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Hydrogen Atom Position in Hydrated Iodide Anion from X-ray Absorption Near Edge Structure

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Hydrogen atom position in the hydrated iodide anion complex is determined from X-ray Absorption Near Edge Structure (XANES) of an aqueous iodide solution at both the K- and L-edges. The spectra are compared with the theoretical ones calculated by using the FEFF method for several model geometries having hydrogen atoms at different positions. Satisfactory agreements are obtained from models with an almost linear alignment of iodine–hydrogen–oxygen atoms, indicating the capability of the XANES analysis when it is combined with the multiple scattering calculations as a method to detect the positions of hydrogen atoms in the first coordination sphere.

X-ray absorption fine structure (XAFS) contains information on the coordination geometries in condensed media.[1–3] Its near edge structure (XANES) has a well-defined structure, which depends essentially on the coordination geometry around the central atom absorbing the X-ray. Consequently, it has been used to investigate the hydration structure of aqua complexes and the localization of hydrogen atoms of ionic complexes in aqueous solutions.[4–6] All these studies have been for cations or metal complexes. Their strong cation–solvent interactions result in spectra with fine structures, and even the structural information for the lightest atom, hydrogen, can be acquired. On the other hand, anion–solvent interactions, in which the hydrogen bonding must play the most important role, are normally too week to be investigated with similar facilitation and accuracy, as in the case of metal complexes. The hydrogen-bond structure has been studied by many other methods, e.g. for supercritical methanol by neutron diffraction[7] and NMR.[8] In supercritical water, the hydration of bromide anion has been studied by an MD method combined with the XAFS.[9] The hydrogen-bond structures in the hydrated halide anions have also been studied by IR,[10] ab initio calculation,[11] Monte Carlo simulation,[12] and MD simulation.[13] These experimental and theoretical studies have been increasing our knowledge of the hydration structures of anions step by step, while other methods have always been desired which are able to detect the position of hydrogen atoms in the hydrated complexes.

The aim of the present work is to study the possibility of detecting the hydrogen atoms by the XANES method. The contribution of hydrogen atoms to the XAFS spectrum has been considered to be minor due to its low scattering power, such that it has often been neglected in theoretical calculation and data analysis. There are, however, a few cases reported in which the presence of hydrogen atoms in the aqueous solution had to be taken into account in the data analysis procedure.[4–6] In the beginning stage of XAFS studies for hydrogen atoms, the hydrogen adsorption was studied. The adsorbed hydrogen atoms influenced the XANES of the substrate atoms (Ni, W, Pt),[14] and a multi scattering calculation could produce the peak induced by the hydrogen adsorption on the Pt surface.[15,16] Recently, for the hydrogen atoms in water, the extended X-ray absorption fine structure (EXAFS) from hydrogen atoms was measured.[17] For the hydrated halide anions, EXAFS data of the bromide anion in a methanolic solution have been analyzed by including the contribution from hydrogen atoms,[18] and for $ZnBr_2$ aqueous solution the analyses were performed by taking into account the multiple-scattering contributions involving hydrogen atoms at the Br K-edge.[19] The Br K-edge EXAFS spectra for bromide anions in aqueous solution at near supercritical condition were analyzed by accounting for the photoelectron focusing effect of hydrogen atom.[20]

In our previous study it was found that the K-edge XANES spectra for iodide anions in solvents[21] have characteristic structures which are sensitive to the kind of solvent that are not present in those of bromide anions.[22] The solvent effects on the spectral features would suggest that the XANES for iodine is sensitive to the presence and the coordination structure of hydrogen atoms in contact with the iodine atom and that the XANES has the potential of detecting hydrogen atoms. It is reported here that in order to theoretically reproduce the XANES spectra both at the K- and L-edges of the iodide anion in aqueous solution it is essential to include the hydrogen atoms at proper positions. The XANES spectra are simulated based on the full multiple-scattering theory using FEFF code (version 8.10).[23] The sensitivity of the calculation to the presence of hydrogen atoms should be used to obtain an insight on the arrangement and orientation of water molecules around the halide anions. The present results will provide a convenient reference for further study on the XANES method.

