

**PHOTOIONIZATION OF INNER VALENCE ELECTRONS OF CO₂ IN THE GAS PHASE:
A SYNCHROTRON RADIATION STUDY
USING PHOTON ENERGIES BETWEEN 40 AND 100 eV**

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The photoelectron spectrum of gaseous CO₂ is investigated in the inner valence electron region, between 20 and 45 eV binding energies for photon energies between 40 and 100 eV using synchrotron radiation. The branching ratio for inner valence ionizations increases considerably as a function of photon energy. We identify 12 ion states in this energy range. Some of the ion states show strong variations in relative intensities. The observed spectra *cannot* be understood on the basis of single-particle considerations. On the basis of many-particle calculations reported in the literature some of the ion states can be assigned.

1. Introduction

The photoelectron spectrum of gaseous CO₂ has been subject to many experimental [1–14] † and theoretical [15–18] investigations. While most interest has been devoted to the study of the outer valence ionizations, namely the $1 \Pi_g$, $1 \Pi_u$, $3 \Sigma_u$, and $4 \Sigma_g$ ion states, only in a few studies have researchers tried to assign and disentangle the rather complex spectrum resulting from ionization of inner valence electrons. The ion states observed in the inner valence regime cannot be assigned to single-electron ionizations. In this regime a complete breakdown of the single-particle picture occurs [15,19]. Consequently the observed spectrum is a rather complicated superposition of many configuration interaction satellites [19]. An early high-energy photoelectron study, covering this energy region by using non-monochromatized

Mg K α radiation, has been published [2]. Due partly to the very low photoionization cross sections for inner valence ion states, interference with X-ray-satellite-radiation-induced ionizations cannot be excluded. This was recognized by Gustafsson et al. [7] in their study of branching ratios using synchrotron radiation. The latter study mainly concentrated, however, on outer valence ionizations. More recently, electron–electron coincidence measurements [10,11] have been used to try to unravel the structure of the inner valence electron spectrum of CO₂. So far, two different theoretical approaches have been used to calculate the inner valence spectrum of CO₂: An ab initio Green's function approach within the two-particle–hole (2ph) Tamm–Dancoff (TD) approximation to the self-energy part [15,20], and the semi-empirical HAM/3 algorithm [17] have been employed. Comparison with experiment has been tried, and some qualitative conclusions have been reached [15, 17]. The present paper is intended to provide well re-

† For condensed CO₂, see ref. [14].

solved photoelectron spectra of the complete inner valence region to test the ability of available theoretical approaches [15,17] to assign these spectra, and in addition serve as reference data for surface studies [21].

We report in this Letter results of a synchrotron radiation study of inner valence shell CO₂ ionizations between 20 and 45 eV binding energies and photon energies between 40 and 100 eV. Our experiments lead to the identification of twelve ion states in this energy range, to be compared with six ion states identified so far [15]. The changes in relative intensities as a function of photon energy allow us to identify the *remnants* of those states derived from ionization of the two σ bonds in CO₂, namely the bonding $3\sigma_g$, and the antibonding $2\sigma_u$ molecular orbitals. This conclusion is supported by comparison with available data taken with Mg K α radiation [2]. The remaining ten ion states are assigned to configuration interaction satellites borrowing intensity from the $3\sigma_g$ and $2\sigma_u$, and the outer valence orbitals. Guidance for this assignment is gained from the *ab initio* calculations of Domcke et al. [15] and the semi-empirical calculation of Chong [17]. Clearly, however, none of the available calculations can provide us with a quantitative description of the spectra.

2. Experimental details and results

The experiments were performed at the BESSY storage ring in Berlin using a toroidal grating monochromator (TGM4) for monochromatization of the radiation [22]. Photoelectrons were detected after passing a double sector cylindrical mirror analyser (CMA) which is placed, and can be rotated, in the plane perpendicular to the photon beam direction to allow angular distribution measurements [23]. Within this plane the angular resolution is $\pm 3^\circ$ and it is $\pm 10^\circ$ perpendicular to this plane. In addition, another one-sector CMA is mounted at a fixed position to monitor an angle-independent signal for intensity calibration. The details of the apparatus have been described [23]. The spectra have been recorded at the quasi-magic angle (Φ_{QM}) at which the measured intensity is directly proportional to the partial cross section σ , i.e.

$$d\sigma/d\Omega = (\sigma/4\pi)[1 + \frac{1}{4}\beta(1 + 3P_1 \cos^2\Phi)], \quad (1)$$

with

$$1 + 3P_1 \cos^2\Phi = 0 \quad \text{for } \Phi = \Phi_{QM}, \quad (2)$$

where P_1 is the first Stokes parameter.

