Assigning x-ray absorption spectra by means of soft-x-ray emission spectroscopy

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The possibility to symmetry assign x-ray absorption spectra using x-ray emission spectroscopy is demonstrated. The oxygen K spectra of CO₂ are used to illustrate the possibility to assign core excitations through excitation-energy and angular dependence of resonantly excited x-ray emission spectra. The Rydbergassociated structures just below the ionization threshold in the O K x-ray absorption spectrum are assigned to be mainly due to excitations to orbitals of σ_g character. The results, which contradict some previous literature assignments, are supported by quantum-chemical calculations. [S1050-2947(98)08001-9]

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I. INTRODUCTION

Inner-shell x-ray absorption spectroscopy (XAS) and electron-energy-loss spectroscopy, which simulate photoabsorption in the limit of small momentum transfer and highimpact energy [1], are powerful techniques for gaining element specific information about the unoccupied orbitals. However, there are still problems in the interpretation and assignments of certain features in many spectra. Even for some of the smaller molecules there are absorption features that have not yet been conclusively assigned. Hence, there is a need for techniques that provide additional symmetry information which can be used for assignments. In recent years angular-resolved ion-yield measurements have given information about the spatial (σ/π) symmetry of the unoccupied orbitals in diatomic and linear triatomic molecules [2,3]. In this work we will use angular-resolved resonant x-ray emission spectroscopy (XES) to obtain the spatial symmetries as well as parities of the unoccupied orbitals. The idea of using fluorescence spectra to gain additional information about the absorption is not new. It has, for example, been used in several recent x-ray studies of solid samples [4], but XES spectra have not been used to reveal the identity of unassigned absorption features of gas-phase molecules before.

High-brightness synchrotron radiation sources have recently enabled x-ray emission studies of molecules in gas phase using well-defined selective excitation energies [5,6]. Previous investigations have shown that the polarization [6,7] and the angular distribution [7,8] of resonant x-ray emission are in general anisotropic, and that the parity is conserved in the full absorption-emission scattering process [5,9]. The anisotropic distributions and the parity selection rule, which are consequences of the electric-dipole nature of both the absorption and the subsequent emission of soft-xray photons, strongly influence the relative intensities of the emission peaks. From the energy and angular dependence of the relative intensities one can determine the parity and spatial symmetry of the unoccupied orbitals reached in the absorption step.

To demonstrate the usefulness of the approach, the O K

x-ray absorption spectrum of CO_2 is studied in detail. The near-edge part of the spectrum consists of one strong and broad peak, a weaker and sharper peak, and a broad structure leading to the ionization continuum. The first of these peaks has been assigned to the O $1s \rightarrow 2\pi_{\mu}$ resonance, but the assignment of the other features below the ionization threshold is still inconclusive. Wight and Brion [10] suggested that the $3s\sigma_{\sigma}$ Rydberg resonance also contributed to the first peak and that the second peak was due to $3p\sigma_u$ and $3p\pi_u$ Rydberg resonances. The remaining structure was assigned to resonances to higher Rydberg levels. Later on, Sham et al. [11] assigned the second peak to the 3s and 3p Rydberg resonances. In a recent ion-yield work by Bozek et al. [12] it was found that the absorption intensity in the region below the ionizaton limit results mainly from excitations to orbitals of σ symmetry. More recent ion-yield measurements made in higher resolution by Hitchcock [13] have verified that those features are predominantly of " σ character." The difference in suggested assignments shows that there is a need for a more conclusive experimental method for this kind of determinations.

In this work, resonant x-ray emission spectra are used to determine whether the different features correspond to excitations to unoccupied orbitals of predominantly σ or π character, and whether the unoccupied orbitals have mainly gerade or ungerade character. The experimental results are compared to calculated XAS spectra.

II. EXPERIMENT

The experiments were made at undulator beamline 7.0 [14] at the Advanced Light Source in Berkeley, California. The grazing-incidence spectrometer [15,16] used to record the x-ray emission spectra provides a choice of three different spherical gratings and has a two-dimensional multichannel detector, which can be translated to the focal position defined by the Rowland circle of the grating in use. In these experiments a slit width of 20 μ m was selected and a 5 m grating with rule density of 1200 lines/mm was used, providing a resolution of about 0.7 eV. The chamber, housing the

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spectrometer and gas cell, is rotatable 90° under vacuum, which makes angle-resolved measurements possible [16]. The CO₂ gas was contained, at a pressure of a few Torr, in a gas cell with thin windows transmitting the radiation. The synchrotron radiation entered the cell through a 1000 Å thick silicon-nitride window and the interaction region was viewed by the spectrometer through a 900 Å thick polyimide window, supported by a polyimide grid and coated with 150 Å of aluminum nitride. The spectrometer was mounted so that its entrance slit was parallel to the synchrotron beam. This configuration enabled a large fraction of the interaction region to be viewed by the spectrometer.

