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# Selective observation of the two oxygens at different site in carboxyl group (-COOH) of liquid acetic acid

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## Summary

A study of the excitation energy dependence of resonant x-ray emission spectra across the O1s absorption edge in combination with x-ray absorption spectroscopy and density functional theory reveals the site-specific valence electronic structure of liquid acetic acid under ambient condition.

The electronic structure of a material is important for many fields of science, because valence electrons play important roles in properties. While many spectroscopic methods are utilized in physics and chemistry to study electronic structure, methods to observe valence electronic states of liquids are limited due to experimental difficulties. Recently, electronic structure studies of liquids were reported for water <sup>1-5</sup> and alcohol <sup>6</sup> using synchrotron radiation based x-ray absorption spectroscopy (XAS) and x-ray emission spectroscopy (XES). However, there are no reports of site-selective observations of the electronic states for liquid phase molecules. Here we demonstrate site-selective observations of liquid molecules using XES. The molecule we studied is acetic acid, an organic chemical compound with the formula  $\text{CH}_3\text{COOH}$ , which has a carboxyl group ( $-\text{COOH}$ ) in a molecule. The carboxyl group appears in a wide variety of important materials with many applications in biology and chemistry. For example, citric acid, which has three carboxyl groups in a molecule, is important for the metabolism of all living beings due to a biochemical reaction called tri-carboxylic acid cycle (TCA cycle). Through site-selective excitation, the two types of oxygens in carboxyl group were clearly distinguished in resonant XES spectra. Atom- and site- specific information of molecular orbitals obtained by resonant XES are expected to provide valuable insights into properties, intermolecular interactions and reactions of liquids and solutions.

XAS and XES spectra were recorded using circularly polarized soft x-rays at BL17SU of SPring-8 <sup>7</sup>. Figure 1 shows a schematic experimental configuration of a compact flange-mounted liquid flow-cell for XAS and XES measurements. The liquid flow-cell uses a 150 nm-thick Au-coated  $\text{Si}_3\text{N}_4$  as a window, for separating the flowing liquid at atmospheric pressure from the high vacuum. The incoming probe photons and the outgoing photons emitted from the sample are transmitted through this window. XAS spectra were recorded as the total fluorescence yield by using a standard 100mm<sup>2</sup> Al-filtered Si photo diode supplied by IRD Corporation, which was placed facing the window. The photoelectrons emitted from the window result in a background and were eliminated from the spectra by using an electrically biased deflector. XES spectra were recorded by using a newly developed slitless grazing incidence soft x-ray spectrometer based on a previous design <sup>8</sup>. The estimated energy resolution of the XAS and XES spectra are 0.1eV and 0.4eV, respectively. Acetic acid with a purity of better than 99.7% (Wako Pure Chemical Industries Ltd., Japan) was used as a sample without further purification. The sample at atmospheric pressure and room temperature was continuously circulated through the liquid flow cell during the experiment in order to ensure negligible radiation induced effects.

Figure 2 shows the O1s XAS spectrum of liquid acetic acid measured over the energy range of 527-548eV. In the absence of any previous study on liquid acetic acid, we make a comparison with O1s XAS spectra of liquid acetone, water and previously reported electron energy loss (EELS) spectra of gaseous acetic acid and acetone <sup>9</sup> to clarify contributions of the two oxygens. In the O1s XAS spectrum of liquid acetic acid, two intense peaks are observed in the pre-edge region (532.3eV and 534.5eV). Previously reported electron energy loss (EELS) spectrum of gaseous acetic acid <sup>9</sup> also shows two peaks in the pre-edge region located at 531.95eV and 535.2eV. Observed peak shift between the gaseous and liquid acetic acid is attributed to hydrogen bonding present in the liquid, because a similar red shift of the first peak and a blue shift of the second peak due to hydrogen bonding was reported for the hydrogen bonded cluster of formic acid, the simplest carboxylic acid <sup>10, 11</sup>.