The quasi-magic angle has been determined for each photon energy separately via an angular distribution measurement for the 1s photoionization in helium with the known asymmetry parameter β (≈ 2 in dipole approximation and outside resonances). This method has been demonstrated to work very well [24]. High-purity CO₂ (99.9999% Linde) was introduced into the photon interaction volume via a multicapillary array. A typical pressure in the interaction region was 2×10^{-4} Torr with a pressure of 1.6×10^{-5} Torr in the recipient. The background vacuum was 1.1×10^{-6} Torr, typically. The spectrometer was operated with constant relative resolution, i.e. $\Delta E/E = \text{const}$. The spectra shown in fig. 1 have been corrected for the energy dispersion effect caused by this mode of operation by dividing each intensity value by the corresponding spectrometer voltage. Thus, the spectra reflect the correct relative intensities of the various photoionization peaks. The dispersion correction may be problematic close to threshold. At high kinetic energies (above 20 eV) there is no problem, namely, the background can usually be approximated by a straight line. However, as the kinetic energy decreases the slope of the background is no longer constant. Close to threshold an unambiguous separation between background and spectral features is almost impossible without the use of additional information.

The regions of inner ionization are shown for several photon energies on an extended scale in fig. 1, and, in addition, on an expanded energy scale in fig. 2. Note at this point that at low kinetic energies there is possibly a cut off in the transmission of the electron spectrometer, and, in addition, scattered electrons can influence the shape of the background. Both effects could possibly only affect the region of high binding energies in the spectrum taken with 40 eV photon energy. Therefore, only in this case has care to be exercised judging relative intensities of peaks. The binding energies are in table 1.

