Determination of dissociation energy for ligand exchange reaction from EXAFS

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EXAFS (extended X-ray absorption fine structure) experiments were performed at several different temperatures for a series of 3d transition metal ions (Cr^{3+}, Fe^{3+}, Fe^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}) in aqueous solutions. Anharmonic EXAFS analyses, which include up to third order cumulant, were carried out to study on the metal-oxygen bonding potential. According to the model in which the dissociation process is dominant for the ligand-water exchange reaction, the dissociation energy has been first evaluated from EXAFS in solution phase.

Keywords: EXAFS, anharmonic potential, cumulant, ligand exchange reaction.

1. Introduction

When the X-ray Absorption Fine Structure (XAFS) spectroscopy is applied to solution systems, it directly gives us the interatomic distances between X-ray absorbing atom and photoelectron scattering atoms and the number of scattering atoms by performing the Extended-XAFS (EXAFS) analysis. The analysis also gives us the disorder in structure or the fluctuation in interatomic distance (the Debye-Waller factor). The factor is concerned with the dynamical disorder in the interatomic distance and/or the static disorder of the atomic position. It should be noted here that the Debye-Waller factor, as determined by EXAFS, differs from that obtained by the diffraction technique for crystals. It has been apparent that the EXAFS spectrum is sensitive to the anharmonicity in the potential energy function and its temperature dependence provides unique information about the anharmonicity. We can determine the anharmonic potential from the temperature dependent analyses of these cumulants in EXAFS using the relation between them. The method of derivation of the anharmonic potential has been applied some solids (Yokoyama *et al*., 1990, Dalba *et al*., 1998) and surface systems (Arvanitis *et al*., 1993).

In this paper, we apply the anharmonic analysis for higher cumulants in EXAFS to solution systems and derive the anharmonic potential between metal ions and water molecules. The dissociation energy in the potential is related to ligand exchange reaction rate.

2. Experimental

All the K-edge X-ray absorption spectra were recorded in a transmission mode at BL-6B and 7C of the Photon Factory (KEK) in Tsukuba. The stations were equipped with Si(111) double-crystal monochromators. To reduce the higher order components in X-rays, the second crystal was detuned or a quartz total-reflection mirror was introduced. The storage ring was operated at 2.5 GeV and the ring current was 200-300mA.

Solid samples of $Cr(ClO4)_3{\cdot}6H_2O$, $Fe(ClO_4)_3{\cdot}8H_2O$, $Fe(ClO_4)_2{\cdot}6H_2O$, $CoSO_4{\cdot}7H_2O$, $Ni(ClO_4)_2{\cdot}6H_2O$, and $Zn(ClO_4)_2{\cdot}6H_2O$ were obtained commercially. The solution samples were prepared by dissolving the above salts into the appropriate acidic water. The concentrations of metal ions in solution were 0.5-1.0 mol dm^{-3} and sample thickness was set to 1mm as to obtain appropriate edge jump around 1.0.

The EXAFS analyses were performed using XANADU code (Sakane *et al*., 1993). The theoretical EXAFS function to determine the structural parameters is as follows.

$$\chi(k) = \frac{B\ f(k,r)}{k\ \ r^2} e^{-2r/\lambda} e^{-2\sigma^2 k^2} \times \sin[2kr + \phi(k) + \frac{2}{3}C_3 k^3] \qquad (1)$$

where r is the interatomic distance between X-ray absorbing and photoelectron scattering atoms, $f(k,r)$ and $\phi(k)$ are the backscattering amplitude and total phase shift functions, which were calculated by using FEFF6 code (Zabinsky *et al*., 1995). The k-range used for the curve-fitting procedure was from about 4 Å^{-1} to 12 Å^{-1}. λ is the photoelectron mean free path being optimized by FEFF6 calculation. C_3 is the third order cumulant representing the anharmonic effect in the interatomic potential. B is a parameter consisting of the coordination number, N, and the reduction factor due to many body effects.

3. Results and Discussion

As the examples of temperature dependent EXAFS for tri-valent and di-valent metal ions, Figures 1 display the EXAFS $k^2\chi(k)$ functions for 3d metal ions of (a) Cr^{3+} and (b) Ni^{2+} in aqueous solutions at several different temperatures. In these figures the quality of the data is quite satisfactory.

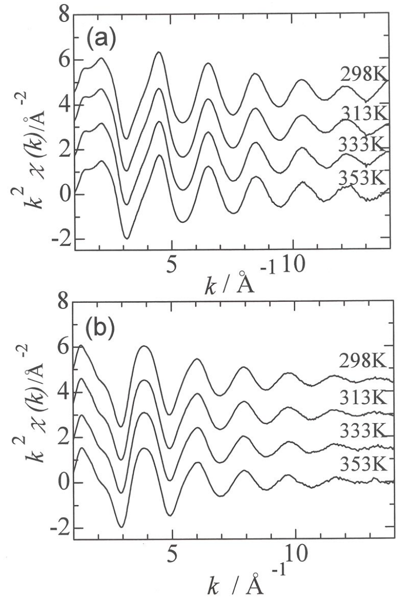

Fig. 1 K-edge EXAFS $k^2\chi(k)$ functions for aqueous solutions of (a) 1.0 mol dm^{-3} Cr^{3+} and (b) 1.0 mol dm^{-3} Ni^{2+} ions at different temperatures.

