論 文 要 約

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Theoretical study of core-electron spectroscopies for gas-phase molecules using Multiple-Scattering theory

多重散乱理論を用いた気体分子の内殻光電子分光に関する理論研究

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Chapter 1   Introduction

The advent of COLTRIMS Reaction Microscope [1], which enabled us photoelectron-ion coincidence measurements with high detection efficient, has become a standard technique to measure angular distributions of photoelectron emitted from molecules in a molecular frame (Molecular-Frame Angular Distributions:MFPADs) and promoted studies of photoionization. Due to the extremely short pulse width and extremely high intensity of X-ray Free Electron Lasers (XFEL), it is expected that pump-probe measurements using COLTRIMS Reaction Microscope and the high-repetition-rate XFEL make us possible to take molecular movies in femto second order. Kastrike *et al.* [2], very recently demonstrated the feasibility of tracing molecular dynamics by using these techniques. Furthermore, a two-color XFEL which delivers two of different color XFEL pulses with controlling the delay time in femto second order, provides multi-ionization of a target molecule, such as photoionization of carbon $1s$ and oxygen $1s$ excitation of CO molecule. These novel measurements open a way to understand fundamental molecular dynamics in photoionization processes.

In 2012, Williams *et al.* [3] reported that carbon $1s$ MFPADs of methane molecule (CH_4) averaged over the polarization-direction (PA-MFPADs) has a shape similar to that of the methane molecule itself. Inspired by this work, PA-MFPADs have been studied on various molecules such as CF_4 and NH_3, and it is expected that the measurement and analysis of PA-MFPADs become a powerful tool to determine molecular structures in the middle of photoionization.

Chapter 2   Theory

In this study, theoretical calculations of PA-MFPADs are performed using Multiple Scattering Theory (MST) with these advances of experimental and theoretical methods in mind. One of the feature of this work is a use of general treatment of the molecular potential beyond Muffin-tin (MT) approximation, so called Full-potential (FP) method. In MT approximation, the system is divided into spherical atomic cells and the interstitial region. The molecular potential and charge density are spherically averaged in the atomic cells, and in the interstitial region, they are set to be negative constant values. Due to the significant reduction of calculation costs and the simplification of theory, MT approximation is widely used and works well for many systems, however, this approximation fails for systems having strong anisotropy. In short, this chapter is composed in the following way. First, it starts from derivation of the FP-MST (the Multiple-Scattering Theory with general potential). After obtaining PA-MFPADs formula within the FP-MST framework, simplified PA-MFPADs formula is derived based on MT-MST. Finally, it is further reduced to the case of hetero-diatomic molecule with single and double scattering.

Chapter 3 Study of oxygen 1s PA-MFPADs of CO^{2+}

In this study, O 1s PA-MFPADs of CO^{2+} are calculated with MT-MST and FP-MST. Comparing the results, it is revealed that MT approximation makes the forward intensity of PA-MFPADs underestimated. The high forward intensity in FP-MST is due to the treatment that weak scattering potential distant from nucleus is correctly taken into account by putting empty cells. Contrary to X-ray Absorption Near Edge Structure (XANES), difference of the shape of PA-MFPADs between the results of MT approximation and FP methods is still visible with a photoelectron kinetic energy of 100 eV. Furthermore, study of electronic state dependence on PA-MFPADs is also performed by calculating PA-MFPADs for three types of excited states. Molecular potentials and charge densities for these PA-MFPADs calculations are constructed from molecular orbital wavefunctions obtained by quantum chemical calculations in Self-Consistent Field (SCF). From the comparison, it is found that the PA-MFPADs of the three excited states have almost the same shapes which indicates that the PA-MFPADs are not sensitive to electronic states.

On the other hand, PA-MFPADs are very sensitive to change of C-O bond length, in other words, PA-MFPADs include rich information about molecular structure. In this study, two methods are proposed to determine the bond length from PA-MFPADs patterns. One is focusing on the oscillations of the ratio of forward (along a direction from absorption atom to the other site) and backward intensity (opposite direction). This ratio is formulated in the framework of MT-MST with single scattering approximation. It explicitly shows that the ratio of intensities oscillates as a function of bond length R with a frequency $2kR$ where k is photoelectron wavenumber. In this work, O 1s PA-MFPADs of CO^{2+} calculated within FP-MST is successfully fitted with this ratio function with errors less than 10 %. The other is focusing on the small lobes which appear between 0 and 180 degrees ("Flower Shape"). In this study, it is revealed that the Flower Shape is dominantly caused from an interference between direct wave and singly-scattered wave. MT-MST with single scattering is applied to interpret this phenomena based on the fact that the peak/valley positions in the Flower Shape are almost the same between the calculation results of MT approximation and FP method. Starting from the equation for the angles of the peaks and valleys under MT-MST with single scattering approximation, a novel formula describing the relationship between the lobe positions and C-O bond length is obtained. This formula is similar to well-known Young's formula. By applying this formula to the calculation results of O 1s PA-MFPADs of CO^{2+} with FP-MST, C-O bond lengths are successfully determined with errors less than 5%.

The theoretical methods established in this work are expected to be a powerful tool to analyse the time-resolved PA-MFPADs obtained by using XFEL-pump XFEL-probe measurement and to be conductive to understand the molecular dynamics in the middle of photo-dissociation.

Reference

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