3. Discussion

In fig. 1 the region of outer valence ionization can

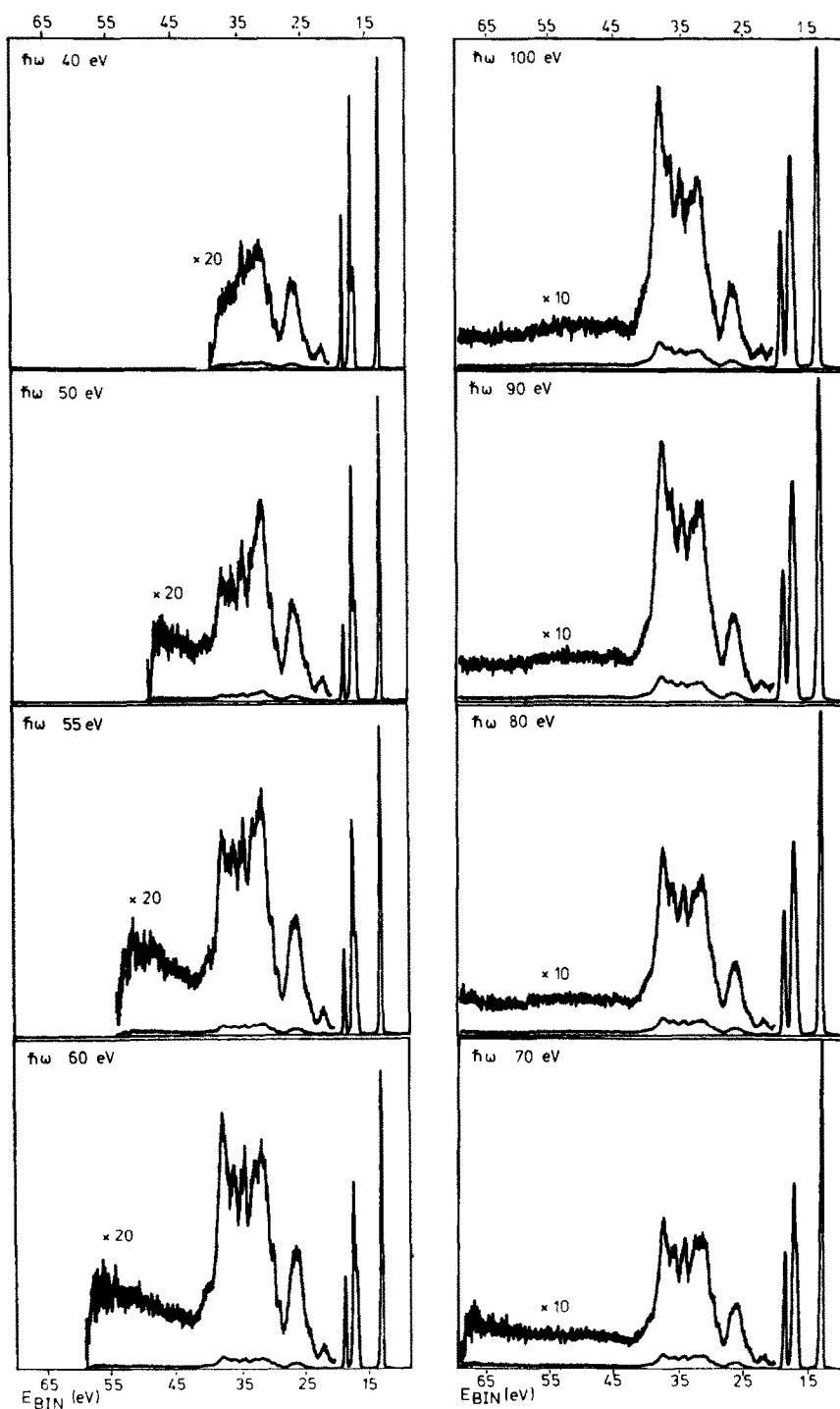


Fig. 1. Complete valence photoelectron spectra of gaseous CO_2 , taken at the quasi-magic angle as defined in the text. Photon energies are indicated. The maximum count rates were between 3000 and 10000 cps, depending on the photon energy range.

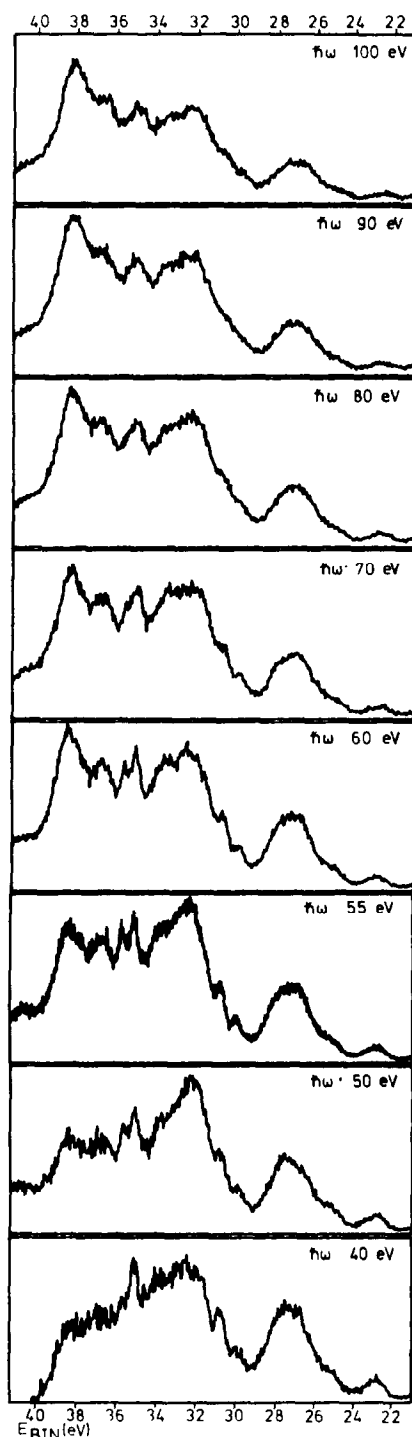


Fig. 2. CO₂ photoelectron spectra of the inner valence region between 40 and 100 eV photon energy.

Table 1
Binding energies of CO₂

Ion state label	E_{BIN} (eV)
1 Π_g	13.79 a)
1 Π_u	17.32 a)
3 Σ_u	18.08 a)
4 Σ_g	19.40 a)
A	22.8
B	25.1
C	26.9
D	29.8
E	30.7
F	32.2
G	33.4
H	35.0
I	35.5
K	36.9
L	38.0
M	40.6

a) Adiabatic ionization potentials of CO₂ from ref. [1].

easily be differentiated from the region of inner valence ionizations: While the outer valence ionizations are characterized by relatively sharp lines with binding energies below 25 eV, the inner valence ionizations with binding energies between 23 and 45 eV appear as a rather broad, structured continuum consisting of a multitude of overlapping lines (see binding energies in table 1).

