Molecular-Frame Photoelectron Angular Distributions of Gas-Phase Molecules

Gas-phase free molecules are randomly oriented in space. Photoelectron angular distributions (PADs) in the laboratory frame defined by the electric vector of radiation are described by an anisotropy parameter β using the expression $I(\theta_e) \propto 1 + \beta P_2 (\cos\theta_e)$, where $P_2(\cos\theta_e)$ is the Legendre second order polynomial and θ_e is the angle between the electric vector and the direction of the electron emission. However, to discuss molecular photoionization the use of a molecular frame is more natural. Furthermore, molecular-frame PADs (MFPADs) have a much more richer structure than the laboratory frame PAD and thus may be used for extracting further information about the target molecule. Due to these evident reasons, significant experimental efforts have been devoted to MFPAD measurements in the last decade or so.

To measure MPFADs, one has to fix the target molecule in space. This has been realized by two alternative ways. To temporary align the molecule in space prior to photoionization, one can use dynamical alignment caused by the pulsed IR laser. Recent pump-probe MFPAD measurements using this approach with ultrafast pulse lasers have been successfully applied to probe the evolution of the electronic structure in time for a photoexcited CS_2 molecule [1]. The alternative way of fixing the molecule in space and measuring MFPADs is to record momenta of electrons and fragment ions in coincidence. When the molecular dissociation is faster than the molecular rotation, one can determine the molecular orientation from the momenta of the fragment ions and thus, by measuring the momentum correlation between the ions and the photoelectron, one can realize MFPAD measurements. Since the pioneering work by Shigemasa *et al.* [2], this approach has been widely used in investigating detailed photoionization dynamics including shape resonance phenomena.

In the present work, we have investigated C 1*s* photoemission from a linear CO_2 molecule. As in other molecules, the C 1*s* photoionization of CO_2 is also governed by the shape resonance that appears at ~14 eV above the C 1*s* ionization threshold. Thus, we have carried out electron-ion coincidence momentum-imaging measurements for CO_2 at several photon energies across the shape resonance [3,4] at beamline **BL27SU**. The employed momentum imaging is based on electron and ion time-of-flight (TOF) measurements with two multi-hit two-dimensional (2D) position-sensitive detectors. A supersonic jet of CO_2 in the vertical direction crosses the photon beam in the horizontal direction. The TOF axis is in the horizontal direction and perpendicular to both the gas and photon

beams. Photoelectrons and fragment ions ejected in all directions are driven to each of the electron and ion detectors using uniform electrostatic and magnetic fields. Each detector is equipped with a 2D multi-hit readout delay-line anode that permits measurements of both the time of detection and the 2D position coordinates and thus allows us to extract 3D momenta. The orientation of the molecular axis at the time of photoemission is extracted from the momentum vectors of the CO^+ and O^+ fragments resulting from the Coulomb dissociation of CO_2^{2+} subsequent to a rapid Auger decay.

To compare the measured and calculated MFPADs, we select the reaction in which the electron is emitted in the plane defined by the molecular axis and the E vector, as shown in Fig. 1. Here, the angle θ_n between the E vector and the molecular axis is shown along the horizontal axis and the electron emission polar angle θ relative to the molecular axis is shown along the vertical axis. The electron emission intensity is plotted on a false color scale at five photon energies. At first glance, the agreement between experimental and theoretical results is reasonable. Theoretically, the shape resonance located at ~312 eV is assigned to electron promotion from the $2\sigma_g$ (C 1*s*) core orbital to the $4\sigma_u$ unoccupied molecular orbital and thus the final
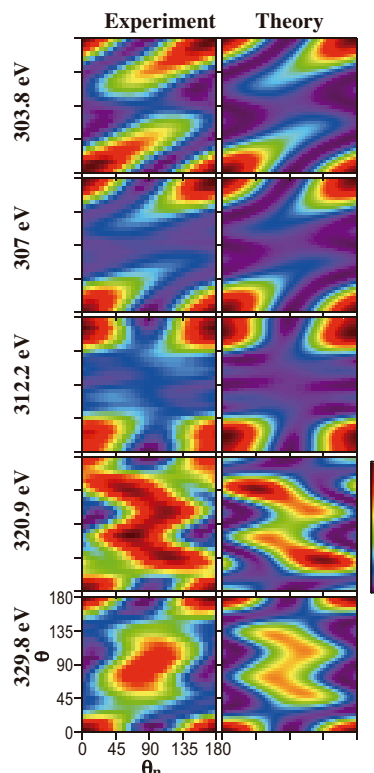
Fig 1. Experimental and theoretical 2D plots of C 1*s* MFPADs of CO_2 at five photon energies across shape resonance at ~312 eV. $\theta = 0°$ and $180°$ are the directions of O^+ and CO^+, respectively [3].

state may be described as $2\sigma_g^{-1} (^2\Sigma_g^+) 4\sigma_u \, ^1\Sigma_u$. This $\Sigma_g \rightarrow \Sigma_u$ photoexcitation is a parallel transition and the ejected electron has predominantly σ_u symmetry. In Fig. 1, $\theta_n = 0°$ and $90°$ correspond to parallel ($\Sigma \rightarrow \Sigma$) and perpendicular ($\Sigma \rightarrow \Pi$) transitions, respectively. The observed electron emission at ~312 eV is mostly at $\theta_n = 0°$ along the molecular axis with a nodal plane at $\theta = 90°$. These observations are consistent with the expectation that the shape resonance is the parallel $\Sigma_g \rightarrow \Sigma_u$ transition emitting photoelectrons of σ_u symmetry.

