DV-Xα MO approach to Zn K-XANES spectra of zinc aqueous solution

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The Discrete-Variational Xα molecular orbital calculations have been carried out for model clusters of Zn(II) ions in the aqueous solution. The coordination structure affects the shape of the unoccupied partial density of states (PDOS) for Zn p-states, corresponding to the Zn K-absorption. The variation of the PDOS shape with change in the coordination structure is fairly consistent with experimental Zn K-XANES spectral shape. (1) The first maximum peak of PDOS is intense for hexacoordinated structure and its intensity decrease with a decrease in the coordination number. (2) The position of rising in the PDOS is also discussed with that of the experimental Zn K-XANES spectra.

1. Introduction

It is well known that the XANES spectrum, especially in the vicinity of the absorption edge, reflects the coordination structure and the electronic structure, which is resulted from the coordination structure. For example, the white line intensity for Zn(II) is related to its coordination number; the white line intensity in the XANES of Zn(II) ion with a hexacoordinated structure is fairly strong and the intensity decrease with a decrease in the coordination number. It has been reported that the XANES of Zn stearate Langmuir monolayer changes with elapsed time and that its white line has several components depending on the age of the Langmuir monolayer (Watanabe et al, 1997). The relation between such XANES spectral shape and the coordination structure has not been clearly explained for Zn K-XANES of zinc aqueous solution.

Recently, several theoretical studies on XANES spectra have been achieving steady results. It has been found that molecular orbital (MO) calculations using the Discrete-Variational Xα (DV-Xα) method (Adachi et al, 1978) on a model cluster give a good description of the near-edge structure of electron energy-loss spectra (ELNES) of α-quartz at both Si L_{23}-edge and O K-edge (Tanaka & Adachi, 1996). The partial density of states (PDOS) in the unoccupied band for a corresponding atom is closely related to the experimental ELNES and XANES spectrum, unless strong core hole effects (Tanaka & Adachi, 1996; Tanaka et al, 1995). As for L-absorption edges of Pu hydrates, XANES calculations performed with the *ab initio* code, FEFF7 (Ankudinov, 1996), which is well known as a multiple scattering code proved to work very well in the EXAFS region, has reproduced the XANES spectral feature (Ankudinov et al, 1998).

We have executed the DV-Xα MO calculations for Zn(II)

ions in aqueous solutions and have evaluated the PDOS for Zn p-state. This paper presents variation of shape of the unoccupied PDOS with change in the coordination structure and the comparison of such PDOS shape with experimental Zn K-XANES spectra. Besides, Zn K-XANES spectra calculated using the code FEFF7 have been achieved. Calculated spectra are also compared with experimental spectra.

2. Calculation

DV-Xα MO calculation.

Calculations were executed for four cluster models $[Zn(OH)_n]^{2-n}$ (n=4,5,6) with different coordination structure as shown in Fig. 1, ie, tetrahedral (T_d), planar (Pl), quadrangular pyramidal (Py) and octahedral (O_h) coordination structure. Clusters consist of a central Zn atom surrounded by oxygen atoms. H atoms surrounded at further 0.096 nm from O atoms put as a terminating atom. Distance between Zn and O was 0.196 nm for Td-$[Zn(OH_4)]^{2-}$ and that in other model was 0.205 nm. Atomic orbitals (AOs) used in the present study are 1s - 4d for Zn, 1s - 3d for O and 1s for H.