An acetic acid molecule has two oxygens:  $\text{O}=\text{C}$  and  $\text{O}-\text{H}$ . Thus, O1s XAS spectrum of acetic acid contains contribution of both oxygens. In order to identify contributions of oxygen in  $\text{C}=\text{O}$  group, we have measured the O1s XAS of liquid acetone that has only

one oxygen, namely C=O. The O1s XAS spectrum of liquid acetone shows an intense peak at 531.3eV. Energy positions of the first peak correspond well to the first peak of acetic acid. On the other hand, the O1s XAS spectrum of liquid water that has no C=O type oxygen shows no peak structure corresponding to the first peak of acetic acid. Hence, we assign the first peak in O1s XAS spectrum of acetic acid to a selective excitation of the  $O_{C=O}$  1s. This assignment is also supported by electron energy loss (EELS) spectrum of gaseous acetic acid <sup>9</sup>, where the first peak at 532eV was assigned to  $O_{C=O}$  1s  $\rightarrow \pi^*$ . The second peak is assigned to the  $O_{OH}$  1s  $\rightarrow \pi^*$  and  $O_{C=O}$  1s  $\rightarrow 3p$  transition according to the EELS study of gaseous acetic acid <sup>9</sup>. However contribution of  $O_{C=O}$  1s excitation to the second resonance is considered to be weak, because the second peak of gaseous and liquid acetone which is attributed to  $O_{C=O}$  1s  $\rightarrow 3p$  is clearly weak. In addition, observed peak shift due to hydrogen bonding indicate that the peak component belonging to the  $O_{C=O}$  1s contribution is shifted toward the higher energy, in the same way as reported for the formic acid cluster <sup>10, 11</sup>. Hence the  $O_{OH}$  1s selective excitation is considered to be dominant in the second peak.

Figure 3 shows the O1s XES spectra of liquid acetic acid for various excitation energies across the absorption edge. The excitation energies are labeled with tick marks in the XAS spectrum of liquid acetic acid (Fig.2). The XES spectra show clear differences between three regions of excitation energies plotted as (i) 531.6-533.5eV, (ii) 533.8-535.4eV and (iii) 536.9 and 538.5eV, respectively. The x-ray emission is a relaxation process following core-hole generation by x-ray absorption. Hence we can select a chemical site by tuning the excitation energy across the absorption edge. The distinct difference observed in these three regions can be assigned to differences of the probed site due to selective excitation.

For region (i), narrow peak structures have a maximum in intensity for the excitation energy corresponding to the top of the first peak (532.3eV) in the XAS spectrum. This peak shows narrowest peak width of 0.55 eV (FWHM), which is nearly comparable to the total resolution (0.4eV). Based on the clear assignment of the first resonance peak in XAS, it is considered that the dominant contribution to features observed in region (i) comes from  $O_{C=O}$  site. The weak feature at higher photon energies marked R can be associated with the Raman shifted component belonging to  $O_{C=O}$  emission, as it is directly correlated with the increase in photon energy beyond 532.3eV.

For region (ii), spectra are different in terms of peak separation, structure and width compared to region (i). The observed peak broadening is known to be due to core hole induced dynamics <sup>12</sup>, a motion of atoms associated with the excited state. XES reflects the motion of atoms within the core hole life time, and thus the probed site with a lighter mass atom shows large peak broadening of XES spectrum due to this effect. Since only the  $O_{OH}$  oxygen has hydrogen as a nearest neighbor atom for acetic acid, XES spectra in region (ii), which is attributed to  $O_{OH}$  selective excitation, have broader peak structures compared to region (i). XES spectra in region (ii) show complex energy dependence in this region, i.e. the main peak first broadens (534.6 eV and 535 eV) and eventually splits into two components on raising the excitation energy to 535.4 eV. Also, since there are no sharp peak structure which can be attributable to  $O_{C=O}$  1s contribution as observed in region (i), it is confirmed that  $O_{OH}$  1s selective excitation is dominant in the XES spectra corresponding to region(ii), i.e. excitation energies associated with the second peak of XAS.

