

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

K. Gunnelin¹, P. Glans², P. Skytt¹, J.-H. Guo¹, J. Nordgren¹, and H. Ågren³

¹Department of Physics, Uppsala University, Box 530, S-75121 Uppsala, Sweden

²Atomic Physics, Physics Department, Stockholm University, Frescativägen 24, 10405 Stockholm, Sweden

³Institute of Physics and Measurement Technology, Linköping University, S-58183, Linköping, Sweden

INTRODUCTION

X-ray absorption spectroscopy and electron-energy-loss spectroscopy are powerful techniques for obtaining information about the unoccupied orbitals of various systems. Yet, there are still uncertainties regarding the assignment of some absorption spectra, even those of some small molecules. Therefore, there is a need for a technique that can provide additional information in those cases. Here a simple method to distinguish between orbitals of different parity and spatial symmetry, using x-ray emission spectroscopy, is presented. To illustrate the usefulness of the method it is applied to the much debated Rydberg transitions in the x-ray absorption spectrum of CO₂.

SYMMETRY ASSIGNMENTS

I. 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.

This rule is valid for dipole transitions in homonuclear diatomics, where there is only one, totally symmetric, vibrational mode [1,2]. 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 parity-forbidden electronic transitions can borrow intensity of parity-allowed ones [3]. 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. If the parameters are such that the symmetry is completely broken, the intensity is the same as that of the corresponding transition in the nonresonantly excited molecule. In the general case the intensity of a “forbidden” transition is, however, lower than that of the corresponding transition following nonresonant excitation. The parity selection rule can therefore be thought of as a “propensity rule”. This 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.

II. Spatial symmetry

When linearly polarized light is used for resonant excitation, the distribution of the emitted light is in general anisotropic. It depends on the spatial symmetries of the initial and final states. Therefore, it is possible to obtain spatial symmetry information by measuring the angular distribution of the

emitted photons. It is possible to make quantitative predictions of the angular distributions of the x-ray emission peaks [4]. The distributions can be accurately modeled for diatomic molecules, as a recent study of CO shows [5]. However, for polyatomic molecules vibronic coupling and the large number of close-lying final states make a quantitative analysis of x-ray emission spectra complicated. Because of these complications a simplified “two-step” model will be used 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 [6]. 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.

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.

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

In Table I we summarize in what direction we expect maximum intensity for different combinations of unoccupied and occupied orbitals. 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.

APPLICATION TO CO₂

The near-edge part of the O K x-ray absorption spectrum of CO₂ is shown in the lower part of Fig. 1. In order to study the absorption spectrum we have recorded x-ray emission spectra at two angles ($\theta=0^\circ$ and $\theta=90^\circ$) 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 high-energy feature and a low-energy feature. 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 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 shake-up transitions 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. To do this we use our knowledge about the emission spectrum. Apart from a participator peak present in four of the emission spectra in Fig. 2, they consist of two main features caused by transitions involving the four outermost valence orbitals [7]. The high energy feature is due to an electron from the $1\pi_g$ orbital filling the core hole. The low-energy feature consists of three vibrationally and instrumentally broadened and overlapping peaks, $4\sigma_g$, $3\sigma_u$, and $1\pi_u$. In comparison to the other two, $4\sigma_g$ is small.

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 orbitals of ungerade parity. From the discussion above 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 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 above. 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 primarily are different at the low-energy side of the low-energy feature. Since this side corresponds to σ emission peaks, the lower ratios at $\theta=90^\circ$ are due to that the relative intensities of the σ peaks are larger at this angle. From these results and Table 1 it can be concluded that the absorption features B and C are mainly due to unoccupied orbitals of σ symmetry.

Calculations have been carried out to further test the validity of this method. The so called static exchange approach has been used to calculate the absorption spectra, and the results support our experimental findings. A complete description of this method for symmetry assignments and the analysis, briefly described in this report, can be found in ref. [8].

CONCLUSION

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 what is found for the O₂ molecule.

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The experiments were performed at the ALS of Lawrence Berkeley National Laboratory operated by DOE under contract No. DE-AC03-76SF00098.

Principal investigator: Joseph Nordgren, Department of Physics, Uppsala University, Sweden. Email: joseph.nordgren@fysik.uu.se. Telephone:+46 18 4713554.

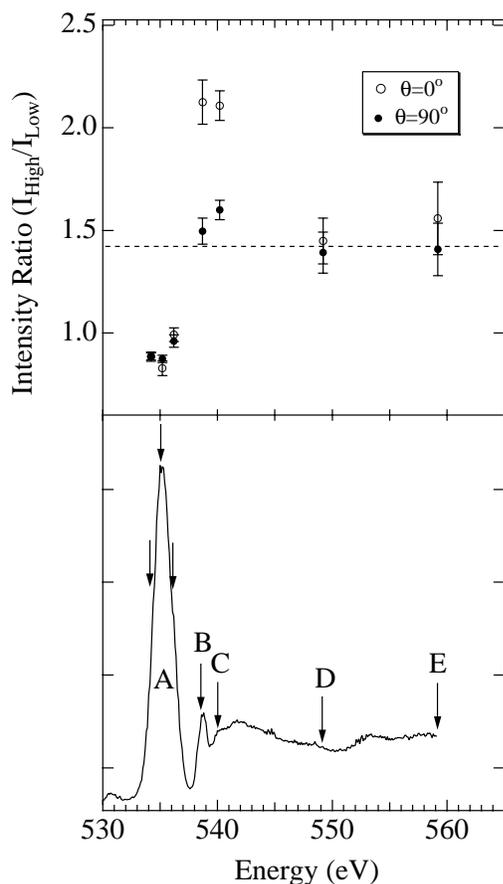


Figure 1. (bottom) X-ray absorption spectrum with arrows indicating at what excitation energies resonant x-ray emission spectra were recorded. (top) Intensity ratios between the high-energy peak (due to $1\pi_g$) and the low-energy peak (due to $1\pi_u$, $3\sigma_u$, and $4\sigma_g$) in x-ray emission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

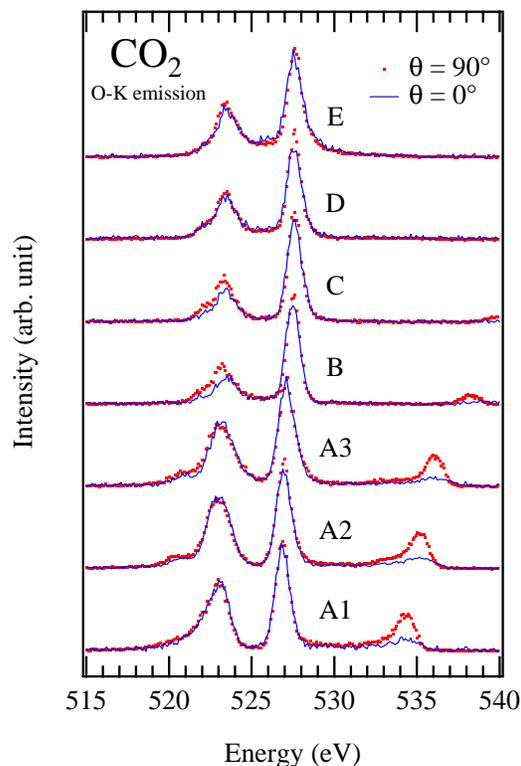


Figure 2. Resonant O K x-ray emission spectra excited at energy positions indicated in Fig. 1, detected perpendicular ($\theta=90^\circ$) and parallel ($\theta=0^\circ$) to the polarization vector of the exciting radiation.