Inner-Shell Photoemission from Free Molecules in the Molecular Frame Probed by the Electron-Ion Coincidence Momentum Imaging Technique

Photoelectrons from molecules are scattered by the anisotropic molecular potential. One can study such scattering effects by measuring photoelectron emission in the molecular frame. The experimental technique we use for such a study is momentum imaging, which is based on the time of flight measurement combined with the measurement of the position of detection for the charged particles. A momentum imaging apparatus was installed on beamline **BL27SU** a couple of years ago and was first used for measuring three-dimensional (3-D) momentum of fragment ions produced via the core excitation of CO_2 molecules [1]. One can also employ this technique for molecular inner-shell photoelectrons. The measurement of the 3-D momentum of a photoelectron in coincidence with fragment ions, emitted over 4π sr, allows us to obtain photoelectron angular distributions in the molecular

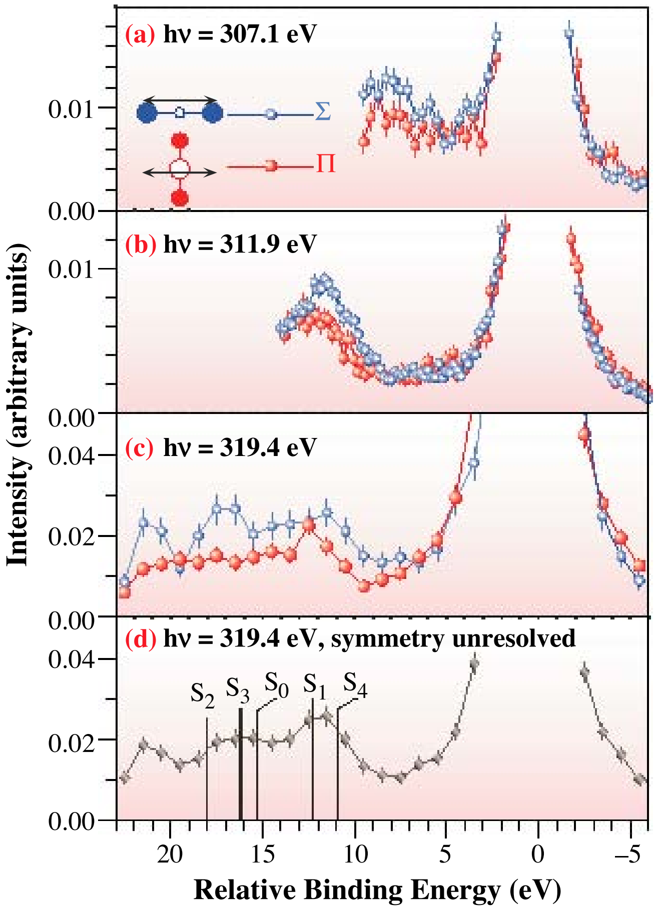

Fig. 1. Photoelectron spectra of CO_2 for the molecular axis fixed in space parallel (Σ), and perpendicular (Π) to the direction of the electric vector of the incident light, ***(a-c)****, and without selection of the molecular axis* ***(d)****.*

frame, as well as photoelectron spectra of selected symmetries for the ionization continuum. Here we present such a photoemission study of CO_2 molecules and the argon dimers.

In Fig. 1, we present CO_2 C1*s* photoelectron spectra for selected symmetry of the ionization continuum with resolution sufficient to resolve the satellite structure. This satellite structure is attributed to the excitation of a valence electron to the unoccupied molecular orbital accompanying core ionization. The energy scale represents the binding energy relative to the main photoline, and the intensity is normalized so that the integrated area of each spectrum is unity. For Σ and Π symmetries of the ionization continuum the molecular axis is parallel and perpendicular, respectively, to the electric vector of the incident light. Thus, we can resolve the symmetries of the continuum channel by filtering the fragment ions emitted at 0° or 90° with respect to the electric vector. From these symmetry-resolved photoelectron spectra, one can learn that the creation of the satellites is more efficient for the Σ rather than the Π channel, stemming from the fact that the slow photoelectron interacts more strongly with the valence electrons when the photoelectron is emitted along the molecular axis [2].

Figure 2 presents photoelectron angular distributions (PAD) for C1*s* ionization of CO_2 molecules in the molecular frame, with the molecular axis oriented along, at 45°, and perpendicular to the electric vector of the incident light. The major features of these measured PADs are fairly accurately reproduced by calculations employing a relaxed-core Hartree-Fock approach, as can be seen in the figure. In contrast to the well-known PAD for N 1*s* ionization of N_2, which exhibits a rich structure dominated by the f-wave (ℓ= 3) at the shape resonance [3], the PAD for C 1*s* photoionization of CO_2 is quite unstructured over the entire observed range

