molecules and clusters

Verification of NEXAFS assignments by a comparison of fragmentation between gaseous and condensed methyl formate

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According to the ion desorption from condensed methyl formate ($DCOOCH_3$) by C 1s electron excitation, C^+ yield was strongly enhanced at 289.1 eV, a higher energy side of C1s(DC) $\rightarrow$ π^*(C=O) peak. This feature could not be clearly assigned. In this work, to clarify the feature, fragment-ion yield curves of gas-phase methyl formate were measured and compared with those of condensed one, since gas-phase and condensed systems are presumed to show more or less similar fragment-ion yield curves under similar excitations. The results demonstrate that fragment-ion yield curves are useful for the assignments of NEXAFS features in both gaseous and condensed polyatomic molecules.

Keywords: soft –x--ray, NEXAFS, methyl formate, photofragmentation, mass spectrometry

1. Introduction

In the past there have been numbers of Near Edge X-ray Absorption Fine Structure (NEXAFS) spectroscopic studies on free and condensed molecules. However, the assignments of NEXAFS features are somewhat unsettled, especially for polyatomic molecule. Therefore, not only calculations but also casual inspection have been used to decide whether a transition terminates at an unoccupied valence shell level or at a Rydberg level. In the inspection, the assignments are decided by shift, broadening and/or missing of Rydberg states due to condensation. Methyl formate is one of the simplest molecules having two carbon atoms in different chemical environments. Since these carbon atoms have different C 1s ionization energies, NEXAFS features are complicated and also difficult to be assigned accurately. Nevertheless, overall gas-phase methyl formate spectra can be interpreted very satisfactorily as the sum of localized inner-shell excitations to unoccupied orbitals characteristics of the molecular chromophores using inner-shell excitation by electron energy loss (ISEELS) technique (Ishii & Hitchcock, 1987). On the other hand, one of NEXAFS features in condensed methyl formate remains to be assigned (Sekiguchi *et al.*, 1996). This feature is in a higher energy side of C1s(DC) $\rightarrow$ π^*(C=O) peak and unique to condensed methyl formate. At this energy, C^+ yield was strongly enhanced. The feature was tentatively assigned to C1s(CH_3) $\rightarrow$ σ^*(O-CH_3) excitation. To verify the assignments of NEXAFS features of condensed methyl formate, we measured fragment-ion yield curves of gas-phase

methyl formate near C K-edge. Fragment-ion yields generally depend on excited states (Eberhardt *et al.*, 1983). The excitations between C1s(C=O) and C1s(CH_3) are expected to be distinguished since a core orbital is generally strongly localized at a specific atom and then fragmentation occurs around the atom
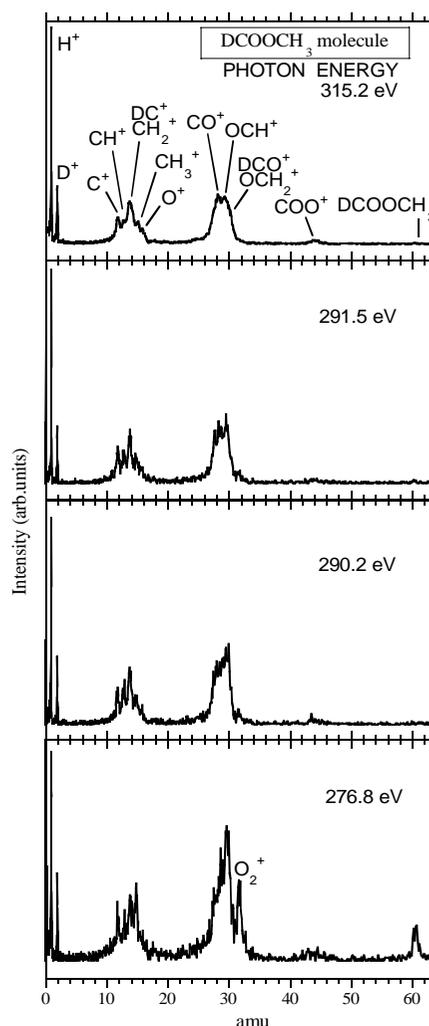