Experimental

X-ray absorption spectra at I K- and L-edges were obtained for iodide anions in aqueous solution at room temperature (25 ± 3

°C). The measurements have been performed at BL01B1 of SPring-8. The storage ring was operated at 8 GeV with a current of 100 mA. The monochromator crystals used were Si (311) and Si (111) for I K- and L-edges, respectively. Higher harmonics have been removed by a double-mirror system coated with rhodium. The iodide solutions were prepared using tetra-*n*-butylammonium and potassium salts at concentrations from 0.01 to 1 mol dm^{-3}. Neither salt nor concentration effects were detected, thus the ion-pair formation can be neglected in the present study, i.e. either the degree of the ion-pair formation is small or the immediate surroundings of the iodide anion are not significantly changed by the ion-pair formation. The solutions were put into cells with polyethylene or poly-tetrafluoroethylene film windows, and the typical cell lengths for 1 mol dm^{-3} concentration were 2 mm and 0.2 mm for the K- and L-edge measurements, respectively. Background subtraction from the experimental spectra and other procedures have been reported in detail previously.[21]

The theoretical XANES spectra were obtained by using the self-consistent muffin tin potential and the full multiple-scattering procedure in the FEFF8.10 code,[23] i.e. the specified cards used were as follows. EDGE_K_0_0, CONTROL_1_1_1_1_1_1, POTENTIALS_0_53_iodine, 1_8_oxygen, 2_1_hydrogen, XANES, SCF_3.5, FMS_4.5, and the cards for ATOMS section.

Results and Discussion

The experimental XANES spectra are shown in Figs. 1, 2, and 3 for the K-, L_3-, and L_1-edges, respectively, at the top of each figure. The K-edge spectrum is characterized by a step-like feature at the edge. This is a feature not observed in the spectrum of the hydrated bromide anion at the Br K-edge[22] which is similar to the I L_1-edge spectrum given in Fig. 3. The spectra of the L_3- and L_1-edges given in this report are identical to those in Ref. 24.

The first FEFF calculation is performed for an octahedral complex consisting of one iodine and six oxygen atoms, as shown in Fig. 4(a). Its I–O distances are set at 3.50 Å which is the result from the EXAFS analysis reported in Ref. 21. The FEFF calculations predict XANES spectra of (a)s in Figs. 1, 2, and 3 for K-, L_3-, and L_1-edges, respectively. The predicted spectra from the model having no hydrogen atoms are not in accord with the experimental ones with regard to either peak positions or peak intensities. The calculated K- and L_1-edge spectra look quite different from the experimental ones, and the calculated L_3-edge spectrum does not exhibit a pre-edge shoulder peak (peak P in Fig. 2). Thus the FEFF calculation obviously fails to reproduce the XANES spectra if no hydrogen atoms are included.

Once the hydrogen atoms are included in the model, the theoretical spectra are improved dramatically. The K-edge spectrum (b) in Fig. 1, which is obtained by using the model (b) in Fig. 4, reproduces four peaks denoted by A, B, C, and D. Moreover, the L_3- and L_1-edge spectra are improved by including the hydrogen atoms as well. The theoretical spectra for model (b) at three edges exhibit almost all the features appearing in the experimental spectra. In the model, the iodine, hydrogen, and oxygen atoms align linearly. The water molecules have the geometry of 0.9575 Å as the O–H distance, 104.30° as the H–O–H angle, and the O–I distance as 3.50 Å. These three parameters are kept the same throughout this work.