For region (iii), the peak structures are different from that of region (ii) and almost similar to non-resonant XES, except for a small excitation energy dependence. In general, non-resonant XES yields non-selective information of the two oxygens, i.e. the spectrum reflects contributions from both  $O_{C=O}$  and  $O_{OH}$  in this case. The similarity to non-resonant XES and the difference from the peak shape in region (ii) indicate that

XES spectra in region (iii) contains both contribution of  $\text{O}_{\text{C=O}}$  and  $\text{O}_{\text{OH}}$  as is expected for non-resonant XES.

Experimental results show that resonant XES works as a selective probe of chemical site by tuning excitation energy to discrete absorption structures of  $\text{O}_{\text{C=O}}$   $1s \rightarrow \pi^*$  and  $\text{O}_{\text{OH}}$   $1s \rightarrow \pi^*$  excitation observed in XAS spectra. In order to study details about the resonant XES spectra of liquid acetic acid, we have performed electronic structure calculations within the framework of density functional theory (DFT). However, since liquids are very complex system with dynamics, it is hard to determine a reliable model of the molecular geometry. As an approximate approach, we have performed calculations for an isolated molecule assuming the electronic structure of molecule in liquid remains essentially unchanged compared to isolated molecule. The spectral calculations were performed using the ground state wave functions by StoBe-deMon code<sup>13, 14</sup>. In this code, Relative intensity of calculated XES spectra are evaluated by dipole transition probabilities between a core and valence orbitals<sup>15</sup>. In order to determine the absolute energy position of the excited states, normal  $\Delta$ Kohn-Sham ( $\Delta$ KS) calculations were performed to compute the ionization energies of the highest occupied molecular orbital (HOMO) and a core orbital. The core-excited oxygen atom was described using the IGLO-III basis of Kutzelnigg et al.<sup>16</sup>, while (5211/411/1) and (311/1) basis sets were applied for carbon and hydrogen atoms, respectively. The non-core-excited oxygen atom was described by effective core potentials<sup>17</sup>. Fig.4 shows experimental and calculated XES spectra. For experimental  $\text{O}_{\text{C=O}}$  selective spectrum, we choose excitation energy at the top of the first peak (532.3eV) in XAS spectrum. For  $\text{O}_{\text{OH}}$  selective spectrum, we choose slightly lower excitation energy (534.2eV) from the second peak (534.5eV) in XAS spectra to eliminate the peak splitting observed in the second peak excitation. Energy axis of calculated XES spectra is shifted to fit experimental XES spectra. Shape of each molecular orbital (MO) are also depicted in the figure. All peak structures observed in the experimental spectra are simulated in the calculation except for small discrepancy in the energy position and intensity which might come from intermolecular interaction such as hydrogen bonding, not included in the calculations.

From the calculations, we have obtained clear connection between site-selective XES spectra and MO distributions i.e. distribution of valence electrons, as follow: MO number 10 which is mainly spread over methyl group ( $-\text{CH}_3$ ) has no intensity in both  $\text{O}_{\text{C=O}}$  and  $\text{O}_{\text{OH}}$  spectra. The MO distributed mainly on carboxyl group ( $-\text{COOH}$ ), that is MO number 1 and 2 exhibit intense peaks in spectra. MO number 9, which is mainly distributed on  $\text{O}_{\text{C=O}}$  and methyl group ( $-\text{CH}_3$ ) site, appears only in  $\text{O}_{\text{C=O}}$  spectra. MO number 1 results in an intense peak in  $\text{O}_{\text{C=O}}$  spectra, but has clearly weaker contribution in  $\text{O}_{\text{OH}}$  due to inhomogeneous distribution between two oxygens.

