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XANES of Aqua Complexes of 3d Transition Metals in Solid and Solution

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A characteristic second peak appears at about 10 eV from a main peak in the XANES (X-ray Absorption Near Edge Structure) spectrum of aqueous 3d transition metal complex of divalent state. This second peak is prominent in solid samples. The peak intensity depends on the kind of central metal or counter anion in solid. Theoretical calculations based on the full multiple scattering formalism provide the information regarding the origin and property of the second peak in XANES. The second peak can be reproduced by the multiple scattering calculation considering only six first coordinating oxygen atoms. The intensity and the position of the peak vary with the charge on the first coordinating oxygen atoms which is affected by the ions or solvent molecules contacting with the metal complex.

The coordination structures of hydrated complexes of 3d transition metals have been studied by X-ray diffraction technique[1)] and EXAFS (Extended X-ray Absorption Fine Structure)[2,3)] which investigate the pair correlation functions. Recently, it has been demonstrated that XANES spectroscopy directly provides higher order correlation function containing the information on geometries around the X-ray absorbing atom.[4)] In the region of XANES are involved the electron transitions from a core level to unoccupied valence levels and multielectron effects (shake up and shake off). This complexity makes the XANES difficult to be applied to the characterization of materials.

We have found that there is a characteristic peak at about 10 eV higher from the main peak in the XANES spectra of hexaaqua 3d transition metal complexes of divalent state and the peak is stronger for solid samples than for aqueous solutions. Such a peak has also been reported in the XANES spectra of $MnCl_2$, $FeCl_2$, and $CoCl_2$, at about 5 eV higher from the main peak. Stern[5)] explained it in terms of multielectron excitation such as shake up process by referring to the results of XPS. Sham[6)] has observed an analogous peak at 6.8 eV higher from the main peak for L_{III}-edge of Pt in K_2PtCl_4 solid. This peak is not present in the spectrum of solution state. He concluded that this peak is most likely due to the density of state effects involving Pt–Pt interaction. In the XANES of Ge, a similar peak is more prominent in crystal state than in amorphous state. Proietti et al.[7)] have attributed the peak to the multiple scattering effect by the second and the third coordination shell.

In this paper, we study the origin of the second peak in K-edge XANES of hexaaqua complexes of 3d transition metals by means of multiple scattering calculation. The XANES calculations are performed according to the scheme described in detail elsewhere[8)] in which the full multiple scattering effect is taken into consideration. The scattering property of each atomic pair is described by a set of scattering phase shifts which depends on the electronic structure of the atom. Thus the charge distribution around the X-ray absorbing atom can be obtained by means of XANES analysis.

Experimental

$Mn(ClO_4)_2 \cdot 6H_2O$ and $Co(ClO_4)_2 \cdot 6H_2O$ were purchased from Kishida Chemicals, Ltd. and $Ni(NO_3)_2 \cdot 6H_2O$ and $Fe(ClO_4)_3 \cdot 6H_2O$ from Nakarai Chemicals, Ltd. $CrSO_4 \cdot 5H_2O$, $Cr(ClO_4)_3 \cdot 6H_2O$, $Fe(ClO_4)_2 \cdot 6H_2O$, $Cu(ClO_4)_2 \cdot 6H_2O$, and $Zn(ClO_4)_2 \cdot 6H_2O$ were prepared according to the text.[9)] The solution of Ti^{3+}, Cr^{2+}, and Fe^{2+} were prepared by the electrolytic reductions of each sulphate (Ti^{4+}, Cr^{3+}) or perchlorate (Fe^{3+}) solutions. The solution of V^{3+} ion was prepared by mixing equal amounts of V^{4+} and V^{2+} sulphate solutions. Since these low valence state ions are very sensitive to air and are easily oxidized, all the procedures for the preparations as well as the X-ray absorption measurements were performed under a dry nitrogen gas atmosphere.

The solid powdered samples were held on adhesive tapes and the liquid samples were placed in airtight polyethylene pouches. The concentrations of metal ions in solution were 1.0 mol dm^{-3}.

All of the K-edge absorption spectra were recorded at BL-7C of the Photon Factory of National Laboratory for High Energy Physics (KEK) in Tsukuba. A Si(111) double crystal monochromator was used. The storage ring was operated at 2.5 GeV and the ring current was 150—200 mA.

