

Asymmetry parameters for CO₂ around the C *K* and O *K* ionization edges from the anisotropy of the ion distributions

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Asymmetry parameter (β) values have been determined from the C⁺, O⁺, and CO⁺ signals in the time-of-flight (TOF) mass spectra and the CO⁺-O⁺ signal in the photoion-photoion coincidence (PIPICO) spectra of CO₂ excited and/or ionized with monochromatic synchrotron radiation around the C *K* and O *K* ionization edges using a rotatable time-of-flight mass spectrometer. Positive β values of 0.4 were found for the C⁺ ions at the C $1s^{-1}2\pi_u^*$ and O $1s^{-1}2\pi_u^*$ resonances, respectively, and negative values between -0.1 and -0.4 were obtained for the other TOF and PIPICO signals at the same photon energies. The difference between these values and the expected value of -1 results from bending the molecule in the excited state before or during its ionic fragmentation. An O-C-O bond angle of 124° was found for CO₂ in the C $1s^{-1}2\pi_u^*$ state from the β value for the O⁺-CO⁺ PIPICO signal. The β values were close to the isotropic value of zero at all other photon energies for the C⁺ ions. β values for the O⁺ and CO⁺ signals in the TOF spectra and the O⁺-CO⁺ signals in the PIPICO spectra were found to be similar. Slightly negative β values were found below the C *K*-edge, rising to a maximum value of 0.9 at the σ_u^* shape resonance at 312.2 eV. Strongly positive β values were found just below the O *K* edge and were assigned to a transition of an O $1s$ electron to an s -type Rydberg orbital coupled with a shape resonance in the σ_g ionization channel. Two maxima were observed in the β values above the O *K* edge and assigned to shape resonances in the σ_g and σ_u continuum channels. The lower energy resonance in the σ_g channel was found at 542.5 eV and the position of the higher energy shape resonance in the σ_u channel was found to be 560 eV. The importance of using mass-resolved ion spectra to determine the β parameters for molecules which undergo a change in geometry upon excitation of a core electron is highlighted by a comparison of these results with the symmetry-resolved ion yield spectra of CO₂.

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I. INTRODUCTION

The inner-shell spectra of simple molecules exhibit resonances both below and above the ionization thresholds that have been associated with the shape of the molecular potential giving rise to the term "shape resonance" to describe the peaks observed above the ionization edge in the cross sections of numerous simple molecules [1]. The shape of the molecular potential is in turn dependent on the geometry of the nuclei and the distribution of their associated electrons. This dependence led Sette and co-workers to correlate the positions of the shape resonances observed around core ionization edges of simple molecules with the internuclear distances between the atoms involved in the bond giving rise to the observed resonance [2-4]. The debate which followed their attempts to describe this relationship centered in part on the experimental evidence required to assign an enhancement in the cross section, particularly above the ionization edge, as a shape resonance [5-8]. In addition to an enhancement in the cross section, it was agreed that

asymmetry parameter measurements for the core level of interest and theoretical calculations should support the assignment of the peak as a shape resonance to make it unequivocal [6,7]. Unfortunately it is difficult to measure the asymmetry parameters for a core level from the photoelectron anisotropy over a wide energy range, requiring a large number of low signal experiments (i.e., a lot of time). Near-edge x-ray-absorption-fine-structure spectroscopy of oriented molecules adsorbed on surfaces provides one means of measuring the molecular asymmetry parameter of a molecule [4]. In the gas phase, however, the sample gas usually has a random distribution of molecular orientations. By measuring the anisotropy of the deexcitation products, be they electrons, ions [9-11], or photons [12-14], however, the orientation of molecules undergoing a specific electronic transition can be determined. The utility of examining the anisotropy of ion yields of the core excited and ionized molecules has been demonstrated to provide a measurement of the molecular asymmetry parameter β_m for a variety of simple diatomic [9-11,15-23] and triatomic [24,25] molecules.

When a molecule absorbs linearly (or elliptically) polarized light, such as synchrotron radiation, it will undergo an electronic transition from an initial state to some final state only when the molecule is specifically oriented with respect to the electric vector of the in-

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cident radiation. The orientation is a function of the symmetries of the initial and final electronic states, the symmetry group of the molecule, and the degree of polarization of the incident radiation. For linear molecules, with $D_{\infty h}$ or $C_{\infty v}$ representations, transitions from initial states with Σ symmetry to final states with Σ symmetry occur only when the molecule is oriented parallel to the electric vector of the incident radiation. Transitions from Σ to Π states occur only when the molecule is oriented perpendicular to the electric vector. If the excited state molecule created in these orientations electronically de-excites and fragments into ions *before* any nuclear motion occurs, then the ions should be ejected along the axis of the fragmenting bond. In the case of core excited and ionized molecules composed of light elements, the principle decay mechanism is Auger decay. The lifetime of the C $1s^{-1}$ core hole has been estimated to be about 9×10^{-15} s by a deconvolution of the vibrational structure in the C K emission band of CO_2 [26]. A similar value of 1×10^{-14} s has also been obtained by theoretical methods [27]. The O $1s^{-1}$ core hole lifetime for CO_2 has not been determined experimentally, but it is also estimated to be about 1×10^{-14} s [28]. These lifetimes are several orders of magnitude shorter than the usual rotational frequencies of simple molecules, so the orientation of the molecule at the instant of excitation should be preserved. Following the Auger transition, the molecule is usually left with two holes in the valence shell, often in a repulsive state that fragments directly. The resulting anisotropic distribution of molecular fragment ions can be detected and the symmetry of the final electronic state of the transition can be inferred.

Results for several diatomic and triatomic molecules of first row elements have been presented previously, demonstrating the validity of the method and its underlying assumptions [9–11,15–25]. One method that shows considerable promise for extension of the technique to more complex polyatomic molecules is the photoion-photoion coincidence measurement [25]. By selecting only specific ion pairs arriving in coincidence at the ion detector, the orientation of a specific bond in the molecule can be probed.

In this paper we report the asymmetry parameter (β) values determined from the time-of-flight (TOF) mass spectra and photoion-photoion coincidence (PIPICO) spectra of CO_2 at photon energies around the C K and O K ionization edges. Cross sections for the two core levels of CO_2 have been studied experimentally by electron energy loss and photoabsorption measurements [29,39] and theoretically [4,40–42] by several groups. The ground state electronic configuration of CO_2 is

$$1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 3\sigma_g^2 2\sigma_u^2 4\sigma_g^2 3\sigma_u^2 1\pi_u^4 1\pi_g^4, \quad {}^1\Sigma_g^+,$$

where the $1\sigma_g$ and $1\sigma_u$ orbitals are linear combinations of the two O $1s$ orbitals and the $2\sigma_g$ orbital corresponds to the C $1s$ orbital. The first three unoccupied orbitals are $2\pi_u$, $5\sigma_g$, and $4\sigma_u$. Using the dipole selection rules, which allow a transition between two states with different inversion symmetries (i.e., $g \rightarrow u$ and $u \rightarrow g$) but forbid transitions between two states with the same inversion symmetry (i.e., $g \rightarrow g$ and $u \rightarrow u$), the C K -edge photoab-

sorption spectrum is expected to exhibit one π^* and one σ^* resonance due to the $2\sigma_g \rightarrow 2\pi_u$ and $2\sigma_g \rightarrow 4\sigma_u$ transitions. The O K -edge spectrum should exhibit one π^* and two σ^* resonances due to the $1\sigma_g \rightarrow 2\pi_u$, $1\sigma_u \rightarrow 5\sigma_g$, and $1\sigma_g \rightarrow 4\sigma_u$ transitions, respectively.