XAS spectra were measured using the photocurrent from an electrode situated inside the gas cell. The signal was normalized by the photocurrent from a clean gold mesh introduced into the beam prior to the gas cell. The bandpass of the synchrotron beam in these recordings was about 0.65 eV at full width half maximum.

III. CALCULATIONS

We have employed the so-called static exchange (STEX) approach to compute the O K x-ray absorption spectrum of CO₂. We have also used results from multiconfigurational self-consistent field (MCSCF) calculations to check the results for the lowest excitations. We refer to the original method descriptions [17,18] for merits and limitations of these approaches. The particular parametrizations for the results which we present here have been tested and used in a previous extended investigation covering a set of carbonyl compounds [19].

Computations are carried out with broken inversion symmetry ($C_{\infty v}$) using the ground state equilibrium internuclear distance and assuming the vertical approach. In order to assist assignments of the parity symmetries, STEX calculations were also performed in full $D_{\infty h}$ symmetry. A selfconsistent-field (Δ SCF) procedure is used for calculating ionization potentials, which are then used in the STEX calculations. The STEX results have also been used for population, quantum defect, and so-called r^2 analysis in order to further characterize the states in terms of atomic decomposition and valence versus Rydberg character.

IV. RESONANT X-RAY EMISSION SPECTROSCOPY

Resonant XES is based on a two-photon scattering process: An incoming x-ray photon excites a core electron which results in a transition to an intermediate, core-excited state. The intermediate state decays by emission of an x-ray photon to a final, valence-excited state. The process may be described in the following way:

$$h\nu + M \Rightarrow M^{\dagger} \Rightarrow M^* + h\nu',$$
 (1)

where ν and ν' are the frequencies of the incoming and outgoing photons, M^{\dagger} designates the core-excited state, and M^* the valence-excited state.

In a resonant excitation the core electron is promoted to an unoccupied (or unfilled) bound orbital. The fluorescence decay may then occur either via a spectator transition, where an electron from one of the occupied orbitals fills the core hole while the excited electron remains as a spectator in the (previously) unoccupied orbital, or via a participator transition, where the excited electron itself fills the core hole. The final state of a spectator transition is a valence-excited state whereas the final state of a participator transition is the electronic ground state. The spectator emission peaks will be designated by the symmetry of the occupied valence orbital from which the electron filling the core hole comes. The Poynting and polarization vectors of the incoming and outgoing photons are designated \mathbf{k}_{in} , ε_{in} and \mathbf{k}_{out} , ε_{out} , respectively.

V. SYMMETRY ASSIGNMENTS

A. Parity

According to the parity selection rule, the parities of the initial and the final states of a one-photon process have to be different. Thus in a two-photon process the parities have to be the same. For the parity of the final state of the emission to be the same as that of the initial ground state, the electron filling the core hole has to come from an orbital of the same parity as the one to which the core electron was promoted, i.e., the unoccupied and occupied orbitals must have the same parity.

This rule is valid for dipole transitions in homonuclear diatomics, where there is only one, totally symmetric, vibrational mode [5,9]. However, in polyatomic molecules vibrational modes of ungerade symmetry can couple nearly degenerate core-excited electronic states of different parity, thereby reducing the molecular symmetry. In this way parityforbidden electronic transitions can borrow intensity from parity-allowed ones [20]. Electronic symmetry forbidden transitions have been observed in, for example, CO₂ [21] and C_{60} [22]. This dynamical vibronic coupling is an example of a case when the Born-Oppenheimer approximation is not valid. The intensity of a "forbidden" transition depends on the strength of the vibronic coupling and on the lifetime of the intermediate state relative to the period of vibration [20]. If the lifetime is short compared to the vibrational period the geometry will not have time to change appreciably before the deexcitation takes place and the inversion symmetry is not broken even if the vibronic coupling is strong. If the lifetime is long compared to the period of vibrational motion then the inversion symmetry is broken in the case of strong vibronic coupling. In intermediate cases the intensity of a forbidden transition is generally lower than that of the corresponding transition following nonresonant excitation, and the parity selection rule can then rather be thought of as a "propensity" rule" [21]. As recently demonstrated [21,23], the symmetry breaking is strongly frequency dependent and the symmetry selection can be restored by detuning the frequency away from resonance. This can be explained by a shorter duration time for the scattering process, which, just as a very short lifetime, quenches the symmetry breaking nuclear motion.