Method of XANES Calculation

The XANES theory used in this paper is based on the short range order multiple scattering theory proposed by one of the present authors.[10)] The $\chi(k)$ is calculated by the same method as the one for EXAFS. $\chi(k)$ is defined as

$$\chi(k) = (\sigma(k) - \sigma_0(k))/\sigma_0(k),$$

where $\sigma_0(k)$ is the photo-absorption cross section of the core orbital of a free atom, $\sigma(k)$ is the cross section in the presence of surrounding atoms, and k is the wave vector of the ejected photoelectron.

For semiconductors and insulators, the core holes are not fully screened and the hole potential felt by a photoelectron is too large to be neglected.[11] One of the simplest models for the hole potential is a $Z+1$ potential. In this paper it is assumed that the system is fully relaxed in the final state and the photoabsorbing atom is replaced with a $Z+1$ atom.

The phase shifts are obtained under the Hartree-Fock approximation by using Pendry's program.[12] Practically it requires the charge densities of atoms calculated from the interatomic distances and the charges of atoms. Usually the distances are obtained from X-ray diffraction data and the charges are from Pauling's method.[13] In the present work, the charges are treated as the unknown parameters for the XANES calculations in order to clarify their contribution to the XANES.

Results and Discussion

XANES Spectra. The structures of the hexaaqua complexes of 3d transition metals are normally octahedral, except for Cr^{2+} and Cu^{2+} in which there are a Jahn-Teller distortion.

The K-edge XANES spectra for trivalent 3d metal complexes are shown in Fig. 1. There is a weak dipole-forbidden 1s–3d transition peak in the pre-edge region of each XANES spectrum. The energy scale refers to this pre-edge peak. The shapes of the XANES for trivalent hexaaqua complexes, especially Ti^{3+}, V^{3+}, and Cr^{3+}, resemble each other. Figure 2 shows the XANES spectra for divalent 3d metal complexes in solid and solution. It is interesting to note that the XANES spectra for hexaaqua complexes in solution (Fig. 2 right) are quite similar to each other, except for Cr^{2+} and Cu^{2+}. The shapes of XANES for Cr^{2+} and Cu^{2+} are different from those for other metal complexes possibly because of the Jahn-Teller distortion. Garcia et al.[14] reported that the theoretical calculation for a CuO_6 cluster, taking into account the Jahn-Teller distortion (>0.3 Å), predicted the presence of the peaks on both low- and high-energy sides of a main peak. In our spectra, there are two peaks on high-energy side of the main peak B in Fig. 2 for Cr^{2+} and Cu^{2+}, and there is a single peak on the edge for $CrSO_4\cdot 5H_2O$ in which the difference in bond length between those for axial and equatrial amounts to 0.43 Å.[15] The distances between peaks in XANES are listed in Table 1. The main peak B shifts to high-energy side with the increase of atomic number of central metal.

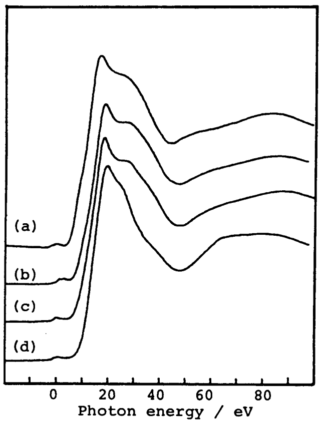

Fig. 1. K-edge XANES spectra for trivalent 3d metal complexes in aqueous solution of (a) Ti^{3+}, (b) V^{3+}, (c) Cr^{3+}, and (d) Fe^{3+} ions. The energy scale refers to the pre-edge peak.

Another characteristic spectral feature for aqua complexes of divalent metals is that the peak C at about 10 eV higher energy side from the main peak is stronger in solid than in solution. This peak is especially strong in the spectra of Zn^{2+} as shown in

