

Solvation Sphere of I^- and Br^- in Water

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Stanford, CA

August 20, 2010

Prepared in partial fulfillment of the requirements of the Office of Science, Department of Energy's Science Undergraduate Laboratory Internship under the direction of Ritimukta Sarangi at the Structural Molecular Group, Stanford Synchrotron Radiation Lightsource.

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ABSTRACT

Solvation Sphere of I⁻ and Br⁻ in Water. MATTHEW D. ANTALÉK (, Binghamton, NY 13902) RITIMUKTA SARANGI (Structural Molecular Group, Stanford Synchrotron Radiation Lightsource, Stanford, CA 94025)

The solvation sphere of halides in water has been investigated using a combination of extended x-ray absorption fine structure (EXAFS) and x-ray absorption near-edge structure (XANES) analysis techniques. The results have indicated that I⁻ and Br⁻ both have an asymmetric, 8 water molecule primary solvation spheres. These spheres are identical, with the Br⁻ sphere about .3 Å smaller than the I⁻ sphere. This study utilized near-edge analysis to supplement EXAFS analysis which suffers from signal dampening/broadening due to thermal noise.

1.0 INTRODUCTION

Halide ions are of fundamental importance to many chemical and biological systems. They play essential roles in protein activation/deactivation, determination of acid-base equilibria, ion transport across cell membranes, and electrolytic and osmological balance found in all organisms [1]. For these reasons it is central to biology and biochemistry to understand the solvation of halide ions in water. In particular knowledge of the the number and coordination geometry of the water molecules around the halide ions will help shed light on their roles in biological systems. The solvation sphere of I^- and Br^- have been extensively studied using both computational and experimental methods. However, studies of these systems, particularly in the solution phase is no trivial undertaking. Thermal motion, as well as dynamic solvation shells make these studies particularly challenging.

To this point, a variety of methods have been used to probe the solvation shell structures of I^- and Br^- solvated in water. These include studies in extended x-ray absorption fine structure (EXAFS), quantum mechanical (QM) simulations, infrared spectroscopy, molecular dynamics (MD) simulations, and density functional theory (DFT) calculations [2],[1],[3]. However, experimental techniques suffer from large errors in determining the coordination number and geometric structure of solvation shells. Studies in x-ray and neutron diffraction, although powerful for probing structures with uniform surfaces and orientations, lack the ability to study dynamic systems such as ions in bulk solution phase. Computational simulations rely on theoretical parameterized inputs and are approximate at producing statistically reliable information on the structural properties of these solvation spheres [3]. As a result, the latest reported aqueous coordination numbers of I^- and Br^- are 7.3 to 9.7 and 5.8 to 6.2, water molecules, respectively [2],[3]. These results agree with the established chemical theory that larger ions have larger solvation shells. This study attempts to analyze these solvation spheres with more rigor and precision than previous studies.

In this study, a combination of data analysis techniques was used to study the solvation

shells of I^- and Br^- in water. Using bromide K-edge and iodide L1-edge EXAFS and near-edge data, structural analysis was performed. EXAFS analysis is a standard structural determination technique, which can be used to probe the local geometric structure near a central absorbing element [4],[5],[6],[7]. EXAFS analysis requires less computational time than near-edge analysis, so this data was fit first to generate models for the near edge analysis. EXAFS fits were used to test structural models (4, 6, 8, and 10 coordinate geometries), which were subsequently used to fit the near-edge data. MXAN has the advantage that it is mostly independent of thermal noise/Debye-Waller factors, which lead to EXAFS signal dampening and broadening. Near-edge analysis was performed using MXAN, a data analysis software that employs full multiple scattering theory, to reproduce the x-ray absorption near edge spectrum (XANES) and the EXAFS region out to 150 eV, using input structural and non-structural parameters[8],[9]. The near-edge analysis used by MXAN is very sensitive to local geometries and can furnish accurate three-dimensional structural information[8],[9],[6]. It is best to use a combination of these data analysis techniques because these methods are complementary and optimize structural model-building.

