

Fingerprint of Dipole Moment Orientation of Water Molecules in Cu^{2+} Aqueous Solution Probed by X-ray Photoelectron Spectroscopy

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The electronic structure and geometrical organization of aqueous Cu^{2+} have been investigated using X-ray photoelectron spectroscopy at the Cu L-edge combined with state-of-the-art ab initio molecular dynamics and a quantum molecular approach designed to simulate the Cu 2p X-ray photoelectron spectrum. The calculations offer a comprehensive insight into the origin of the main peak and satellite features. It is illustrated how the energy drop of the Cu 3d levels (≈ 7 eV) following the creation of the Cu 2p core hole switches the nature of the highest singly occupied molecular orbitals from the dominant metal to the dominant molecular orbital nature of water. It is particularly revealed how repositioning the Cu 3d levels induces the formation of new Bonding (B) and Antibonding (AB) orbitals, from which shake-up mechanisms toward the relaxed H-SOMO operate. As highlighted in this study, the appearance of the shoulder near the main peak corresponds to the characteristic signature of shake-up intra-ligand ($1a_1 \rightarrow \text{H-SOMO} (1b_1)$) excitations in water, providing insights into the average dipole moment distribution ($\approx 36^\circ$ degrees) of the first-shell water molecules surrounding the metal ion and its direct impact on the broadening of the satellite. It is also revealed that the main satellite at 8 eV from the main peak corresponds to ($\text{metal}/1b_2 \rightarrow \text{H-SOMO} (1b_1)$) of water) excitations due to a Bonding/Antibonding (B/AB) interaction of Cu 3d levels with the deepest valence O2p/H1s 1b2 orbitals of water. This finding underscores the sensitivity of XPS to the electronic structure and orientation of the nearest water molecules around the central ion¹.

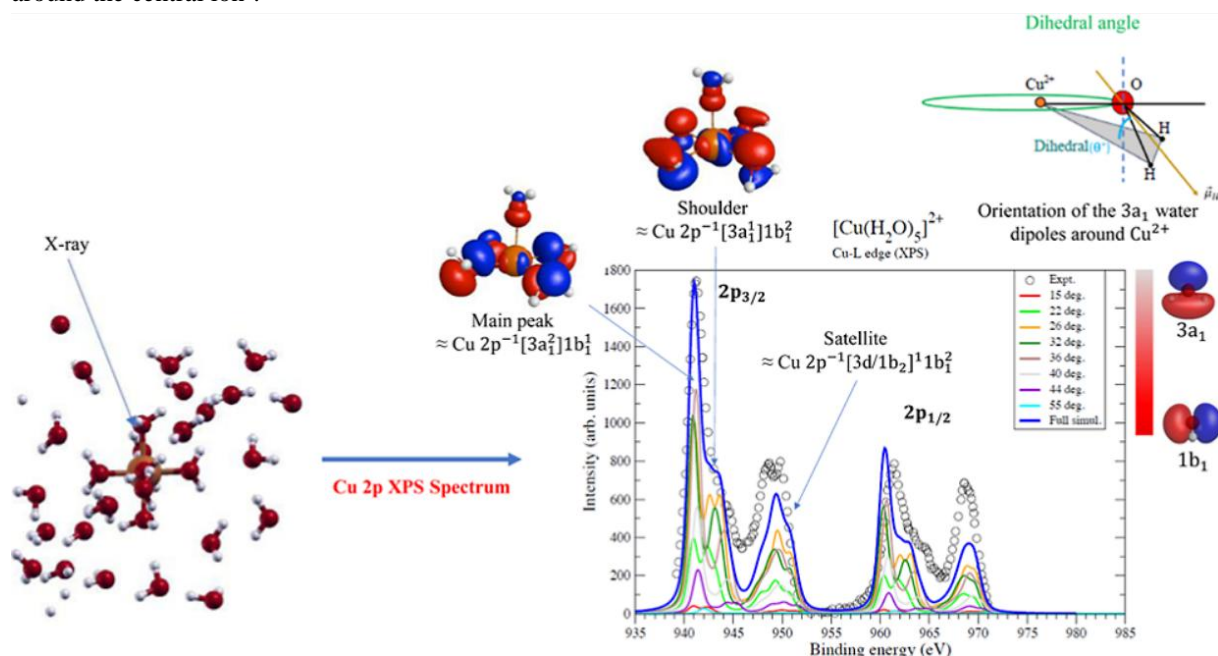


Figure 1. The illustration of the developed . In the left, the cluster is displayed. In the right panel, spectra are computed for different values of the dihedral angle.

Keywords: Ab initio, Molecular Dynamics, X-ray photoelectron spectroscopy

1 Mosaferi, M. et al. Fingerprint of Dipole Moment Orientation of Water Molecules in Cu^{2+} Aqueous Solution Probed by X-ray Photoelectron Spectroscopy. Journal of the American Chemical Society.

