

Influence of multielectron excitations on the O 1s photoionization in CO₂

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High-resolution O 1s photoelectron spectra of the CO₂ molecule have been measured in the region of the resonant features above the O K edge. The cross sections and asymmetry parameters were determined for the vibrational components of the O 1s photoelectron line. The vibrational fine structure is completely dominated by the antisymmetric stretching mode, which arises due to vibronic coupling. The O 1s line is accompanied by a rich satellite structure. Auger electron spectra have been measured at the energies of the continuum resonances and used as an indirect probe for multielectron excitations. The shoulder on the low-energy side of the 4σ_u shape resonance is due to double excitations that decay via spectator processes. [S1050-2947(98)02111-8]

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I. INTRODUCTION

Shape resonances and multielectron excitations often dominate the x-ray absorption cross sections of small molecules in the threshold region for core-level photoionization. Shape resonances are essentially one-electron processes and can be regarded either as due to the trapping of the emitted photoelectron by a potential barrier [1] or, in an alternative description, as due to transitions into virtual, antibonding molecular orbitals in the continuum [2]. Double excitations, on the other hand, consist of simultaneous transitions from a core level and a valence level into unoccupied orbitals. The influence of shape resonances and multielectron excitations on C 1s partial cross sections, vibrational branching ratios, and β parameters have already been studied for several molecules; see, e.g., [3–14]. In this photon energy region soft x-ray undulators and grazing incidence monochromators are now able to provide the high flux and resolution that are essential for shape resonance studies in individual vibrational channels. At the oxygen edge the situation is different. Firstly, the lifetime of the oxygen core hole (binding energy ~540 eV) is even shorter than that of carbon (binding energy ~300 eV), making it more difficult to observe vibrational spacings. Secondly, the energy resolution and photon flux from typical monochromators normally decrease with increasing photon energy. However, the recent change of grating of the grazing-incidence monochromator on the X1B beam line at the NSLS, Brookhaven National Laboratory, has sufficiently improved its performance that vibrational resolution is now possible in O 1s photoelectron spectroscopy of small molecules [15].

In a first approximation, only totally symmetric vibrational modes are expected to appear in the photoelectron spectrum of a molecule. This is due to the Born-Oppenheimer approximation, in which the total wave func-

tion is separated into its electronic and vibrational parts, and the resulting Franck-Condon principle. For polyatomic molecules with high symmetry, however, the problem may be different. Although the extent of the interaction between equivalent core orbitals may be almost negligible, the core molecular orbitals are actually nondegenerate. These electronic states, which may be separated in energy by only a few meV, can couple through the movement of the nuclei. This phenomenon is termed vibronic coupling and can induce the excitation of nontotally symmetric modes, as was predicted by Domcke and Cederbaum [16]. Specifically, they treated O 1s ionization in the CO₂ molecule and calculated that the antisymmetric stretch mode would dominate the O 1s vibrational fine structure at the expense of the symmetric stretch. This prediction has only recently been confirmed by experiment [15]; the measurements actually showed no indication of the totally symmetric mode. In the present paper we report further details of the O 1s ionization in CO₂. Particularly interesting is the extent to which the continuum resonances present in the absorption spectrum affect the cross section and angular distribution of the vibrational fine structure on the O 1s photoelectron line.

The first angle-resolved O 1s photoelectron studies of CO₂ in the near edge region were performed by Schmidbauer *et al.* [17]. Both the O 1s cross section and the asymmetry parameter were found to be influenced by double excitations and the shape resonance. The analysis, however, was handicapped by the moderate photon energy resolution, which was about 1 eV at the oxygen edge. Our angle-resolved measurements yield the spectroscopic constants of the O 1s⁻¹ state in CO₂ as well as the partial photoionization cross sections and asymmetry parameters β of the individual vibrational lines. Additionally, by scaling to the absolute absorption cross section (see Fig. 1) [18], the partial photoionization cross sections can be given in absolute units (Mb).