Experimental and theoretical calculation results indicate that resonant XES provides site-specific valence orbital information of liquid acetic acid. Especially  $\text{O}_{\text{C=O}}$  selective observation using  $\text{O}_{\text{C=O}}$   $1s \rightarrow \pi^*$  transition provides pure information of valence electronic structure without core hole induced dynamics, in the absence of nearest neighbor hydrogen. It is also worth mentioning that the peak splitting observed in  $\text{O}_{\text{OH}}$  selective observation is similar to the peak splitting observed in recent high resolution XES spectra of water<sup>4, 5</sup>, which is attributed to species with different hydrogen bonding configuration. However at present, the XES spectra can not be separated out due to broadening of core hole induced dynamics. Further experiments, such as temperature dependence and/or other experiments like isotope effect studies are important to resolve this issue.

In summary, we have observed strong excitation energy dependence of oxygen 1s XES spectra for liquid acetic acid through site-selective excitation of two oxygens in carboxyl group ( $-\text{COOH}$ ). Detailed study of experimental XAS and XES results combined with

DFT calculation reveals that resonant XES works as a selective probe of chemical site for liquid molecules. The present results demonstrate the utility of resonant XES in site-selective studies of the electronic structure of liquids under ambient condition.

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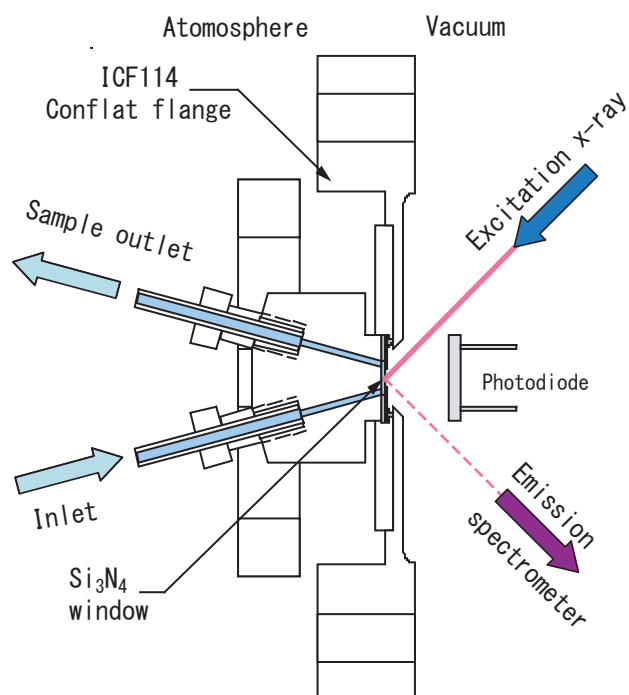


Fig.1

Schematic view (cross-sectional view) of the experimental geometry. The focal point of the incident beam is located on the Au-coated  $\text{Si}_3\text{N}_4$  membrane window mounted in the middle of the mount flange. The incident angle of the beam to the window surface normal is 45 degrees. The spectrometer is located at the other side to detect soft x-ray emission. In order to reduce the polarization correlation, circularly polarized x-rays were used for the experiment.