2.0 MATERIALS AND METHODS

2.1 Sample preparation

A 500 mM solution of KI in de-ionized (DI) water was prepared by mixing solid KI in DI water until completely dissolved. A 500 mM solution of KBr in DI water was prepared by mixing solid KBr in DI water until completely dissolved.

2.2 Data collection

Iodide L1-edge XAS data were collected on the 20-pole 2T wiggler unfocused beamline 4-3 under the standard ring operating condition of 3 GeV and 200 mA ring current. A fully tuned Si(111) double crystal monochromator was used for energy selection. Other upstream optics included a Ni-coated vertically collimating and harmonic rejection mirror.

Room temperature measurements were performed on the sample in fluorescence mode using a passivated implanted planar silicon (PIPS) detector. The samples were housed in a teflon cell with 5 μm polypropylene windows. The cell was sealed with 37 μm Kapton tape. Energy calibration was achieved by setting the first inflection point at 5280 eV [10]. Bromide K-edge data was previously collected on BL 9-3 by Dr. Ritimukta Sarangi.

2.3 Data analysis

Before analysis the data was processed to remove background radiation. To accomplish this, each spectrum was viewed using MVIEW, a program in the suite EXAFSPAK, to check the quality of data files. The spectra were then added together and averaged. A second degree polynomial was then fit to the pre-edge region of the averaged data using PySpline. This polynomial was then subtracted from the entire spectrum as background. This process was used to normalize both the I- and Br- data.

Theoretical EXAFS phase and amplitude parameters were calculated using *FEFF* (version 7.0), and fit to the experimental data using EXAFSPAK. Hydrogen atoms were excluded during the fitting process because of their minor contribution to the overall EXAFS signal. Structural parameters that were varied during the fitting process included bond distance (R) and bond variance (σ^2), which is related to the Debye-Waller factor, resulting from thermal motion. The nonstructural parameter E_0 , (the energy where $k=0$), was also varied between fits but was linked for every component in a given fit. Coordination numbers were varied but remained constant in a given fit. The reduced error (χ^2) and visual analysis were used to determine the goodness of the fits. The I⁻ spectrum was fit over $k=2-10.1 \text{ \AA}^{-1}$. The Br⁻ spectrum was fit over $k=2-12.5 \text{ \AA}^{-1}$.

Experimental XAS spectra were theoretically modeled using MXAN, which performs full multiple scattering analysis to obtain structural information [8],[9]. Starting structures were taken from the best three-dimensional models that included the coordination numbers 4, 6, 8, and 10 with radial metrics obtained from EXAFS analysis. The data were fit over a $E-E - 0$ range of -6.5 eV to 120 eV for I⁻ and -6.0 eV to 120 eV for Br⁻. After each

step of structural parameter refinement a step of non-structural parameter refinement was performed. Refinements were closely monitored for large fluctuations in both the structural parameters and non-structural parameters. No such fluctuations were observed. The least squares error and visual analysis were used to determine the accuracy of the fits.

3.0 RESULTS

3.1 Iodide

In I⁻ EXAFS analysis, the best fit was achieved with a coordination number of 8 water molecules, as the reduced χ^2 error was 0.000672 (see Table 1, Figure 3). However, the fit with 10 water molecules coordinated to the I⁻ anion also yielded a very low error with reduced χ^2 error = 0.000884 (see Table 1, Figure 4). Both fits used two iodide-oxygen paths in which one path was about 0.3 Å longer than the other (see Table 1). Both fits correlated well with coordination numbers and distances suggested in previous studies [3]. Due to the similarities between the two fits it was impossible to distinguish between the two models. Fits with coordination numbers of 6 and 4 yielded much higher error (see Table 1).

In XANES analysis, the best fit was achieved with a coordination number of 8 water molecules with the \sum square residuals = 0.57718 (see Figure 7). In this particular model, the four water molecules in a plane with the central anion were coordinated over a range of distances (see Figure 9), from 3.30 to 3.70 Å from the central I⁻ to the O of the water molecules. The two remaining pairs of water molecules had distances of 3.54 Å from the I⁻ ion to the O of the water molecule. These distances agree with findings in previous studies as well as distances observed in EXAFS analysis [3]. The fit with a coordination number of 10 yielded a fit that was about three times poorer than a coordination number of 8 with \sum square residuals = 1.8835 (see Figure 7). Coordination numbers of 4 and 6 yielded poor fits to the data (see Figure 7).