The experimental C K -edge cross section is dominated by a π^* resonance below the ionization edge and a σ^* shape resonance above the ionization edge [29,38]. Several smaller resonances have been identified below the ionization edge at high photon resolution and assigned as transitions to the $3s$, $3p$, $3d$, $4s$, $4p$, $5p$, and $6p$ Rydberg orbitals [39]. Additional features were also observed above the edge and assigned to shake-up excitations [38]. The O K -edge cross section also exhibits a strong π^* resonance below the edge but the positions of the Rydberg resonances have not been clearly identified in the experimental spectra [29,38]. Two σ shape resonances have been assigned to the continuum region, one near threshold due to the $1\sigma_u \rightarrow 5\sigma_g$ transition and another ~ 19 eV above threshold due to the $1\sigma_g \rightarrow 4\sigma_u$ transition along with additional structure due to shake-up of valence electrons accompanying the O K ionization [38].

The π^* resonances observed in the cross sections of CO_2 below the two core edges are much broader than the experimental bandpass [29,39]. The breadth of these peaks has been ascribed to the excitation of a large number of vibrational modes in the core excited molecule due to the large difference in equilibrium nuclear geometries of the ground and excited states [29,43]. When a core electron is promoted to the empty π^* orbital, the equilibrium geometry of the CO_2 molecule changes from linear in the ground electronic state to bent in the excited state [44]. The O—C—O bond angle in the C $1s^{-1}\pi^*$ excited state has been previously estimated to be about 135° [29].

The positions of the shape resonances in the photoabsorption spectra of CO_2 do not correlate well with the C—O bond length in the δ - R diagram for the other C—O bond containing molecules in the scheme developed by Sette and co-workers [2–4]. One of the reasons given for the discrepancy is the uncertainties in the positions of the σ^* resonances. The position of the high energy resonance is not clear as there is an overlapping contribution to the photoabsorption cross section from shake-up transitions. Characterization of the low energy resonance as a shape resonance (i.e., by the measurement of β values) is also not yet complete. The measurements reported here clarify some of the ambiguities about the nature of these resonances.

II. EXPERIMENT

Synchrotron radiation from the Teras electron storage ring [45] operating at 750 MeV was monochromatized with a Grasshopper monochromator [46] equipped with a 1200 line/mm grating. The resolving power of the monochromator ($\lambda/\Delta\lambda$) was estimated to be about 300 in the C K -edge region and about 150 in the O K -edge region. An effusive molecular beam of CO_2 (99.9% purity) was crossed with the photon beam at the center of

a TOF mass spectrometer. The high vacuum regions of the electron storage ring and beam line optics were separated from the experimental chamber using two stages of differential pumping allowing a background gas pressure of $\leq 3.0 \times 10^{-5}$ Torr in the experimental chamber to be tolerated without windows between the light source and the interaction region.

The TOF spectrometer employed in this study has been described in detail elsewhere [9,46] and consists of a mutually orthogonal arrangement of the monochromatized photon beam emerging from the differential pumping, a nozzle for the introduction of an effusive jet of the sample gas, and a microchannel plate (MCP) detector and flight tube with a MCP detector mounted opposite each other to detect the electrons and ions. Charged particles generated in the interaction region of the sample gas with the photon beam were accelerated to the MCP detectors using a series of grids biased to the appropriate potentials.

The TOF spectra were obtained in two modes, photoelectron-photoion coincidence (PEPICO) mode and photoion-photoion coincidence mode. No energy analysis was applied to the electrons used to provide a start signal in the measurement of the TOF spectra. TOF spectra in PEPICO and PIPICO modes were measured at angles of 0° , 55.9° , and 90° with respect to the direction of polarization of the synchrotron radiation. Electric fields of 8.1 or 16.2 and 32.6 or 16.2 V/mm were applied to the interaction region of the spectrometer in the PEPICO and PIPICO modes, respectively. The spectra were measured using two different extraction fields to ensure that no other signals underlie the peaks of interest and that the peak shapes, and hence the β parameter values obtained, are not dependent upon the extraction field used to measure the spectra.

III. RESULTS & DISCUSSION

A. TOF spectra

Time-of-flight mass spectra of CO₂ photoexcited to the shape resonance above the C K edge (312.2 eV) measured with the axis of the flight tube at 0° and 90° with respect to the mean electric vector of the elliptically polarized synchrotron radiation are shown in Fig. 1. Signals for four ions C⁺, O⁺, CO₂²⁺, and CO⁺ are present in these spectra and the assignments are given in the bottom frame of the figure. The spectra are reasonably consistent with previously reported spectra [47] both in the relative intensities of the peaks and the kinetic energy distributions of the ions [48]. The detection of CO₂²⁺ on a time scale of about 3 μ s indicates that some portion of excited molecules electronically decay to a stable or long-lived metastable doubly charged molecular ion. The CO₂⁺ molecular ion, which is expected to have a flight time of 4.4 μ s in the TOF spectrometer in the present conditions, was not detected because the range of the time to amplitude convertor was set to 2 μ s (plus an offset of 2 μ s).

The shapes and relative intensities of the peaks in the

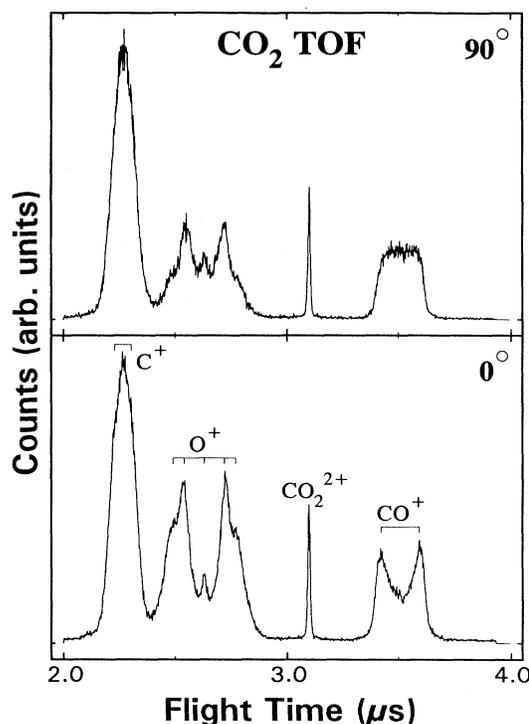


FIG. 1. Time-of-flight mass spectra of CO₂ photoionized with 312.2 eV monochromatized synchrotron radiation measured at angles of 0° and 90° .