Core-level ionization is often accompanied by valence level (Val) excitations, which result in so-called shake-up satellite lines on the high-binding-energy side of the single hole line. These correspond to ionic configurations of the type 1s⁻¹Val⁻¹Val. Shake-off states corresponding to 1s⁻¹Val⁻¹ are also possible although normally the threshold energy for these double ionization processes is not readily visible in the photoelectron spectrum. Our previous

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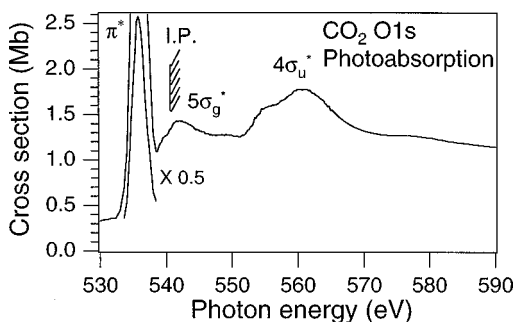


FIG. 1. Photoabsorption spectrum of the CO_2 molecule at the O K edge after Kempgens *et al.* [18].

work on CO and C_2H_2 [6,12] has shown that conjugate processes can also occur in the near-threshold region and lead to conjugate satellites as well as to a conjugate contribution to normal satellites. We have therefore also measured the O $1s$ satellite spectrum of CO_2 as a function of photon energy.

Core-excited states of first-row molecules decay almost exclusively via electron emission, so that any differences in their electronic configuration should be reflected in the corresponding Auger spectra. Above threshold, electronic decay from the core-ionized $1s^{-1}$ single hole state accounts for most Auger features. Additional contributions appear, however, when the simultaneous excitation or ejection of a valence electron (double excitation and shake-up, respectively) become energetically possible. Extra resonant decay features have indeed been observed for the core-hole doubly excited states and for shake-up satellites of N_2 [19,20]. In contrast, the shape resonance was not found to create any additional features in the N_2 decay spectrum. We therefore also present in this paper Auger decay spectra of CO_2 measured over the resonances at a number of photon energies and show in particular that the 555-eV continuum resonance has to be assigned to core-hole double excitations.

II. EXPERIMENTAL DETAILS

High-resolution O $1s$ photoelectron and Auger spectra of CO_2 were measured on the undulator beamline X1B at the National Synchrotron Light Source (NSLS). A new holographically manufactured laminar grating (800 lines/mm) has been installed in the spherical grating monochromator (SGM) and been found to improve significantly the photon flux and energy resolution at the oxygen edge. The kinetic energies of the emitted electrons were determined with a magic-angle cylindrical mirror analyzer (CMA), along the axis of which the photon beam reaches the target region. The electrons collected are those emitted in the reverse direction to the incoming beam at the magic angle. The electron spectrometer has a circular microchannel plate detector, which is divided into eight segments each spanning 45° . The eight simultaneously measured spectra thus monitor electrons at different emission angles relative to the electric field vector of the incoming beam and can be used to determine the asymmetry parameter β of the photoelectron lines, when the degree of linear polarization of the exciting radiation is known. Applying the general cross-section formula of Huang [21] to our specific measuring geometry [22] and integrating over the horizontal and vertical segments, we obtain for the

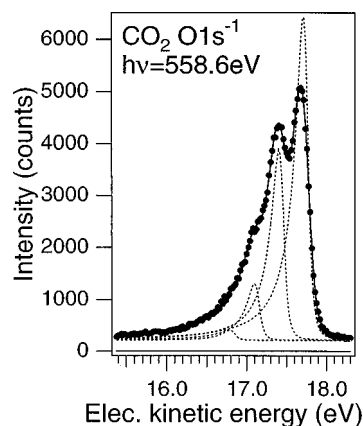


FIG. 2. Vibrationally resolved O $1s$ photoelectron spectrum of CO_2 measured at a photon energy $h\nu=558.6$ eV. The result of a least-squares fit is shown: the individual lines of the vibrational fine structure after convolution with the instrument profiles give the full line through the data points.

product of the asymmetry parameter β and the degree of polarization P :

$$\beta P = \frac{\pi}{\sqrt{2}} \frac{I_1 - I_3 + I_5 - I_7}{I_1 + I_3 + I_5 + I_7}. \quad (1)$$

P is the Stokes parameter resulting from the normalized difference in light intensity polarized parallel and perpendicular to the horizontal. I_i are the integrated intensities of a spectral feature measured on segment i . Segments 1 and 5 are symmetric about the horizontal, 3 and 7 about the vertical. P was determined to be ~ 0.83 by measuring the Ne $2s$ photoelectron line, whose β value is known to be 2. The beamline has been described in detail previously [23].