Several observations on relative intensities can be made on the basis of fig. 1: (i) the relative intensities in the outer valence region vary moderately as a function of photon energy, (ii) the intensity of the complete inner valence electron ionization region increases considerably for increasing photon energies relative to the intensity in the outer valence region, (iii) within the inner valence region strong changes in relative intensities of individual components occur.

Observation (iii) can be confirmed in more detail from fig. 2. Obviously, the peaks above 36 eV binding energy increase in intensity relative to those peaks at lower binding energies. In particular, the peak at 38.5 eV binding energy shows a pronounced increase with increasing photon energy. This behaviour continues into the soft X-ray region as shown in fig. 3. In fig. 3 our spectra taken at 55 and 100 eV photon energies are compared with a spectrum recorded with Mg K α radiation by Allan et al. [2]. In this figure twelve ion

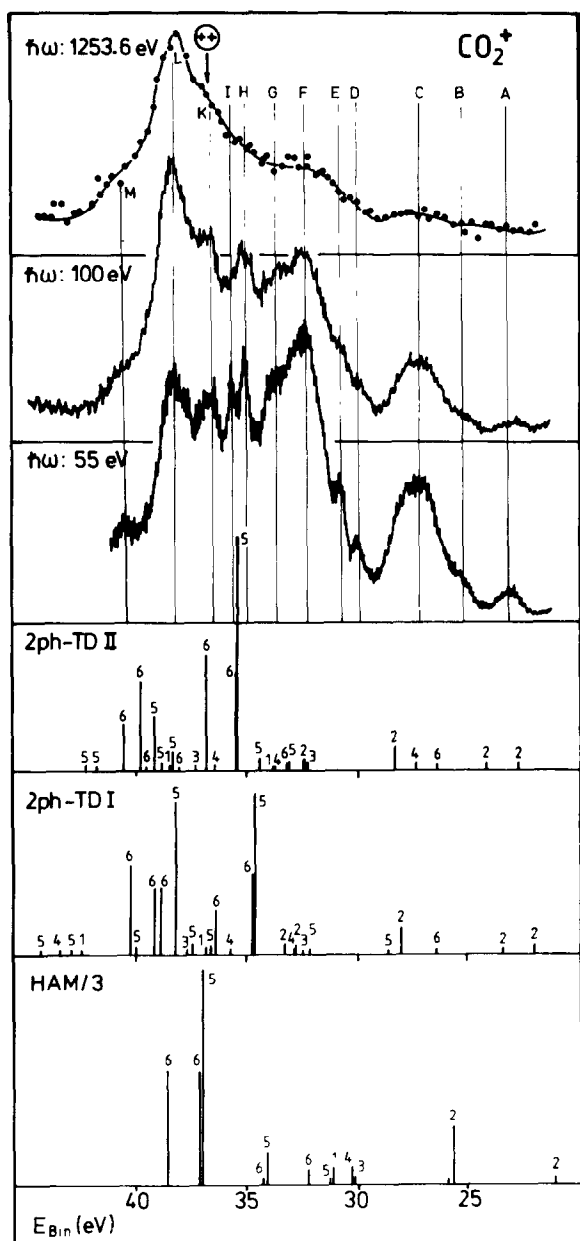


Fig. 3. Comparison of inner valence photoelectron spectra of CO_2 at 55 and 100 eV photon energy with a soft X-ray-induced spectrum (Mg $K\alpha$: 1253.6 eV) [2] and with results of theoretical calculations [15,17] as discussed in the text. (1: $1\pi_g$, 2: $2\pi_u$, 3: $3\sigma_u$, 4: $4\sigma_g$, 5: $2\sigma_u$, 6: $3\sigma_g$).

states according to table 1 are indicated by vertical lines as they show up experimentally as peaks or shoulders in fig. 2. In the following we shall discuss

observations (i) to (iii) with emphasis on (iii) using the calculational results of Domcke et al. [15] and of Chong [17]:

(i) According to Gustafsson et al. [7] and to Brion and Tan [10] the cross sections of the outer valence ionizations smoothly decrease above 40 eV photon energy. The lines due to the $1\Pi_u$ and $3\Sigma_u$ states (not resolved in refs. [7,10]) decrease more rapidly than the $1\Pi_g$ line at lowest binding energy and the $4\Sigma_g$ ion state at highest binding energy with increasing photon energy. Our spectra indicate that this trend continues to 100 eV photon energy. However, at 100 eV the relative intensities are still very different from those at 1200 eV photon energy. Obviously, the high contribution of s character to the σ -type orbitals, which is thought to determine the relative cross section of σ and π orbitals for soft X-ray photon energies ($\approx 0.1 \text{ \AA}$) [25] does not dominate at 100 eV ($\approx 1.2 \text{ \AA}$) photon energy for outer valence orbitals.