TOF spectra in Fig. 1 are dramatically different for the different ions and change more subtly between the spectra measured at the two angles. The doubly charged molecular ion is formed with only thermal kinetic energies and hence the peak shape is very narrow and Gaussian on this scale. As expected, the shape of this peak does not change with the orientation of the analyzer. Peaks for the other ions, which are created by breaking bonds in the molecule, are much broader than this thermal contribution and receive varying degrees of kinetic energy from the fragmentation. The breadth of the peak is a rough indication of the kinetic energy of the ions, so the O⁺ ions are created with much larger kinetic energies than the C⁺ ions, for example. The peaks are roughly symmetric about the center point with flight times shorter than the median value corresponding to ions initially directed towards the TOF tube, hence arriving first, and flight times longer than the median value resulting from ions initially directed away from the flight tube. The direction of propagation of these ions must first be reversed by the applied electric field before they can be accelerated towards the TOF tube, resulting in a longer flight time. Ions arriving at the median flight time (the center of the peak) are those created with little kinetic energy in the direction parallel to the flight tube.

Differences in the peak shapes between the two spectra in Fig. 1 measured at 0° and 90° result from anisotropy in the distributions of fragment ions of CO₂ at this photon energy (312.2 eV). The most obvious case is CO⁺, where the peak shape is a doublet with maxima near the extents of the peak in the spectrum measured at 0°

while it is almost rectangular in shape in the spectrum measured at 90° . This is consistent with the CO^+ ions being formed with kinetic energy directed along the electric vector of the polarized radiation. Similarly for the O^+ ions the peak shape is indicative of the ions having kinetic energy directed parallel to the electric vector of the incident radiation, with greater relative intensities at the extents of the peak in the spectrum measured at 0° than the spectrum measured at 90° . The shapes of these two ion peaks therefore suggest that the CO_2 molecule is oriented parallel to the electric vector of the incident radiation when it is excited into the shape resonance, quickly decays electronically and fragments, directing CO^+ and O^+ ions along the bond axis, parallel to the electric vector. The shape of the C^+ peak does not change significantly between the two spectra measured at 0° and 90° . The width of the C^+ peak is much greater than the thermal width of the CO_2^+ peak. These two observations are consistent with C^+ being formed with an isotropic distribution of momentum vectors. It is not surprising that C^+ ions are isotropically distributed and formed with less kinetic energy than either the O^+ or CO^+ ions, since both bonds in the molecule must be broken to form C^+ , a process that can occur either simultaneously or in two steps. This is discussed further in the following sections.

B. β values

Rather than discussing the spectra measured at 0° and 90° to determine the orientation of the molecule at each photon energy studied, it is convenient to quantify the degree of anisotropy observed in the distributions for each ion using the asymmetry parameter (β) value. The method used to extract β values from the TOF spectra has been presented in detail previously [9,15–17,49–55] and will only be outlined here. Shapes of the peaks in the experimental TOF spectra depend on several factors: the kinetic energy distributions of the ions, the physical characteristics of the spectrometer, the degree of polarization of the incident radiation, and the angular distribution of the ions. In order to determine a β value, which is related to the angular distribution of the ions, the other factors contributing to the peak shape must be accounted for. These factors can be determined from a TOF spectrum measured at 55.9° (the magic angle in the xy plane assuming 90% polarization of the incident radiation) by considering the physical characteristics of the spectrometer. At this angle, contributions to the peak shape from the anisotropy of the ions cancel out and the peak shapes are determined by the other factors. Asymmetry parameters can then be determined by a fit of the experimental spectra measured at 0° and 90° by allowing only the β value to change while keeping the other parameters fixed at the values determined from the spectrum measured at the magic angle. The validity of this method has been demonstrated by the similarity of results obtained using this method [9,15–17,23,25] with complementary results from other methods [10,11,18–22].

Several sources of error in the β values determined in this way must be considered. The polarization of the

incident radiation is assumed to be 90% based on the acceptance angles of the beam line optics. If the actual polarization differs from this value erroneous β values will result from the method. The β values determined at a specific photon energy will also contain contributions from other photon energies because of the finite photon resolution of the monochromator and higher-order contributions to the monochromatized photon beam. This is of particular interest in the region below the ionization threshold where many sharp resonances are often observed. β values at the positions of these resonances are therefore averaged by contributions from other resonances or base line within the photon width determined by the monochromator. Statistical errors in the fitting procedure and experimental spectra also contribute to the total error in the β values. The β values reported here should therefore be considered to be subject to a confidence limit of ± 0.1 , especially in the pre-edge region of the spectra.

Kinetic energies of 0.09, 0.36, 0.81, 1.44, 2.25, 3.24, 4.41, 5.76, and 7.29 eV were used to fit the C^+ signals while energies of 0.01, 0.09, 0.36, 0.81, 1.44, 2.25, 3.24, 4.41, 5.76, 7.29, 9.0, 10.89, 12.96, 15.21, 17.64, and 20.25 eV were used for the O^+ peaks, and 0.01, 0.09, 0.36, 0.81, 1.44, 2.25, 3.24, 4.41, and 5.76 eV for the CO^+ peaks. These values have no physical significance other than to provide a basis set of peaks with which to fit the experimental line shape. The values are chosen to be equally spaced in flight time rather than in energy. The experimental peak shapes are fit using the envelope of peaks described above in order to extract numerical β values from the shapes of the ion peaks at different angles.

C. Asymmetry parameters from the TOF spectra

1. C K edge

The asymmetry parameter values resulting from these fitting calculations are shown for the C^+ , O^+ , and CO^+ fragment ions of CO_2 at photon energies around the C K edge in Fig. 2. In the top frame of Fig. 2 a total electron yield determined by measuring the count rate on the electron MCP while scanning the photon energy is given. This total electron yield is an approximation of the photoabsorption cross section to identify the positions of the resonances and illustrate the photon resolution of the monochromator. The relative intensities of the peaks in the total electron yield spectrum in Fig. 2 do not compare well with the previously reported spectra owing to variations in the ionization efficiency (η) across the core ionization edge.

The photoabsorption cross section of CO_2 in the vicinity of the C K edge has been studied previously by several methods. Wight and Brion reported the first cross section measured using electron energy loss spectroscopy and identified all of the structure observed here [29]. The lowest energy peak was assigned to a transition of a C $1s$ electron into the lowest unoccupied molecular orbital, the $2\pi_u$ orbital. The resulting excited state molecule was

