Oxygen *K*-edge x-ray-emission–threshold-electron coincidence spectrum of CO$_2$

Johan Söderström,[1,*] Marcus Agåker,[1] Robert Richter,[2] Michele Alagia,[3,4] Stefano Stranges,[3,4,5] and Jan-Erik Rubensson[1,6]

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

[2]*Sincrotrone Trieste, I-34012 Trieste, Italy*

[3]*Istituto per lo Studio dei Materiali Nanostrutturati, CNR, Sezione Roma 1, Piazzale Aldo Moro 5, I-00185 Roma, Italy*

[4]*TASC-CNR, Area Science Park, Basovizza, I-34012 Trieste, Italy*

[5]*Dipartimento di Chimica, Universitá di Roma La Sapienza and INSTM Unit, Piazzale Aldo Moro 5, I-00185 Rome, Italy*

[6]*BESSY, Albert-Einstein Strasse 15, D-12489 Berlin, Germany*

The oxygen *K*-edge x-ray-emission–threshold-electron coincidence spectrum of CO$_2$ is presented. A two-step model, describing the result as a threshold-photoelectron spectrum free from post-collision interaction effects, predicts the salient features of the measured spectrum. Small discrepancies from the predictions are discussed in terms of threshold ionization dynamics.

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I. INTRODUCTION

The application of threshold-photoelectron (TPE) spectroscopy to atomic and molecular core levels [1] is limited due to the post-collision interaction (PCI) effect, which tends to shift (to higher excitation energy) and broaden the spectral features. As PCI is associated with the Auger decay the effect would be eliminated if the core hole state decays via the alternative radiative channel. In x-ray-emission–threshold-electron coincidence (XETECO) [2–4] spectroscopy, TPEs are detected in coincidence with x-ray photons emitted in the subsequent core hole decay as the excitation energy is varied over the core ionization threshold. Assuming that the first step of the process is threshold ionization, and that the emitted TPE is not influenced by the electron rearrangement associated with the second radiative decay step, XETECO spectra can be interpreted as PCI-free TPE spectra.

Recently the limits of this simple two-step picture were theoretically investigated, and it was shown that interference effects associated with the fact that only a few decay channels are considered may appear in molecules, especially when transition rates are strongly geometry dependent [5]. The XETECO spectrum may also derive intensity from states excited just below threshold decaying via the radiative Auger process [6,7], and from secondary processes as the final (valence excited) state of the process further decays.

In this paper we present the oxygen *K*-edge XETECO spectrum of CO$_2$. The spectrum has improved statistics compared to previously presented molecular XETECO spectra [3,4], facilitating a detailed discussion of the peak shape, quantitative comparison to x-ray-photoemission (XPS) spectra taken far above threshold, and theoretical predictions.

Vibrational excitations associated with th O 1*s* ionization in the linear CO$_2$ molecule have previously been extensively studied [8–13], and dynamic symmetry breaking associated with excitations of the antisymmetric stretch mode has attracted much attention.

We demonstrate that the simple two-step model gives a good description of the XETECO spectrum. The general correspondence with a recently presented experimental state-of-the-art XPS spectrum [11], as well as theoretical XPS predictions [12] is good, which implies that there are no dramatic threshold effects in the photoionization cross section. So far experimental XPS spectra have mostly been analyzed in terms of the single antisymmetric stretch vibrational progression. In the analysis of the present XETECO data also the symmetric stretch progression is included. This is partly in line with the theoretical prediction [11,12] of the O 1*s* XPS spectrum, but additional intensity for some of the components in the symmetric stretch vibration would improve the agreement between experiment and theory.