3.2 Bromide

In bromide EXAFS analysis the best fit was achieved with coordination number of 10 water molecules with a reduced χ^2 error of 0.0167 (see Table 2, Figure 5). The fit with coordination number of 8 was slightly poorer with a reduced χ^2 error of 0.0189 (see Table 2, Figure 6). Due to the similarities between these two fits, and since the Debye-Waller factors make coordination number determination difficult, both 8 and 10 coordinated models must be regarded as feasible structural models for the Br^- solvation sphere. Fits with coordination numbers of 4 and 6 water molecules did not fit the data well (see Table 2).

The MXAN analysis resulted in a much clearer pattern. The fit with 8 water molecules coordinated to the central Br^- anion yielded the best fit and the \sum square residuals was 2.9440. Structurally, this model is similar to the I^- model with 8 water molecules, however the distances between the central anion and the O of the water molecules is slightly shorter (see Figure 10). The four water molecules in a plane with the central Br^- anion have a distance of 3.25-3.44 Å from the Br^- ion to the O of the water molecules. The two remaining pairs of water molecules are placed such that the Br-O distances are 3.30 Å in three of the water molecules and 3.63 Å in the remaining water molecule. These distances agree with previous studies, as well as distances observed in EXAFS analysis [3]. The fit with 10 water molecules coordinated to a central Br^- anion produced a fit about three times worse than the fit with 8 water molecules (see Figure 8).

4.0 DISCUSSION

The solvation sphere of I^- and Br^- has been determined using a combination of EXAFS and MXAN data analysis techniques. Both anions have an asymmetric eight coordinate solvation sphere (see Figures 9,10). In the I^- model, 4 of the water molecules lie in a plane around the central anion, with the oxygen atoms between 3.30 Å and 3.72 Å from the iodide anion. The remaining four molecules are in pairs above and below the central plane with the oxygen atoms approximately 3.54 Å from the iodide anion (see Figure 9). This model is consistent

with both the EXAFS and MXAN analysis and correlates strongly to distances obtained in previous studies[3].

The Br⁻ solvation shell is nearly structurally identical to the I⁻ solvation shell (see Figure 10). Four water molecules lie in a plane about the central Br⁻ anion with the oxygen atoms between 3.26 Å and 3.44 Å from the central Br⁻ anion. The remaining four water molecules are in pairs oriented in orthogonal planes to each other, with the oxygen atoms between 3.27 Å and 3.63 Å from the central Br⁻ anion(see Figure 10). This is a strong model because the Br-O distances match what previous literature suggested, as well as correlating strongly to the results we saw in both EXAFS and XANES analysis [2], [3]. Although some aspects of this study correlate to reported values in previous literature, the structural results described in this study are different from earlier EXAFS publications [3] [2]. This study especially contrasts previous reported values with respect to coordinate geometry of the water molecules.

The use of MXAN which includes the XANES region of the absorption spectrum, was a very powerful tool in this study. MXAN allows the optimization of a wider variety of structural and non-structural parameters. MXAN includes edge region, where effects from Debye-Waller broadening and dampening are minor, which uniquely allows inclusion of geometric structure analysis. While EXAFS analysis using FEFF is a very powerful technique for local structure determination, the error associated with EXAFS especially in room temperature data studies does not allow the precise determination geometric structures because EXAFS is only capable of giving radial information. The EXAFS equation does not include an angular dependence term. A combination of these data analysis techniques is a more powerful way to analyze XAS data and determine geometric structures. EXAFS analysis can produce starting models with the correct coordination number and bond distances relatively quickly. MXAN can then be used to optimize the geometry as well as non-structural parameters not included in EXAFS analysis.

Near-edge XAS investigation has determined that the solvation spheres of both I⁻ and

Br^- are nearly identical in geometry and number. This is counterintuitive since a large anion might be expected to have a larger solvation sphere by classical chemistry. The data show that although the coordination number remains the same, the bond distances for Br^- are shorter by 0.24 Å, indicating the decrease in ionic radii in Br^- . These data indicate that the classical theory of increasing the number of solvating water molecules with increasing ionic radius must be revisited. Other reasons, such as charge delocalization, charge density and steric hindrance effects of nearby water molecules may play major roles in determining the solvation sphere. We are currently exploring the solvation sphere of Cl^- to get a more complete understanding of solvation in halides.