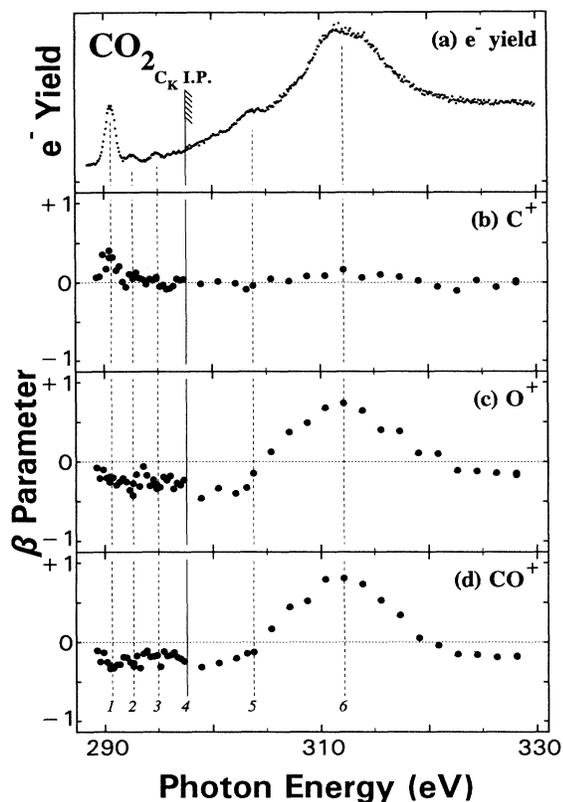


FIG. 2. β parameters obtained from the C^+ , O^+ , and CO^+ ion signals in the TOF spectra of CO_2 measured around the C K edge. The total electron yield spectrum measured at the same photon resolution is included in the top frame and the C $1s$ ionization edge is indicated on the figure by the hatched bar. Several positions corresponding to bound excitations and shape resonances are indicated by the broken vertical lines and are summarized in Table I.

predicted to be bent in its equilibrium geometry with a bond angle of about 135° resulting in the broad peak observed in the spectrum [29]. The photon energy scale used here was calibrated against the position of this peak reported previously [29]. Positions and assignments of other peaks in the electron yield spectra of CO_2 around both the C K and O K ionization edges as well as the edge positions were taken from a more recent report of the photoabsorption spectra [38].

Between the π_u^* peak and C K ionization potential several less intense peaks have been observed and ascribed to transitions of a C $1s$ electron into s and p Rydberg orbitals. Recently the photoabsorption spectrum of CO_2 in the region of the Rydberg excitations has been reported at very high photon resolution ($\Delta h\nu = 70$ meV) and Rydberg transitions up to $n = 6$ identified along with numerous vibrational bands [39].

Owing to the inversion symmetry, only one shape resonance is observed above the C K edge with several other peaks resulting from two electron transitions. The only two electron transitions clearly observed in the electron yield spectrum in Fig. 2 is the shake-up peak centered at about 303.8 eV. The position of the shape resonance is

not clear from the photoabsorption spectrum since there is a large overlapping contribution from shake-up in the same photon energy range. We have chosen the position of the maximum in the β values as discussed below, 312.2 eV, as the position for the shape resonance.

The positions and assignments of the features in the total electron yield spectra indicated by the dashed vertical lines across Fig. 2 are summarized in Table I along with the β values from the different ions at these positions. The experimental β values [$\beta_{\text{expt}}(h\nu)$] reported in Table I and those presented in the text have been corrected for the underlying background ionization (valence ionization in the case of the C K edge) by Eq. (1) derived from the definition of the asymmetry parameter as the difference between the photoabsorption strengths for parallel and perpendicular molecular orientations with respect to the electric vector of the incident radiation [16]:

$$\beta_{\text{expt}}(h\nu) = \beta_{C\ 1s}(h\nu) \frac{\sigma_{C\ 1s}(h\nu)}{\sigma_{C\ 1s}(h\nu) + \sigma_{\text{background}}(h\nu)} + \beta_{\text{background}}(h\nu) \times \frac{\sigma_{\text{background}}(h\nu)}{\sigma_{C\ 1s}(h\nu) + \sigma_{\text{background}}(h\nu)}, \quad (1)$$

where $\beta_{C\ 1s}(h\nu)$ is the asymmetry parameter for electronic excitation and ionization involving only the C $1s$ electrons, $\beta_{\text{background}}(h\nu)$ is the asymmetry parameter for the background ionization, $\sigma_{C\ 1s}(h\nu)$ is the C $1s$ TOF cross section, and $\sigma_{\text{background}}(h\nu)$ is the background TOF cross section, all involving the ion of interest. Relative yields of the individual ions have been determined recently from their peak areas in the TOF spectra measured over this energy range [48]. The β values in the figures have not been corrected for the underlying ionization continua.

Except for a maximum at the C $1s^{-1}2\pi_u^*$ resonance, the β values from the C^+ fragment are nearly isotropic at all photon energies. A positive β value at a π_u^* resonance is at odds with results for all of the linear molecules previously studied using this and other ion detection techniques. When a C $1s$ electron is promoted into the $2\pi_u^*$ orbital ($2\sigma_g \rightarrow 2\pi_u$), the total symmetry of CO_2 changes from Σ to Π . The molecule should therefore be oriented perpendicular to the electric vector and ions ejected along the bond axis would yield β values of around -1 , as observed for N_2 [9–11,16,19], O_2 [11,15,18,20], NO [17,21], CO [18,22,23], and N_2O [25]. The positive β value obtained here, however, indicates that the C^+ ions are ejected parallel to the electric vector of the polarized synchrotron radiation.

The nearly isotropic distribution of C^+ ions at the other photon energies is not surprising if the mechanisms that produce these ions are considered. The C^+ ion can only result from a simultaneous rupture of both bonds in the CO_2 molecule or in two steps in which first one C—O bond ruptures producing an unstable or metastable CO fragment followed by the rupture of the second C—O bond. In the first case, if the atoms are colinear prior to the bond rupture, the two O atoms will carry away most of the momentum leaving the C^+ ion with none and hence no anisotropy. In the second case, the CO fragment pro-

TABLE I. Summary of the resonance positions in the electron yield spectra of CO₂ and β parameter values from the TOF and PIPICO signals around the C *K* and O *K* ionization edges. The peak labels refer to the labels on Figure 2 and 5 around the C *K* edge and Figs. 3 and 6 around the O *K* edge.

Figure peak label	Energy (eV)	Assignment	β parameters			PIPICO O ⁺ -CO ⁺
			C ⁺	TOF O ⁺	CO ⁺	
2,5-1	290.7	C 1s ⁻¹ 2 π_u^*	0.4	-0.2	-0.4	-0.3
2,5-2	292.7	C 1s ⁻¹ 3s Rydberg orbital	0.1	-0.5	-0.4	-0.3
2,5-3	295.0	C 1s ⁻¹ 3p Rydberg orbital	0.1	-0.5	-0.3	-0.2
2,5-4	297.5	C 1s ⁻¹ IP				
2,5-5	303.8	shakeup	-0.1	-0.2	-0.1	-0.1
2,5-6	312.2	σ_u^* shape resonance	0.2	0.8	0.9	0.8
3,6-1	535.0	O 1s ⁻¹ 2 π_u^*	0.4	-0.2	-0.1	-0.3
3,6-2	539.3	O 1s ⁻¹ 3s,4p Rydberg orbitals	0.1	1.6	0.9	0.9
3,6-3	541.3	O 1s ⁻¹ IP				
3,6-4	542.5	σ_g^* shape resonance	0.0	0.9	0.7	0.7
3,6-5	554.2	shakeup	0.1	0.2	0.0	0.1
3,6-6	560	σ_u^* shape resonance	0.2	0.4	0.3	0.2

duced by the rupture of the first C—O bond will have momentum in a direction opposite to that of the O atom released. If the CO fragment is formed in a metastable state, it may have time to rotate before it fragments, leading to a loss of the anisotropy. Alternatively, if the second C—O bond ruptures quickly with respect to the rotational period of the CO fragment, the C⁺ ion will be released in the opposite direction to the momentum imparted to the CO fragment in the first bond rupture and will again have little momentum and hence little anisotropy. These arguments are consistent with the narrower width (narrower kinetic energy distribution) of the C⁺ ion peak with respect to the O⁺ peak in the TOF spectra in Fig. 1.