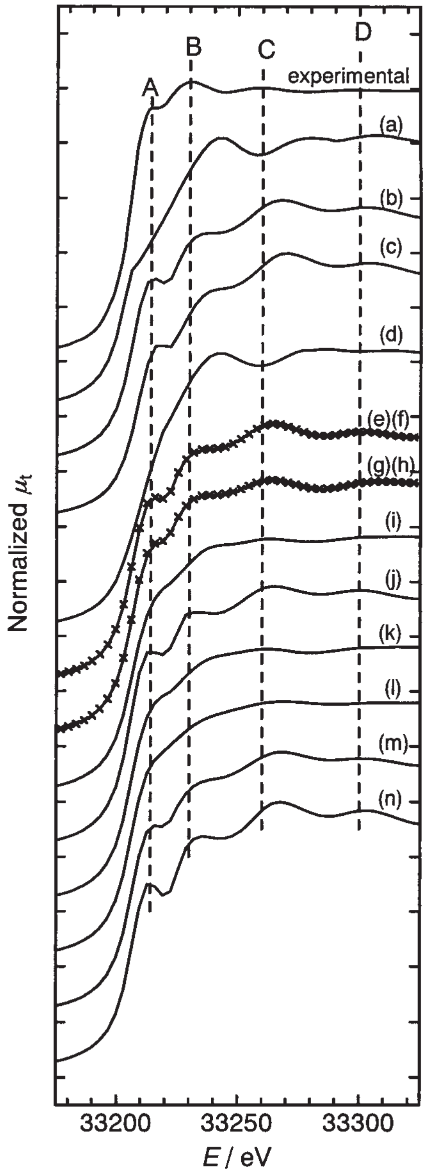

Fig. 1. I K-edge experimental XANES spectrum and the predicted ones by FEFF8 method. The spectra from (a) to (n) correspond to the theoretical results for hydrated iodide clusters shown in Fig. 4. The spectra (e) and (g) are indicated by lines and those for (f) and (h) are indicated by mark ×.

In such linear arrangements the multiple-scattering effect is expected to contribute significantly, especially for an O–H–I–H–O linear structure. In order to check this point, several calculations have been performed using slightly bent models with regard to O–I–O angles. However, the results are not different from those of the linear structure. It seems that the long distance of O–I–O (O to O distance of 7 Å) attenuates the multiple-scattering probability. This is also confirmed by the results for a tetrahedral model with nonlinear O–I–O, (m) in Fig. 4, for which the FEFF calculation predicts fairly good spectra. An eight-hydration structure (n) in Fig. 4 is again a good model, predicting similar quality spectra, though exhibiting too much amplitudes in the fine structures. Even the model (l),

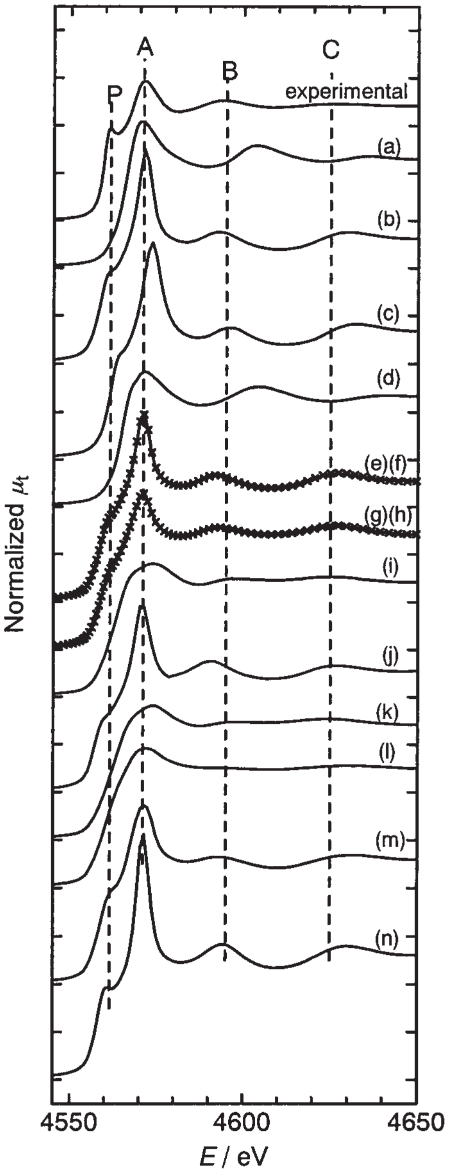

Fig. 2. I L_3-edge experimental XANES spectrum and the predicted ones by FEFF8 method. The spectra from (a) to (n) correspond to the theoretical results for hydrated iodide clusters shown in Fig. 4. The spectra (e) and (g) are indicated by lines and those for (f) and (h) are indicated by mark ×.