This study of the first solvation shell of I^- and Br^- is of fundamental importance to the bio-chemical community. Knowledge of the solvation sphere gives us a better understanding of how these anions interface with other molecules in aqueous systems. This is of particular importance in biological systems, since how these anions interact with proteins as well as how they determine equilibria may be related to the solvation sphere that surrounds these anions in aqueous systems. In addition, the impact of halide solvation on the structure of water can now proceed from a geometrically explicit solvation model. Further studies could look at how this solvation structure changes in protein solution, and if the presence of a protein matrix decreases the number of solvated water molecules.

5.0 CONCLUSION

This paper has reported on the solvation first sphere of I^- and Br^- in water. Using EXAFS and XANES analysis, strong models which describe the geometric configuration of water molecules coordinated to a central anion have been developed. The combination of these techniques has provided us with a more substantiated argument than relying solely on one or the other. An important finding of this study is that the size of the anion plays a smaller role than previously assumed in determining the number of coordinating water molecules.

Further experimental and theoretical investigation is required to understand why the size of the anion plays a minor role in determining the number of water molecules bound.

6.0 ACKNOWLEDGMENTS

I would like to thank Dr. Ritimukta Sarangi for mentoring me on this project and contributing the KBr K-edge data used. I would also like to thank Dr. Maurizio Benfatto for the resources and expertise he has provided in using MXAN. I would like to thank Dr. Steven Rock for the direction and organization he has provided, as well as the other staff who have helped run the SULI program at SLAC. I would also like to thank Dr. Patrick Frank for his guidance and input on this manuscript. This research was funded by the U.S. Department of Energy, the Stanford Linear Accelerator Center and the Stanford Synchrotron Radiation Lightsource. The calculations were carried out at the computing center in Frascati, Italy, at the Istituto Nazionale di Fisica Nucleare.

REFERENCES

- [1] K.J.Tielrooij *et al.*, “Cooperativity in ion hydration,” *Science*, vol. 328, pp. 1006–1009, 2010.
- [2] S. Raugei and M. L. Klein, “An ab initio study of water molecules in the bromide ion solvation shell,” *Journal of Chemical Physics*, vol. 116, no. 1, pp. 196–202, 2002.
- [3] V.T.Pham *et al.*, “The solvent shell structure of aqueous iodide: X-ray absorption spectroscopy and classical, hybrid qm/mm and full quantum molecular dynamics simulations,” *Journal of Chemical Physics*, vol. 371, pp. 24–29, 2010.
- [4] B. Teo, *EXAFS: Basic Principles and Data Analysis*. New York: Springer-Verlag, 1986.

- [5] J. M. de Leon *et al.*, “Ab initio curved-wave x-ray-absorption fine structure,” *Physical Review, B: Condensed Matter*, vol. 44, no. 9, pp. 4146–4156, 1991.
- [6] E. Stern, *In EXAFS, SEXAFS and XANES*, D. Koninberger, Ed. New York: John Wiley and Sons, 1988, vol. 1.
- [7] G. George, “Exafspak and edgefit,” Stanford Synchrotron Radiation Laboratory, Stanford Linear Accelerator Center, Stanford University, Stanford, CA, 2000.
- [8] M. Benfatto and S. D. Longa, “Geometrical fitting of experimental xanes spectra by a full multiple-scattering procedure,” *Journal of Synchrotron Radiation*, vol. 8, pp. 1087–1094, 2001.
- [9] M. Benfatto *et al.*, “Advances in the theoretical analysis of the xanes (x-ray absorption near edge structure) energy region for quantitative structural use,” *Physica Scripta*, vol. T115, p. 28, 2005.
- [10] F. E. Huggins *et al.*, “Modes of occurrence of trace elements in coal from xafs spectroscopy,” *International Journal of Coal Geology*, vol. 32, no. 1, pp. 31–53, 1996.