Vibrationally resolved O $1s$ photoelectron spectra were measured with the entrance and exit slit of the SGM set to $5 \mu\text{m}$ (equivalent to a photon bandwidth of about 100 meV) and pass energy of the CMA set to 15 eV (equivalent to a kinetic energy resolution of about 110 meV). Thus, a total energy resolution of about 150 meV was achieved. For the measurement of the shake-up satellites, which occur over a wider energy window, the flux of the incident radiation had to be increased. The entrance and exit slits of the SGM were therefore set to $40 \mu\text{m}$ and $30 \mu\text{m}$, respectively. The total energy resolution in this case was about 330 meV. The Auger decay spectra were measured with a photon bandwidth of 0.7 eV on the continuum resonances between 550 and 564 eV. They were measured with an 80 eV CMA pass energy, which corresponds to an electron kinetic energy resolution of 0.6–0.7 eV. The photon energy scale was calibrated using results from electron energy loss spectroscopy (EELS) measurements [24]. All photoelectron spectra were normalized to the incident photon flux by alternate measurements of the Ne $2p$ spectrum at each photon energy.

III. VIBRATIONAL FINE STRUCTURE ON THE O $1s$ LINE

The O $1s$ photoelectron main line of CO_2 measured at a photon energy of $h\nu=558.6$ eV is shown in Fig. 2. At least three distinct components of the vibrational fine structure are

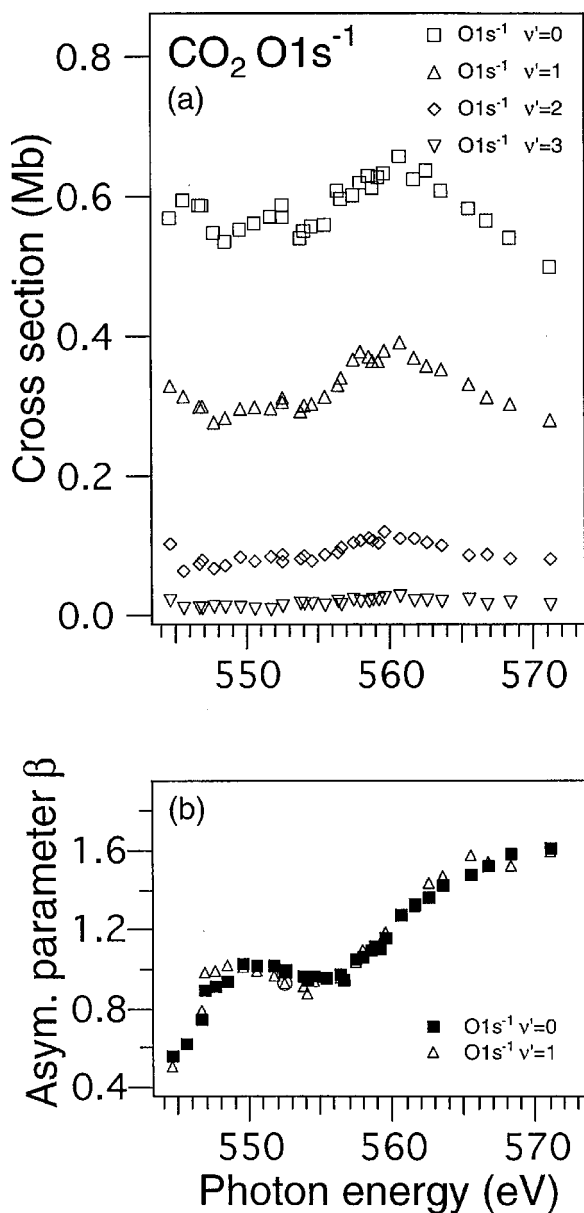


FIG. 3. (a) The O $1s$ partial photoionization cross sections for the vibrational channels $\nu'=0,1,2$ showing the $4\sigma_u^*$ resonance around 560 eV. (b) The corresponding asymmetry parameter β also shows the influence of the shape resonance and the multielectron excitations.