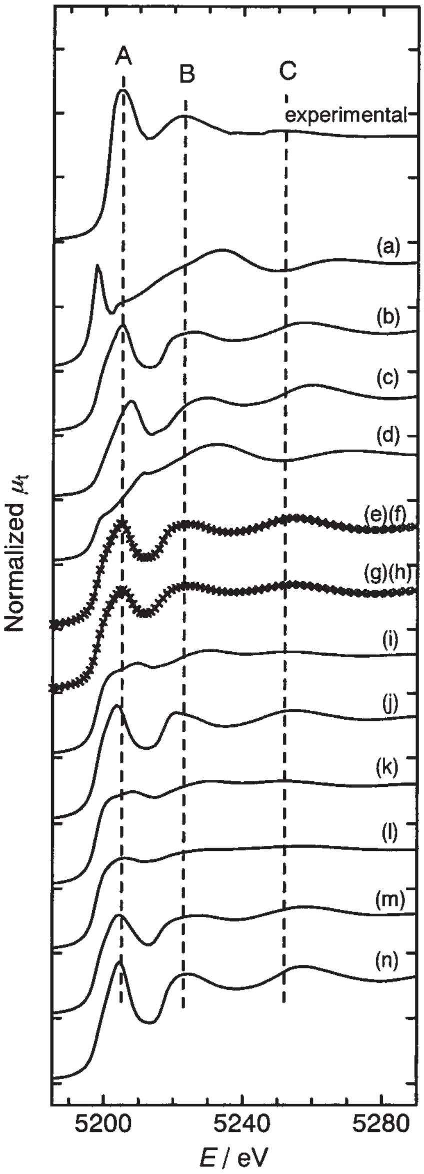

Fig. 3. I L_1-edge experimental XANES spectrum and the predicted ones by FEFF8 method. The spectra from (a) to (n) correspond to the theoretical results for hydrated iodide clusters shown in Fig. 4. The spectra (e) and (g) are indicated by lines and those for (f) and (h) are indicated by mark ×.

having only a single water molecule, presents quite excellent spectra if they are compared with spectra (a)s in Figs. 1, 2, and 3. In all the models (l), (m), and (n), the I–H–O bonds are linear. Consequently, in order to reproduce the XANES spectra for the hydrated iodide anion, one need focus only on the relative configuration between I, H, and O atoms. For this reason further FEFF calculations are performed using only the octahedral model with hydrogen atoms at various positions.

The water molecules in model (b) can be rotated on the linear I–H–O axis changing the relative distance between the hydrogen and oxygen atoms, each belonging to different water molecules. This might affect some contribution from the multiple-scattering path along these atoms. The calculations for these models, however, result in undistinguishable spectra from those for the model (b), indicating that the contributions from hydrogen atoms at distant positions are due only to the single scattering effect. A similar discussion has been reported concerning Ni hydrides.[6]

Although the XANES structure is not sensitive to the positions of hydrogen atoms if they are distant, its sensitivity to the presence of a hydrogen atom itself is striking. When some of the hydrogen atoms are removed from the model (b), the theoretical XANES spectra lose a lot of their resemblance to the experimental ones. The model (c), having six hydrogen atoms in between I–O and no outer hydrogen atoms, leads to good