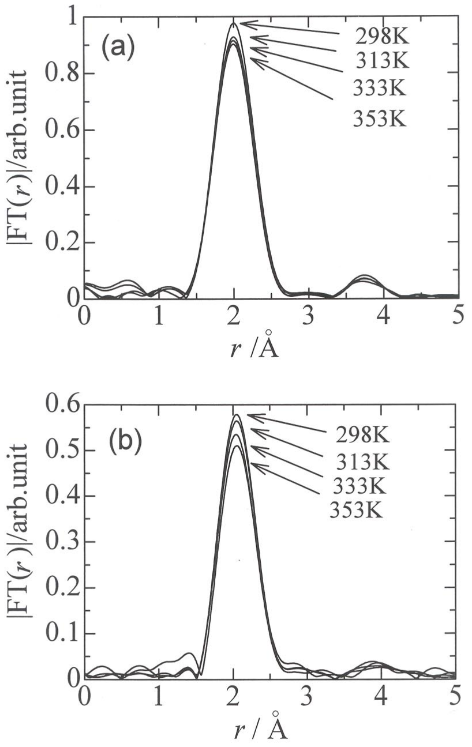

Fig. 2 Fourier transformed spectra for aqueous solutions of (a) 1.0 mol dm^{-3} Cr^{3+} and (b) 1.0 mol dm^{-3} Ni^{2+} ions at different temperatures.

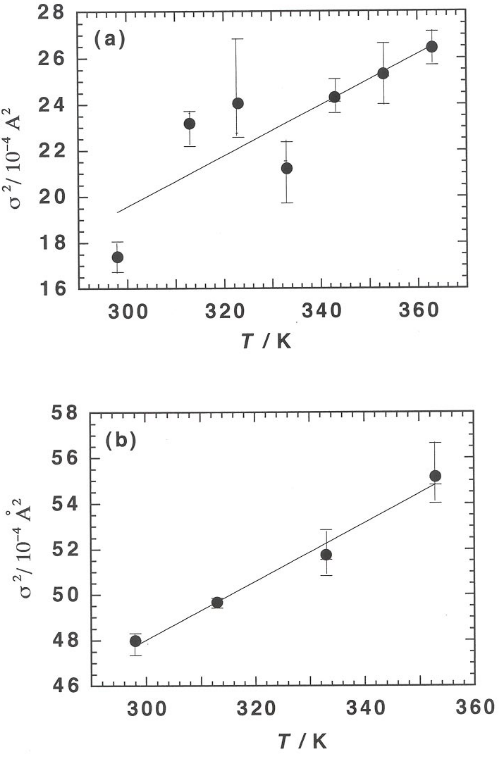

Fig. 3 Temperature dependence of σ^2 for aqueous solutions of (a) 1.0 mol dm^{-3} Cr^{3+} and (b) 1.0 mol dm^{-3} Ni^{2+} ions. Error bars in the figure show the statistical errors for the several times of the measurements.

Figures 2 are the Fourier transforms of the EXAFS data for 3d metal ions of (a) Cr^{3+} and (b) Ni^{2+}. In these figures, the main peaks correspond to the six oxygen atoms in the first coordination water molecules. The peak intensity decreases as temperature increases due to the thermal motion. We can find the clear peaks at about 3.75 Å for Cr^{3+} (a) and at 4 Å for Ni^{2+} (b) corresponding to the second hydration shell and the multiple scattering effect, which was pointed out by Munoz-Paez and coworkers (Munoz-Paez *et al*., 1995, Sakane *et al*., 1998). The differences of the distance and intensity between them correspond to that of ionic radius and the amplitude of the multiple scattering.

By the curve fitting method, the interatomic distance between the metal ion and oxygen atoms for the first hydrated water, the values of the second order cumulant σ^2, or the Debye-Waller factor, and third order cumulant, C_3, were determined as unknown parameters.

Now we assume that the anharmonic potential for M^{n+}-O resembles to the Morse function as

$$V(x) = D(e^{-2\alpha x} - 2e^{-\alpha x}) \qquad (2)$$

where x represents the relative deviation from the equilibrium interatomic distance a between M^{n+} and O, that is $x = (r-a)/a$. D is the dissociation energy and α is the curvature of the potential. Following the theory for the diatomic model (Fujikawa & Miyanaga, 1993, Miyanaga & Fujikawa, 1994) with a high temperature approximation, σ^2 is proportional to temperature, T, as,

$$\sigma^2 \propto \frac{a^2}{\pi \ D\alpha^2} \ k_B T \qquad (3)$$

where a is the interatomic distance between the metal ion and oxygen atom. k_B is the Boltzmann constant. Figures 3 show the temperature dependences of σ^2 values for 3d metal ions of (a) Cr^{3+} and (b) Ni^{2+}. Error bars in the figure show the statistical errors for the several times of the measurements. The term σ^2 arises mainly from the harmonic part in the interatomic potential. The straight lines in the figures are the results from the least-square fitting calculation in accord with eq.(3). For the other four metal complexes good linear fits were also obtained, indicating that the high temperature (classical) approximation holds in the temperature region used in the present study.

