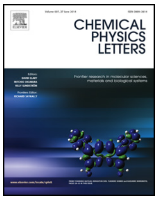
Chemical Physics Letters 640 (2015) 55–60

Contents lists available at ScienceDirect

Chemical Physics Letters

journal homepage: www.elsevier.com/locate/cplett



A theoretical study on the selective oxygen K-edge soft X-ray emission spectroscopy of liquid acetic acid

Naohiro Nishida[a], Seiji Kanai[a], Takashi Tokushima[b], Yuka Horikawa[c], Osamu Takahashi[d,*]

[a] Department of Chemistry, Hiroshima University, Higashi-Hiroshima 739-8526, Japan
[b] RIKEN SPring-8 Center, Sayo-cho, Sayo, Hyogo 679-5148, Japan
[c] Department of Physics and Information Science, Yamaguchi University, Yamaguchi 753-0841, Japan
[d] Institute for Sustainable Science and Development, Hiroshima University, Higashi-Hiroshima 739-8526, Japan

ARTICLE INFO

Article history:
Received 6 August 2015
In final form 11 October 2015
Available online 23 October 2015

ABSTRACT

We have performed theoretical calculations to reproduce the site-selective X-ray emission spectroscopy (XES) spectra of liquid acetic acid at the oxygen K-edge ($O_{C=O,1s}$ and $O_{OH,1s}$). Structure sampling of an acetic acid cluster model was performed from the ab initio molecular dynamics trajectory. Relative XES intensities for the core–hole excited state dynamics simulations were calculated using density functional theory. We found that the theoretical XES spectra reproduced well the experimental spectra and that these calculations gave us electronic and molecular structure information about liquid acetic acid.

1. Introduction

An understanding of the electronic structure of materials is important in many scientific fields. In particular, the valence electronic structure plays an important role in the properties of materials. Recently, direct observation of the valence electronic structure becomes available for liquid and solutions by means of soft X-ray spectroscopies [1–4], such as X-ray emission spectroscopy (XES) and X-ray absorption spectroscopy (XAS) which are powerful tools to probe molecular electronic structure. Soft X-rays are produced in synchrotron radiation facilities such as the SPring-8 facility in Japan.

When a molecule is irradiated with soft X-rays, a core–electron of a particular atom is excited and the core ionized state is produced. This state is unstable and a valence electron rapidly transfers to the core orbital. The excess energy of this transition is released as either emission of an Auger electron or soft X-ray fluorescence. Since the X-ray fluorescence yield increases as atomic number increases, intensity of the X-ray fluorescence is weak for lighter elements. Especially, if the atomic number is less than 30, the Auger electron yield is larger than the K-shell fluorescence [5]. Recently, because of the development of soft X-ray spectroscopy, the soft X-ray fluorescence of lighter elements can also be observed. The XES which analyzes emitted photon energy of soft X-ray fluorescence allows the interpretation of the electron density distribution of the valence electronic states. An important characteristic of XES is that the spectra is dependent on the local chemical environment of the excited site. Thus, XES spectra yield information on the environment of a particular excited atom.

To interpret experimental XES spectra in liquid-state, many attempts have been made to reproduce the XES spectra from theoretical models of the liquid. Guo et al. measured the XES spectrum the oxygen K-edge in liquid water and reproduced the XES spectra using theoretical calculations, and revealed electronic structure information about liquid water clusters [1]. Kashtanov et al. measured the XES spectrum at the oxygen K-edge in liquid methanol and predicted that liquid methanol has a structure consisting of 6–8 molecules with an intermolecular chain or cyclic structure [2].