β values obtained from the shapes of the O⁺ and CO⁺ fragment ion peaks in the TOF mass spectra of CO₂ have similar profiles around the C *K* edge. Both sets of data have weak minima at the 2 π_u^* resonance, scattered but negative β values in the region of the Rydberg transitions, and broad maxima of positive β centered at about 312.2 eV, the position of the σ_u^* shape resonance above the C *K* edge. The feature in the total electron yield spectrum at \sim 304 eV, which has previously been assigned as due to shake-up excitations [38], has no apparent effect on the β values observed for the O⁺ and CO⁺ ions. The positive β values for the C⁺ ions and negative β values for the O⁺ and CO⁺ ions are consistent with the CO₂ molecule being bent in the C 1s⁻¹2 π_u^* excited state. When the bent molecule fragments and O⁺ ions or atoms are ejected along the C—O bond directions, by conservation of momentum, the C⁺ ions are ejected in a direction perpendicular to the bond axis of the ground state molecule. Increased probabilities of the C⁺ ions being directed perpendicular to the axis of the ground state molecule, which is itself oriented perpendicular to the polarization vector of the incident light, give rise to positive β values for the C⁺ ions at the 2 π_u^* resonance. It cannot be determined from these data whether the molecular geometry changes before, during, or after the electronic relaxation of the core hole or even whether

the molecular geometry changes before or during ionic fragmentation of the molecule.

2. O *K* edge

β values from the C⁺, O⁺, and CO⁺ ion signals in the TOF spectra of CO₂ at photon energies around the O *K* edge are summarized in Fig. 3. The β values at the positions of the resonances indicated on Fig. 3 have been corrected for the underlying valence and C 1s ionization continua by Eq. (1) and are summarized in Table I. The total electron yield spectrum shown in Fig. 3 illustrates the nature of the resonances observed in the spectrum at the photon resolution employed. The positions and assignments of the resonances indicated on Fig. 3 by the dashed vertical lines were taken from a previous study of the photoabsorption spectrum of CO₂ [38] and are summarized in Table I. The position of the O *K* edge, which is also indicated on Fig. 3, was also taken from the same study [38]. The photon energy scale was calibrated using the previously reported position of the intense 2 π_u^* resonance below the edge [29].

In previous studies of the cross sections of CO₂ around the O *K* edge a strong resonance attributed to excitation of an O 1s electron into the first unoccupied molecular orbital 2 π_u^* was observed as the first peak below the ionization edge. The appreciable width of this resonance (considerably wider than the C 1s⁻¹2 π_u^* resonance), even when measured at high resolution, is thought to be due to the excitation of a large number of bending levels resulting from the bent equilibrium geometry of the molecule in this excited electronic state [29,43]. In addition, the creation of a localized O 1s core hole in the CO₂ molecule leaves the two oxygen atoms inequivalent, lowering the symmetry of the molecule, and results in a lengthening of the C—O bond involving the excited oxygen atom and an accompanying shortening of the other C—O bond in the equilibrium geometry of the excited state molecule [56,57]. A significant number of asymmetric stretching

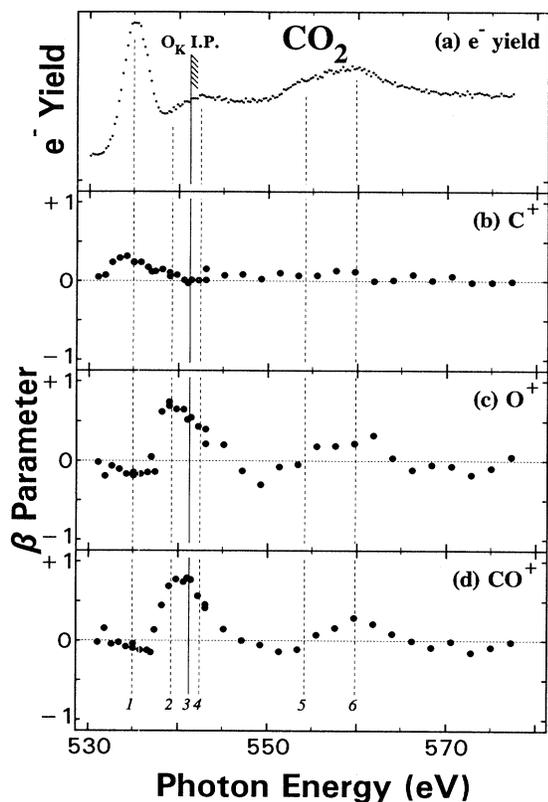


FIG. 3. β parameters obtained from the C⁺, O⁺, and CO⁺ ion signals in the TOF spectra of CO₂ measured around the O *K* edge. The total electron spectra yield spectrum measured at the same photon resolution is included in the top frame and the C 1*s* ionization edge is indicated by the hatched bar. Several positions corresponding to bound excitations and shape resonances are indicated by the broken vertical lines and are summarized in Table I.

vibrational levels are therefore populated in the excitation, contributing additional width to the peak. A less intense resonance with considerably narrower width observed below the O *K* edge has been attributed to excitation of an O 1*s* electron into 3*s* and 3*p* Rydberg orbitals [38]. Above the ionization edge, two resonances have been observed previously, one close to threshold and a second about 19 eV above threshold. Molecular orbital considerations and theoretical calculations have assigned these as shape resonances in the $k\sigma_g$ and $k\sigma_u$ channels, respectively [38]. Shake-up of the valence electrons accompany the ionization of an O 1*s* electron causes the broad enhancement in the cross section centered at 554 eV [38].

Asymmetry parameter values from the C⁺ ion signals in the TOF spectra of CO₂ exhibit positive values at the $2\pi_u^*$ resonance and nearly isotropic values at the most other photon energies. This behavior can be explained in the same way as below the C *K* edge. The isotropic β values result from a simultaneous three-body dissociation or a two-step dissociation of the excited or ionized linear molecule. The positive values at the O $1s^{-1}2\pi_u^*$ resonance arise from ionic dissociation of the molecule in

a bent geometry, with the C⁺ ions ejected perpendicular to the axis of the molecule in its ground state, which was oriented perpendicular to the electric vector of the polarized incident radiation.

β values from the O⁺ and CO⁺ ions are similar around the O *K* ionization edge with two broad maxima in the profiles in Fig. 3. Neither the O⁺ nor the CO⁺ ions exhibit significant anisotropy at the O $1s^{-1}2\pi_u^*$ resonance, although β values from both are slightly negative. The first broad maximum in the β values straddles the O *K* edge and may be either a single resonance located near the ionization threshold or due to two contributions, one below the edge and one at or just above the edge. The effects of the higher energy shape resonance are clearly seen as weak maxima in the profiles of the β values for O⁺ and CO⁺ (6 of Fig. 3). The shake-up states (5 of Fig. 3) do not have a distinguishable effect on the β values of the O⁺ or CO⁺ ions.