The propensity rule can be utilized to determine the parity of unknown absorption features. If there are two (or more) well-separated features in the emission spectra, each feature corresponding to electrons from either gerade or ungerade orbitals filling the core hole, then an intensity ratio of a "gerade feature" to an "ungerade feature" can be obtained. Comparing this ratio to the ratio of the corresponding transitions for nonresonant excitation will tell which transition is allowed and which is forbidden in the resonant case. From this information the parity of the unoccupied orbital can be deduced.

The reason that we can use a nonresonant spectrum as a reference is that when the excitation energy is tuned above the ionization threshold the core electron is promoted to the continuum and the outgoing photoelectron may have either parity. Far above threshold, the probability for producing gerade and ungerade photoelectrons is the same, owing to the infinite degeneracy of states and the spherically symmetric ionic field. In that case, the spectral intensities are not affected by the parity selection rule, or rather it is not necessary to invoke the parity selection rule to calculate or explain the emission spectrum.

Now, if the intensity ratio of a gerade feature to an ungerade feature is smaller than in the nonresonant case, then the core electron was promoted to an orbital of ungerade parity or, in the case of overlapping absorption resonances, mainly to ungerade orbitals. If the ratio instead is larger, transitions to one or several gerade orbitals dominate. In this way the parities of the unoccupied orbitals can be determined, and the corresponding features in the absorption spectrum assigned.

At high photon energies, far above threshold, shakeup and shakeoff accompanying the core ionization are likely and multiple vacancy satellites will become important. These satellites normally appear on the high-energy side of the nonresonant emission spectrum, but typically overlap the diagram lines. To avoid these satellites it is in practice better to record a nonresonant spectrum at a photon energy close to the threshold, below the shake thresholds. However, close to threshold photoelectrons referring to gerade and ungerade levels might not be produced with the same probability [24]. This is especially true in the vicinity of a shape resonance. In a recent study of N₂ we showed that exciting at the σ_u shape resonance dramatically increased the emission peaks corresponding to ungerade electrons filling the core hole [9], as expected. Therefore to obtain a reference nonresonant spectrum the photon energy has to be selected with some care in a region where a spherical symmetry distribution of the photoelectrons may be assumed.

B. Spatial symmetry

When linearly polarized light is used for resonant excitation, the distribution of the emitted light is in general anisotropic. When the polarization ε_{out} is not detected the equation for the angular distributions takes the form [25]

$$I(\theta) = I_0 [1 + R(\frac{3}{2} \sin^2 \theta - 1)], \qquad (2)$$

where the intensity $I(\theta)$ of the emitted light for each final state is a function of the angle θ between ε_{in} and \mathbf{k}_{out} , and the polarization anisotropy parameter *R*. The latter parameter depends on the spatial symmetries, defined by the irreducible representations, of the initial and final states. Therefore it is possible to obtain spatial symmetry information by measuring the angular distribution of the emitted photons.

By utilizing Eq. (2) it is possible to make quantitative predictions of the angular distributions of the x-ray emission peaks. The distributions can be accurately modeled for di-

TABLE I. The angles θ at which the emission of x rays is expected to be most intense for various combinations of unoccupied and occupied orbitals.

Occupied orbital	Unoccupied orbital	Maximum emission intensity at
σ	σ	90°
π	π	90°
	σ	0°

atomic molecules, as a recent study of CO shows [8]. However, for polyatomic molecules vibronic coupling can mix final states of different spatial symmetry and as a result the angular distribution of the emission peaks might be more isotropic than given by Eq. (2).

In addition to vibronic coupling a quantitative analysis of x-ray emission spectra for polyatomic molecules is also often complicated by the large number of close-lying final states. Because of these complications we will not use Eq. (2) but instead use a simplified "two-step" model to describe the angular distributions in a qualitative way.

Let us restrict the discussion, for simplicity, to linear molecules and K-shell resonant x-ray emission spectra. Then the absorption strength of a core excitation to an unoccupied orbital is determined by the local atomic p-type character of the orbital according to the one-center model [26]. For excitation to σ (p_z) orbitals the absorption rate is largest if the polarization vector ε_{in} is parallel to the molecular axis and thus the smaller the angle between the molecular axis and ε_{in} the more likely it is that the molecule gets core excited. For excitation to a π (p_x , p_y) orbital the absorption rate is largest when the molecular axis is perpendicular to ε_{in} . In other words, an aligned ensemble of core-excited molecules is created by the linearly polarized photons and the preferential orientation of those molecules depends on the spatial symmetry of the unoccupied orbital [27].

