

Theoretical Calculations of Structure and Core-loss Spectrum of Liquid

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In-situ observations of chemical reactions, fractures, applying electric voltages, and so on, are recently available inside of transmission electron microscopy (TEM), and it enables us to observe their dynamic behaviors with high spatial resolution [1, 2]. By using special sample holders equipped with microcapsules or/and dedicated microscopes with differential pumping systems, it is possible to do in-situ observation in liquid environments. So far, many kinds of important chemical reactions, such as catalytic reactions, corrosion reactions, and adsorption reactions, have been reported at the liquid/solid interface. The developments of the in-situ observation techniques have potential to unravel detailed mechanisms of those reactions in liquids. In order to investigate the detailed changes in atomic structures and electron transfers during the reactions, not only atomic resolution observation but also chemical analysis using electron energy loss spectroscopy (EELS) is indispensable.

On the other hand, theoretical calculation is indispensable to interpret near edge structures of EELS (ELNES). So far, theoretical calculations of ELNES of crystalline solids have been extensively performed [3-5]. It has been known that almost all ELNES can be adequately calculated by selecting suitable theoretical framework [3]. Contrary to the ELNES calculation of crystalline solids, ELNES calculations of liquids have not been reported so far within author's best knowledge. It is partially because molecules in liquid and gas do not have long periodicity and thus making models is difficult.

In this study, we examined atomic structures of methanol gas and liquid methanol by using molecular dynamics (MD) calculations with different temperatures, and utilized the calculated structures to the ELNES calculations.

MD calculations of methanol gas and liquid methanol were performed. Figure 1 shows the calculated structures containing an isolated molecule and several molecules of methanol. They correspond to gas and liquid states, respectively. In the MD calculations, empirical potential with cvff molecular force field was employed [6]. Time step was set at 0.1fs and total simulation time was carried out up to 1.0ps.

By using the calculated structures by the MD calculation, C-K ELNES of methanol gas and liquid methanol were performed. The ELNES calculations were carried out using a first principles pseudopotential method (CASTEP code). The pseudopotential method is more efficient than the all-electron method because core-orbitals are not explicitly calculated. In the pseudopotential calculation, the core-hole effect can be taken into account by employing a special pseudopotential designed for the excited atom with a core-hole. Using this method, not only the spectral features but also the chemical shift of the spectrum can be calculated [7]. This ELNES calculation employing the pseudopotential method is considered to have a great advantage over the all-electron method in that the plane wave pseudopotential method

allows for efficient calculation of ELNES in large and complex systems, such as amorphous and liquid.

In the present calculation, plane-wave cut off energy was set to 500eV, and the core hole was introduced to carbon-1s orbital. Since the supercell of the liquid state has several methanol molecules, C-K ELNES calculations of all carbon sites were separately performed. The calculated spectra were compared with experimental spectra reported in literature [8].

It was found that the calculated C-K edge spectrum of the isolated methanol molecule satisfactorily reproduces the experimental spectrum of methanol gas, while it is different from the experimental spectrum of liquid methanol. It was found that the reproducibility of the liquid spectrum is greatly improved by calculating C-K edge of the liquid model. This indicates that the spectral profiles of ELNES reflects molecule-molecule interactions, including coulomb interactions and van der Waals interactions, and local structure fluctuations of molecules, such as stretching and bending [9].

References

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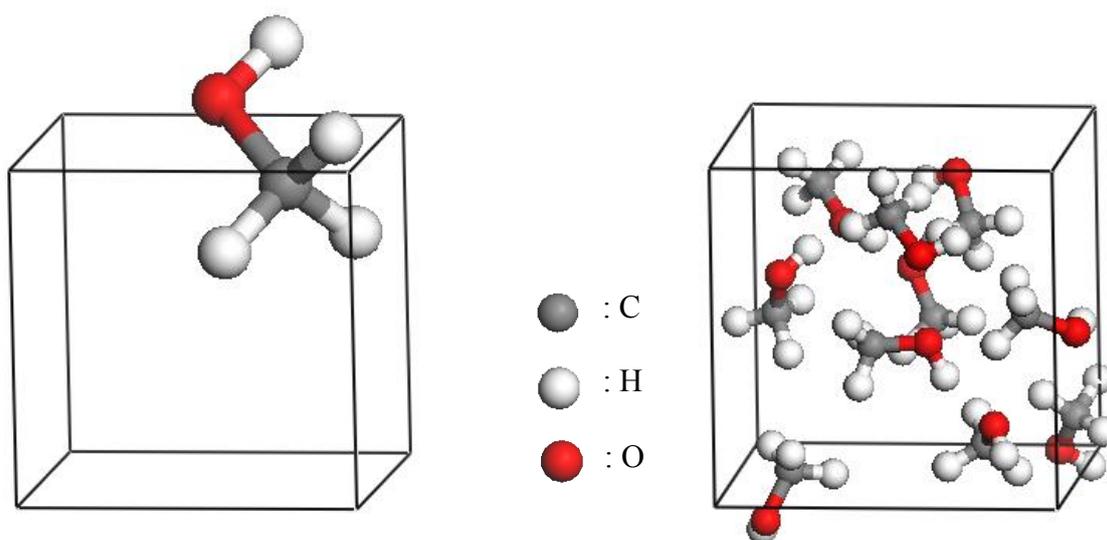


FIG. 1. Atomic structures of (left) isolated methanol molecule and (right) liquid methanol.