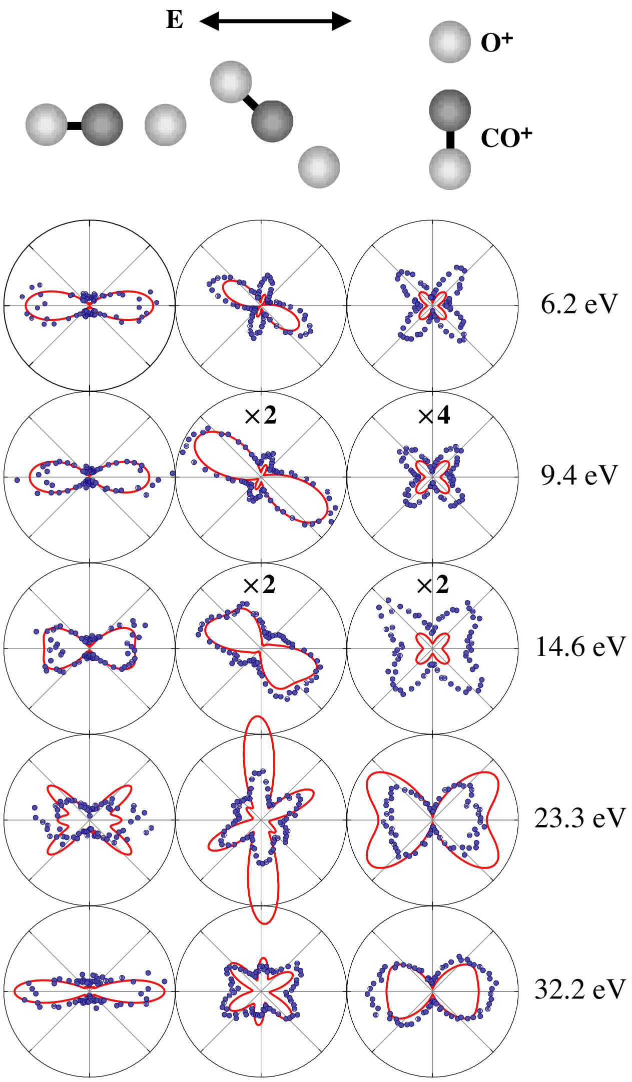

Fig. 2. Polar plots of C 1s photoelectron angular distributions of CO_2 molecules in a molecular frame, at electron kinetic energies of 6.2, 9.4, 14.6, 23.3 and 32.2 eV. The dots and curves correspond to measurements and calculations, respectively. The direction of the electric vector of the incident light, E, is horizontal. The molecular axis is at 0°, 45°, and 90° with respect to E.

across the shape resonance, illustrating that more than one partial wave contribute to the formation of the shape resonance, and that these waves interfere with each other [4].

In Fig. 3, we present PADs for the argon 2*p*-shell ionization of argon dimers. Here the PAD's dependence on the direction of the electric vector of the incident light has been removed by integrating over all relative orientations of the dimer axis with respect to the electric vector. The photoemission events belonging to the dimers have been filtered out with the momentum imaging of two Ar^+ ions by requiring momentum conservation for the fragments; the event is attributed to the dimer only if the two Ar^+ have opposite momentum vector. Comparison with *ab initio* calculation is necessary to interpret the process, and this will be performed in the near future.

In the future we intend to systematically extend this electron-ion coincidence momentum imaging technique to a photoemission study of three-dimensional polyatomic molecules.

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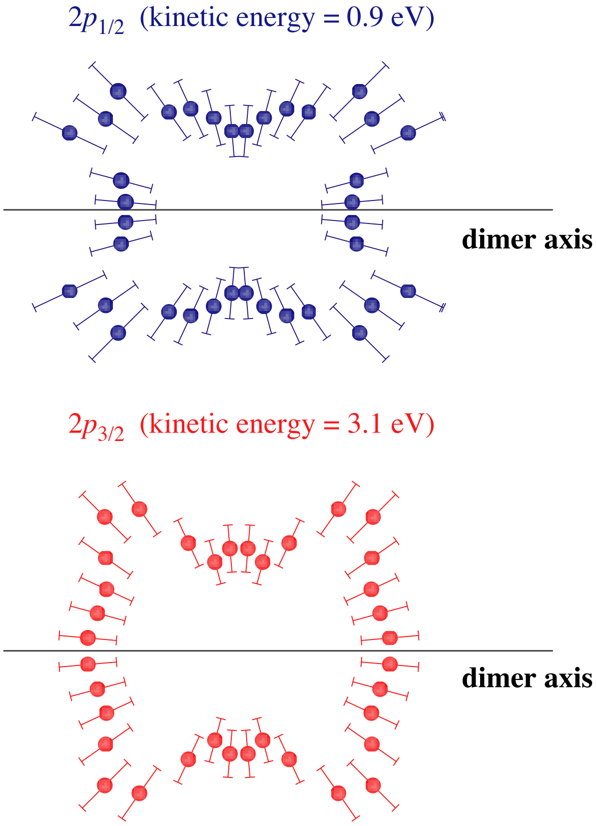
$2p_{1/2}$ (kinetic energy = 0.9 eV)

$2p_{3/2}$ (kinetic energy = 3.1 eV)

Fig. 3. Polar plots of Ar $2p_{1/2}$ and $2p_{3/2}$ photoelectron angular distributions of argon dimers in the molecular frame. The dependence on the relative orientation between the dimer axis and the electric vector of the incident light is removed by integrating over the all possible relative orientations.

References

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