The core-excited molecules may then decay by emitting x-ray photons. It should be noted that the lifetime of the core-excited molecules is much shorter than any rotational motion and the molecular axis can therefore be assumed to be frozen during the absorption-emission process. If a valence electron from a σ orbital fills the core hole the photons are mostly emitted perpendicular to the molecular axis with their polarization vector, ε_{out} , parallel to the molecular axis, whereas a transition from a π orbital gives maximum emission intensity parallel to the molecular axis.

From the simple reasoning above it can be inferred that (1) in the x-ray absorption step an aligned ensemble of coreexcited molecules is created; the preferential direction of the molecular axis depends on the spatial symmetry of the unoccupied valence or Rydberg orbital; and (2) the angular distributions of the emission are anisotropic with respect to the molecular axis and they depend on the spatial (σ or π) symmetry of the valence orbital involved in the decay. The final angular distribution will depend on the spatial symmetries of both the unoccupied orbital and the occupied valence orbital taking part in the scattering process. In Table I we summarize in what direction we expect maximum intensity for different combinations of unoccupied and occupied orbitals.

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Using Table I and measuring how the relative intensities of the σ and π emission peaks change going from $\theta = 0^{\circ}$ to $\theta = 90^{\circ}$ the spatial symmetry of the unoccupied orbital can be obtained.

Finally, it should be noted that we assume that nonresonant excitation to the continuum leads to an isotropic distribution of core-ionized molecules and hence isotropic x-ray emission. This assumption might not be valid close to threshold, as is the case if the excitation is at or near a shape resonance.

From the foregoing discussion and Table I it should be clear that it is possible to determine the spatial symmetry of the unoccupied orbital reached at a certain excitation energy by measuring how the relative intensities of σ and π spectator emission peaks change as a function of detection angle in the resonant x-ray emission spectra.

It should be mentioned that with a polarization-sensitive spectrometer the spatial symmetry information can be obtained by measuring the polarization of x rays emitted at one angle (preferably at $\theta = 90^{\circ}$) instead of measuring the angular dependence [6].

VI. RESULTS AND DISCUSSION

A. Experiment

The near-edge part of the O K x-ray absorption spectrum of CO_2 is shown in the lower part of Fig. 1. The spectrum consists of one strong and broad peak (A), a weaker and sharper peak (B), and a broad structure (C) leading to the ionization threshold at 540.8 eV [28]. In the region just above the threshold a σ_{ρ}^{*} shape resonance contributes and at higher energies, between 550 and 570 eV, there are contributions from double excitations [29] and a σ_u^* shape resonance [11,30]. In order to study the O K x-ray absorption spectrum of CO_2 we have recorded x-ray emission spectra at two angles ($\theta = 0^{\circ}$ and 90°) for seven different excitation energies, five below the ionization threshold and two above. The arrows in Fig. 1 indicate the energy positions at which the x-ray emission spectra were recorded. The XES spectra are shown in Fig. 2. All the emission spectra show a highenergy feature and a low-energy feature at about 527 and 523 eV, respectively. The upper part of Fig. 1 shows the intensity ratios of the high-energy to low-energy features, obtained from the emission spectra recorded at the corresponding excitation energies. The error bars include both statistical errors and errors due to uncertainties in the integration limits. The dashed line is the estimated intensity ratio in the case of an isotropic angular distribution and no parity selectivity, obtained as the average value of the experimental ratios from the spectra recorded at the energy position D, which is above the ionization threshold and the σ_g^* shape resonance but below the double excitations and the σ_u^* shape resonance.

The intensity ratios presented in the upper part of Fig. 1 might be used to assign the symmetries of the absorption features *A*, *B*, and *C*, but to do this we need to examine the emission spectra in some more detail. The ground state configuration of CO₂ is $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 3\sigma_g^2 2\sigma_u^2 4\sigma_g^2 3\sigma_u^2 1\pi_u^4 1\pi_g^{4-1}\Sigma_g^+$, where the $1\sigma_g$ and $1\sigma_u$ are linear combinations of the two O 1s orbitals and the $2\sigma_g$ orbital corresponds to the C 1s orbital. In the upper part of Fig. 3 a nonresonant O



FIG. 1. (bottom) X-ray absorption spectrum with arrows indicating at what excitation energies resonant x-ray emission spectra were recorded. (top) Intensity ratios between the high-energy peak (due to $1 \pi_g$) and the low-energy peak (due to $1 \pi_u$, $3 \sigma_u$, and $4 \sigma_g$) in x-ray emission spectra recorded at $\theta = 0^\circ$ and $\theta = 90^\circ$.