visible. The spectrum has been fitted using a nonlinear least-squares algorithm resulting in the full line. The fit is a convolution of an experimentally determined CMA profile, the monochromator profile modeled by a Gaussian shape and the intrinsic line shapes (see, e.g., Ref. [6] for further details). The latter (dashed lines) are strongly asymmetric towards lower electron kinetic energy due to postcollision interaction (PCI) between the slow outgoing photoelectron and the subsequently emitted Auger electron. In the threshold region the PCI effect strongly changes the line shape as a function of photon energy so that several spectra have been fitted simultaneously in order to determine reliably the lifetime broadening and the vibrational spacing. CO_2 possesses four normal vibrational modes: the totally symmetric stretching mode ν_1 of σ_g symmetry, the antisymmetric stretching mode

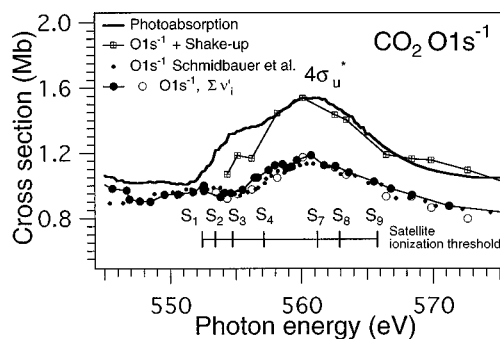


FIG. 4. O $1s$ single hole cross section for CO_2 . The full line shows the photoabsorption cross section after subtraction of an extrapolated smooth contribution from the valence and C $1s$ absorption.

ν_3 of σ_u symmetry, and two degenerate bending modes ν_2 of π_u symmetry. From the fit of the photoelectron spectrum with a single progression a vibrational energy of 307 ± 3 meV is obtained. In the molecular ground state ν_1 (σ_g) and ν_2 (π_u) have lower vibrational energies: 165 and 83 meV, respectively [25]. On the other hand, the ground-state frequency of ν_3 is 291 meV. In keeping with the observation that vibrational energies only change marginally upon core ionization we attribute the vibrational fine structure of the O $1s$ line to the antisymmetric stretching mode. *Ab initio* calculations within the Hartree-Fock formalism for the O $1s^{-1}$ state of CO_2 give a similar vibrational energy for the antisymmetric stretch [26]. The fit thus indicates that the excitation of the antisymmetric stretching mode totally dominates. In fact, attempts to fit with a second vibrational progression with an energy similar to that of the symmetric stretch in the neutral ground state show that such a contribution cannot be greater than a few percent. The 20 year old predictions of Domcke and Cederbaum [16] are thus confirmed, although their calculations at the time suggested a stronger contribution from the symmetric stretch. The lifetime broadening of the O $1s$ core hole, as extracted from the fit, is 165 ± 10 meV. A more detailed account of the analysis of the O $1s$ vibrational structure can be found in [15].

IV. SINGLE HOLE PHOTOIONIZATION CROSS-SECTION AND ASYMMETRY PARAMETER

Figures 3 and 4 show the partial photoionization cross sections for the vibrational substates corresponding to the fine structure on the O $1s$ main line (open squares, triangles, and diamonds) as well as their sum, i.e., the total O $1s$ main line or single hole cross section (connected filled circles). Another single hole data set obtained from lower resolution measurements is depicted with open circles (Fig. 4). The summed intensity of the O $1s$ main line and of the shake-up satellites is also shown (connected crossed squares). The latter has been scaled at $h\nu=560$ eV to the photoabsorption curve [18] from which the extrapolated contributions of the valence level and C $1s$ photoionization have been subtracted. In the earlier measurements of Schmidbauer *et al.* [17] the vibrational fine structure on the single hole line could not be resolved. For comparison, their results have been rescaled to the photoabsorption cross section (dots in Fig. 4). The statis-