Looking at Fig. 1 carefully, we note that the measured MFPADs at ~312 and ~321 eV do not show a complete symmetry relative to the center, though the calculated MFPADs always exhibit a complete point symmetry because of the assumed $D_{\infty h}$ molecular symmetry. To confirm this asymmetry, in Fig. 2, we made polar plots of the electron emission at $\theta_n = 0°$ for these two energies. The observed asymmetry is evidence of the breakdown of the theoretical model in Ref. [3], which is commonly employed for the description of the MFPADs. A recent theoretical study by Miyabe *et al.* [5] successfully elucidated the origin of the asymmetry. According to Miyabe *et al.*, the memory of the instantaneous position of the nuclei at the time of photoionization is imprinted on the final dication state, provided that the Auger decay occurs before the vibrational motion on the transient core-hole surface can erase that memory. They therefore incorporated the asymmetric-stretch motion of the neutral target into the observed MFPAD by confining the average to half of the allowed range of nuclear geometries, where one CO distance is elongated relative to the other. In Fig. 2, their calculations are shown by a solid black line. We can see that the observed asymmetry is well accounted by their model.

The upper panel of Fig. 3 shows the electron spectrum recorded at ~312 eV. In addition to the main line, we can see the satellite at a binding energy of ~12 eV relative to the main line. MFPADs for the main line and the satellite, measured within the reaction plane in Fig. 1, are compared in the lower panel of Fig. 3. The satellite emission is mostly at $\theta_n = 0°$, revealing the predominance of the $\Sigma_g \rightarrow \Sigma_u$ transition, as shown in the case of the main line. In contrast
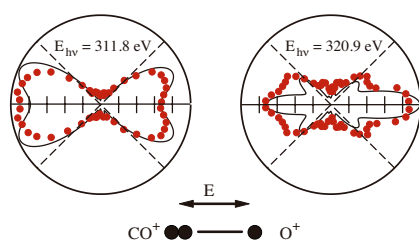
to the main line, however, the satellite clearly shows a maximum intensity at $\theta = 90°$. These observations suggest that the plausible assignment for the major contribution to the satellite is $2\sigma_g^{-1} 1\pi_g^{-1} 2\pi_u^* (^2\Sigma_u)\varepsilon\sigma_g \, ^1\Sigma_u$, which is the parallel $\Sigma_g \rightarrow \Sigma_u$ transition emitting photoelectrons of σ_g symmetry. This assignment implies that this satellite is of the conjugate type, where the symmetry of the ionic final state ($^2\Sigma_u$) is different from that of the main line ($^2\Sigma_g^+$). A well-known shake-up mechanism, however, cannot excite this conjugate satellite state. We can conclude that this satellite is excited by internal inelastic scattering, where a photoelectron ($2\sigma_g \rightarrow \varepsilon\sigma_u$) and a valence electron ($1\pi_g$) collide and one of them is promoted to $2\pi_u^*$ and the other is ejected to $\varepsilon\sigma_g$. The present observation is the first experimental evidence of a conjugate satellite excited by internal inelastic scattering.
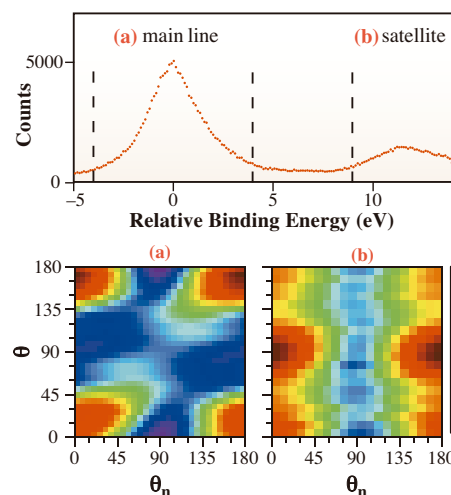
Fig. 3. Upper panel: photoelectron spectrum of CO_2 recorded at 311.8 eV. Lower panel: 2D plots of MPFADs for **(a)** C 1*s* main line and **(b)** lowest satellite of CO_2 recorded at photon energy of 311.8 eV [4].

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Fig. 2. Polar plots of C 1*s* MFPADs of CO_2 with molecular orientation parallel to E vector at photon energies of 311.8 eV and 320.8 eV. Experimental points (red dots), from Ref. [3]; theoretical curves (black solid curves) [5].

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