K x-ray emission spectrum is shown. The spectrum was obtained with an excitation energy of 549.2 eV, and consists of two main features caused by transitions involving the four outermost valence orbitals [31]. The $1\pi_g$ peak at about 527 eV is by far the strongest, which is due to the fact that the $1\pi_g$ orbital is more or less a pure O 2*p* orbital. The low-energy feature at about 523 eV consists of three vibrationally and instrumentally broadened and overlapping peaks, $4\sigma_g$, $3\sigma_u$, and $1\pi_u$. The O 2*p* character of the $4\sigma_g$ orbital is rather small and the corresponding peak is weak in comparison to the nearby ungerade peaks [32].

The lower part of Fig. 3 shows a resonant x-ray emission spectrum obtained by tuning the excitation energy to the maximum of the $2\pi_u$ absorption peak ($h\nu = 535.2 \text{ eV}$). This spectrum is noticeably different from the nonresonant spectrum in the upper part. An additional strong and vibrationally broadened peak is observed at about 535 eV. It is due to participator transitions and will not be discussed further. The other features have changed shape and are shifted slightly



FIG. 2. Resonant O K x-ray emission spectra excited at energy positions indicated in Fig. 1, detected perpendicular ($\theta = 90^{\circ}$) and parallel ($\theta = 0^{\circ}$) to the polarization vector of the exciting radiation.

towards lower emission energies because of the extra $2\pi_u$ spectator electron. However, the effect that is of interest for the symmetry assignment is that the relative intensity of the two features is completely different in the two spectra.



FIG. 3. Upper part: nonresonant O K x-ray emission spectrum of CO₂. Lower part: O $1s \rightarrow 2\pi_u$ resonant x-ray emission spectrum. The spectra were recorded at $\theta = 90^\circ$.

To determine the parities of the unoccupied orbitals we note that the high-energy feature is due to an occupied orbital of gerade parity, whereas the low-energy feature is mainly due to levels of ungerade parity. From the discussion in Sec. V A we expect the intensity ratios in Fig. 1 to be well above the value given by the dashed line if the excitation is to a gerade unoccupied orbital and, vice versa, well below the line if the unoccupied orbital has ungerade parity. It is clear from the figure that for both recording angles the ratios are below the dashed line at absorption peak A whereas the ratios are above the line at the other two features, B and C. The data, thus, indicate that peaks A, B, and C are due to unoccupied orbitals of ungerade, gerade, and gerade parities, respectively. The first assignment is in accordance with the fact that mainly the $2\pi_u$ resonance contributes to peak A.

The high-energy feature in the emission spectra is due to an occupied π orbital $(1\pi_g)$ whereas the low-energy feature is due to occupied orbitals of both σ $(3\sigma_u, 4\sigma_g)$ and π $(1\pi_u)$ symmetry, with the σ contribution on the low-energy side of the feature. The fact that the spatial symmetry character of the two emission features is different can be used to obtain the spatial symmetries of the unoccupied orbitals, as described in Sec. V B. To do that we consider how the intensity ratios in the upper part of Fig. 1 vary with the angle θ .

At absorption features *B* and *C* the intensity ratios are clearly different at the two angles. At both energies the ratios are smaller in the $\theta = 90^{\circ}$ spectra. Furthermore, it can be observed in Fig. 2 that the spectra are primarily different at the low-energy side of the low-energy feature. Since this side corresponds to σ emission peaks, the lower ratios at θ = 90° are due to the fact that the relative intensities of the σ peaks are larger at this angle. From these results and Table I it can be concluded that the absorption features *B* and *C* are mainly due to unoccupied levels of σ symmetry. This conclusion is in agreement with what was found previously from angular-resolved ion-yield work [12,13].