II. EXPERIMENT

The experiment was done using the ARPES end station at the gas phase beamline [14] at Elettra in Italy. TPEs were detected using a penetration field threshold photoelectron analyzer [15] mounted perpendicular to the polarization plane of the incoming radiation. The emitted photons were detected by two multichannel plate (MCP) detectors mounted symmetrically with respect to the TPE analyzer, at ∼25° angle to the polarization plane and ∼115° angle to the path of the electrons in the lens of the TPE. A schematic picture of the layout can be found in Ref. [3]. A polyimide filter is mounted in front of each MCP detector to discriminate against charged particles and metastable fragments. The filter has less than 1% transmission below 30 eV [16], and at lower energies (below 12 eV), where the transmission is larger, the MCP has a very low efficiency; therefore the MCP detectors measure primarily photons with higher energies. Several meshes are mounted in front of the MCP detectors to further discriminate against charged particles and prevent leak fields from penetrating into the interaction region. The incident photon flux was measured after the interaction region by a photodiode.

Energy calibration was facilitated by aligning the peak at 540.01 eV in the fluorescence yield (FY) spectrum to absorption spectra in the literature [17,18]. As the energy distance to the ionization threshold is small, this introduces an additional error of not more than 10 meV. As FY, XETECO,
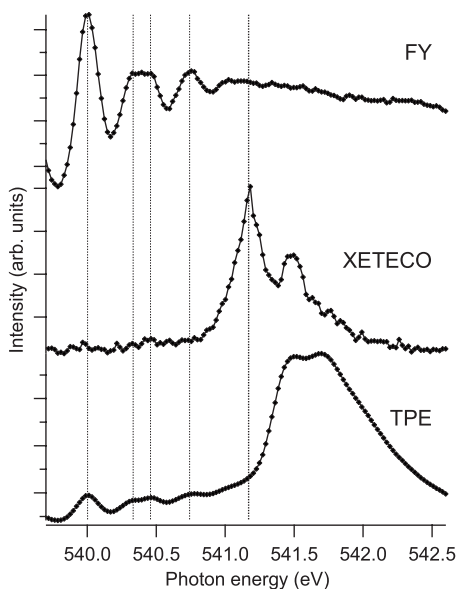
*johan.soderstrom@fysik.uu.se

FIG. 1. FY, XETECO, and TPE spectra recorded at the O K edge of CO_2. Vertical dashed lines mark the energy positions of the Rydberg features, and the principal XETECO peak, which appears very close to the nominal ionization threshold determined by extrapolation of the resolved Rydberg series [17,18]. The error bars for both the FY and TPE spectra are smaller than the point size while the error bars for the XETECO spectrum are indicated in Fig. 3. The experimental ionization energy obtained by fitting Voigt profiles to the XETECO spectra is very close to 541.17 eV, indicated by the vertical line at the XETECO maximum.

and TPE spectra are recorded in the same scan the error in their relative energy calibration is negligible.

A Voigt fit of the peak at 540.01 eV, assuming a natural linewidth to be in the 155–175 meV range, close to the width of the core ionized state [10], results in a monochromator width in the range of 85–98 meV. For further analysis we choose 90 meV as the experimental width. The energy resolution of the TPE analyzer is around 10 meV, and thus contributes little to the experimental resolution on this scale. Further experimental details can be found in Ref. [3].

III. RESULTS AND DISCUSSION

In Fig. 1 we show the FY, TPE, and XETECO spectra of CO_2. The FY spectrum has a narrow peak centered at 540.01 eV, which can be assigned to the $5s/4p\sigma_g$ excitation, and a double structure with maxima at $\sim$540.30 eV and $\sim$540.48 eV, which is assigned to the $4p\pi_u(001)$ $+5s/4p\sigma_g(001)$ and $5p\pi_u+6s/5p\sigma_g$ resonances, respectively [17]. Some further structures are resolved as the Rydberg series approach threshold, where the intensity variations as a function of energy are small. The FY spectrum closely resembles previously presented absorption spectra [17,18].