FIGURES

| Coordination# | R (Å) | σ^2 | E_0 (eV) | Reduced Error (χ^2) |
|----------------------|---------------------------|------------------------------|------------------------------|--|
| 4 | 3.51 | 0.02347 | -3.9119 | 0.0015 |
| 6 | 3.54 | 0.03378 | -2.9505 | 0.00208 |
| 8 | 3.52 | 0.02149 | -1.3404 | 0.000672 |
| | 3.83 | 0.04573 | | |
| 10 | 3.54 | 0.0248 | -1.1247 | 0.000884 |
| | 3.87 | 0.04474 | | |

Figure 1: Table 1 displays coordination number, bond distances, Debye-Waller factors, E_0 , and Reduced Error (χ^2) for EXAFS fits with iodide. Note that two paths were used for fits with 8 and 10 water molecules coordinated.

| Coordination# | R (Å) | σ^2 | E_0 (eV) | Reduced Error (χ^2) |
|----------------------|---------------------------|------------------------------|------------------------------|--|
| 4 | 3.27 | 0.01328 | -5.5179 | 0.0718 |
| 6 | 3.27 | 0.01209 | -5.6423 | 0.0407 |
| 8 | 3.27 | 0.02514 | -5.6574 | 0.0189 |
| 10 | 3.27 | 0.02113 | -5.7119 | 0.0167 |
| | 3.6 | 0.04452 | | |

Figure 2: Table 2 displays coordination number, bond distances, Debye-Waller factors, E_0 , and Reduced Error (χ^2) for EXAFS fits with bromide. Note that two paths were used for fit with 10 water molecules coordinated.