When exciting to absorption feature A, which is due to the $2\pi_{\mu}$ unoccupied orbital, we would expect the intensity ratios to be stronger at $\theta = 90^{\circ}$. However, the intensity ratios appear to be more or less insensitive to the angle θ . There are two reasons for this apparent lack of anisotropy. First of all, because of the Renner-Teller effect the promotion of an electron to the $2\pi_{\mu}$ molecular orbital will induce bending mode vibrations, leading to more isotropic emission than would be the case otherwise. The other reason, which is probably more important, is the fact that for most organic molecules emission to the $\pi^{-1}\pi^{*-1}\Sigma^{+}$ final state(s) is weaker and shifted in energy compared to that of the $\pi^{-1}\pi^{*-1}\Sigma^{-1}$ and $\Delta^{-1}\Delta$ final states [33]. An example of this is the resonant XES spectra of CO recorded at the π^* (2 π) resonance, where no clear evidence of contribution from transitions to the $1\pi^{-1}2\pi^{-1}\Sigma^+$ final state was found [8]. When the ${}^{1}\Sigma^{+}$ contributions are missing the angular distributions of the π emission peaks are similar to those of the σ emission peaks [8] and spectra recorded at $\theta = 0^{\circ}$ and 90° will appear very similar, as was found in the CO case.

At *D* the excitation energy ($h\nu$ =549.2 eV) is in a region where we expect isotropic emission (no alignment of the core-excited molecules) and the intensity ratios are equal within the error bars. At *E* the excitation energy ($h\nu$ =559.2

TABLE II. STEX calculation of O K XAS of CO₂ in C_{2v} symmetry. The ionization potential is 540.71 eV. The oscillator strengths, f^L and f^V , are calculated with both length (L) and velocity (V) gauges, δ is the quantum defect. The last column shows the expectation value of the \hat{r}^2 operator (a.u.). The unoccupied orbitals are specified by their dominant atomic character (O and C) and atomic *nl* quantum number as well as their molecular symmetry.

Energy (eV)	Term energy (eV)	Character	Symmetry	f^L	f^V	δ	r^2
536.21	-4.50	(O+C) 2p	π^*	0.0391	0.0478	0.261	20.84
536.26	-4.45	C 3 <i>s</i>	σ	0.0012	0.0033	1.252	43.28
538.24	-2.47	C 3 <i>p</i>	π	0.0004	0.0001	0.653	55.05
538.45	-2.26	(C+O) 3 <i>p</i>	σ	0.0022	0.0013	0.545	70.12
538.80	-1.91	O $(3p + 4s)$	σ	0.0010	0.0016	1.330	66.61
539.23	-1.48	O 3 <i>d</i>	δ	0.0000	0.0000	-0.029	79.47
539.31	-1.40	O(3d + 4p)	π	0.0005	0.0004	-0.114	73.33
539.33	-1.38	O 4 <i>p</i>	σ	0.0000	0.0000	0.864	85.76
539.74	-0.97	O 4 <i>p</i>	π	0.0006	0.0003	0.267	67.71
539.76	-0.95	O 5 <i>s</i>	σ	0.0022	0.0020	0.205	96.25
539.96	-0.76			0.0000	0.0003		
540.20	-0.51			0.0000	0.0000		
540.33	-0.38			0.0008	0.0005		
540.37	-0.34			0.0000	0.0002		
540.62	-0.09			0.0000	0.0000		

eV) is in the region of the σ_u^* shape resonance. However, the error bars are too large to determine a specific symmetry at this absorption energy. The larger error bars at this energy are due to shakeup and shakeoff satellites overlapping the diagram lines in the emission spectra. Since these satellites typically appear on the high-energy side the intensity ratios might be slightly overestimated at this excitation energy.

It can be noted that except for excitation energies near the $2\pi_{\mu}$ resonance (absorption peak A) the core-excited states should only be affected weakly or not at all by vibronic coupling through the Renner-Teller effect. This means that the angular distributions at the other energies should be well described by Eq. (2) and if the symmetries of the final states are known it is possible to calculate the angular distributions for the different emission peaks. If we assume that absorption feature B is due to unoccupied orbitals of σ symmetry it is possible to decompose the low-energy feature in the emission spectra recorded at absorption feature B into a σ part (due to $3\sigma_u$ and $4\sigma_g$) and a π part (due to $1\pi_u$) by taking difference spectra and utilizing Eq. (2). The I_0 intensity of the π part was found to be roughly 1.5 (±0.5) times larger than that of the σ part. As indicated by the large error bars this value is very sensitive to various parameters in the analysis (choices of background etc.) and although the analysis shows that it is possible to decompose the low-energy feature in the emission spectra at absorption peak B into a σ and a π part, the statistics in the spectra do not warrant such a decomposition (the decomposed spectral parts are therefore not shown).