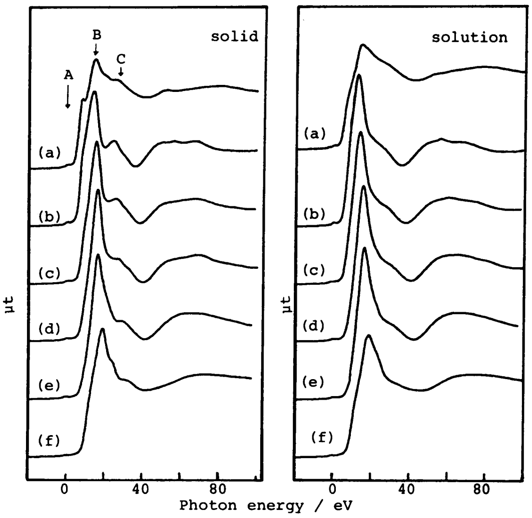

Fig. 2. K-edge XANES spectra for 3d metal complexes of (a) $CrSO_4\cdot 5H_2O$, (b) $Mn(ClO_4)_2\cdot 6H_2O$, (c) $Fe(ClO_4)_2\cdot 6H_2O$, (d) $Co(ClO_4)_2\cdot 6H_2O$, (e) $Ni(NO_3)_2\cdot 6H_2O$, and (f) $Cu(ClO_4)_2\cdot 6H_2O$ (left) and corresponding metal solutions (right).

Table 1. Intervals between Peaks in eV

	Cr^{2+}	Mn^{2+}	Fe^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}
A–B (solid)	14.3	13.7	16.2	16.9	17.1	19.2	—
A–B (solution)	14.3	12.5	15.1	16.9	15.9	18.9	—
B–C (solid)	6.1 11.3	10.5	11.3	11.2	12.6	5.4 13.9	11.9

Fig. 3. The order of the intensities of this peak is $Zn^{2+} > Mn^{2+} > Fe^{2+} > Co^{2+} > Ni^{2+}$. Regarding the origin of the peak C, the possibility of the multielectron effect observed in XANES for 3d metal chlorides[5] can be ruled out because (1) the peak intensities are different in solids and solutions and (2) the peak appears remarkably in Zn^{2+} compounds in which 3d orbitals are filled with valence electrons exhibiting no shake up peak in XPS. It has also been reported[16] that the plasmon satellites are featureless and probably lost in the background in the low kinetic energy region in XPS and this would make the shake up phenomenon quite weak in XANES region. It is possible that the appearance of the peak C is caused by the multiple scattering effect of photoelectrons. The multiple scattering calculation for ZnSe by Matsuura,[17] reproduces the second peak at about 10 eV higher from the main peak when the second shell scattering is included for the calculation. In the case of Ge crystal,[7] the peak is caused presumably by the multiple scattering by the shell extending further than the second shell. The XANES spectra for Zn^{2+} crystals having various counter anions are shown in Fig. 3. The second peak is observed in each spectrum, with the intensity order of $ClO_4^- > NO_3^- > SO_4^{2-}$. The peak is also observed in solution though it is rather weak. The XANES spectra for Zn^{2+} solutions are the same regardless of the kind of the anion. From the results of solutions, it is inferable that the second shell is less important, and that the electron scattering by only nearest six coordinating oxygen atoms would make the peak appear.

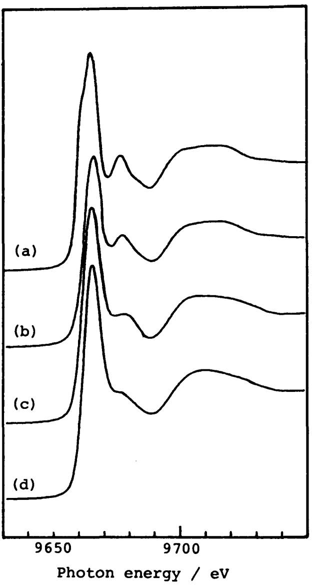

Fig. 3. K-edge XANES spectra for Zn^{2+} compounds, (a) $Zn(ClO_4)_2 \cdot 6H_2O$, (b) $Zn(NO_3)_2 \cdot 6H_2O$, (c) $ZnSO_4 \cdot 7H_2O$, and (d) Zn^{2+} aqueous solution.

Multiple Scattering Calculation. $[Zn(OH_2)_6]^{2+}$ complex is chosen as a model in order to reveal the character of the second peak or the peak C in XANES, because the second peak for Zn^{2+} is the most prominent among the 3d transition metals and the calculation is expected to be the simplest owing to the fully occupied 3d orbitals.