tical error on the intensity of the O 1s photoelectron line in the present data is about 2%. Normalization errors due to fluctuations in incident photon flux are significantly higher for high-resolution measurements at the oxygen edge than at the carbon edge because smaller slit widths are needed to achieve vibrational resolution. This increases the counting time, in particular for the Ne 2p measurements. Normalization errors comprise the largest contribution to the total error and are estimated to be about 8%. The photoabsorption cross section itself is thought to be accurate to be within 2%. Additionally, the scaling to the O 1s plus shake-up intensity introduces a further possible error of $\sim 3\%$. Taken together, the maximum total error in the absolute photoionization cross section is therefore about 15% for photon energies higher than 550 eV.

Theory predicts two shape resonances [27] for O 1s excitation in CO₂, whereas at the C 1s edge only one is expected. This can be understood in terms of dipole selection rules: if the shape resonances are regarded as the virtual $5\sigma_g^*$ and $4\sigma_u^*$ molecular orbitals, then the transition into both is allowed for the O 1s σ_g and σ_u core molecular orbitals. For the C 1s core orbital of σ_g symmetry only the transition into the $4\sigma_u$ orbital is allowed. The component in the fine structure (Fig. 2) corresponding to the vibrational ground state of the O $1s^{-1}$ ion is the strongest and shows the resonance around 560 eV (Fig. 3), as in the absorption curve and the single hole cross section. We assign this feature to the $4\sigma_u^*$ resonance. (In the C 1s data of Schmidbauer *et al.* [17] the $4\sigma_u^*$ resonance occurs at an energy of 13.5 eV relative to threshold compared to 19.2 eV in the present O 1s data.) It is also observed in the $\nu' = 1$ and 2 vibrational components but, in contrast to the results for the shape resonance in N₂ [10] and CO (C 1s) [4], appears to remain at constant energy. In these molecules the 1s cross sections of the different vibrational substates have maxima at different photon energies, indicating non-Franck-Condon behavior. In valence level photoelectron spectroscopy similar observations have been made: the shape resonance associated with the direct ionization of the $3\sigma_g$ level in N₂ shows strong non-Franck-Condon behavior, whereas there is no significant enhancement of higher vibrations in the $4\sigma_g$ partial cross section of CO₂ in the resonance region [28]. There is possibly a slow increase in the single hole cross section from 547 eV down towards threshold (Fig. 3), which may be due to the $5\sigma_g^*$ shape resonance. According to theory the latter is expected at 542 eV just above the O 1s threshold [27].

The major difference between the absorption curve and the O 1s partial cross section (below 552 eV the single hole cross section) in Fig. 4 is the shoulder on the shape resonance at about 554 eV. Since it is not present in the O 1s partial cross section, it has to be explained in terms of multielectron excitations that do not autoionize into the single hole state, but rather decay directly via spectator processes. The additional decay structures appearing in the Auger spectrum at these excitation energies are discussed in Sec. VI. The recent symmetry-resolved ion yield spectrum of CO₂ by Watanabe *et al.* [29] shows a resonance at 554 eV in the $\sigma \rightarrow \pi$ channel, indicating double excitations to final states of π symmetry. Stöhr [30] has argued that the shoulder at ~ 554 eV might in fact be the $4\sigma_u^*$ resonance. In the light of

