelastic threshold. The valence-excited core-ionized states  $\text{CO}_2^{+*}(2\sigma_g^{-1}v_i^{-1}v_j)$  thus created influence the intramolecular interference in the C  $1s$  single-hole ionization. The  $i$  feature and the resonant energy shift

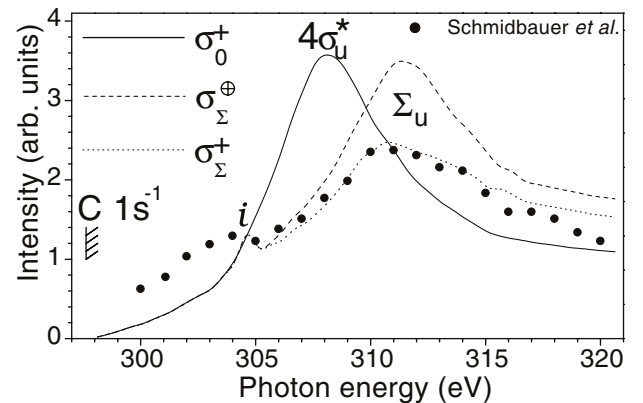


FIG. 3. The dashed and dotted lines show  $\sigma_{\Sigma}^{\oplus}$  and  $\sigma_{\Sigma}^+$ , respectively, computed taking account of the PEVE coupling, whereas a continuous line shows  $\sigma_0^+ (= \sigma_{\Sigma}^{\oplus} = \sigma_{\Sigma}^+)$  computed neglecting the PEVE coupling. Closed circles represent the experimental single-hole ionization cross section  $\sigma^+$  from Ref. [5].

originate from the change in the interference due to the additional photoelectron wave phase shift caused by the PEVE coupling.

In describing the PEVE coupling in the quasiatomic model, the core-level photoelectron impact is approximated by the low-energy electron impact to the neutral molecule. The valence-excited states of CO<sub>2</sub> ( $^3\Pi_g$ ,  $^3\Sigma_u^+$ ,  $^1\Pi_g$ ,  $^3\Delta_u$ ,  $^3\Sigma_u^-$ ,  $^1\Sigma_u^-$ ,  $^1\Delta_u$ ) lie 7.5–8.3 eV above the ground state [19]. Thus the photoelectron-impact satellites are expected to appear for  $\epsilon > \sim 7.5$  eV. Indeed the satellites in Fig. 2 appear for  $\epsilon > \sim 6$  eV. The difference of  $\sim 1.5$  eV is due to the core-hole relaxation effect on the valence transitions neglected in the present model and correlates with the calculations of Porwol *et al.* [22].

Note that the *i* feature appears at 305 eV in Fig. 3, i.e., 7.5 eV above the inelastic threshold. Indeed the C 1*s* photoionization cross section [5], presented in Fig. 3 by closed circles, exhibits irregular behavior at  $h\nu \sim 304$  eV, which can be obviously assigned to the predicted feature *i*. Furthermore, the calculated spectral dependence of  $\sigma_{\Sigma^+}^+$  is in reasonable agreement with the one  $\sigma^+$  measured without resolving symmetry [5]. The agreement between the calculated and measured spectra in Fig. 3 provides evidence of the existence and importance of the PEVE coupling. Thus we may state that the distorted shape resonance  $\Sigma_u$  is associated with the temporary trapping of the C 1*s* photoelectron by the molecular ion deformable in the photoelectron field.

The intramolecular impact process occurs also for the  $\Pi$  transition. Because this process is connected with the photoelectron transmission through the anisotropic molecular barrier, it depends on the molecular orientation relative to the direction  $\mathcal{E}$ . Indeed Eq. (3) shows that  $\nabla J$  depends on the photoelectron angular distribution. The C 1*s* photoelectrons ejected from CO<sub>2</sub> oriented perpendicularly to  $\mathcal{E}$  (i.e., the  $\Pi$  transition) couple with valence electrons more weakly than those from the molecule directed along  $\mathcal{E}$  (i.e., the  $\Sigma$  transition). This explains the strong symmetry dependence of the satellite spectra at 319.4 eV.

In conclusion, satellite excitations accompanying C 1*s* photoionization in CO<sub>2</sub> differ for  $\Sigma$  and  $\Pi$  transitions near the C 1*s* ionization threshold. These satellites are found relatively stronger and the satellite structure is richer for the  $\Sigma$  transition. The present results are clear evidence that the PEVE interaction plays a significant role in the satellite formation. The PEVE interaction shifts the energy where the cross section takes maximum as compared to single particle calculations. We thus suggest that one

regard the broad resonance at  $\sim 312$  eV in photoionization and photoabsorption spectra as the *distorted* shape resonance of  $\Sigma_u$  symmetry.

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\*Corresponding author.

Email address: ueda@tagen.tohoku.ac.jp

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