First, the cluster consisting of 35 atoms having Zn at the center, $ZnO_{26}N_8$, is adopted as the model for solid $Zn(NO_3)_2 \cdot 6H_2O$. The positions of the selected atoms are within 5 Å from Zn and fixed according to the X-ray diffraction results.[18] For the phase shift calculations of the central Zn atom and the first coordinating oxygen atoms, a diatomic molecule, Zn–O, is considered and its bond length is assumed to be 2.08 Å which is observed in solution.[1] The charges on Zn and O atoms are unknown parameters. They are determined by putting the trial values to get the best fit between the theoretical result and the experimental spectrum. Figure 4 (a) shows the

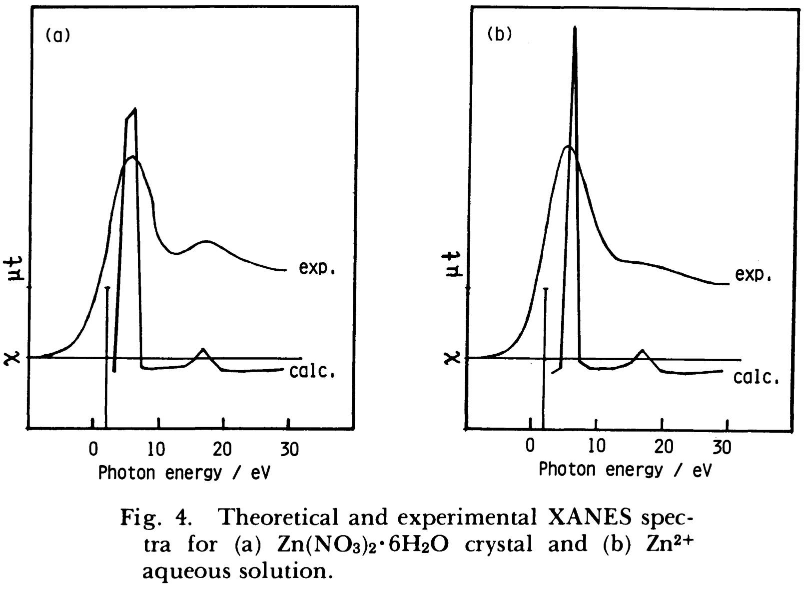

Fig. 4. Theoretical and experimental XANES spectra for (a) $Zn(NO_3)_2 \cdot 6H_2O$ crystal and (b) Zn^{2+} aqueous solution.

XANES spectrum of $Zn(NO_3)_2 \cdot 6H_2O$ and the calculated XANES spectrum for the $ZnO_{26}N_8$ cluster model when the charge of Zn atom is 1.2 (that of O atom is −1.2). The charge of NO_3 is fixed as neutral. The charges of Zn and the first coordinating O atoms are determined so as to reproduce the positions of the main B and the second peak C of the experimental spectrum. In the present work, only the intensity and the position of the second peak are important. Therefore the theoretical XANES spectra are not corrected for the absolute intensity and the widths of the peaks, which can be estimated by considering the absorption cross section of free atom and the life time of the excited state.

Next, the calculation was performed on the model of a ZnO_6 cluster representing the complex present in aqueous solution. The second coordinating atoms are those in solvent molecules and they cannot contribute to produce the fine structure in XANES and EXAFS because their positions are randomly distributed. The shape of the cluster is octahedral and the distance of Zn–O is 2.08 Å.[1] The calculated XANES spectrum for the solution model is shown in Fig. 4 (b). This is a very important result which indicates that the multiple scattering effect confined only in the ZnO_6 moiety gives rise to the second peak. We had expected that the intensity of the second peak in the calculated spectrum for the solid model should be stronger than that for the aqueous solution model. The intensities and the positions of the second peaks.are, however, almost the same.

Subsequently, the effect of solvent molecules in this calculation is studied just in case. Twelve oxygen atoms of water molecules are added to the ZnO_6 cluster. It is assumed that the water molecules bond to the complex through the hydrogen bonding and that the distance of O–O in Zn–O–H···O–H and the angle of Zn–O–H are 2.5 Å and 140° in this model. Further, the multiple scattering calculations are performed for the models having the water molecules at various places which simulate the distribution of the solvent molecules. However, the results are not different from those of the ZnO_6 cluster and the solid. We conclude that the second shell atoms and/or the atoms outside of the second coordination shell atoms should not contribute much to the appearance of the second peak in XANES for the 3d metal aqua complexes.

The Effect of the Charge on Oxygen. From the full multiple scattering calculation the following conclusions are derived. (1) In order to produce the second peak in XANES only the first coordination shell atoms are neccessary. (2) Addition of the second shell atoms results in no alteration in the strength or in the position of the second peak. (3) Thus it is impossible only by placing the scattering atoms around the central atom to reproduce the experimental facts that the second peak is lower for solution sample than that for solid sample and that the peak height for the solid sample is quite sensitive to the kind of counter anion.