We have recently measured the site-selective observation of X-ray emission spectra for two oxygen sites of acetic acid in liquid-state by tuning the excitation energy to a specific atomic K-edge ($O_{C=O,1s}$, $O_{OH,1s}$) [3]. Site-selective XES spectra can be measured even if the liquid is multicomponent. For example, in aqueous acetic acid, when the pH value is high, almost all of the acetic acid is ionized. This drastically changes the XES spectrum obtained by $O_{C=O,1s}$ K-edge excitation energy [4]. In these studies, spectral structure of XES was assigned based on DFT theoretical calculations. However, the calculation was modeled only one molecule, and it was too simplistic a model to reproduce the true liquid-state. In the present study, we performed theoretical calculations to reproduce the site-selective oxygen K-edge XES spectra (for $O_{C=O,1s}$ and $O_{OH,1s}$) in liquid acetic acid using a cluster model. Furthermore, core–hole

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* Corresponding author.
E-mail address: shu@hiroshima-u.ac.jp (O. Takahashi).

http://dx.doi.org/10.1016/j.cplett.2015.10.021
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excited state dynamics are included in present calculation since several recent studies pointed out the importance of core–hole excited state dynamics to explain peak shape of XES spectra [6–8].

2. Theoretical and experimental methods

2.1. Theoretical methods

To obtain theoretical XES spectra of the liquid, an equilibrated MD snapshot is needed. Therefore, we performed classical MD simulations using GROMACS [9] version 4.5.5. An NVT ensemble MD simulation comprising 40 molecules modeled using the OPLS [10,11] force field was performed. The temperature during the simulation was 300 K, which was controlled using the Nosé–Hoover [12,13] thermostat. The simulation cell was a cubic cell with a cell length of 15.6 Å. The density of acetic acid in the simulation cell was 1.049 g/cm^3 which was in good agreement with the experimental density (1.044 g/cm^3 at atmospheric pressure and at 298.15 K) [14]. The simulation was performed with a time step of 0.1 fs and a total time of 200 ps. From this, one snapshot was obtained and this was used as the starting configuration for a DFT ab initio NVT ensemble MD simulation using VASP [15,16]. This was performed to more accurately model the liquid. A plane wave basis set with an energy cutoff of 400 eV was used, and PAW potentials [17,18] were applied to all atoms. The Perdew, Burke, and Ernzerhof (PBE) exchange correlation functional was used [19,20]. 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). Intermolecular radial distribution functions obtained from both the classical and ab initio NVT-MD simulations are shown in the supporting information as Figures S1 and S2, respectively. These radial distribution functions are in good agreement with the experimental data, which were obtained from liquid acetic acid by X-ray scattering at atmospheric pressure and at 298 K [21].

Next, structure sampling from the obtained ab initio MD trajectory was performed. One characteristic of XES spectra is that they are representative of the chemical environment of the excited site. Because we expected that acetic acid would form strong intermolecular O—H$\cdots O_{C=O}$ hydrogen bonds between H at O—H and O at C=O (H_O and $O_{C=O}$ respectively) site in the liquid phase, the structure sampling was based on the atomic radial distribution functions to identify molecules that formed these hydrogen bonds. The $H_O\cdots O_{C=O}$ radial distribution function was calculated from the ab initio MD trajectory: A 16-molecule cluster was sampled with the condition that the $H_O\cdots O_{C=O}$ distance (between a molecule at the center of cluster and that formed an intermolecular $H_O\cdots O_{C=O}$ interaction) corresponded to a peak in the $H_O\cdots O_{C=O}$ radial distribution function. Typical 16-molecule clusters are shown in Figure S3 of the supporting information.

For the 16-molecule cluster obtained by structure sampling described above, an acetic acid molecule at the center of these clusters was used to model the $O_{C=O,1s}$ or $O_{OH,1s}$ core–hole state and the core–hole excited state dynamics simulations. The time step in this simulation was 0.25 fs and the core–hole excited state dynamics simulations were propagated for 20 fs. These MD simulation time lengths are sufficient for the required spectral resolution for comparison with the experimentally determined decay process. The core-excited oxygen atom was described using the IGLO-III [22] basis set of Kutzelnigg et al., and the TZVP [23] basis set was employed for all the other atoms. The non-core-excited oxygen atoms were described by effective core potentials. During the 20 fs simulation, $O_{C=O,1s}$ and $O_{OH,1s}$ excited dynamics were modeled and each snapshot was used to calculate the relative line intensities.