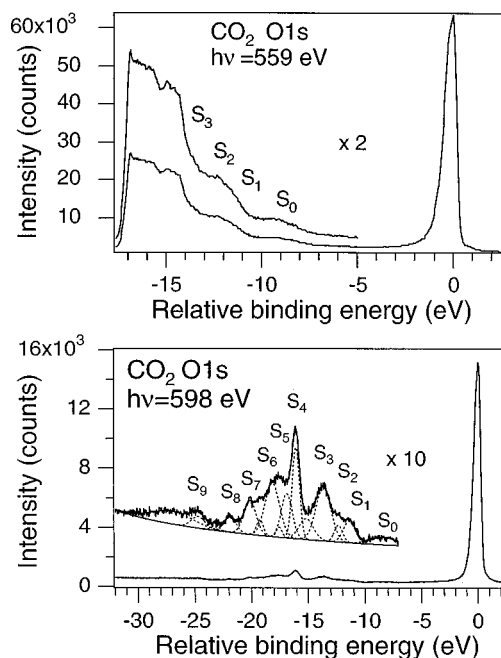


FIG. 5. O 1s shake-up satellite spectra of CO₂ measured at $h\nu = 559$ eV and $h\nu = 598$ eV.

the present results this is very unlikely and demonstrates the problems of identifying shape resonances on the basis of absorption spectra rather than the corresponding single hole cross sections. In addition to double electron excitations the thresholds for satellite excitations also occur in this region; the shake-up satellites account largely for the difference in the single hole cross section and the absorption curve. In the region around 552 eV the first shake-up satellites appear; their intensity increases strongly with photon energy, eventually reaching about 30% of the main line. Moreover, the threshold behavior of the satellites (see below) also exaggerates the contribution of the shape resonance to the absorption cross section. Above 565 eV shake-off processes also occur, leading directly to $1s^{-1}Val^{-1}$ double hole states, although this is not apparent in Fig. 3.

Similar to the cross sections, the asymmetry parameter, β , for the $\nu' = 0$ and $\nu' = 1$ states shows a strong perturbation in the region of the multielectron excitations and the shape resonance at $h\nu = 560$ eV. Strong oscillations, as are found around the multielectron excitations and the shape resonances in CO and N₂, do not occur. On the other hand, there is a smooth variation of the asymmetry parameters, which might be explained by many double excitations that cannot be resolved. From the onset of the shape resonance at around $h\nu = 560$ eV the β values (of both $\nu' = 0$ and $\nu' = 1$) start to increase steadily, reaching a value of about 1.6 at $h\nu = 570$ eV.

V. SATELLITES

Figure 5 shows wide energy window O 1s spectra at photon energies of $h\nu = 559$ eV and $h\nu = 598$ eV, illustrating the rich satellite structure. Peaks S_1 – S_9 are known from the Mg $K\alpha$ data of Allan *et al.* [31] corresponding to the sudden limit. The prominent satellite lines S_1 , S_3 , S_4 , S_6 , S_8 , and S_9 are well resolved, but there appears to be further unre-

TABLE I. Summary of the core level shake-up data for CO₂ O 1s at $h\nu=598$ eV compared to the data of Allan *et al.* obtained with Mg $K\alpha$ radiation. Relative intensities are estimated to be accurate to $\pm 15\%$ in this paper and $\pm 20\%$ in Allan *et al.* [31].

Satellite (see Fig. 5)	Shake-up energy (eV) this paper $h\nu=598$ eV	Relative intensity (%)	Shake-up energy (eV) Allan <i>et al.</i> [31] $h\nu=1253.6$ eV	Relative intensity (%)
S_0	8.5 ± 0.2	0.8		
S_1	11.5 ± 0.2	1.4	11.5 ± 0.2	0.9
S_2	12.4 ± 0.2	0.7	12.7 ± 0.2	1.4
S_3	13.8 ± 0.1	4.9	13.8 ± 0.2	3.6
S_4	16.2 ± 0.1	4.3	16.1 ± 0.2	5.8
S_5, S_6			17.9 ± 0.2	3.1
S_7	20.3 ± 0.5	2.3	19.9 ± 0.2	2.8
S_8	22.0 ± 0.2	1.0		
S_9	24.9 ± 0.2	0.9	22.3 ± 0.4	0.2 ± 0.1

solved lines contributing to the broad structures. In Table I the shake-up energies of prominent satellite structures and their intensities from our measurement at $h\nu=598$ eV are compared with data from Allan *et al.* [31]. The binding energies and the intensities were determined using a line profile analysis in which the individual satellite bands were described by asymmetric Gaussians. An extrapolated secondary electron background formed part of this fitting procedure, as shown in Fig. 5.