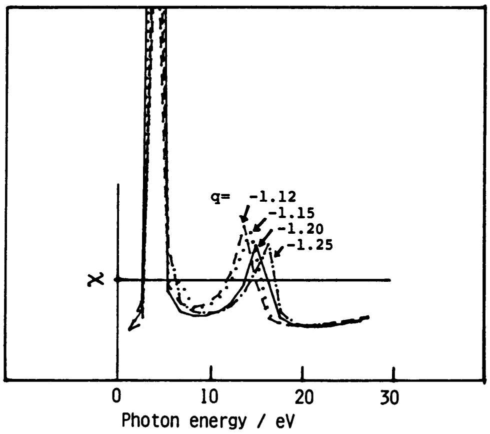

Fig. 5. Calculated XANES spectra for various charges (−1.12—−1.25) on the first coordinating oxygen atoms. The charge on Zn atom is fixed at 1.2.

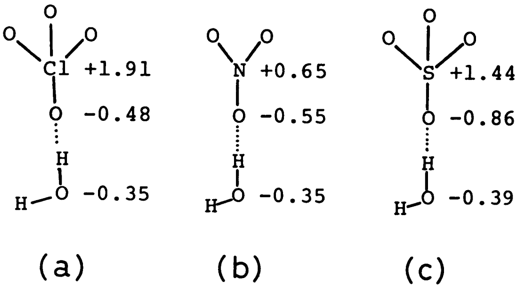

Fig. 6. Charge distributions on water molecule and counter anions determined by MNDO calculations: (a) ClO_4^-, (b) NO_3^-, and (c) SO_4^{2-}.

In order to explain the effect of the counter anion on the second peak in XANES, the charge of the first coordinating oxygen atoms should be incorporated into the calculation. Figure 5 shows the calculated XANES spectra for the various charges (−1.12—−1.25) of the first coordinating oxygen atoms in ZnO_6 cluster model, where the charge of Zn is fixed to be 1.2. The intensities and positions of the second peak change according to the charge of the first coordinating oxygens. The more the negative charge on oxygens, the lower the second peak height and the lower the peak position in energy. Then, in order to estimate the charge on the oxygen atoms, or the alteration of the charge due to the anions, we perform MNDO calculations, which are recognized as the useful quantum chemical method to predict the charges of the atoms up to Cl atom in periodic table.[19,20] The calculations performed here consider only the counter anion and water molecule. The results of the calculations are shown in Fig. 6. The lengths of the hydrogen bondings between H_2O and counter anions are optimized by the calculations so that they are not necessarily the same as those for the crystals. The calculations indicate that SO_4^{2-} ion induces more negative charge on the oxygen atom than ClO_4^- or NO_3^- does. The experimental result that the crystal with the ClO_4^- or NO_3^- counter ion gives the stronger second peak is in accordance with the theoretical prediction that these anions induced less negative charge on the oxygens, thus the intensities for these crystals are stronger. The peak shifts are also well-predicted with the present model calculation. In this way, the characteristics of the intensity and the position of the second peak can be explained qualitatively by taking into account the variation of the charge on the first coordinating oxygens.

In the case of solution sample, the second coordinating water molecules take various positions around the first coordinaing water molecules. Thus, the charge on the first coordinating oxygens fluctuates depending on the length of the hydrogen bonding between the first and the second water molecules. It may be concluded that the fluctuation of the charge on the first coordinating oxygen atoms would smooth out the second peak in XANES because the position of the peak shifts according to the charges of the first coordinating oxygens. In conformity with this view, the reason why the second peak for Mn^{2+} or Zn^{2+} having a larger ionic radius is stronger than the other complexes is understandable. That is, the negative charge induced by the central metal cation on the oxygen atoms of the first coordinating water molecules must be smaller for larger ionic radius cations.

In conclusion, we believe that the second peak in XANES of the aqueous 3d metal complex appears due to the multiple scattering effect in the system consisting of the central metal and only six first coordinating oxygen atoms, and that its intensity and position vary with the charge on the first-coordinating oxygen atoms which is affected by the second and/or further coordinating atoms. The feature at the higher energy region of several eV from the main peak in XANES seems to contain the information concerning the second coordinating atoms which are too far from the central atom to be studied by means of EXAFS.

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