Figure 1
Time-of-flight mass spectrum of methyl formate photoionized with 276.8 eV, 290.2 eV , 291.5 eV and 315.2 eV monochromatized synchrotron radiation.

where the excitation takes place. It was also found that a polyatomic molecule on surface strongly depend on an antibonding character of excited state (Sekiguchi *et al.*, 1996). Since gas-phase and condensed systems are presumed to show more or less similar fragmentation patterns under similar excitations, we compared the gas-phase results with those of condensed methyl formate. Ab intio molecular orbital calculations were also done and compared with the experimental data.

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2. Experimental

Measurements were carried out using a soft X-ray beamline (Saito *et al*., 1989) consisting of a Grasshopper monochromator (Mark XIV) (Brown *et al*., 1978) and a time-of-flight (TOF) mass spectrometer (N. Saito et al., 1989) at TERAS of the Electrotechnical Laboratory (Tomimasu *et al*., 1983). The optical resolution in the experiment was about 1.5 eV near the carbon *K*-edge. The soft X-ray beam was incident on the sample region through a photon-flux monitor of gold mesh. All yield spectra were normalized by this flux to correct for the energy dependent changes in the incident photon flux from the monochromator. Methyl formate sample was obtained commercially at high purity. The liquid sample was degassed with repeated freeze-pump-thraw cycles.

3.   Results and discussion

3.1. *C1s Electron Excitation and Fragmentation*

Figure 1 shows ion TOF spectra, observed at 276.8 eV, 290.2 eV, 291.5 eV and 315.2 eV photon energy. These energies roughly correspond to off resonance, $C1s(CH_3) \rightarrow \pi^*(CH_3)$, $C1s(DC) \rightarrow \sigma^*(D\text{-}C)$ and continuum, respectively. It was found that O_2^+ and $DCOOCH_3^+$ ions are strongly enhanced at off resonance. $DCOOCH_3^+$ ions are only observed below C *K*-edge, while O_2^+ ions are slightly observed at resonant excitations above C *K*-edge. Although TOF spectra are not different greatly above C *K*-edge, mass 13 is relatively enhanced in the TOF spectrum at 290.2 eV compared with that at 291.5 eV. This suggests that $C1s(CH_3) \rightarrow \pi^*(CH_3)$ excitation enhances a production of CH^+ ions. Mass 30 consists of DCO^+ and OCH_3^+ ions. Considering that $C1s(DC) \rightarrow \sigma^*(D\text{-}C)$ excitation occurs at 291.5 eV, DCO^+ ions are expected to be decreased at this energy. Actually, mass 30 is relatively suppressed at 291.5 eV.