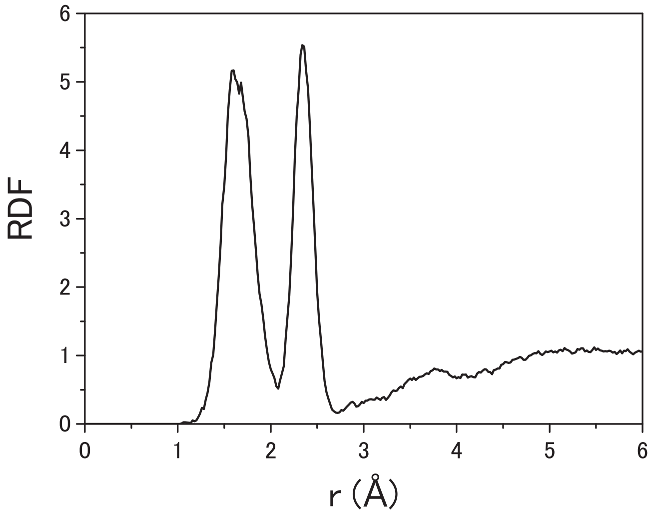

Figure 1. $H_O\cdots O_{C=O}$ radial distribution function obtained from ab initio MD trajectory for liquid acetic acid.

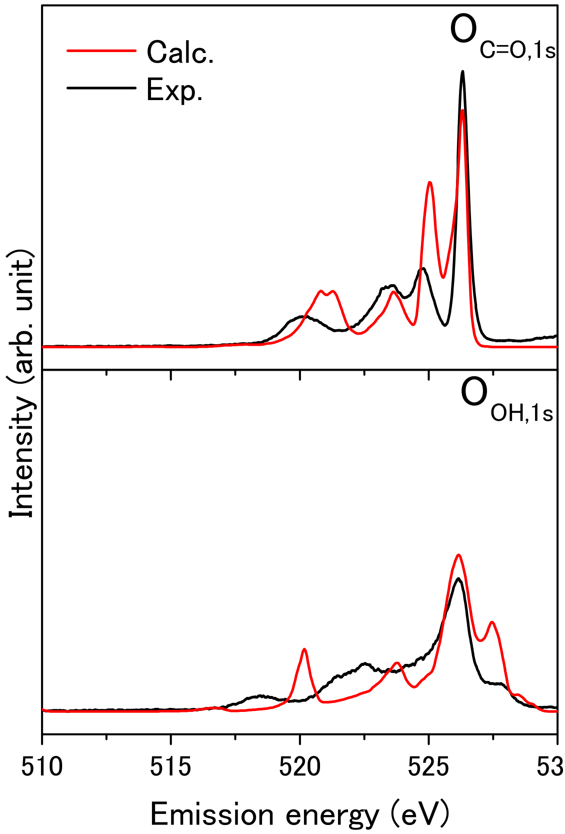

Figure 2. Comparison of theoretical and experimental XES spectra for liquid acetic acid. Theoretical XES spectra calculated from the total core–hole excited state dynamics, obtained from structure sampling based on the $H_O\cdots O_{C=O}$ radial distribution function (Figure 1). The calculated XES spectra are shifted to lower energy by 3.22 and 2.03 eV for $O_{C=O,1s}$ and $O_{OH,1s}$, respectively to fit the experimental XES spectra.

Relative intensities of the XES spectra from the core–hole excited state dynamics simulation were calculated within the framework of DFT using the deMon2k code [24]. The PBE exchange and correlation functionals [19,20] were used. The relative intensities were evaluated from the dipole matrix elements between the core and valence orbitals. Dipole matrix elements between the core and valence orbitals of different molecules of the cluster