

## 3-D Mapping of Photoemission from a Single Oriented H<sub>2</sub>O Molecule

3-D O 1s photoelectron angular distributions from a fixed-in-space H<sub>2</sub>O molecule have been observed for the first time by the quadruple coincidence measurements of O 1s photoelectron-O<sup>+</sup>-H<sup>+</sup>-H<sup>+</sup>. Obtained results for the non-axially-symmetric molecules revealed the symmetry-imposed restrictions of the C<sub>2v</sub> symmetry group on the angular distributions and their strong orientation. Characteristic features of the angular distributions are explained in terms of Huygens' approach to electron de Broglie waves.

Very promising and challenging classes of experiments to determine molecular frame photoelectron angular distributions (MF-PAD) are those which achieve the full detection of products after photo-excitation of the ground state to the continuum states. Following the absorption of a photon, the set of momentum vectors of a photoelectron and all fragments from a free molecule can be measured in coincidence by imaging and timing techniques.

Figure 1 shows the vector correlation image of three particles, O<sup>+</sup>, H<sup>+</sup>, and H<sup>+</sup>, produced by three-body break-up of H<sub>2</sub>O<sup>3+</sup> following double Auger decay after O 1s photoemission. The H<sup>+</sup> ion is emitted in a narrow angular range with respect to the O<sup>+</sup> ion and the momentum distributions of two H<sup>+</sup> ions are mirror symmetric to each other. It is also shown that the correlation angle between two H<sup>+</sup> momenta is slightly larger than the ground state bond angle (∠HOH = 104.5°) because of the Coulomb repulsive force. These results verify that the Coulomb

explosion leading to three-body break-up of H<sub>2</sub>O<sup>3+</sup> is immediate, maintaining the ground state shape of H<sub>2</sub>O. Then, from the momentum vectors of the three fragment ions, the molecular orientation and intrinsic shape of H<sub>2</sub>O in space at the instance of the O 1s photoionization can be determined. By extending this approach to the quadruple coincidence measurements of photoelectron-O<sup>+</sup>-H<sup>+</sup>-H<sup>+</sup>, O 1s photoemission measurements from H<sub>2</sub>O molecules fixed in space were successfully performed [1-3].

A simple photoelectron diffraction model involving only a single scattering based on Huygens' approach was applied, to obtain an intuitive understanding of MF-PADs. When the electron de Broglie wavelength λ<sub>e</sub> (= 2π/k in atomic units) is comparable to the molecular size of H<sub>2</sub>O, 1.9 in atomic units (~1 Å), like our experiment of λ<sub>e</sub> = 6.2 (3.3 Å), the wave nature of the electron should manifest through interference, similarly to what macroscopic waves experience as they meet macroscopic ob-

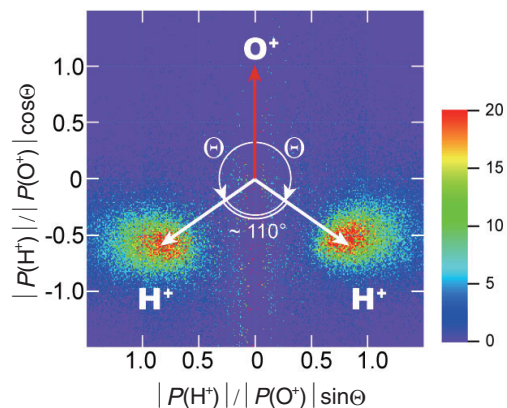


Figure 1  
Momentum vector correlation among O<sup>+</sup>, H<sup>+</sup>, and H<sup>+</sup> ions created in O 1s photoionization of H<sub>2</sub>O. The O<sup>+</sup>-ion momentum aligned parallel to the ordinate direction (0, 1.0) is normalized to unity. Signal intensities of H<sup>+</sup>-ion pairs are plotted with color dots showing the relative intensities in arbitrary units. The distance from the origin corresponds to the magnitude of H<sup>+</sup>-ion momentum relative to the O<sup>+</sup>-ion. White arrows indicate a unit vector of H<sup>+</sup>-ion momentum with an angle Q of 125°.

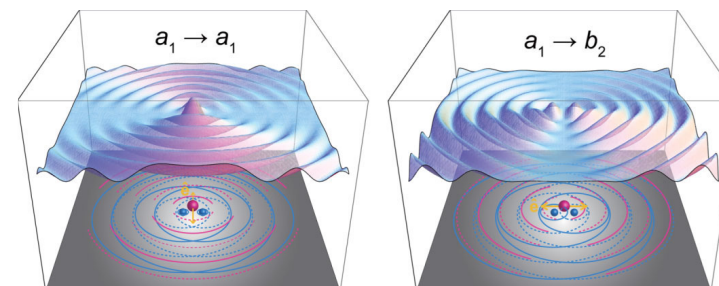


Figure 2  
O 1s photoionization of H<sub>2</sub>O molecules by linearly polarized soft X-ray undulator radiation creates primary photoelectron waves which are subsequently scattered from the two hydrogen atoms. Interference between the primary and scattered waves appears in photoelectron angular distributions from a single oriented H<sub>2</sub>O molecule. The upper parts illustrate plan views of the total wavefield, for the two types of transitions. The lower parts depict wave fronts, where red and blue curves represent primary and scattered waves, respectively.

jects. That is, from Huygens' point of view, the O atom acts as an emitter of primary waves which are subsequently scattered against the two H atoms. The total wavefield was constructed as a coherent sum of the primary and scattered waves. For the two types of transitions of O1s (*a*<sub>1</sub>) → *a*<sub>1</sub> and O1s (*a*<sub>1</sub>) → *b*<sub>2</sub>, a plan view of the total wavefield is shown in Fig. 2. The modulation from the primary wave can be seen as the up-down asymmetry on the intensity of the total wavefield. This simple photoelectron diffraction model can reproduce the experimentally determined MF-PADs, which are not shown here.

As reported here, full 3-D MF-PAD, which has never been attempted for non-linear molecules, is an extremely sensitive direct probe of the 3-D anisotropic multi-centre molecular potential and photoionization dynamics. The development of experimental methods will provide new insights into molecular photoionization processes. The present results enable the full 3-D MF-PAD from a single oriented molecule to be compared with photoelectron diffraction patterns from the relevant adsorbed

molecules on the surface. This is interesting, because it might clarify the interaction between molecules and surfaces. Even more importantly, successful application of the simple scattering model to MF-PAD suggests that it will be possible to determine the local structure of a single protein molecule from full 3-D MF-PAD measurements, if its orientation in space can be controlled, by using an X-ray laser in future.

### REFERENCES

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### BEAMLINER

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