

XAS and RIXS study of acetic acid and methyl formate in liquid

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Abstract. Structure of acetic acid (AA) and methyl formate (MF) in the liquid phase is studied using X-ray absorption spectroscopy (XAS) and X-ray emission spectroscopy (XES) experimentally and theoretically. Two distinct XES spectra are observed by tuning photon energy for both molecules. Model structure in the liquid phase is constructed using the classical and first principle molecular dynamics simulations, and XES spectra are calculated using density functional theory. Calculated XES spectra are consistent with experimental ones. The effect of core-hole induced excited state molecular dynamics are discussed.

1. Introduction

Soft X-ray spectroscopy is now one of powerful tools to investigate a local structure of various materials in the gas or condensed phases [1, 2]. Experimental technique to observe spectra under ambient conditions has been developed for more than fifteen years. To interpret the observed spectra theoretical analysis with the model structure is needed.

Previously Tokushima and his coworkers investigated structure of acetic acid (AA) in the liquid phase using resonant X-ray emission spectroscopy (resonant XES) [3], a technique that can also be called resonant inelastic X-ray scattering (RIXS). XES spectra of the two oxygen atoms at different sites in the carboxyl group can be distinct by tuning incident photon energy. In the previous study theoretical calculations performed for a single molecule and these results supported their experiments. Calculations using more applicable models is challenging work at the liquid phase.

In the present study, we investigate methyl formate (MF) in the liquid phase using X-ray absorption spectroscopy (XAS) and XES in comparison with AA [4]. MF and AA are isomers of $C_2H_4O_2$. And, it is expected that molecular interaction through a hydrogen bond (H-bond) is different between MF and AA because OH functional group is not included in MF. For AA, strong intermolecular interaction such as $OH \cdots O$ H-bond may be operated. On the other hand, for MF, weak interaction such as $CH \cdots O$ H-bond may be operated only. To elucidate feature of XES spectra of these liquids theoretical model structure was constructed using the first principle molecular dynamics simulations, and XES spectra were produced within the framework of density functional theory (DFT) using the cluster model. Note that Robin et al. [5] reported studies for AA in the gas phase by electron energy loss spectroscopy (EELS).

2. Experimental measurements



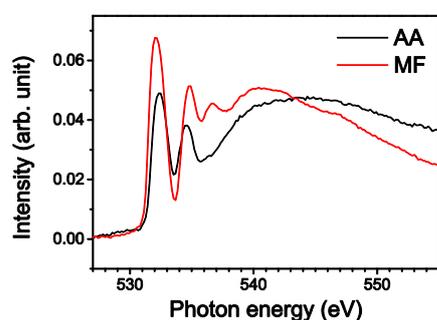


Figure 1. Experimental XAS spectra of AA and MF.

XAS and XES spectra of AA and MF were recorded at synchrotron radiation facility SPring-8 at the beamline BL17SU using an X-ray emission spectrometer. All the spectra were measured using a liquid flow cell with a 150 nm-thick Au-coated thin-film SiC window to separate the liquid flowing at atmospheric pressure from the high-vacuum region. Circularly polarized X-rays were used to eliminate any polarization dependence effects. The energy resolution of the O_{1s} XES measurements is typically about 0.35 eV. The background signals from oxygen impurities in the SiC window, i.e., natural surface oxides, were estimated by measuring the XES spectra of pure acetonitrile and these were subtracted from the sample spectra.