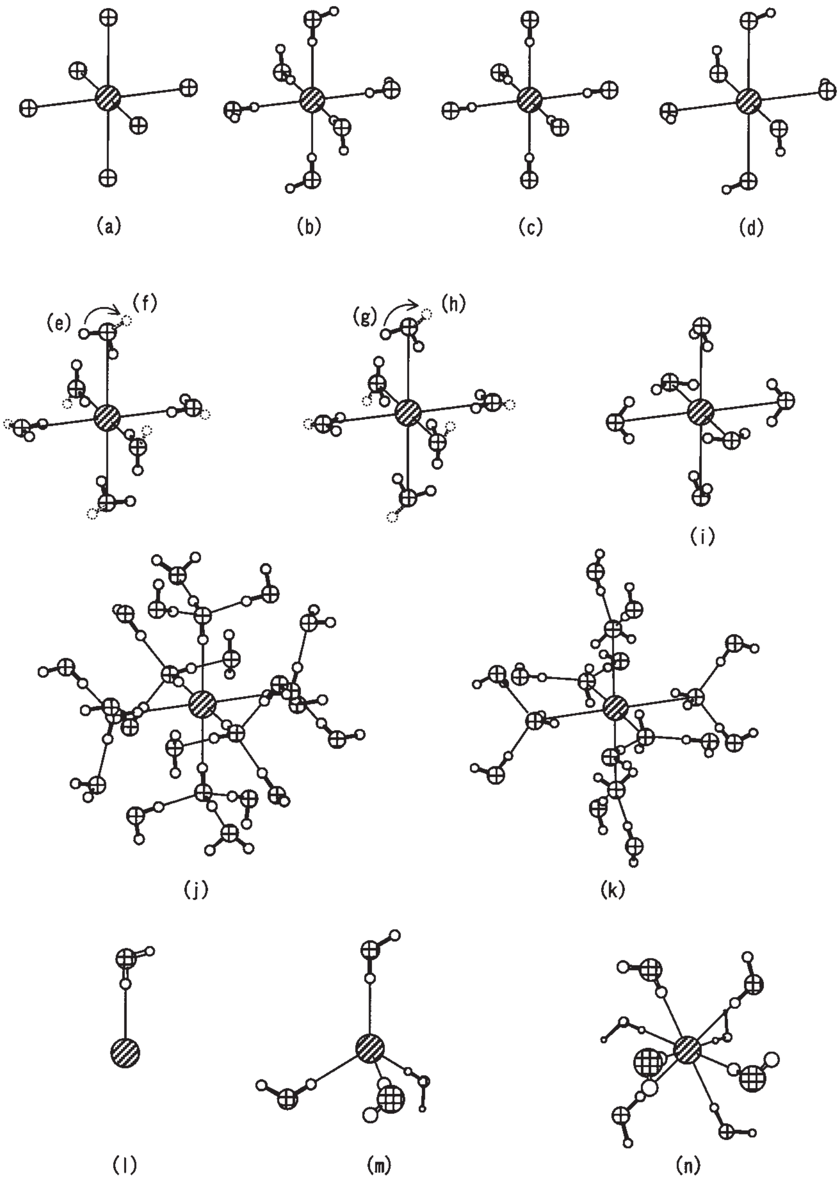

Fig. 4. Geometrical configuration of the hydrated iodide anion clusters used for the FEFF8 calculations. The central largest circle represents the iodide anion, while the other smaller circles stand for the oxygen and hydrogen atoms. The models (f) and (h) indicate different configurations concerning the positions of the hydrogen atoms from those of (e) and (g), respectively. For details see the text.

theoretical spectra, however, a couple of the first peaks move to incorrect positions in energy, while the peaks in the EXAFS regions are predicted correctly. Consequently, the presence of hydrogen atoms next to iodine is very important in predicting the XANES and can lead to the XANES fairly well and the EXAFS excellently, but is not enough to predict the structures at extreme edges. The addition of only outside hydrogen atoms to model (a) does not improve the spectra, cf. spectra (d)s in Figs. 1, 2, and 3.

Further calculations have been performed using different configurations regarding the hydrogen atoms. In model (e) the water molecules are so tilted that the angle I–O–H becomes 13°, keeping the geometry of water molecules and the I–O distances the same as those in model (b). The theoretical spectra for model (e) are shown in Figs. 1, 2 and 3 by solid lines. The improvements by the tilting operation are not significant, but in fact they are better than those for model (b) in some aspects. The third peak C in Fig. 1 comes closer to the experimental position, and the fourth peak located around 4625 eV in Fig. 2 and the third peak around 5250 eV in Fig. 3 appear closer positions, too. For the model (e) the hydrogen atoms located outside can be rotated keeping the angle I–O–H same. When the hydrogen atoms come to the most remote positions, the theoretical spectra are those denoted by (f) and drawn with × marks in the figures. There are no differences found between spectra (e) and (f). This indicates that the scattering by the hydrogen atoms at distant positions contributes weakly, even in the XANES region.