The details of the computational DV-Xα method have been described in elsewhere (Adachi et al, 1978). The exchange scaling parameter α in Slater's exchange potential (Slater, 1951) was taken to be 0.70 for all atoms. The PDOS was obtained from AO coefficient for each MO and each MO energy was broadened by Gaussian function of 1.2 eV FWHM.
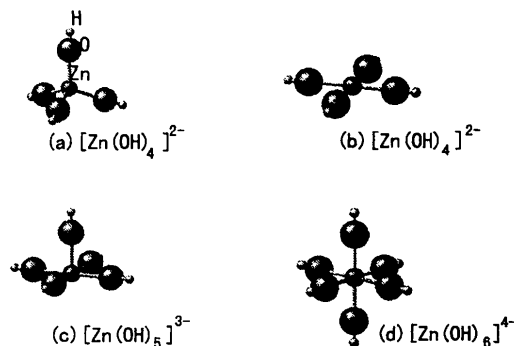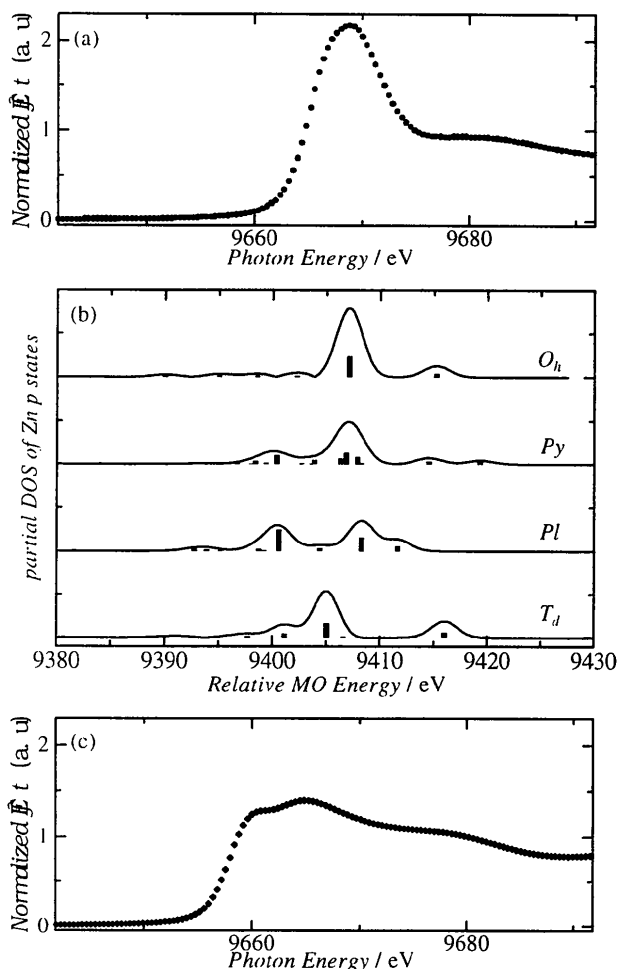

Figure 1
Model clusters $[Zn(OH)_n]^{2-n}$ used for the calculations.

Multiple scattering calculation by FEFF7.

Models used in multiple scattering XANES calculations withh FEFF7 were same ones that used in DV-Xα MO calculations except that H atoms were not used in multiple scattering calculations. The Debye temperature was assumed to 315.0 K. The calculation at experimental temperature of 10 K was performed. According to recommendations given by Ankudinov et al (Ankudinov et al, 1998), number of the multiple scattering paths was taken to be larger than 1000 and overlapped muffin-tin potential was used.

3. Results and Discussion

The PDOS for unoccupied Zn p-state is plotted in Fig.2b. Energy is taken to be relative to eigen value of ground state Zn 1s orbital. Vertical solid lines in Fig.2b indicate MO levels correlated to Zn p-state. The length of line shows the population of Zn 3p component obtained from the Mulliken's population analysis. The PDOS of O_h-structured Zn shows
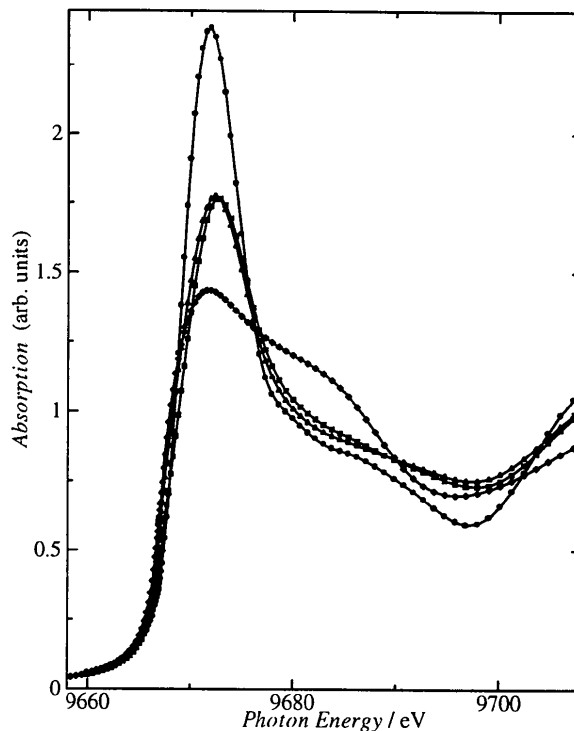
Figure 2