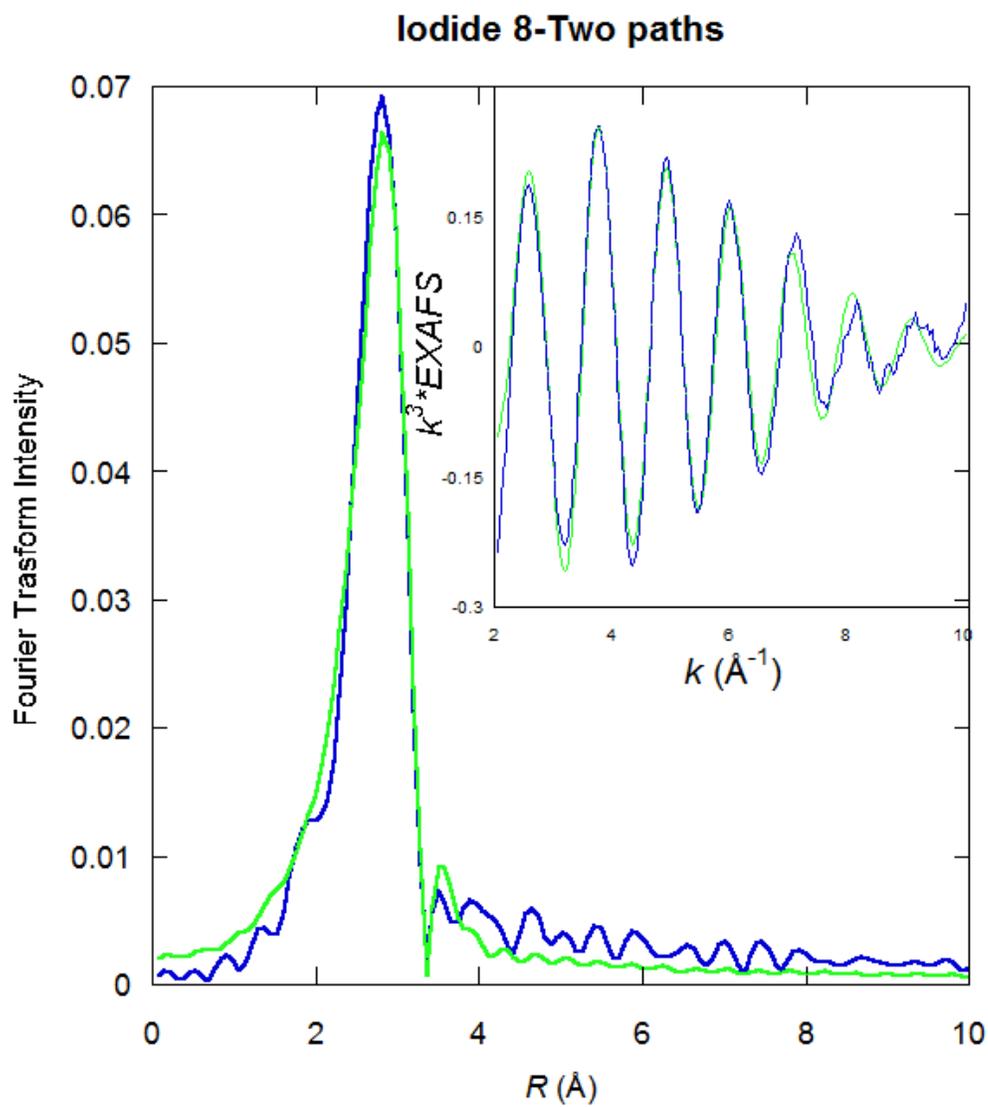


Figure 3: Fourier Transform and EXAFS data, Iodide coordination number 8. Blue lines indicate experimental data, green lines indicate theoretically reproduced spectra.