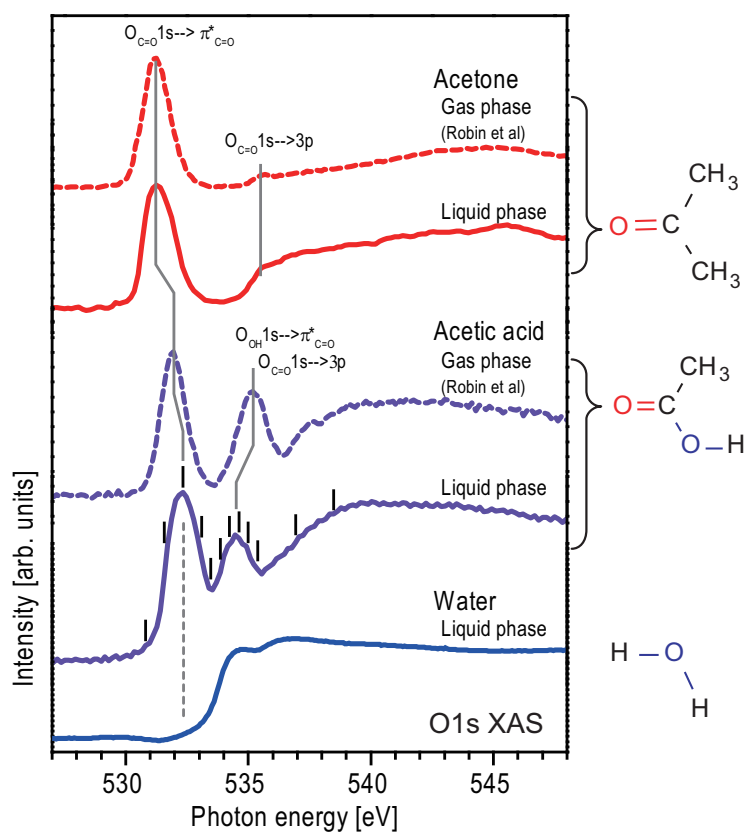


Fig.2  
O1s XAS Spectra of liquid acetic acid. EELS spectrum of gaseous acetic acid (Robin et al.<sup>9</sup>) are also shown. O1s XAS spectra of other liquids contains C=O and OH structure, acetone and water, are included for comparison. Molecular structures of each molecule are depicted on right side of the figure. Tick marks in the x-ray absorption spectrum of liquid acetic acid indicate excitation energies of x-ray emission spectra in Figure.3.



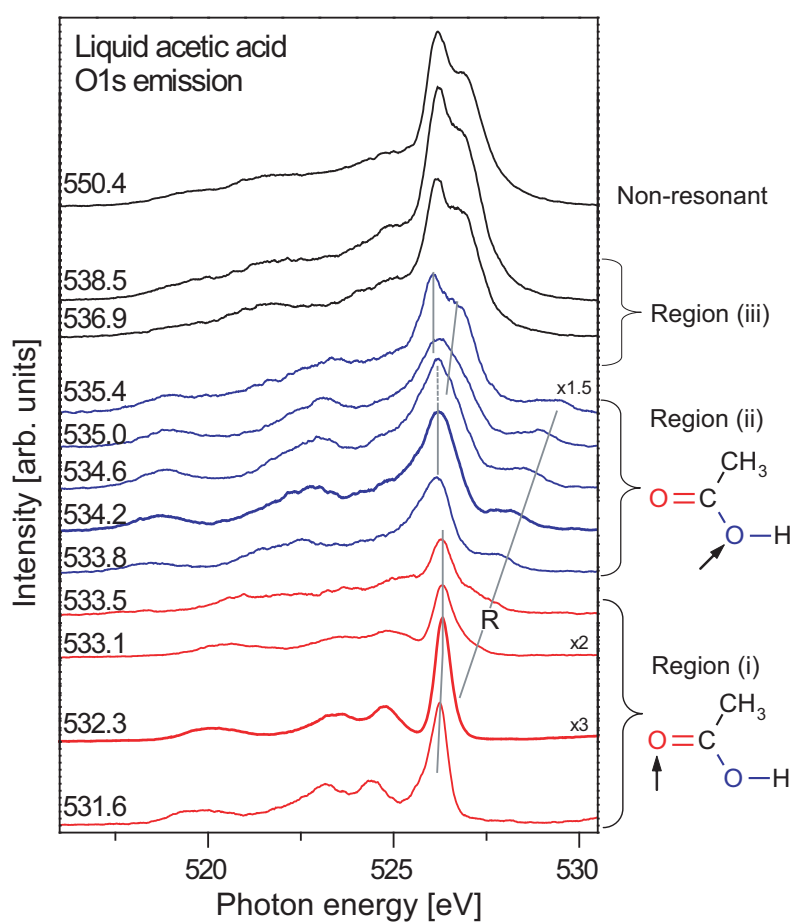


Fig.3

Excitation energy dependence of XES spectra of liquid acetic acid across O 1s edge excitation. The excitation energies are labeled on the XES spectra. Three energy regions (i), (ii) and (iii), are indicated by labels at right side of the figure. Non-resonant XES spectrum is also depicted as a reference. For region (i) and (ii), excited sites are also indicated as arrows in molecular structure diagrams.