Comparison of experimental Zn K-XANES spectra and PDOS for Zn p-state. (a)Experimental Zn K-XANES spectrum for Zn(II) hexahydrate ion, (b)the unoccupied PDOS for Zn p-state and (c)experimental Zn K-XANES spectrum for tetrahydroxozincate(II) ion. O_h, Py, Pl and T_d show octahedral, quadrangular pyramidal, planar and tetrahedral coordinations, respectively. Energy in (b) is relative to unexcited Zn 1s orbital. Vertical lines inserted in (b) depict MO levels associated with Zn p-state.

Figure 3

Calculated XANES spectra for several coordination structures using the FEFF7 code. Lozenge, square, triangle and circle denote T_d, Pl, Py and O_h coordination, respectively.

intense one peak and such peak is weakened and broadened and several small peaks appear in the PDOS of Py-structured Zn. By taking Pl-structure, two peaks with almost same intensity appear in PDOS. For T_d-structured Zn, rather intense peak is observed but the intensity is small as compared with such peak in the PDOS of O_h-structured Zn. Here, extremely weak peaks in PDOS are neglected since such peaks come from the bonding to external H atoms, owing to simplest cluster model.

For comparison, experimental hexacoordinated and tetracoodinated Zn K-XANES spectra are also shown in Figs. 2a and 2c, respectively. The above-mentioned peak intensity variation is clearly consistent with the difference in the white line intensity between hexacoordinated and tetracoordinated Zn(II). Further, the difference in energy for both absorption

edge might be correlated to the variation of the PDOS shape, ie, the absorption edge energy for tetracoordinated Zn(II) is smaller than that for octacoordinated one, while intense peak in T_d-structured Zn has smaller energy than that in O_h-structured Zn. It is obvious that the present DV-Xα MO calculations predict complex structures in XANES spectra but can not work well as for reproducing the spectral shape, especially a shape of a rising at the absorption edge. This is owing to a lack of higher AOs in the present calculations and the fact that an atomic background is virtually excluded in the MO calculation.

To reproduce the XANES spectral feature, it has been reported that the multiple scattering XANES calculation with the FEFF7 code is more advantageous than the MO calculation(Ankudinov, et al, 1998). Thus the multiple scattering calculation using the FEFF7 code has been achieved for the present Zn compounds. Calculated XANES spectra are plotted in Fig. 3. The white line for O_h-structured Zn is more intense than that for T_d-structured Zn. This result is consistent with the experimental one very well. On the other hand, the white line intensity for Pl-structured Zn is a little more intense than T_d-structured Zn though both takes 4 O atoms. And its spectral shape is similar to that for Py-structured Zn where Zn takes 5 O atoms. Moreover, the energy of the absorption edge for all models is almost similar. This tendency is, unfortunately, different from the experimental evidence, ie, the energy of the absorption edge for T_d-structured Zn has lower than that for O_h-structured Zn for Zn aqueous solution.

In conclusion, XANES calculations using the FEFF7 code reproduce the white line intensity and the general spectral

shape for Zn aqueous solution. Besides, the present variation in the PDOS shapes with the coordination structure change appears that the DV-Xα MO approach can describe the complicated change in XANES spectral shapes with the coordination structural change, though the calculation with cluster model similar to more real species is necessary.

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