

Theoretical calculation of X-ray absorption near edge structure and photoelectron angular distribution for gas-phase molecule

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X-ray Free Electron Laser (XFEL) opens a new research for revealing tiny geometrical change of molecules in femto second order due to its very high intense pulse in very short time range. Recent improvement of experimental technique for alignment of gas-phase molecule using optical laser opens us measurement of photoelectron angular distributions (PAD) in the molecular frame, so called MFPAD, with XFEL. Since the PAD pattern appears as the result of interference of photoelectron waves scattered by the molecular potential, we can obtain geometrical information of the molecule by analyzing the PAD. Thus the MFPAD is expected as an effective tool to investigate photoionization processes of gas molecule.

For improvement of MFPAD calculation, we studied Multiple Scattering (MS) theory. In the MS theory, the molecular potential and charge density are divided into parts (sites), then the photoelectron wave is constructed from the T-matrices of the sites prepared by solving the local Schrödinger Equation (SE) and the free propagators connecting all the sites. The input potential and density for the local Schrödinger equation are usually just composed by the superposition of free atomic ones, hereafter we indicate these with “non-SCF”. More rigorous way is that we first calculate molecular wave functions in Self-Consistent Field (SCF) by using a quantum chemistry code, then construct the potential from them. In contrast, we call a result with this scheme by “SCF”. The SCF potential takes into account covalent bonds properly.

The most common way for dividing the system for MS calculation is the Muffin-tin (MT) approximation, in which the system is divided to spherical atomic regions centered on each atom and the interstitial region. Inside the atomic spheres, the potentials and charge densities are spherically averaged, while they are set to constant value in the interstitial region. While the MT approximation greatly simplifies the MS calculation as a consequence of spherical symmetry, the detail of the structure of system, i.e. anisotropy of electronic structure such as covalent binding, is ignored. More precise way beyond the MT approximation is Full-Potential (FP) method, in which the system is divided by polyhedrons instead of spheres in order to eliminate interstitial region, at the same time the potentials and charge densities inside the cells are treated exactly. We have implemented this in the FPMS code [1].

In this work, we have done calculations of the MFPAD patterns and X-ray Absorption Near Edge Structure (XANES) spectra for carbon K-edge of CO and CO₂ free molecules by the FPMS code in order to study the role of the details of potential, so that we compared the results for non-SCF/SCF potential and the MT/FP method. The calculations were performed in high-energy

region (kinetic energy of photoelectrons above 50 eV) which is normally regarded as not sensitive to the details of potential. For the SCF potential and density, we used the quantum chemistry code "Gaussian 09"[2].

From the calculation results we observed that the shapes of the MFPAD patterns are very sensitive to the conditions, while the XANES looked rather inert. In the presentation we show this tendency in detail and discuss the roles of approximations.

References

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2. M.J. Frisch *et al.*, Gaussian09 Revision E.01, Gaussian Inc. Wallingford CT (2009).