

Anion formation following core level photoexcitation of CO₂

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Recently, a series of anion yield spectroscopy experiments has been performed at beam line 8.0 at the ALS, which have yielded some very interesting results. In CO, it has been found that the shape resonance, which is a major contribution to the total photoabsorption cross section just above the ionization threshold, does not contribute to the negative ion yield cross section [1]. In methanol, the negative ion production turns out to be core-hole dependent, resulting in 100% selectivity [2]. In this abstract, results for similar a experiment with CO₂ is reported.

The experiment was performed at beam line 8.0 at the ALS. The partial ion yield spectra were recorded with approximately 0.15 eV resolution at the C1s edge, and 0.25 eV resolution at the O1s edge. The fragments were selected with a magnetic sector mass spectrometer. Both anion and cation spectra were recorded, but only the anion data are presented here. The production of negative ions was checked for dependence on pressure, to rule out the possibility of secondary processes such as electron attachment.

In figure 1, the O⁻ partial ion yield spectrum recorded in the vicinity of the C1s edge is presented. As can be seen, there is only one strong feature, and this is the (C1s)⁻¹(π^{*}) resonance. Rydberg states and the photoionization continuum, including a shape resonant contribution, are not visible in this spectrum, unlike the situation in the total ion yield spectrum. The explanation of why the photoionization continuum does not contribute to the negative ion yield cross section is conceivably that the decay for the core-ionized state is dominated by emission of an Auger electron. This leaves the ion in a doubly charged state, from where the further dissociative decay into a negative fragment and a triply charged positive fragment is unlikely. The O⁻ fragment was the only negative fragment found in this energy region.

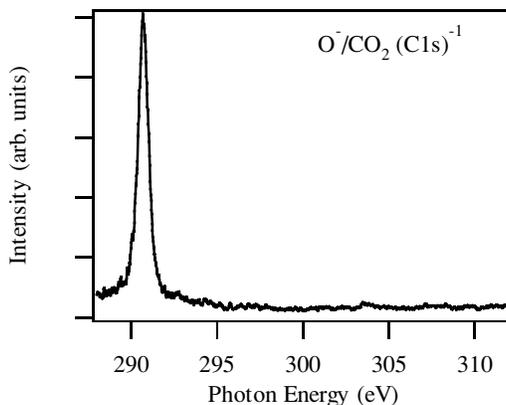


Figure 1. Anion yield spectrum of CO₂ in the vicinity of the C1s threshold. O⁻ was the only negative fragment found in this energy region.

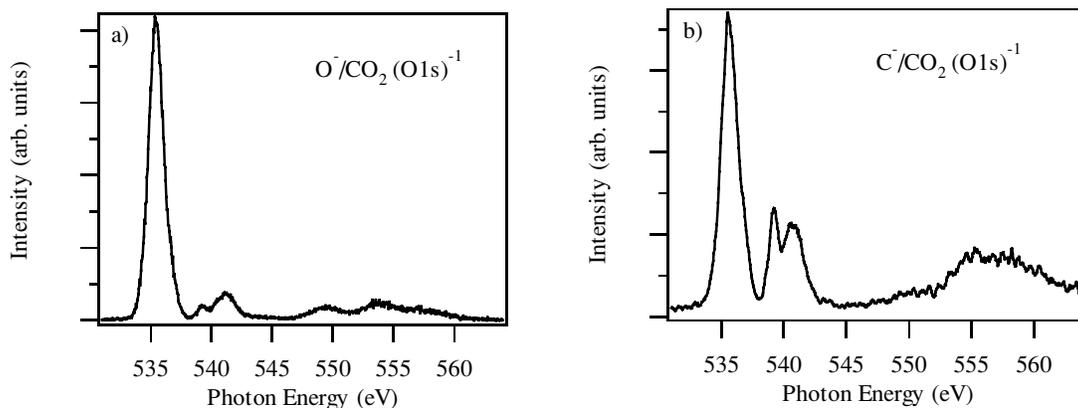


Figure 2. Anion yield spectra of CO_2 in the vicinity of the O1s threshold. The O^- yield is shown in figure a) and the C^- yield is shown in figure b).

In figure 2, the O^- (a) and C^- (b) anion yield spectra in the vicinity of the O1s edge are presented. These spectra show more structure than the O^- yield spectrum at the C1s edge. The first strong feature is the π^* resonance, which overlaps the 4s Rydberg state, which can be seen as a hint of a shoulder on the high energy side. Above this feature, there are several overlapping Rydberg states leading up to the ionization edge, where the intensity drops off. The line shape above the edge is a quasi-exponentially decreasing curve, considerably wider than the photon band width, which can be explained as a post collision interaction (PCI) effect. After the Auger decay takes place in the core-ionized molecule, there is a possibility of recapture of the photoelectron as it is passed by the much faster Auger electron. This probability of this recapture can be shown to decrease quasi-exponentially with kinetic energy [3], which is consistent with the present finding if the formation of anions is made impossible by the Auger decay leading to doubly charge ionic states. Above the edge, the spectrum is quite different from the total ion yield spectrum. There is no photoionization continuum, which in the total ion yield spectrum is dominated by a strong shape resonance with a maximum at 560 eV. Instead, several discrete resonances are observed, which are not seen in the total ion yield spectrum. These are attributed to multielectron states, and as they do not match the known photoelectron correlation satellites in energy, they are most likely double excitations. These states are swamped by the photoionization continuum contribution to the cross section in the total ion yield spectrum.

In conclusion, we have recorded anion yield spectra of CO_2 for photon energies in the vicinity of the C1s and O1s core levels. These spectra show the same interesting properties as other recently recorded negative ion yield spectra: The production of these ions is dependent on the core level which is excited, and the continuum contribution to their partial ion yield cross sections is very small, particularly the usually dominating shape resonant contribution is missing. This exciting new technique can thus yield results unobtainable in other ways.

REFERENCES

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