The TPE spectrum exhibits the same features below the ionization threshold as in the absorption spectra. Such structures are often observed in TPE spectra, and have been assigned to double Auger processes and secondary processes subsequent to the Auger decay [1]. The spectrum is domi-
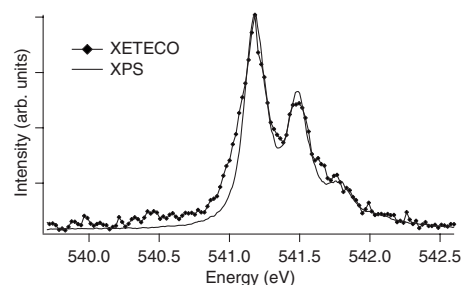

FIG. 2. The XETECO spectrum compared to the XPS spectrum from Ref. [11]. The energy shift for the XPS spectrum is chosen to give a good visual agreement. The spectra are normalized at peak and background.

nated by a broad feature with maxima in the 541.5–542 eV region, some tenths of an eV above the ionization limit. We assign this peak to threshold ionization of oxygen $1s$ electrons, shifted away from the ionization threshold and asymmetrically broadened due to the PCI effect. The main feature of the XETECO spectrum is narrower and peaks at 541.17 eV, close to the adiabatic threshold energy, as determined by extrapolation of the resolved Rydberg series [17,18]. This is the behavior expected in the simple two-step model according to which the PCI effect is turned off when threshold electrons are measured in coincidence with the radiative decay. In the following we will make a detailed comparison to experimental and theoretical photoemission results.

In Fig. 2 we compare the XETECO spectrum to a recently presented XPS spectrum excited at 700 eV [11], where PCI and resonant effects are small. The overall agreement between the two spectra is very good, and most fine structure in the XETECO spectrum finds its counterpart in the XPS spectrum. The resemblance gives further support for the interpretation of the XETECO spectrum as a PCI-free TPE spectrum. It also implies that there are no strong resonant effects in the ionization cross section at threshold.

The XPS spectrum has been well described theoretically [11,12]. In Fig. 3 the XETECO data is compared to a theoretical prediction based on SDCI (singles and doubles configuration interaction) theory from Ref. [12] [the CC-SD(T), coupled-cluster singles and doubles with noniterative triplets and calculations in Ref. [11] give very similar results], and the two-step model, which implies a spectrum composed of a series of independent Voigt peaks. For the theoretical spectrum in Fig. 3 we have assumed a Gaussian width of 90 meV and a Lorentzian width of 165 meV [10]. For the interpretation we show also predictions of the contribution from each vibrational mode. The fine structure in the peak is dominated by excitations of the antisymmetric stretch mode, but there is also a small contribution from the symmetric stretch mode. This has almost one-half the vibrational frequency of the antisymmetric stretch [12], and appears most clearly in Fig. 3 for $v=2$, and for combinations of the two modes. The bending vibration and the gerade and/or ungerade splitting is neglected for the theoretical curve. The equivalent core approximation at the SDCI level does not influence the picture significantly, but theories at lower level of sophistication, presented for comparison in Refs. [11,12] clearly fail to describe the XETECO spectrum (not shown).
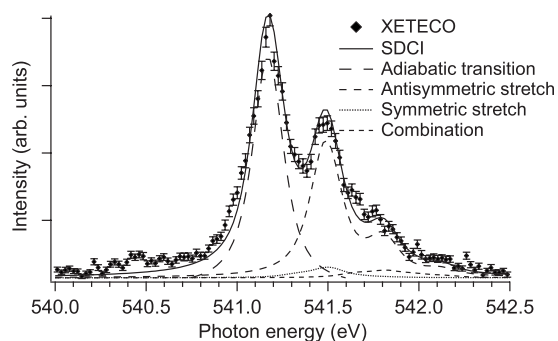
FIG. 3. The XETECO spectrum compared to a description based on the two-step model and the theoretical prediction of the nonresonant XPS spectrum based on SDCI calculation in Ref. [12]. The various predicted vibrational modes are shown separately. The energy shift for the theoretical spectrum is chosen to give a good visual agreement. The spectra are normalized at peak and background. The error bars indicate the statistical error $\sqrt{N_{True}}$ where N_{True} is the total amount of true coincidences ($N_{True} = N_{Total} - N_{Random}$).