On the other hand, the third order cumulant C_3 expresses the anharmonicity in the interatomic potential. In the high temperature approximation, C_3 depends on T^2 as

$$C_3 \propto \frac{a^3}{\pi^2 D^2 \alpha^3} (k_B T)^2 \quad . \qquad (4)$$

Figures 4 show the variation of the value of C_3 with T^2 for 3d metal ions of (a) Cr^{3+} and (b) Ni^{2+}.

Using eq.(3) and (4), the parameter D can be evaluated from the following relation

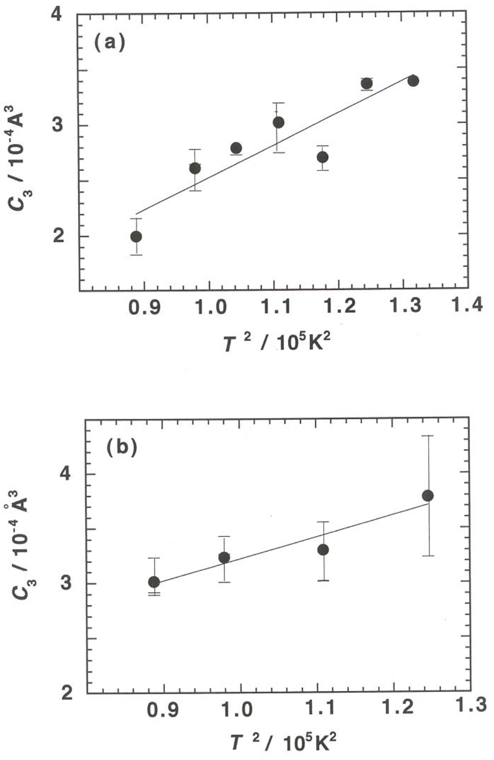

Fig. 4 Temperature dependence of C_3 for aqueous solutions of (a) 1.0 mol dm^{-3} Cr^{3+} and (b) 1.0 mol dm^{-3} Ni^{2+} ions. Error bars in the figure show the statistical errors for the several times of the measurements.

$$D = F\,\frac{\vartheta^3}{\xi^2} \tag{5}$$

where $\vartheta = \sigma^2/T$ and $\xi = C_3/T^2$. The factor F is a constant calculated for a diatomic model (Miyanaga & Fujikawa, 1994). Here we apply the Arrhenius theory to the water-exchange reaction in solution.

$$k_1 = A\exp(-E_\mathrm{a}/k_\mathrm{B}T) \tag{6}$$

where k_1 is the ligand exchange rate constant, E_a is the activation energy, and A is the frequency factor. Strictly speaking, the water-exchange reactions of 3d metal ions are classified as neither a complete dissociative nor a complete associative process but intermediate of these. However, for simplicity we assume here that the reaction proceeds predominantly dissociatively, which is the conclusion of the recent theoretical study (Akesson *et al*., 1994), and that the Morse-type interatomic potential is operative as a reaction coordinate, thus D can be considered as E_a. In Fig. 5 are plotted the D values from the EXAFS experiments against log k_1 for the present six hydrated metal complexes. It is interesting to find that the extrapolation of the points in Fig. 5 to $D = 0$ comes close to the point of log $k_1 = 10$ for the diffusion-limited reaction in water.

In Fig. 5, the theoretical results by Akesson *et al*. (Akesson *et al*., 1994) are also included. They calculated the D values using the self-consistent molecular orbital method with the dissociation model. It is noted that although the values of D from EXAFS are slightly smaller than the theoretical ones, the D values from both methods are comparable and the behavior of D against the log k_1 value is quite similar each other. This result shows that it is possible to determine the dissociation energy in solution phase directly first from EXAFS.

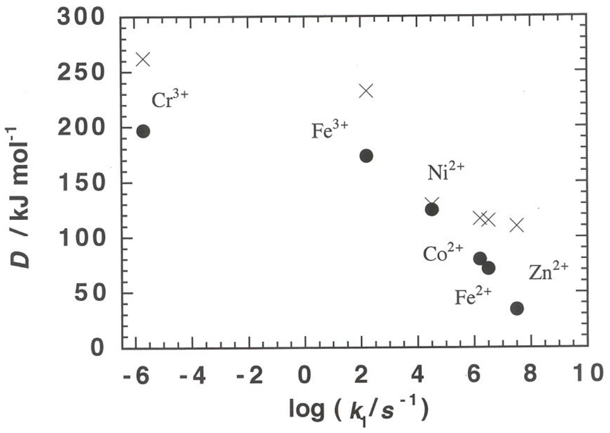

Fig. 5 Relation between the dissociation energy D evaluated from EXAFS (solid circle) and log k_1 (Burgess, 1978). The data points with cross represent the theoretical results by Akesson *et al*. (Akesson *et al*., 1994)

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