(ii) Brion and Tan [10] realized in their study that the branching ratios for ionization of inner valence electrons increase approximately linearly with photon energy and reach a value of 30% (sum over the inner valence region) of the total photoionization cross section in the region of 60 eV photon energy. Our results are in good agreement with their findings: For increasing photon energies beyond 60 eV the relative intensity of the inner valence shell ionizations still increases by a factor of two towards 100 eV photon energy. This reflects the high density of states due to multiple electron processes in the inner valence region. Domcke et al. [15] showed that the high density of multiple electron processes in CO_2 leads to a complete breakdown of the single-particle picture in this energy range. In particular the oscillator strengths for ionizations of the CO σ -bond orbitals, which are situated in this energy range, are predicted to be distributed over several ion states [15]. These states can be represented within a configuration interaction picture to be associated with wavefunctions that are mixtures of configurations.

(iii) Fig. 3 shows in the lower three panels the results of ab initio 2ph TDA calculations by Domcke et al. [15] with two different basis sets, and a semi-empirical HAM/3 calculation by Chong [17]. Both types of calculations use the sudden limit [26] to calculate intensities as given by

$$I \propto \left| \sum_{\alpha=1}^N \langle x_f | p | \phi_e \rangle \langle \Phi_{\alpha}^f | a_e | \Phi_0 \rangle \right|^2. \quad (3)$$

Given the ejection of a particular electron in orbital ϕ_e , the first factor is the dipole matrix element between the bound orbital ϕ_e and the continuum orbital x_f . The second factor is the spectroscopic amplitude and describes the result of annihilating the electron to be ejected from the true neutral ground state Φ_0 , and overlaps this frozen ion state Φ_{α}^f . In both calculations [15,17] the relative intensities are estimated by the sum of the squared spectroscopic amplitudes, thus neglecting the contributions of the dipole matrix elements. Even though it is clear from fig. 3 that none of the calculations shows quantitative agreement with the experimental data, the theoretical results are useful for an interpretation of the spectra.

The spectra shown in figs. 2 and 3 reveal at least three ion states (A, B, C) below 30 eV binding energy in the inner valence region. So far the shoulder (B) had not been identified [15]. It is very likely that these three states originate from the 2ph configuration $1\pi_g^{-2}2\pi_u$ which can be envisioned as the ionization of a $1\pi_g$ electron with simultaneous $1\pi_g \rightarrow 2\pi_u$ excitation into the lowest unoccupied orbital. This configuration may couple to the $1\pi_u$ outer valence ionization [15]. The configuration $1\pi_g^{-2}2\pi_u$ leads to five spectroscopic states, namely three ${}^2\Pi_u$, one ${}^4\Pi_u$, and one ${}^2\Phi_u$ states [27]. Since multielectron excitations gain their intensities through intensity borrowing from single electron excitations, only doublet states are important. The ${}^2\Phi_u$ state has vanishing intensity because there is no single ionization of ϕ_u symmetry. However, there is a single-electron ionization of π_u symmetry to which the three π_u multielectron excitations can couple. Note that Chong's calculation [17] predicts only two satellites of π_u parentage, while Domcke's calculation [15] shows three satellites^{††}. Also, the ab initio calculation predicts two more states having Σ_g symmetry in the energy range of the Π_u satellites. Experimentally we have no

indication of the existence of these states although the linewidths in the experimental spectrum are large enough to cover up more states. We can speculate on the cause of the relatively large linewidths: Walsh [28] has shown that the CO₂ molecule bends if the $2\pi_u^*$ orbital is occupied. Therefore, on $1\pi_g \rightarrow 2\pi_u$ excitation, for example, the CO₂ molecule assumes C_{2v} symmetry. It costs about 8.0–8.5 eV [29] to create the triplet, and about 12.6 eV [29] to create the singlet $1\pi_g \rightarrow 2\pi_u$ excitation, respectively. Roughly estimating the shakeup energy by adding these excitation energies to the $1\pi_g$ ionization energy yields 21.8–22.3 eV, and 26.4 eV, respectively, which is close to the experimentally observed energies in table 1. Therefore, it is quite possible that the expected strong vibronic coupling to the bending mode in those states leads to the large linewidths. It would be highly desirable to have calculations on CO₂ at hand that can take such effects into account. Such calculations were recently reported by Köppel et al. [30] for several other small molecules.