We conclude that the vibrational excitations at threshold are similar to those expected for a nonresonant XPS spectrum. This is in contrast to previously presented XETECO spectra of other small molecules [3,4], where a dramatic redistribution of vibrational intensities has been observed. As the close-lying shape resonance does not influence the relative vibrational intensities appreciably [19] a significant change in cross section at threshold is not expected. This can be compared to, e.g., N_2O where the shape resonance does change the relative vibrational intensities significantly [20] and there is a significant change in the cross section at threshold compared to above threshold [4]. It is also worth to note that the gerade and ungerade electronic states are almost degenerate, and cannot be resolved, which makes any intensity redistribution between the gerade and ungerade component, as seen in N_2 [3], difficult to observe.

Considering finer details in the spectrum some significant discrepancies from the theoretical description remain. These include (a) the low-energy tail extending in the 540–541 eV region, (b) a statistically significant sharp substructure in the strongest peak at 541.17 eV, and (c) the increased relative intensity at ~541.65 eV. Here we briefly discuss these deviations.

(a) Although the statistics is limited we observe an intensity enhancement in the XETECO spectrum corresponding to the resolved Rydberg excitations in the absorption spectra at 540.01, 540.30, and 540.48 eV. Closer to threshold, where individual Rydberg states can no longer be resolved there is a general increase in intensity appearing as a low-energy tail of the main peak. A similar behavior below threshold has been observed in XETECO spectra of other molecules [3,4], and we have earlier pointed out some possible mechanisms that could lead to the emission of a soft x-ray photon and a slow electron at excitation just below the core ionization threshold. First, the Rydberg excited states can decay by the direct

radiative Auger process [6,7] or shake-off processes associated with the electronic and nuclear rearrangement during the radiative decay. Such specific relaxation processes would be the counterpart to PCI in the radiative channel. There is also the possibility that a slow electron is emitted subsequent to the x-ray-emission process in the further decay of the valence-hole–Rydberg-electron state. With the degrees of freedom in a molecule, several rotational-vibrational-electronic states just above the ionization limit may autoionize with the emission of an electron with a kinetic energy, sufficiently low for detection in the TPE analyzer. We have seen earlier that improvement in the resolution of the TPE analyzer reduces the intensity of XETECO features below threshold.

(b) The sharp substructure in the main peak at 541.17 eV cannot be accounted for in a simple way. In this context it may be relevant to mention the dynamic symmetry breaking associated with excitations of the antisymmetric vibrational stretch mode, and the near degeneracy of the gerade and ungerade core hole states. Any steep variation in transition rates associated with this process would make the shape of each peak more complicated than implied by the simple two-step model. In addition, interference effects specific for the channels selected by the coincidence requirement in this experiment could in such a case influence the spectrum [5]. To quantitatively describe this feature of the XETECO spectrum further theory development is needed.

(c) Compared to the theoretical prediction additional intensity is found in the XETECO spectrum at ~541.65 eV. According to the prediction this is the range where the contribution to the spectra from the symmetric stretch vibration becomes noteworthy. The intensity at ~541.65 eV could be accounted for if the symmetric stretch vibration were given somewhat more intensity than what is predicted for the nonresonant XPS spectrum. This observation could be rationalized if excitations of symmetric stretch vibrations indeed are enhanced at threshold and/or if states where the symmetric stretch mode is excited are emphasized in the XETECO measurement, e.g., due to larger fluorescence branching ratio than states where the antisymmetric stretch mode is excited.

IV. CONCLUSIONS

We have presented the O *K*-edge XETECO spectrum of CO_2. By comparing to state-of-the-art theoretical and experimental XPS data we demonstrate that the spectrum is well described by a two-step model as a PCI-free TPE spectrum. We do not find any dramatic resonant effects in the photoemission cross section at threshold. Smaller discrepancies are discussed in terms of enhancement of the symmetric stretch mode and dynamic effects.

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