Photofragmentation yield curves of H^+, D^+, C^+, CO^+ and a component of CH^+, CH_2^+ and CD^+ are shown in fig. 2 together with a total ion yield (TIY) curve. Features of these yields were previously assigned (Ishii & Hitchcock, 1987). The assignment is denoted in Fig. 2. It is found that these ion yields depend on the photon energy. The D^+ yield is decreased at the $C1s(CH_3) \rightarrow \pi^*(CH_3)$ excitation in comparison with the TIY, while the H^+ and C^+ yield is increased. In the methyl formate ($DCOOCH_3$), the C 1*s* electrons of a methoxy group (OCH_3) are selectively excited at the $C1s(CH_3) \rightarrow \pi^*(CH_3)$. After the transition creating a $C1s(CH_3)$ hole, final ionic states with a hole in a valence molecular orbital localized on the methoxy carbon atom are expected to be formed preferentially, due to the overlap between the core and valence wave functions. It is, therefore, reasonable that the D^+ yield is suppressed and the H^+ and C^+ yields are increased at the $C1s(CH_3) \rightarrow \pi^*(CH_3)$ excitation. The increased component of C^+ ions is expected to be derived from the methoxy carbon atoms. As compared to the ISEELS (Ishii & Hitchcock, 1987), the CO^+ and the component of CH^+, CH_2^+ and CD^+ yield curves are presumed to be resemble to an absorption spectrum. Then, it is suggested that the D^+ yield is slightly enhanced at the $C1s(DC) \rightarrow \sigma^*(C\text{-}D)$ excitation. On the other hand, the D^+ yield from condensed methyl formate was strongly enhanced at the $C1s(DC) \rightarrow \sigma^*(C\text{-}D)$ excitation.
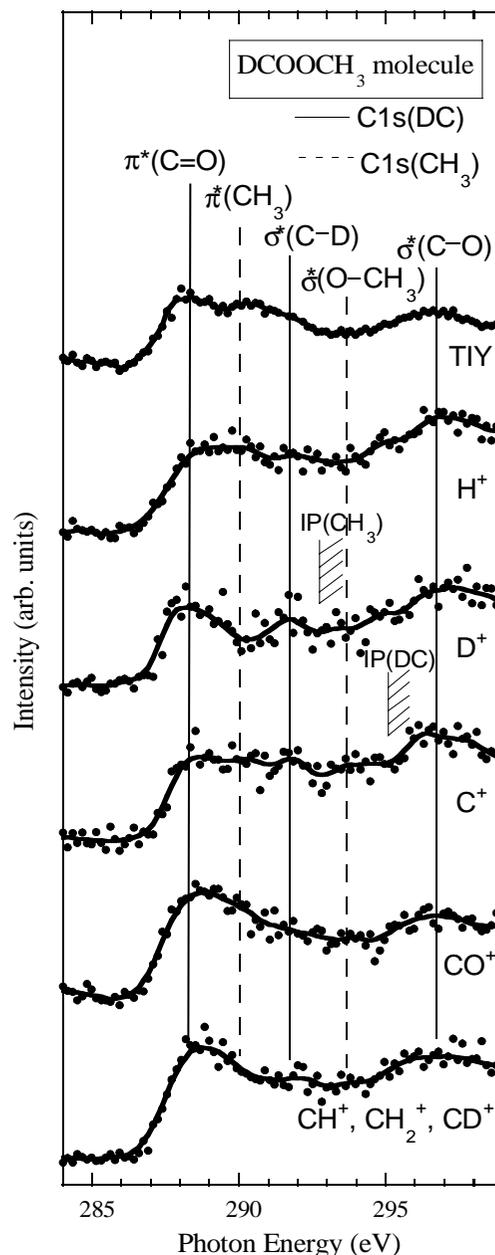

Figure 2

Total ion yield curve and H^+, D^+, C^+, and a component of CH^+, CH_2^+ and CD^+ fragment-ion yield curves of gas-phase methyl formate with the photon energy width of 1.5 eV as a function of excitation energy near the C *K*-edge.

3.2. *Unknown NEXAFS feature of condensed methyl formate compared with calculations*

In our previous paper (Sekiguchi *et al*., 1996), the NEXAFS features of condensed methyl formate were tentatively assigned by comparing with the gas-phase ISEELS spectrum (Ishii & Hitchcock, 1987). Although the NEXAFS features of condensed methyl formate are almost similar to those of gas-phase one, a

