Low kinetic energy photoelectron diffractions for C 1s and O 1s electrons of free CO molecules in the EXAFS region

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Abstract. We have measured molecular-frame photoelectron angular distributions from carbon 1s and oxygen 1s levels of CO molecules up to a photoelectron kinetic energy (KE) of \(~150\) eV. The backward-scattering intensities exhibited a strong modulation as a function of the kinetic energy of the photoelectrons, whereas the intensities for the forward-scattering gradually increased and then became nearly constant over KE \(~100\) eV. Multiple scattering calculations with a muffin-tin potential qualitatively reproduced the experimental results. The present results may be considered as the observation of low-energy photoelectron diffraction patterns for gaseous free CO molecules, which are involved in modulations in extended X-ray absorption fine structure (EXAFS) spectra.

1. Introduction
Photoelectron diffractions yield extensive knowledge, particularly for interfaces and adsorbed systems [1]. Modern photoelectron diffraction theory, in which the continuum final states must be treated, successfully reproduces diffraction patterns and spectra for such materials with a few parameters and approximations. Comparison with experimental data for a simple, well-known physical system is expected to produce improvements in the theory and a proper understanding of photoelectron diffraction. Thus, a rigorous test of the theory for photoelectron diffraction requires an experimental result for free molecules, since effects from the surrounding circumstances and substrates are best avoided. However, few photoelectron diffraction pattern data are available [2,3], because molecular rotational motion averages the angular distribution of photoelectrons in conventional methods.

We have developed a method to measure the photoelectron angular distribution in molecular frame (MFPAD) for studying core-level and inner valence-level molecular photoionization dynamics [2]. To make the measurement of MFPADs more efficient, we constructed a spectrometer that records velocity-map images of both photoelectrons and fragment ions ranging over the entire solid angle [4]. A few years ago, this spectrometer (coincidence velocity-map image spectrometer; CO-VIS) was

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improved so it can measure MFPADs with KE of up to 150 eV [5,6], which enables the study of the elementary process of low kinetic energy photoelectron diffraction for free molecules. Also, systematical data for MFPADs having the higher kinetic energy must improve our understanding of molecular photoionization dynamics.

To elucidate the general perspective on molecular photoionization dynamics, we chose CO molecules as the target and measured C 1s and O 1s PADs for fixed-in-space molecules, which are considered to represent the photoelectron diffraction patterns for isolated molecules without any surrounding effects. In particular, we focus on the intensities of the MFPADs in the backward-scattering direction.

2. Methods
The experiment was performed on the soft x-ray undulator beam line BL-2C [7] at the Photon Factory 2.5 GeV storage ring. Photoelectrons and photoions from CO molecules were measured with a multi-coincidence, velocity-map imaging spectrometer [4,5]. This enabled us to measure multi-coincidence events among angle-resolved photoelectrons and photoions. A homogeneous extraction field of 540–680 V/cm was applied to the collision region. All electrons and photoions having a kinetic energy (KE) of up to 150 eV were collected into the detectors under near-velocity-focusing conditions. To detect photoelectrons and fragmented ions, we used the products of RöntDek Handels GmbH [8] to record time information in a list format. After the measurements, we selected the e−-C⁺-O⁺ triple coincidence events with specified emitted directions from the recorded data to obtain MFPADs in different relative arrangements between the electric vector of the incident light and the molecular axis (experimental geometry). Figure 1(a) shows the parallel geometry as an example.

Calculation was performed using the multiple scattering formula [9,10] with a muffin-tin type potential. The potential included the polarization effect caused by emitted photoelectrons with the optical potential [11].