B. Calculations

From the experimental results we assigned the *B* and *C* features in the O *K* absorption spectrum of CO₂ to unoccupied orbitals of σ_g symmetry. To test these assignments we have also performed calculations in both full and broken symmetry using the STEX method. Table II and Fig. 4 show

the results of the STEX calculations made in broken symmetry and Table III and Fig. 5 the corresponding results from the calculations made in full symmetry. The STEX calculations give a large number of states, of different symmetries, up to the ionization limit. Of those states only five have oscillator strengths larger than 0.001. Because the rest of the transitions are so weak they are not discussed further. The first two of the five states can safely be assigned to absorption peak A, the next two to peak B, and the last one to feature C.

The symmetries of the unoccupied orbitals for the two states contributing to peak *A* are found to be π_u and σ_g , respectively. The orbital of π_u symmetry is the $2\pi_u$ molecu-



FIG. 4. Static exchange calculated O K x-ray absorption spectra of CO₂ in broken symmetry using length and velocity gauges.

TABLE III. STEX calculation of O K XAS spectra of CO₂ in D_{2h} symmetry, both gerade (g) and ungerade (u) orbitals are included. The ionization energy is 553.1 eV. The oscillator strengths, $f_{g,u}^L$ and $f_{g,u}^V$, are calculated with both length (L) and velocity (V) gauges. The unoccupied orbitals are specified by their dominant atomic character (O and C) and atomic *nl* quantum number as well as their molecular symmetry.

Energy (eV)	Term energy (eV)	Character	Symmetry	$f^L_{g,u}$	$f_{g,u}^V$
548.35	-4.75	(O+C) 2 <i>p</i>	π_u	0.0921	0.0827
548.64	-4.46	C 3 <i>s</i>	σ_{g}	0.0074	0.0066
550.62	-2.48	C 3 <i>p</i>	π_u°	0.0001	0.0001
550.89	-2.21	(C+O) 3 <i>p</i>	σ_u	0.0006	0.0005
551.16	-1.94	O $(3p + 4s)$	σ_{g}	0.0047	0.0043
551.57	-1.53	O 3 <i>d</i>	δ_u	0.0000	0.0000
551.67	-1.43	O $(3d + 4p)$	π_{g}	0.0011	0.0011
551.70	-1.40	O 4 <i>p</i>	σ_{g}	0.0000	0.0000
552.12	-0.98	O 4 <i>p</i>	π_u°	0.0003	0.0003
552.24	-0.86	O 5 <i>s</i>	σ_{g}	0.0042	0.0038
552.33	-0.77		u a	0.0004	0.0004
552.58	-0.52		и	0.0000	0.0000
552.76	-0.34		2	0.0019	0.0017
552.81	-0.29		s g	0.0001	0.0001

lar orbital, and the transition to this orbital has by far the largest oscillator strength. Using the parametrization of Ref. [19] the oscillator strength (in the velocity gauge) was found to be 0.048 by STEX in broken symmetry and 0.054 by a complementary MCSCF calculation. These values are approximately 15 times larger than the corresponding values of 0.0033 and 0.0034 calculated for the transition to the neighboring σ_g orbital. Wight and Brion [10] suggested, based on reasonable term energy values, that the $3s\sigma_g$ Rydberg orbital should contribute to the first absorption peak (peak A). Our



FIG. 5. Static exchange calculated O K x-ray absorption spectra of CO₂ using length and velocity gauges in the full symmetry of the molecule. (a) gerade part, (b) ungerade part, and (c) total spectrum.

calculations support this proposal by showing that there should be a contribution from a σ_g orbital to the high-energy side of peak *A*.

The much larger strength of the transition to the $2\pi_u$ orbital explains that all the XES spectra recorded at absorption peak A indicate ungerade parity of the unoccupied orbital(s) and show no clear evidence of the $3s\sigma_g$ orbital. However, a closer inspection of the experimental intensity ratios in Fig. 1 suggests that there might be contributions from a gerade orbital on the high-energy side of absorption peak A. The intensity ratios at $h\nu = 536.2$ eV, which is at the high-energy side of peak A, are at both angles slightly larger than the ratios at the lower excitation energies. The somewhat higher ratios could be due to O $1s \rightarrow 3s\sigma_g$ excitation contributions. In fact, if peak A were entirely due to the $2\pi_{\mu}$ orbital we would expect the ratios at $h\nu = 536.2$ eV to be lower (or about the same) than at the center of the absorption peak $(h\nu = 535.2 \text{ eV})$. The reason is that as the excitation energy is detuned from resonance the effect of vibronic coupling will become smaller (less symmetry breaking) and therefore the ratio of "forbidden" peaks to "allowed" peaks will decrease. We refer to Refs. [21,23] for a detailed account of the symmetry breaking problem of the core-excited O $1s^{-1} 2\pi_{\mu}$ state. Therefore the present XES results are weakly indicative of a $3s\sigma_{q}$ resonance on the high-energy side of peak A. A more detailed x-ray emission study with spectra recorded at more energies, with narrower bandpass, and with better statistics might shed more light on the position of the $3s\sigma_{o}$ resonance.