D. PIPICO spectra

It was found previously that β values determined from the PIPICO signals of two fragment ions comprising the entire molecule are a better reflection of the molecular asymmetry parameter β_m than are the values from the noncoincident signals in the TOF spectra of polyatomic molecules [25]. This is because the PIPICO signals must result from electronic relaxation processes of the core hole that yield only a doubly charged molecular ion, removing contributions from the underlying single valence ionization and autoionization of the core excited states which can result in metastable ions which may rotate before dissociating. The proportion of CO₂ in the C $1s^{-1}2\pi_u^*$ and O $1s^{-1}2\pi_u^*$ excited states that autoionizes to a singly charged molecular ion is small [58,59], but use of the PIPICO signal eliminates its contribution altogether. The PIPICO signals also eliminate contributions from three-body and two-step dissociation mechanisms which may lower the anisotropy of the noncoincident ions in the TOF spectra. However, other mechanisms exist that can contribute isotropic components to the distributions of the coincident ions. Double valence ionization occurs with some probability in the photon energy ranges of interest and will contribute to the PIPICO signal. Its effects can be subtracted using Eq. (1).

Metastable doubly excited states of CO₂²⁺ are known to exist and if they dissociate before traveling too far down the flight tube may contribute isotropic distributions of coincident ions. Doubly charged metastable CO₂²⁺ molecular ions generated by direct double ionization have been identified with lifetimes on the order of 10 ns–2.2 μ s [60]. The fraction of metastable CO₂²⁺ exhibiting metastable charge separation was found to be as high as 24.4% when 30.4 nm light was used as the ionization source. These long-lived metastable ions have sufficient lifetimes to allow for rotation of the doubly charged molecular ion and will result in some isotropic contribution to the PIPICO peak shape. Since many more doubly charged electronic states are accessible through the Auger decay of a core hole than by direct double ionization, the proportion of the O⁺-CO⁺ PIPICO signal resulting from

CO_2^{2+} formed in a metastable state is unknown.

PIPICO spectra of CO_2 obtained at a photon energy of 312.2 eV and with the TOF spectrometer oriented at 0° and 90° are shown in Fig. 4. There are peaks in the spectra corresponding to O^+-O^+ , C^+-O^+ , and O^+-CO^+ ions detected in coincidence. Only the O^+-CO^+ signals are considered here. Comparing the shapes of the O^+-CO^+ peaks in the spectra measured at 0° and 90° , it is apparent that the ions are traveling in directions parallel to the electric vector of the synchrotron radiation, with peak shapes similar to those observed for O^+ and CO^+ in the TOF spectra measured at the same photon energy in Fig. 1. β values have been extracted from the spectra using the methods described in Sec. IIIB and the results are discussed below.

1. C K edge

The β values from the O^+-CO^+ signals in the PIPICO spectra of CO_2 at photon energies around the C K edge are summarized in Fig. 5 together with the total electron yield. At the $\text{C } 1s^{-1}2\pi_u^*$ resonance below the C K edge the β values from the PIPICO spectra have a minimum value of -0.3 , comparable to the β values from the O^+ and CO^+ ions, whereas the values from the C^+ signals in the TOF mass spectra were positive. The minimum value at the π_u^* resonance is not very close to the expected value -1 , due to the bent equilibrium geometry of the excited state molecule, and contradicts previous

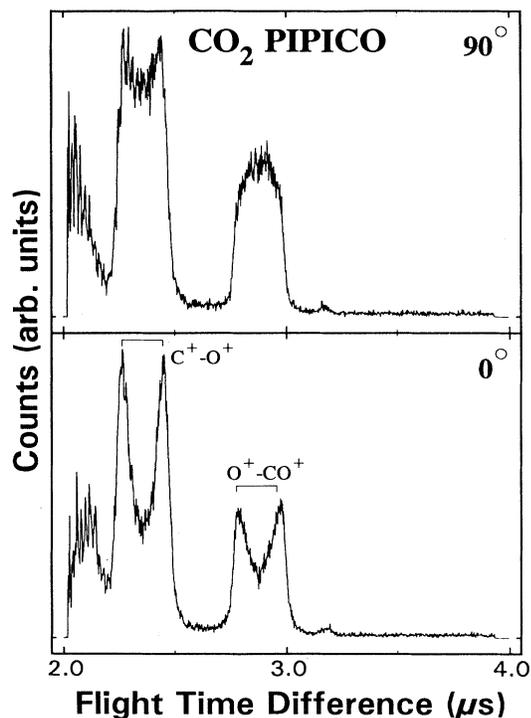


FIG. 4. Photoion-photoion coincidence mass spectra of CO_2 photoionized with 312.2 eV monochromatized synchrotron radiation measured at angles of 0° and 90° .

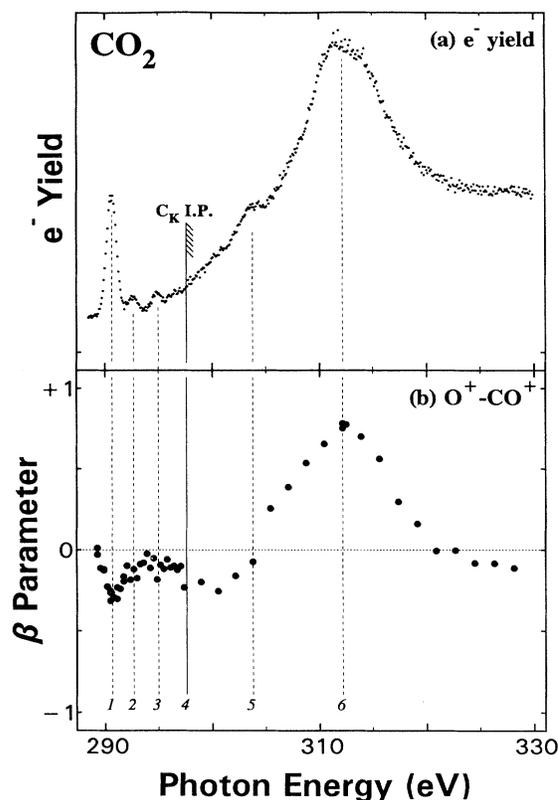


FIG. 5. β parameters obtained from the O^+-CO^+ coincidence signals in the PIPICO spectra of CO_2 measured around the C K edge. The total electron yield spectrum measured at the same photon resolution is included in the top frame and the C $1s$ ionization edge is indicated by the hatched bar. Several positions corresponding to bound excitations and shape resonances are indicated by the broken vertical lines and are summarized in Table I.

work which postulated that CO_2 may be linear in the $\text{C } 1s^{-1}2\pi_u^*$ excited state [61].