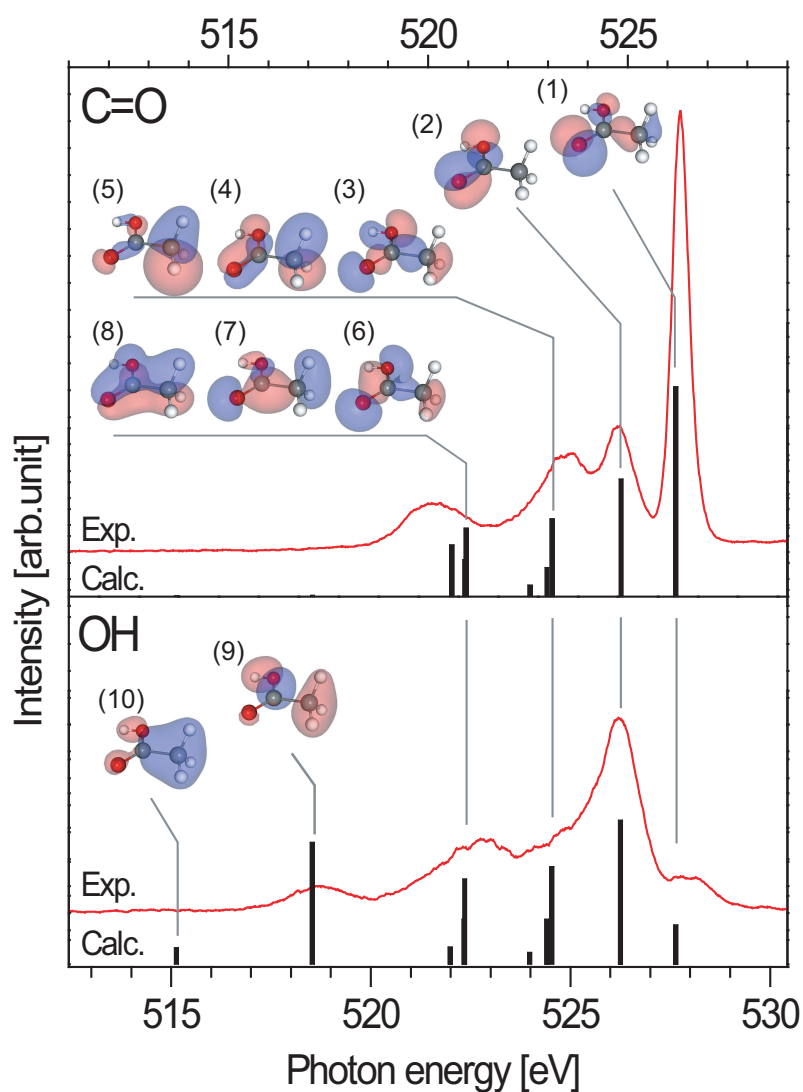


Fig.4  
Assignments of XES spectra of liquid acetic acid to molecular orbitals based on DFT calculation. Upper panel shows the  $\text{O}_{\text{C=O}}$  site selective spectrum and lower panel shows the  $\text{O}_{\text{OH}}$  site selective XES spectrum. Energy axis of two spectra is arranged by shifting 1.43 eV to clarify corresponding peak structure. Calculated XES spectra are shifted toward lower energy by 1.25 eV and 1.95 eV for  $\text{O}_{\text{C=O}}$  and  $\text{O}_{\text{OH}}$  respectively to fit experimental XES spectra.