3. Theoretical methods

Molecular dynamics simulations of AA and MF were performed under periodic boundary conditions with OPLS force field using GROMACS version 4.5.5. An NVT ensemble MD simulation comprising 40 molecules modeled using the OPLS force field was performed. The temperature during the simulation was 300 K, which was controlled using the Nosé-Hoover thermostat. The simulation cell was a cubic cell with a cell length of 15.6 Å. The density of the simulation cell was 1.049 g/cm³ which is in good agreement with the experimental density (1.044 g/cm³ at atmospheric pressure and at 298.15 K). The simulation was performed with a time step of 0.1 fs and a total time of MD was 200 ps. One snapshot was obtained as a final structure, and this was used as the starting configuration for a DFT ab initio NVT ensemble MD simulation using VASP. This was performed to model the liquid more accurately. A plane wave basis set with an energy cutoff of 400 eV was used, and PAW potentials were applied to all atoms. The Perdew, Burke, and Ernzerhof (PBE) exchange correlation functional was used. The simulation temperature was 300 K, controlled by the Nosé-Hoover thermostat. The time step was 0.2 fs and the total time was 4.0 ps. The first half of the simulation was used as the equilibrium time (2.0 ps). Theoretical XES spectra were calculated using deMon2k code with the extension of X-ray electron spectroscopy parts. Initial geometries of 16 molecules cluster were sampled and 40 geometries were studied. Core-hole induced excited state (CHES) MD calculations were propagated within 20 fs with the time step of 0.25 fs. XES spectra were calculated at every step and weighted together according to the exponential lifetime decay constant of 4.1 fs.

4. Results and Discussion

Experimental XAS spectra of AA and MF are shown in Figure 1. The first and second resonant peaks at 532.3 eV and 534.6 eV are assigned as $O(C=O) \rightarrow \pi^*$ and $O(OH) \rightarrow \pi^*$ excitations, respectively. In the same way, two resonant peaks at 532.2 eV and 534.7 eV for MF are assigned as $O(C=O) \rightarrow \pi^*$ and $O(OCH_3) \rightarrow \pi^*$ excitations. Thus by tuning photon energy, site-selective XES spectra can be also observed for MF.

In Figure 2, XES spectra of AA and MF in the liquid phase are illustrated. In a similar manner to AA, observed spectra of MF are different depending on excitation energy. In addition a behavior of peak broadening for AA and MF are quite similar although peak positions are slightly different depending on

molecules. This means that difference of H-bond behavior may not be the reason of the peak broadening of O(OH, OCH₃) excited XES spectra, and other driving force may work in such situations.

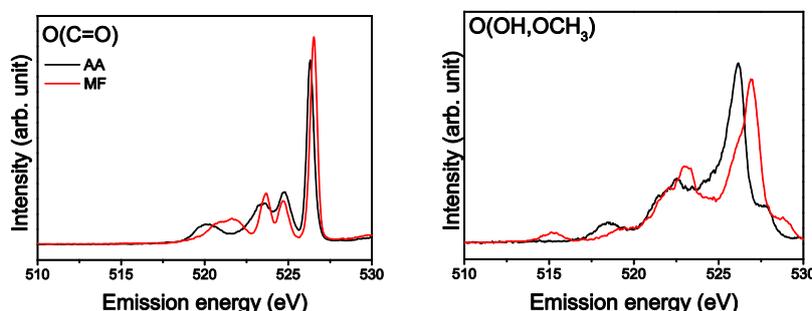


Figure 2. Experimental XES spectra of AA and MF in the liquid phase.

To understand the reason of the peak broadening of AA and MF in the XES spectra in detail, CHES dynamics calculations were performed. We measured the variations in the C=O, C-O, and O-H bond lengths ($d_{C=O}$, d_{C-O} , d_{O-H}) of AA and C=O, C-O, and O-CH₃ bond lengths ($d_{C=O}$, d_{C-O} , d_{O-CH_3}) of MF during the 20 fs simulation period, as depicted in Figure 3. In the cluster model, average bond lengths of the different dynamics generated from the various initial cluster configurations are shown. The error bars in these figures indicate the standard deviation about the averaged bond lengths at each time step. First we discuss about AA. In the case of O(C=O) excitation for a single molecule, the displacement of these three bonds is small. In contrast, at the O(OH) excitation (Figure 3(b), dashed lines), an elongation of the C-O bond is observed. This dynamics is specific at the O(OH) excitation. In the case of both O(C=O) and O(OH) excitations for the cluster model, the enhancement of O-H stretching was observed (Figures 3(a) and (b), solid lines). These dynamics are due to the intermolecular OH...O hydrogen bonds. The O-H stretching at the O(OH) excitation is larger than that at the O(C=O) excitation. And period of vibration of the O-H bond at the O(OH) excitation is shorter than that at the O(C=O) excitation. These results suggest that a chemical bond which is near from a core-excited site is excited more aggressively. Furthermore, the elongation of C-O bond occurs at the O(OH) excitation for both the single molecule and cluster models. The speed of this elongation for the cluster model is slower than that for the single molecule model due to the condensed configuration. A shape of XES spectra depends on chemical