The CO_2 molecule in the $\text{C } 1s^{-1}2\pi_u^*$ state has been estimated to have a bond angle of 135° [29]. The β value which results from this bond angle can be calculated using Eq. (2) if the CO_2 molecule is assumed to undergo the $\text{C } 1s \rightarrow 2\pi_u^*$ transition when it is oriented perpendicular to the electric vector of the incident radiation:

$$\beta = 2P_2(\cos \chi), \quad (2)$$

where $P_2(\cos \chi) = (3 \cos^2 \chi - 1)/2$ is the second Legendre polynomial and χ is the angle between the electric vector of the polarized radiation and the bond that is broken. A bond angle of 135° [29] yields a β value of -0.56 . The minimum β value at the $\text{C } 1s^{-1}2\pi_u^*$ resonance from the PIPICO spectra, -0.3 , gives a $\text{O}-\text{C}-\text{O}$ bond angle of 124° and the minimum β value for CO^+ , -0.4 , gives a bond angle of 129° . Considering that contributions from metastable dicationic molecular ions will yield a more isotropic distribution of fragment ions than the collection of orientation vectors of the parent molecules, the bond angle of 124° calculated above is probably too

low, i.e., the actual molecular orientation parameter is more anisotropic than the experimental β value from the PIPICO spectra, but it does provide a good lower limit estimate of the value.

In the symmetry-resolved ion yield spectra of CO₂ [62], the β value obtained from the intensities of the Σ and Π components of the yields at the C $1s^{-1}2\pi_u^*$ resonance is -0.1 . The agreement with the present results is poor considering that the symmetry-resolved ion yields usually yield slightly more anisotropic β values than the present method owing to differences in photon resolution, background subtraction, and other experimental factors. However, because the total yield of all ions with kinetic energies of greater than a certain threshold in directions parallel and perpendicular to the electric vector of the polarized synchrotron radiation is used to obtain the symmetry-resolved ion yields, the C⁺ ions, which have positive β values, will contribute signal primarily to the Σ ion channel, while the O⁺ and CO⁺ ions, which have negative β values, will contribute signal primarily to the Π channel. Mass differentiation is therefore required to study the anisotropy of ion distributions in bent heteronuclear molecules.

At the positions of the $3s$ and $3p$ Rydberg resonances below the C K edge, the β values are definitely negative. Recently reported high resolution symmetry-resolved ion yield spectra support this observation with a much greater yield of ions at the detector oriented perpendicular to the electric vector of the polarized incident radiation than at the detector perpendicular to the polarization vector [62]. This observation contradicts previous assignments of the resonance observed at 292.7 eV as an excitation of a C $1s$ electron to a $3s$ Rydberg orbital [29,38,39,30] as this would be expected to have a positive β value. The C $1s(2\sigma_g) \rightarrow 3s(\sigma_g)$ transition should be forbidden by the dipole selection rules. Hence the $3s$ Rydberg resonance is probably mixed with a vibrational motion giving it π character. The ν_2 normal mode of CO₂ has π_u symmetry. Coupling between the electronic and bending states therefore makes the C $1s(2\sigma_g) \rightarrow 3s(\sigma_g) + \nu_2(\pi_u)$ transition more intense than expected.

Above the C K ionization edge the β value profile in Fig. 5 is very similar to that obtained for the CO⁺ and O⁺ ions from the TOF spectra. The β values rise from negative values at threshold through to the shake-up peaks to a broad maximum at the position of the σ_u^* shape resonance at 312.2 eV before falling to below zero above 320 eV. The position of the shape resonance is consistent with the position determined from the C KVV Auger and C $1s$ photoelectron cross sections and asymmetry parameters [63–66].

Cross sections of CO₂ above the C K edge have been calculated previously by frozen-core Hartree-Fock (FCHF) [42], Stieltjes-Tchebycheff moment theory (STMT) [40], and multiple-scattering (MS) $X\alpha$ [4] methods. All of the methods underestimate the energy of the σ shape resonance above the ionization edge but reproduce the shape of the peak relatively well. Theoretical partial channel cross sections have been reported only for the FCHF calculations. The molecular orientation param-

eter (β_m) is related to the σ and π components of the photoionization cross section (σ_Σ and σ_Π , respectively) by

$$\beta_m = \frac{2(\sigma_\Sigma - \frac{1}{2}\sigma_\Pi)}{\sigma_\Sigma + \sigma_\Pi}. \quad (3)$$

Using the FCHF calculated partial cross section values, a β_m value of 1.5 is obtained, which is about twice the experimentally observed value.

2. O K edge

The β values from the O⁺-CO⁺ PIPICO signals at photon energies around the O K edge are shown in Fig. 6 together with the total electron yield spectrum. Unlike the β values from the TOF spectra, there is a distinct minimum at the O $1s^{-1}2\pi_u^*$ resonance. The β values are similar to the values from the O⁺ and CO⁺ TOF signals at the other photon energies, with maxima centered around the ionization threshold and ~ 19 eV above the edge.

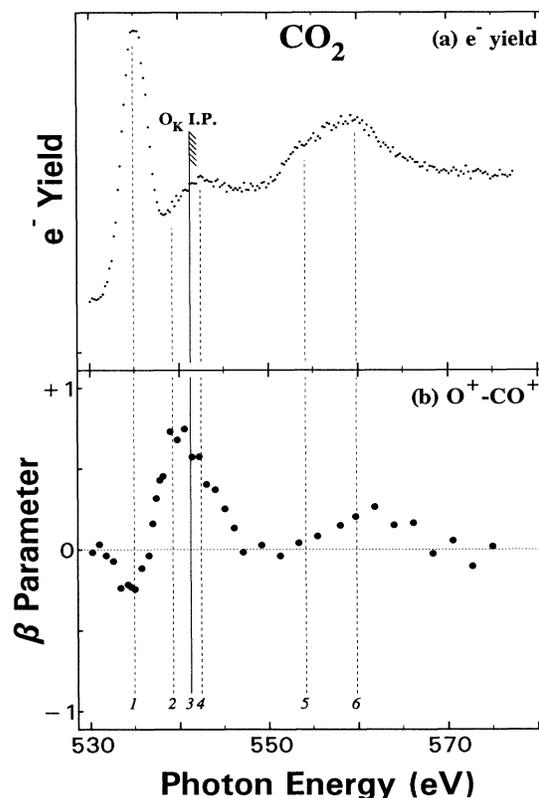


FIG. 6. β parameters obtained from the O⁺-CO⁺ coincidence signals in the PIPICO spectra of CO₂ measured around the O K edge. The total electron yield spectrum measured at the same photon resolution is included in the top frame and the C $1s$ ionization edge is indicated by the hatched bar. Several positions corresponding to bound excitations and shape resonances are indicated by the broken vertical lines and are summarized in Table I.