The unoccupied orbitals of the three states contributing to absorption peaks *B* and *C* all have σ symmetry according to the calculations, confirming the experimental finding of this work and the previous ion-yield work [12,13]. As seen in Table II the broken symmetry STEX calculations turn out as quite gauge dependent. For instance, we find for the two σ resonances contributing to peak *B* that the first is the stronger in the length gauge while the second is stronger in the velocity gauge. Considering the good agreement for velocity gauges between STEX and MCSCF for the first two excitations some preference can be given to the velocity gauge. Calculations in full symmetry give most intensity to the second of the two *B* resonances, and assign them as σ_u and σ_g , respectively. Likewise the σ resonance at feature *C* is clearly of gerade symmetry. The full symmetry STEX calculations give intensities that are quite gauge independent but energies that are overestimated because of lack of relaxation in the calculation of the ionization potential, which is an inherent problem in Δ SCF calculations of core-hole states made in full symmetry (absolute STEX energies refer to the ionization potential). If we, on the other hand, compare the term energies for the two STEX calculations, a much better agreement is obtained.

The two *B* resonances found in the calculations can be attributed to the $3p\sigma_u$ and $4s\sigma_g$ Rydberg orbitals. As mentioned above, the relative strengths of these two resonances are very different in the broken and full symmetry calculations. Our experimental data suggest, like the full symmetry calculations, that the $4s\sigma_g$ is the stronger of these two resonances. It should be noticed that the $3p\sigma_u$ resonance occurs at a slightly lower energy than the $4s\sigma_g$ resonance. The former should therefore contribute mostly to the low-energy side of absorption peak *B*, where it might be possible to reveal its signature by recording XES spectra.

The orbital symmetry assignments as well as the calculated transition energies and oscillator strengths are listed in Tables II and III. In addition, the tables give the dominant atomic orbital characters of the different unoccupied orbitals, based on population analysis, quantum defects, and r^2 expectation values. The r^2 analysis assigns, as expected, the most compact character to the $2\pi_{\mu}$ orbital. The strong dominance of σ_g character for the discrete states and the weak nature of the σ_g^* shape resonance, appearing just above threshold, indicate mixings of σ_g^* valence and Rydberg character in the discrete region. The r^2 numbers in Table II are irregular, and do not indicate truly compact orbitals, as the $2\pi_u$ orbital, nor pure Rydberg orbitals. With respect to the valence-Rydberg mixing, the O K x-ray absorption spectrum of CO_2 is similar to that of O₂, which is much debated. We refer to two recent studies concerning particular aspects of computing XAS spectra with strong valence-Rydberg mixing [34,35].

VII. SUMMARY

In this work it is demonstrated that symmetry assignments of x-ray absorption spectra, can be obtained utilizing the symmetry selectivity and angular dependence of resonant xray emission. The oxygen K x-ray absorption spectrum of CO₂ was used as a test case. The results shed light on the assignments of the core-excited states above the $2\pi_u$ resonance in the Rydberg region. Static exchange and multiconfiguration self-consistent field calculations of the x-ray absorption spectrum further support the interpretation of the experimental observations. These results indicate some of the prospects of resonant x-ray emission for spectral assignment of x-ray absorption spectra, and have highlighted the use of the parity selectivity and angular anisotropy of resonant x-ray emission for this purpose.

We can conclude that the experimental results and the assignments from the calculations agree well, giving more weight to the combined result. The symmetry of the transitions can thus be summarized as follows: The first absorption peak is dominated by an intense transition to the $2\pi_u$ orbital. The calculations give that the first Rydberg resonance, of σ_g symmetry, should appear on the high-energy side of the first absorption peak with about 1/15 intensity of the $2\pi_u$ resonance. At higher energy two groups of transitions are found below the ionization threshold. The experimental and calculated results show that these are predominantly due to excitations to σ_g orbitals. The results indicate a considerable valence-Rydberg mixing in the discrete region of the O K x-ray absorption spectrum of CO₂ similar to that found for the O₂ molecule.

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