In general, the near-threshold region is characterized by a satellite behavior where the conjugate component of the transition moment becomes important, causing the conjugate contribution to normal satellites to become stronger, or even new, conjugate satellites to appear. The latter are forbidden in the sudden limit. A conjugate state results from a dipole transition of a core electron into a valence state accompanied by a monopole excitation of a valence electron into the continuum. Figure 6 shows the cross sections of the satellites S_3 and S_4 as well as those of satellites S_1 and S_2 . The S_1 and S_2 lines could not be separated, so that the added contribution is shown. While the cross section of satellites S_3 and S_4 stays

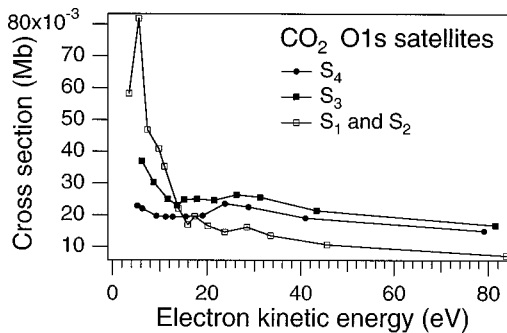


FIG. 6. Cross section of the shake-up satellites S_3 , S_4 and that of the satellites S_1 and S_2 (together) in the threshold region. For the labeling of the satellites, see Table I. S_3 and S_4 are clearly normal shake-up satellites, whereas S_1 and S_2 show a conjugate contribution.

nearly constant with photon energy, a very large increase occurs in the cross section of the combined S_1 and S_2 satellite near threshold, which is indicative of a conjugate excitation. Unfortunately, it is not possible to say from the experimental data in which of the two channels conjugate enhancement occurs or, indeed, whether a new, accidentally degenerate conjugate satellite appears. Calculations would help here. The density of points on the photon energy scale is rather low, so that the slight increase in intensity in the S_3 and S_4 curves between 20 and 30 eV above threshold may not be significant. The $4\sigma_u$ shape resonance is expected in these channels at approximately this energy.

VI. AUGER ELECTRON SPECTRA

“Normal” Auger decay tends to obscure transitions from other, less strongly populated core-hole states such as those generated by double excitations and shake-up transitions [32]. Indeed, in order to confirm the assignment of the reso-

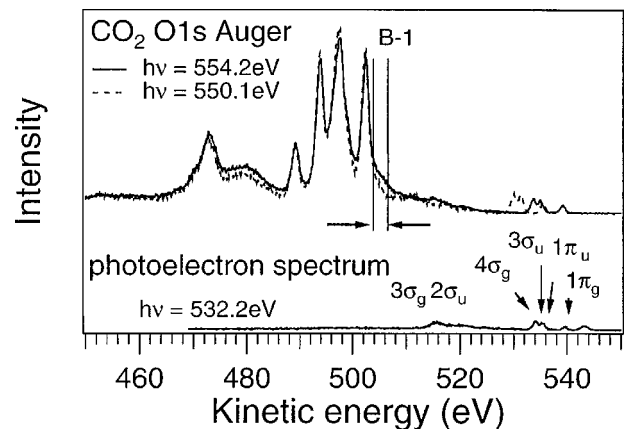


FIG. 7. Resonant Auger spectrum of CO₂ measured on the low kinetic energy shoulder of the shape resonance at 554.2 eV compared to an Auger spectrum just below at 550.1 eV.