The β values at the $2\pi_u^*$ resonance below the O K edge are similar to those at the $2\pi_u^*$ resonance below the C K edge, indicating that the molecule also has a bent equilibrium geometry in the O $1s^{-1}2\pi_u^*$ state. At higher photon energies the β values rise to maxima below the ionization threshold at ~ 539 eV. The β values begin rising to positive values about 4 eV below the ionization edge. The photon resolution of the monochromator in the present experimental conditions at this photon energy is about 3.6 eV, so it is not possible to unequivocally determine whether the positive β values result from the σ_g shape resonance at the O K ionization threshold or a $\Sigma \rightarrow \Sigma$ transition below the ionization edge. The sharp jump in the β values from negative to positive values as well as the slight drop in the β values across the ionization edge suggest that a $\Sigma \rightarrow \Sigma$ transition in the discrete portion of the photoabsorption spectrum is responsible for at least a part of the positive β values observed here. Higher resolution symmetry-resolved ion yield spectra of CO₂ by Kosugi and co-workers [67] show a sharp peak atop a broad maximum in the Σ ion yield channel at this photon energy, supporting this conclusion. Transitions to $3s$ and $3p$ Rydberg orbitals have been assigned to the resonance observed in the O K -shell photoabsorption spectra at this position previously. The strongly positive β values in this region indicate that transitions to Rydberg orbitals with s character dominate the cross section in this region.

Two maxima are seen in the β values from the CO⁺-O⁺ PIPICO signals above the O K edge, similar to the features observed in the β values from the O⁺ and CO⁺ TOF signals, corresponding to shape resonances in the σ_g and σ_u ionization channels, respectively. The position of the shape resonance in the σ_g channel is within 1 eV of the ionization threshold. The position of the shape resonance in the σ_u channel is 560 eV as indicated by the maximum in the β values from the CO⁺-O⁺ PIPICO signal and the O⁺ and CO⁺ TOF signals. The shake-up states centered at 554 eV do not have a definite effect on the β values. Symmetry-resolved ion yield spectra of CO₂ in the region of the shake-up states and the σ_u shape resonance indicate that the shake-up states result in a small ($\sim 25\%$) contribution to the Π channel with a maximum contribution at about 554 eV [67]. The maximum in the Σ channel, resulting from the σ_u shape resonance, is at about 559 eV, in good agreement with the results presented here, although the resulting β value, about 0.5, is more anisotropic than the value of 0.2 obtained here. The positions and magnitudes of the maxima in the β values around the O K edge also compare favorably with the values determined by Kim *et al.* [68].

Cross sections calculated by MS $X\alpha$ [4] and STMT calculations [41] are in good agreement with the experimental observation of two shape resonances in the σ ionization channels above the O K edge. Results from earlier STMT calculations [40] and from FCHF [42] calculations do not reproduce the lower energy shape resonance. The STMT calculation correctly predicts the positions of the resonances at 542 and 560 eV while positions determined from the MS $X\alpha$ calculation, about 1 and 14 eV above the edge, incorrectly predict the position of the higher

energy resonance. β_m values at the resonance positions determined from the partial channel cross sections from the STMT calculation [41] and Eq. (3) are 0.14 and 0.21 for the σ_g^* and σ_u^* shape resonances, respectively. While the calculated value for the σ_u^* resonance is in good agreement with the experimental value, the calculated value for the σ_g^* shape resonance is not. From the FCHF partial cross sections, a β_m value of 0.66 is obtained at the position of the σ_u^* shape resonance which is not in such good agreement with the experimental data.

The position of the higher energy shape resonance, 18.6 eV above the O K edge, leads to poor agreement of the bond length versus mean resonance position for CO₂ (9.9 eV) with the other C-O containing molecules reported by Sette *et al.* [2–4]. The position of the lower energy shape resonance may be below the ionization threshold however, at the position of the maximum in the β values, between 537 and 539 eV. This would result in a mean σ resonance position of between 7 and 8 eV, in much better agreement with the trend observed for the other C-O containing molecules.

IV. SUMMARY

Asymmetry parameter values have been determined from the TOF and PIPICO spectra of CO₂ measured with a TOF mass spectrometer oriented at 0°, 55.9°, and 90° to the orbital plane of the synchrotron using monochromatized radiation at photon energies around the C and O K edges. The experimental spectra were fit by a model calculation to determine the β values from the shapes of the experimental C⁺, O⁺, and CO⁺ TOF peaks and O⁺-CO⁺ PIPICO peaks. Profiles of the β values for the C⁺ ions were found to be close to the isotropic value of zero at all photon energies except at the positions of the π_u^* resonances below the two core edges. β values from the other TOF and PIPICO signals were similar to each other.

At the π_u^* resonances below the C and O K edges the β values from the C⁺ ions were positive with maximum values of 0.4 at the C $1s^{-1}2\pi_u^*$ and O $1s^{-1}2\pi_u^*$ resonance positions. β values from the other ions were negative at these positions however, with minimum value of -0.4 and -0.3 , respectively. These results are inconsistent with the β values of close to -1 observed at the positions of π^* resonances below the core edges of other diatomic and linear triatomic molecules studied with the same or similar techniques. These results support the idea that the equilibrium geometry of the molecule is bent in the π_u^* excited state. If the molecule is assumed to be oriented perpendicular to the electric vector of the incident radiation when it undergoes the $1s \rightarrow \pi_u^*$ transition and it bends symmetrically about the central carbon atom then, upon ionic fragmentation of the molecule, the C⁺ ions will be directed perpendicularly to the original orientation of the molecular symmetry axis and the O⁺ ions will be directed along the directions of the C—O bonds in the bent excited state molecule. Distributions of the C⁺ ions will therefore have a positive β value while those of the O⁺ ions will depend on the O—C—O bond an-

gle. Using the experimentally determined β values from the O⁺-CO⁺ PIPICO signals, an O—C—O bond angle of 124° was found for the C 1s⁻¹2 π_u^* excited state of the molecule.

The β values were found to be slightly negative at the Rydberg resonances below the C K edge, suggesting that the assignment of the peak observed in the photoabsorption spectra at 292.7 eV as C 1s⁻¹3s is incorrect. However, the 3s Rydberg resonance is possibly mixed with the ν_2 vibrational mode, giving this transition the π character. A maximum was found in the β values at the position of the shape resonance above the C K edge, supporting the assignment of this peak as a shape resonance in the σ_u ionization channel.

Just below the O K edge the β values exhibited a strong maximum. This maximum could be due to either a transition to an s Rydberg orbital or a σ_g shape resonance below the ionization edge. Two maxima were found in the profiles of the β values above the O K edge, supporting the previous assignments of shape resonances in the σ_u and σ_g ionization channels at photon energies close to threshold and ~ 19 eV above threshold, respectively. The position of the high energy shape resonance in the σ_u channel leads to a large deviation in the mean resonance position versus bond length for CO₂ compared to other C—O bond containing molecules. If the position

of the lower energy shape resonance in the σ_g channel is located below the ionization threshold, however (i.e., at the position of the maximum in the β values found below the O K edge), a mean resonance position of 7–8 eV results, which is in reasonably good agreement with the trends observed for the other C-O containing molecules.

The results at the positions of the π_u^* resonances highlight the utility of determining β values from the mass-resolved ion yield spectra. In these results it is apparent that the C⁺ ions are directed parallel to electric vector of the incident polarized radiation while the O⁺ and CO⁺ ions are directed at angles closer to the direction of the normal. Using other methods in which the ions are not mass resolved, only an isotropic distribution of ions is observed and the directions of ejection of the individual ions cannot be determined.

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