The tilting angle is increased to 26° for the model (g), which gives slightly improved theoretical spectra concerning the peak positions of C in Fig. 1 and B in Fig. 2. The rotation of remote hydrogen atoms again does not affect the spectra, cf. spectra (g) and (h) with × marks. The model (i) is the extreme case of water molecule rotation in which the two hydrogen atoms face toward iodine at equal distance, i.e. the angle of I–O–H is 52.15°. One can discard this model because of its poor features appearing in all of its theoretical spectra if compared with the experimental ones. In conclusion, the present XANES analysis predicts the model (e) or (g), indistinguishable from (f) and (h), respectively, as the hydration structure for the iodide anion in water.

Additional calculations have been performed to investigate the effect of a second hydration shell on the XANES spectra. In model (j) each water molecule in the first solvation shell of model (b) is coordinated by three water molecules through hydrogen bonding (O–O distance: 2.75 Å). The results are quite comparable to those for the original model (b). Model (k) is another example which has the second hydration shell, i.e. two water molecules attached to each first hydration molecule of model (i). In this case, again, the second hydration shell does not affect the theoretical spectra. The XANES spectra are satisfactorily described by taking into account the first hydration shell only.

The L-edge measurement constitutes one of the methods to investigate the electronic state of the hydrated complex. Its advantage is that the lifetime broadening effects for L-edges are less pronounced than that for the K-edge leading to narrower and larger amplitude structures in the XANES spectra. In Fig. 1 the ratio of the amplitude of the oscillating structure to the edge jump for the K-edge is very small, reflecting the lifetime broadening effect for I K-edge at 33 keV compared to those in Fig. 2 and 3 for L-edges. The L_3-edge spectrum is especially interesting not only because of the sharp and detailed structures in it, but the sensitive appearance/disappearance of the peak P depending on the model structure. The peak does not appear if the hydrogen atoms are removed from the neighbor shell of the iodine atom, as indicated in Fig. 2(a) and (d). An addition of only one hydrogen atom is enough to clearly produce the peak, as indicated in Fig. 2(l). If the hydrogen atoms are kept away from the iodine atom, as in the case of model (i), the peak almost disappears although the number of hydrogen atoms is twelve. The peak P corresponds to a $2p$-to-s symmetry transition and has a different symmetrical character from that of peak A in the K-edge spectrum of Fig. 1. Such fine structure does not appear in the L_1-edge spectrum. Therefore, one would not extract more information from the spectrum of the L_1-edge than that of the L_3-edge.

Conclusion

The hydrogen atom is, in most cases, not detectable by the XAFS method. This is generally true for the EXAFS region where the low scattering power of the hydrogen atom makes its contribution to the amplitude of EXAFS oscillation very small. For the XANES region, however, its contribution is not negligible, but definitely should be taken into account. The present study treats the iodine atom, a very heavy atom, surrounded by hydrogen atoms, the lightest atoms. Against the naïve prediction of weak or undetectable effects of the hydrogen atoms on the core shell transition in such a heavy atom system, the FEFF theory predicts relatively large effects from hydrogen on XANES spectra.

It is shown here that the inclusion of hydrogen atoms to the model for the FEFF calculation not only improves the theoretical results of the K-edge spectrum in shape, but also produces a pre-edge peak in the L_3-edge spectrum. The FEFF calculations are performed placing the hydrogen atoms at different positions. By comparing the calculated spectra with the experimental ones at both K- and L-edges by paying attention not only to the very first or second peaks, but also the third peaks, it can be concluded that the hydrogen atoms lie almost on the iodine–oxygen axis.

It seems that the results presented here provide a new insight into the study of these hydrated anions by means of XANES spectroscopy combined with the multiple-scattering approach, leading to an analysis of the problem through the inclusion of the hydrogen bond, which by X-ray spectroscopy has been considered not feasible or at least to be extremely difficult.

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