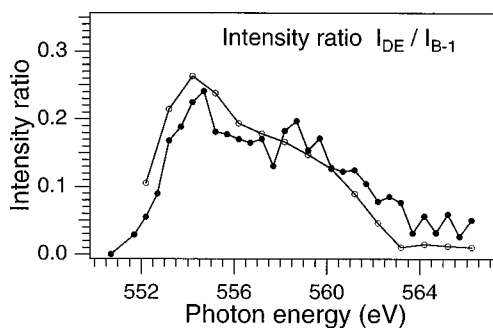


FIG. 8. Ratio of the decay intensity for the double excitations and the $B-1$ Auger line as a function of photon energy. Strong double excitations are apparent at about 554 eV.

nant structures seen in the absorption curve near threshold, we have also measured Auger spectra in the photon energy range 550 to 566 eV. In Fig. 7 a decay spectrum taken on the shoulder at 554.2 eV is compared with an Auger spectrum obtained at 550.1 eV. The intensities of the Auger spectra have been scaled to the $4\sigma_g$ single hole valence line. Additionally, a valence photoemission spectrum measured at $h\nu = 532.2$ eV, which is out of resonance, is shown. It has been shifted on the kinetic energy scale to coincide with the 554.2 eV resonant Auger spectrum. The differences in structure between the two Auger spectra are due to the decay of doubly excited states and/or shake-up states occurring in the one taken at 554.2 eV. In particular, the changes on the high-kinetic-energy tail of the $B-1$ Auger line (notation from [33]) can be used to indicate the occurrence of multiple-hole initial states, as has been shown for N_2 and C_2H_2 [19,34]. From the photoelectron spectrum of Fig. 7 we note that direct valence photoionization does not give rise to any significant intensity at kinetic energies below ~ 512 eV. Furthermore, for the C_2H_2 Auger decay spectra it has been observed that double participator processes, where one excited electron fills the core hole and the other is ejected (leading to valence $1h$ final states), are very unlikely [34].

To study this region more carefully we have measured a series of decay spectra in the range $h\nu = 550-566$ eV and integrated the intensity of the $B-1$ Auger line within the 501–503 eV kinetic energy range, I_{B-1} , as well as the intensity in the range 504–506 eV just above, I_{DE} . The open and filled circles in Fig. 8 show the corresponding intensity ratios as a function of photon energy for the two sets of data. I_{DE} has been set to zero at 550.7 eV on the assumption of negligible multiple excitations at this photon energy. With increasing photon energy the ratio increases strongly to

about 554 eV and then decreases at higher photon energy. Since only a few shake-up states can be excited at 554 eV, the shoulder on the shape resonance is therefore most probably due to doubly excited states, thus confirming the conclusions drawn from Fig. 4. These doubly excited states decay predominantly via spectator transitions where one or both of the excited electrons are not involved in the resonant Auger decay process, leading to $2h1p$ or $3h2p$ final states, respectively. For the C_2H_2 and CH_4 molecules resonant decay spectra have been observed where in a similar way one or both of the excited electrons remain as spectators during resonant Auger decay [34,35]. Another probable decay channel of the double excited states in C_2H_2 , however, is autoionization into the $C 1s^{-1}$ state, which can be explicitly observed for the $1s^{-1}1\pi_u^{-1}1\pi_g^2$ states in the $C 1s$ single-hole photoionization cross section [12].

VII. CONCLUSION

We have investigated the resonant structures in the photoabsorption cross section of CO_2 above the $O 1s$ threshold. Photon energy-dependent single hole $O 1s$ cross sections have been measured at high resolution. The line shape analysis of the vibrational fine structure gives a lifetime broadening of 165 ± 10 meV and indicates that only one vibrational mode, the antisymmetric stretch ν_3 , is excited with a vibrational energy of 307 ± 3 meV. Formally dipole forbidden, it can only arise via vibronic coupling. The difference between the $O 1s$ single hole cross section and the photoabsorption curve at 554 eV, giving rise to a shoulder on the $4\sigma_u^*$ shape resonance, is largely due to double excitations. Moreover, satellite thresholds and conjugate effects exaggerate the shape resonance in the absorption curve. We have also measured decay spectra on the continuum resonances. The Auger spectra show additional structure mainly at the photon energy of 554 eV, reinforcing the conclusion that strong double excitations make the most important contribution to this shoulder. In contrast to the diatomics, CO and N_2 , strong non-Franck-Condon effects appear to be absent in the region of the shape resonance.

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