Theoretical study of Polarization-Averaged Molecular-Frame Photoelectron Angular Distributions with full-potential multiple scattering theory

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X-ray Free Electron Lasers (FELs) that deliver extremely short x-ray pulses down to a few femtoseconds allow us to visualize femtosecond-scale temporal variations of structure. In two years, Linac Coherent Light Source II (LCLS II) will start high repetition-rate operation in the soft to tender X-ray regions and two color XFEL operation. Having such high repetitions, one can record all or most of ions produced from a single molecule consisting of two to ten atoms, in coincidence with electrons ejected from the same single molecule, in a momentum resolved manner. Furthermore, two color XFEL operation allows measurements of 2 different orbital ionizations such as C 1s and O 1s. Noting these advances in mind, we have started a series of simulation studies for molecular-frame photoelectron angular distributions (MFPADs) of di-cationic molecules that go structural changes.

We report here our first such study on carbon monoxide (CO) molecule. The pump pulse removes an electron from C 1s orbital and results to the singlet $5\sigma^{-2}$ states [1–3]. The probe pulse further eliminates an electron from O 1s orbital, consequently, the doublet $1\sigma^{-1}5\sigma^{-2}$ state is produced. The theoretical simulation of polarization averaged (PA-) MFPADs was performed using full-potential full-multiple scattering theory [4], and the charge density and Coulomb potential were prepared by using the MOLCAS 8.2 quantum chemistry package [5] with the multi-reference second-order perturbation theory with restricted active space (RASPT2) level of theory [6,7] and the ANO-RCC-QZVP basis set. Figure 1 shows the calculation results of O1s PA-MFPADs of CO di-cation. We see the PA-MFPADs pattern changes much, so that it is sensitive to the C-O bond length within the order of 0.1 Å. Figure 2 shows the forward- and backward-scattering intensities of PA-MFPADs as a function of C-O bond length, both of them behave like EXAFS signal as $\cos(2kR)$. It can be qualitatively interpreted by a double-scattering theory.
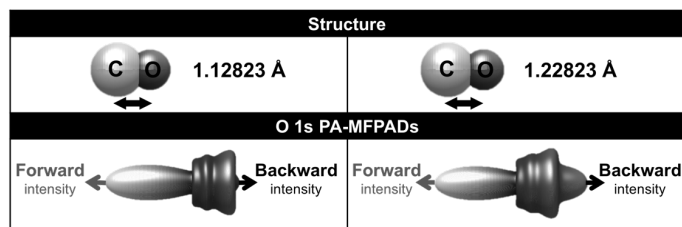

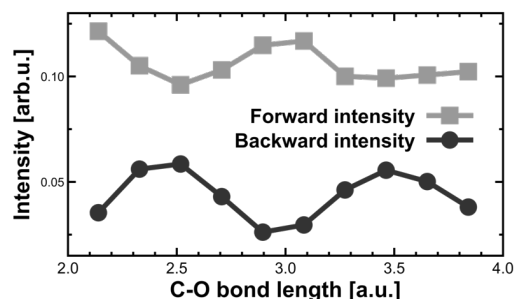**Figure 1.** Oxygen 1s PA-MFPADs of CO di-cation with Photoelectrons having 100 eV of kinetic energy.

Figure 2. Forward- and backward- intensities of PA-MFPADs with changing C-O bondlength.

[1] J. A. Kelber, D. R. Jennison, and R. R. Rye, J. Chem. Phys. 75, 652 (1981).
[2] V. Feyer et al., J. Chem. Phys. 123, 224306 (2005).
[3] L. S. Cederbaum et al., J. Chem. Phys. 95, 6634 (1991).
[4] K. Hatada et al., J. Phys. Condens. Matter 22, 185501 (2010).
[5] F. Aquilante et al., J. Comput. Chem. 37, 506 (2016).
[6] P. Å. Malmqvist et al., J. Chem. Phys. 128, 204109 (2008).
[7] V. Sauri et al., J. Chem. Theory Comput. 7, 153 (2011).