3. Results and Discussion
Figure 1(b,c,d) show polar plots for the C 1s MFPADs at KE = 150 eV in three different experimental geometries for CO molecules. These results show that the intensities in the electric vector direction are rather large, and that they are different from the pure p-wave pattern. The 1s photoionization is fundamentally the local 1s → εp transition on the photoabsorbing atom [12,13]. We expected that the MFPADs in the perpendicular geometry would show almost a pure p-wave pattern, because the intensity of the direct photoelectron wave on the scattering atom side is weak. The experimental results indicate that the MFPADs are strongly affected by scattering with a neighbor atom even with the perpendicular geometry. Our preliminary calculation shows that the intensity of the scattered wave is much weaker than that of the direct 1s → εp wave, and that the interference between the direct wave...
photoelectron wave and the scattered one deforms the MFPADs [14,15]. We concentrate our discussion on the C 1s and O 1s MFPADs in the parallel geometry (i.e., PADs in a plane, including both the polarization and propagation vectors of the incident light). MFPADs in the other experimental geometries will be reported elsewhere in detail [15].

Figure 2 shows the C 1s and O 1s MFPADs in the parallel geometry as the kinetic energy of the photoelectrons varies. Some plots include MFPADs calculated using the multiple scattering theory. The calculated results have well reproduced the experimental ones at higher kinetic energy. At lower kinetic energy, the calculations do not reproduce the shape of the experimental data well. In the present calculation, the lower limit for attempting to reproduce the diffraction pattern is found to be a kinetic energy of about 100 eV.

To focus on the characteristic behavior of MFPADs as a function of the kinetic energy of the photoelectrons, the intensities of the differential cross sections (DCSs) in the directions of forward and backward scattering are shown in Figure 3. (Following scattering theory terminology, we call the scattered atom side the forward direction, which is the right-hand side in Fig.2, and the emitter atom side the backward direction, which is the left-hand side.) These results are shown with a normalization, assuming the partial cross section for the 1s → εσ transition to be constant. The results show that the intensities in the forward direction increase, and then remain nearly constant over about 100 eV. On the other hand, the intensities in the backward direction clearly decrease, and then start to increase over 100 eV. The calculated DCSs in the forward- and backward-scattering directions reproduce qualitatively the corresponding experimental results [14]. Figure 3(c) shows the calculated DCS in the backward-scattering direction for the C 1s photoionization with restriction of the number of scatterings (n). The result of n = 2 is almost converged to that of n = ∞ (full scattering). These

Figure 3 Differential cross sections (DCSs) for C 1s (triangles) and O 1s (squares) photoionizations of CO molecules and calculated DCSs for the C 1s photoionization a) in the forward-scattering direction and b) in the backward-scattering direction. A similar plot for the C 1s photoionization has been reported by U. Becker et al. [16] c) Calculated intensity χ(KE) of the scattering modulation function for C 1s photoionization of CO molecules with photoelectron diffraction theory [9,10].
results means that the change of intensity in the backward-scattering direction comes from double scattering at most. Also, the variation in the intensity of the backward scattering has basically the same origin as an EXAFS oscillation.

Differences appear between experimental results for C 1s and O 1s photoionizations, particularly in the backward-scattering direction. These differences have two probable origins. One is the phase shifts caused by scattering, because a phase shift in the first scattering would strongly affect the entire angular distribution. Another is the difference of equilibrium distance in the 1s ionized states: 1.079 Å in the C 1s hole state and 1.167 Å in the O 1s hole state [17]. It seems difficult to explain the difference by only the effect of the difference between their bond lengths from our preliminary calculation.

4. Conclusion

We have measured C 1s and O 1s MFPADs in the region from a kinetic energy of 50 eV to 150 eV for CO molecules. These MFPADs are the low kinetic energy photoelectron diffraction patterns for fixed-in-space molecules without surrounding effects. The intensities for backward scattering for C 1s and O 1s photoionizations showed strong variation in the interval between KE \sim 50 eV and \sim 150 eV. These behaviors may be related to EXAFS oscillations. This confirms that for free molecules, the measurement of MFPAD enables us to obtain more sensitive EXAFS spectra than the conventional absorption method.

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