The assignment of peaks in the region between 30 and 35 eV binding energy is less clear. From the spectra we can identify at least six ion states (D–I) in this range. Four states (D, E and H, I) lead to relatively sharp lines, and they are situated pairwise at higher (H, I) and lower (D, E) binding energies of two overlapping broad maxima (F, G). At highest binding energies two intense lines, K and L, and a rather weak shoulder M are observed. On the basis of the calculations a quantitative assignment is difficult. Several states with different parentage are calculated for this energy range. However, it is suggested that the complete group of bands between 30 and 40 eV has some CO σ -bond parentage: Domcke et al. [15] calculate six or seven rather intense components distributed over 6–7 eV. Of these components four or five have Σ_g , two Σ_u character. The Σ states are calculated [15] to have higher binding energies on the average compared with the Σ_u states. It is interesting to note that, according to Domcke et al. [15], the dominating configurations contributing to the wavefunctions of the Σ_u states do not involve excitations into the lowest unoccupied $2\pi_u$ orbital. Only rather high-lying orbitals are involved. Since occupation of these orbitals does not lead to a bending of the CO₂ molecule, the small linewidths of the ion states above 30 eV, compared to the satellites below

^{††} The reason for this discrepancy is not clear. Chong [17] reports a third very low intensity peak in this energy range (see fig. 1e of ref. [17] and lower panel of fig. 3 in this work). The origin of this peak, however, has not been discussed by Chong [17].

30 eV binding energy, may be explainable. It is indicated in fig. 3 by (++) that the states K, L, and M are energetically situated within the double-ionization continuum [31]. Domcke et al. [15] realized that due to the vicinity of the double-ionization threshold those states can hardly be described accurately with finite basis set methods. Also, at higher binding energies 3p2h excitations that are not included in their expansion of the self-energy part [15] become more important. An extended TD calculation as reported by Schirmer and Walter [32] for CO would be of interest in the present case.

The photon energy dependence of relative line intensities shown in fig. 2 and compared to a soft X-ray-induced spectrum in fig. 3 is consistent with the discussion presented above. The remnants of the σ -bond orbital ionizations (K and L in fig. 3) with the largest s character increase quite dramatically with increasing photon energy. At 100 eV they are already the most intense lines in the spectrum, and at 1253 eV they completely dominate the inner valence spectrum. In contrast the peaks A, B, and C decrease in relative intensity with increasing photon energy and almost disappear in the high photon energy spectrum [2]. This is consistent with the decreasing intensity of the $1 \Pi_u$ peak in the outer valence region [15], which is supposed to be the parental peak for those ion states. The various peaks centering around state F also decrease in intensity when the photon energy increases but not quite as strongly as the Π_u states. At photon energies above 1200 eV there is still some intensity in the corresponding spectral region. This suggests that part of the oscillator strengths observed between 30 and 35 eV binding energy results from couplings to the outer valence ionizations. This is reasonable since states of Σ_g and Σ_u parentage can couple to the $3\sigma_g$ and $2\sigma_u$ ionizations in the inner as well as the $4\sigma_g$ and $3\sigma_u$ ionizations in the outer valence region.

Very recently, Roy et al. [33] have measured the inner valence region of the ionization spectrum of CO₂ in the gas phase, and have determined the asymmetry parameter β between 30 and 55 eV photon energy. Their results also suggest that the peaks A, B, and C have Π_u parentage in contrast to the peaks at higher binding energy. Their assignment, therefore, based on angular-dependent measurements seems to be consistent with our results based on photon energy dependences over a more extended range of photon energies.

4. Conclusions

We have presented a photon-energy-dependent study of the CO₂ photoelectron spectrum in the gas phase. It is shown that for higher photon energies the branching ratios for the ionization of inner valence electron states increase considerably. Based on qualitative considerations, supported by theoretical calculations reported in the literature [15,17], we find a consistent assignment of twelve peaks in the inner valence region of CO₂. The qualitative considerations lead to predictions for the photon energy dependence of the observed lines which are basically met by the experimental findings. However, clearly, the theoretical calculations [15,17] do not produce quantitative agreement with experiment. There is a need for more sophisticated calculations, taking vibronic coupling, and higher excited configurations, and possibly the continuum into account.

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