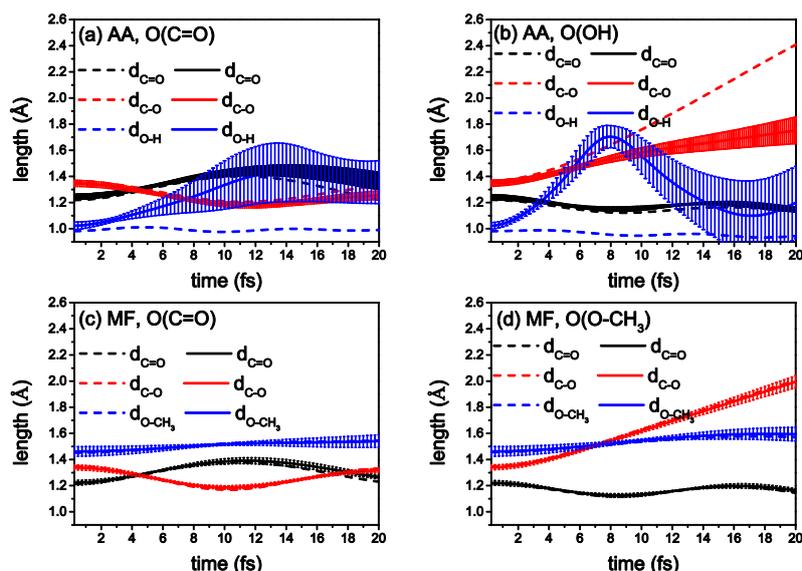


Figure 3. (a), (b) Time propagation within 20 fs of three bonds during two oxygen 1s excitations of AA. Dotted and solid lines correspond to monomer and cluster models. The standard deviations of trajectories by cluster models due to different initial geometry samplings are also included. (c), (d) Those of MF.

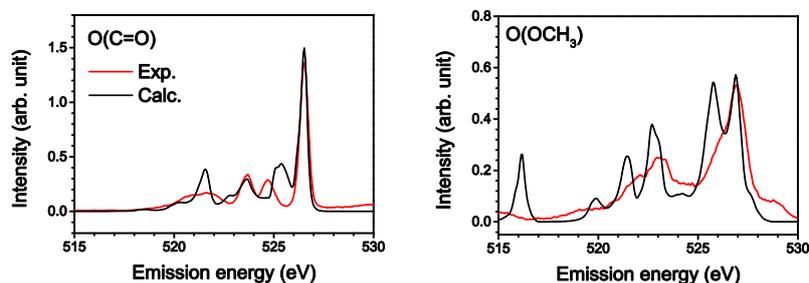


Figure 4. XES spectra of MF. Red and black lines correspond to experimental and theoretical spectra.

environment around a core-excited molecule and its CHES dynamics. Contrary to AA, bond deviations of MF are small in general. Common feature which was observed at the O(OH) excitations of AA and the O(OCH₃) excitations of MF is the elongation of C-O bond. We conclude that the feature of spectra of AA at the O(OH) excitation and MF at the O(OCH₃) excitation is originated with the elongation of C-O bond following core-excitation.

Direct comparisons of experimental and calculated XES spectra of MF are depicted at O(C=O) \rightarrow π^* and O(OCH₃) \rightarrow π^* excitations in Figure 4 [4]. At O(C=O) \rightarrow π^* excitation, the sharp features due to slow CHES dynamics are well reproduced. At O(OCH₃) \rightarrow π^* excitation, the elongation of C-O bond contributes to the broad feature of XES spectra. It should be noted that such trends can be observed on AA experimentally and theoretically. Theoretical XES spectra were produced the above geometries with initial geometry samplings from MD calculations.

5. Conclusion

We explained the features of XES spectra of AA and MF in the liquid phase by dynamical geometry samplings combined with DFT. The strength of H-bond is reflected on the CHES dynamics for both molecules. The broad features of XES spectra at O(OH) and O(OCH₃) \rightarrow π^* excitation of AA and MF can be explained by the elongation of C-O bond, which takes place in both molecules.

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