

Photoexcitation and Auger decay of the Renner-Teller split C $1s^{-1}\pi^*$ state in CO₂

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INTRODUCTION

Molecular inner-shell photoabsorption spectra usually exhibit prominent pre-edge structures due to the excitation of core electrons to unoccupied molecular orbitals. Such transitions in the photoabsorption or electron energy loss spectra of triatomic and larger molecules are often unresolved and difficult to interpret, mainly because of the large number of vibrational modes that can be excited. In the case of CO₂, the symmetric stretch (ν_1), bend (ν_2) and asymmetric stretch (ν_3) vibrational modes are to be considered. The core excitation in CO₂ can also involve changes in molecular geometry, since two Renner-Teller split components – linear and bent – exist. Due to this variety of transitions, the carbon $1s$ excitation to the π^* molecular orbital gives rise to a broad peak in the absorption spectrum, with no resolved structure[1]. In the present study[2], vibrationally resolved photon-energy-dependent resonant Auger electron spectroscopy was used to probe the underlying structure of the carbon $1s$ excitations and to map the potential energy surfaces of the two Renner-Teller split states.

EXPERIMENT

The experiment was performed at the ALS at Beamline 9.0.1 (relocated later to 10.0.1). Total ion yield spectra were measured using a gas cell into which the photon beam entered through a 1000 Å thick Al window. The ion current was detected from two 15 cm long electrodes placed at both sides of the gas cell. An apparatus based on a Scienta SES-200 hemispherical energy analyser was

used for measuring the Auger electron spectra. The target gas was introduced into a gas-cell with differentially pumped openings for the photon beam.

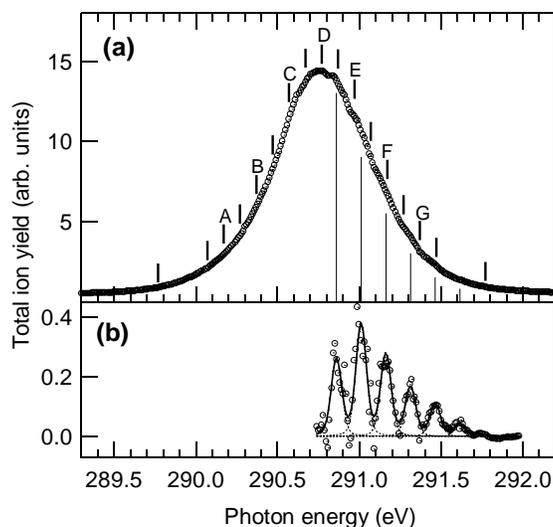


Figure 1. (a) Total ion yield spectrum over the carbon $1s \rightarrow \pi^*$ resonance. Vertical bars mark the energies at which the Auger spectra were measured. (b) Residual structure at the high-energy side after subtracting a broad Gaussian profile, assigned to the symmetric stretch vibrations of the linear Renner-Teller component.

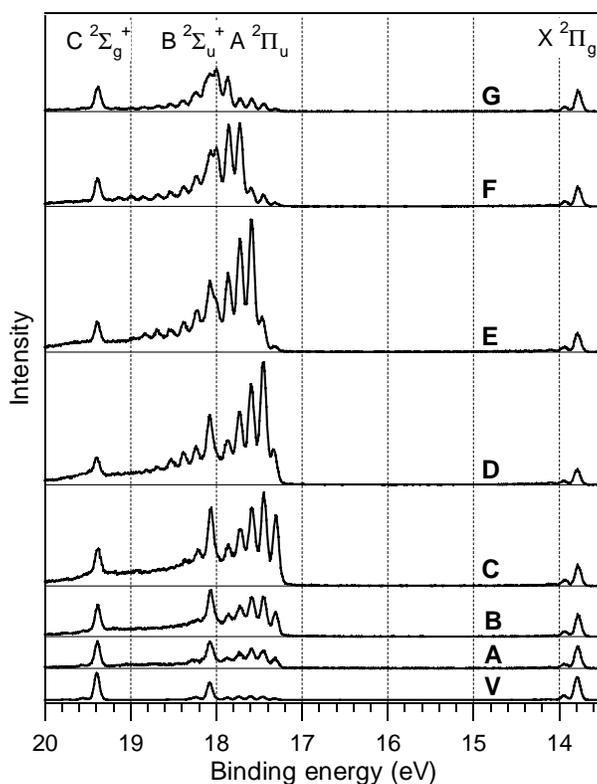


Figure 2. A series of resonant Auger electron spectra measured at different photon energies, as shown by the corresponding labels in Figure 1. The spectrum (V) is a nonresonant valence photoelectron spectrum, taken at 280 eV.

RESULTS

A total ion yield spectrum measured over the $C\ 1s^{-1}\pi^*$ resonance is shown in Fig. 1. Resonant Auger electron spectra were measured at a number of photon energies across the absorption peak. Some of these spectra are shown in Fig. 2, their labels denoting the corresponding photon energies of the core excitation in Fig. 1. The vibrational structure of this series of spectra was quantified using least-squares curve fitting. The behavior of the vibrational envelopes as a function of photon energy was then studied.

Among the lowest-energy ionic states, only the transitions to the $A\ ^2\Pi_u$ state display strong resonant enhancement due to participator Auger decay. The analysis was therefore concentrated on this state. It is obvious already from Fig. 2, that the vibrational structure of the $A\ ^2\Pi_u$ state changes dramatically as the photon energy is scanned across the resonance peak. More detailed analysis was based on the predicted properties of the Renner-Teller pair of the core-excited states, using the $Z+1$ model and the known properties of the NO_2 ground electronic state. A simplified model was also developed to calculate the energy levels and wavefunctions for the symmetric stretch and bending vibrations in both bent and linear geometries. The following general conclusions emerged:

1) In lower-energy part of the absorption peak, the bent component of the core-excited state is populated. The vibronic transitions from the ground state reach mainly the vibrational levels that are close to the central maximum of the double-well potential energy surface of the excited state. In the subsequent Auger decay, mostly the lowest level of the bending mode of the final state is

populated. However, substantial intensity goes also to highly excited states of the bending mode, which gives rise to a pronounced low-energy tail in the Auger spectra, as observed. The symmetric stretch progression in the Auger electron spectra is very similar to the progression in direct valence photoionization and is insensitive to the changes in photon energy. That suggests that the bond length of the bent core-excited state is close to that of the ground electronic state.

2) Excitations to the linear component of the $1s^{-1}\pi^*$ state become energetically possible at 290.55 eV photon energy. Above this energy, the vibrational structure in the Auger spectra changes very rapidly. The structure is assigned to the symmetric stretch mode excitations and the changes reflect different vibrational levels of the excited state, from which the Auger decay originates. The bending mode excitations play a secondary role in the excitation-decay of the linear state, as no changes in the equilibrium geometry are involved.

In addition, quantitative information about the potential energy surfaces, such as bond lengths, some vibrational constants and excitation energies, was obtained. Finally, based on the above results, the absorption spectrum of the core excitation was calculated, taking into account the Renner-Teller splitting and vibrational excitations.

REFERENCES

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This work was supported by the Office of Basic Energy Sciences, Chemical Sciences Division, of the U.S. Department of Energy and by the DOE Facilities Initiative.

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