new feature was observed between π^*(C=O) and π^*(CH$_3$) states at 289.1 eV. We tentatively assigned it to the C1s(CH$_3$) $\to$ σ^*(O-CH$_3$) excitation, since C$^+$ yield is strongly enhanced at this state. Actually, in Oxygen 1s excitation region, O1s(O-CH$_3$) $\to$ σ^*(O-CH$_3$) excitation strongly enhances CH$_n^+$(n=0-3) ions. However, a previous calculation of methyl formate using the equivalent-cores approximation and the 3-21G basis set (Ji & Thomas, 1994) done with the GAUSSIAN 86 shows that LUMO (the lowest unoccupied molecular orbital) is π^*(CH$_3$) in the C1s(CH$_3$) ionization. It is, therefore, questionable that the C1s(CH$_3$) $\to$ σ^*(O-CH$_3$) excitation exists above the C1s(CH$_3$) $\to$ π^*(CH$_3$) excitation. Since Ji and Thomas only calculated the C1s(C=O) $\to$ π^*(C=O) and the C1s(CH$_3$) $\to$ π^*(CH$_3$) near the C K-edge, we tried to calculate methyl formate using the basis set of HF/6-311++G* and the GAUSSIAN 92 (Frish *et al.* 1992). Steric structure of methyl formate was proposed that vapor, liquid and solid all preferentially give a *cis*-type geometry. The carbon-oxygen skeleton is planar with the methyl group *cis* to the carboxyl oxygen. Bond lengths were selected from the data (Ji & Thomas, 1994). The results of calculations were not complete but consistent with the experimental data. The results did not agree with the previous result using smaller basis set (Ji & Thomas, 1994). Using the HF/6-311++G* basis set, it was found that a σ type state with very small oscillator strength exists below the C1s(CH$_3$) $\to$ π^*(CH$_3$) in the C1s(CH$_3$) ionization.

3.3. *Assignment of unknown NEXAFS feature of condensed methyl formate approached by comparison between gas-phase and condensed methyl formate fragmentation*

To assign the unknown NEXAFS feature of condensed methyl formate at 289.1 eV, we compared fragment-ion yields between gas-phase and condensed methyl formate. This is because gas-phase and condensed methyl formate are presumed to show more or less similar fragmentation patterns under similar excitations. The gas-phase ion yields of C$^+$ is enhanced at the C1s(CH$_3$) $\to$ π^*(CH$_3$) excitation as shown in Fig.2. This enhancement is in agreement with that of the unknown feature of condensed methyl formate (Sekiguchi *et al*, 1997). This suggests that the unknown NEXAFS feature of condensed methyl formate corresponds to the C1s(CH$_3$) $\to$ π^*(CH$_3$) excitation. Actually, in the case of condensed acetone (CH$_3$COCH$_3$) which has methyl groups, C1s(CH$_3$) $\to$ π^*(CH$_3$) excitation enhances the production of CH$_n^+$ ions (n=0-3) (Sekiguchi *et al.*, 2000). However, C1s(CH$_3$) $\to$ π^*(CH$_3$) excitation was observed at 290.7 eV in condensed methyl formate. In general, desorbing ions come from only a few surface layers of multilayer. Then, desorbing ion yield curves can reflect on surface states (Rosenberg *et al*. 1992; Coulman *et al*. 1995; Sekiguchi and Sekiguchi, 1997). Thus, the newly observed feature between C1s (DC) $\to$ π^*(C=O) and C1s(CH$_3$) $\to$ π^*(CH$_3$) in condensed methyl formate is considered to a surface state of C1s(CH$_3$) $\to$ π^*(CH$_3$) excitation. There was a bulk state of C1s(CH$_3$) $\to$ π^*(CH$_3$) excitation at 290.7 eV which was clearly observed at a total electron yield curve corresponding to an absorption spectrum. On the other hand, a surface state was observed as a small shoulder feature in higher energy side of C1s (DC) $\to$ π^*(C=O) peak. Although the unknown NEXAFS feature

of condensed methyl formate can be assigned to a surface state of C1s(CH$_3$) $\to$ π^*(CH$_3$) excitation by a comparison of fragmentation between gas-phase and condensed system, the authors do not deny a possibility of co-existence of a σ type state around this energy (see section 3.2.).

4. Conclusions

To verify the assignments of NEXAFS features of condensed methyl formate, we measured fragment-ion yield curves of gas-phase methyl formate near C K-edge. The obtained results show that the C1s(CH$_3$) $\to$ π^*(CH$_3$) excitation enhances the C$^+$ yield, differently from the D$^+$ yield. The efficient production of C$^+$ ions is in agreement with the results of condensed methyl formate. Considering that desorbing ions come from only few surface layers, the feature can be assigned to a surface state of C1s(CH$_3$) $\to$ π^*(CH$_3$) excitation. The results demonstrate that fragment-ion yield curves are useful for the assignments of NEXAFS features in both gaseous and condensed polyatomic molecules.

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