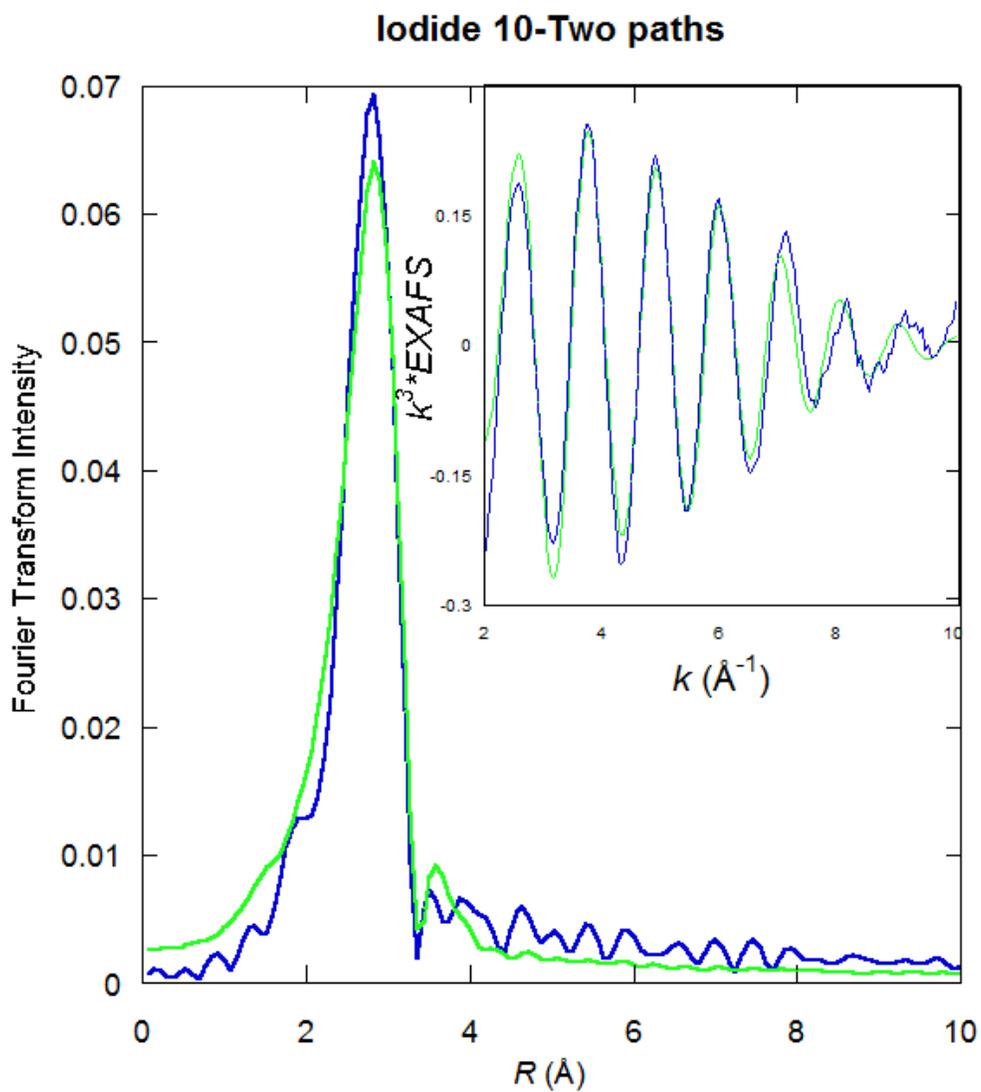


Figure 4: Fourier Tranform and EXAFS data, Iodide coordination number 10. Blue lines indicate experimental data, green lines indicate theoretically reproduced spectra.

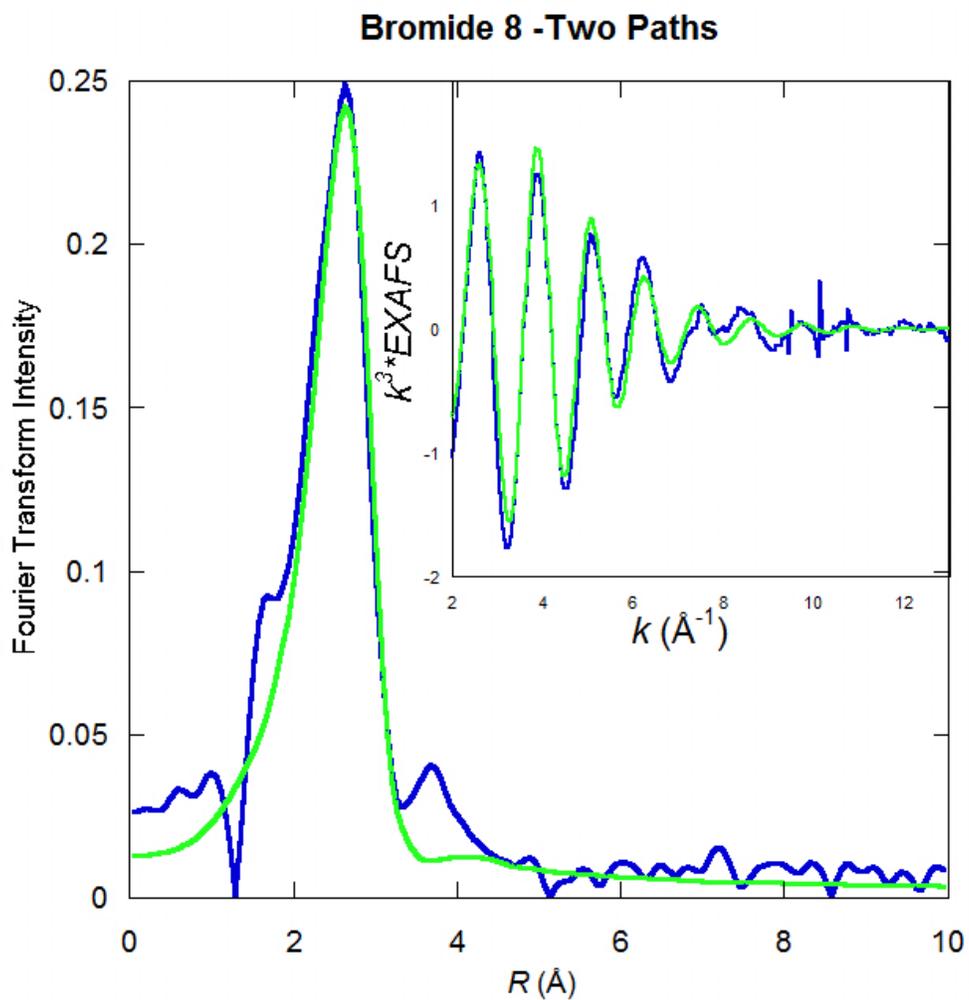


Figure 5: Fourier Tranform and EXAFS data, Bromide coordination number 8. Blue lines indicate experimental data, green lines indicate theoretically reproduced spectra.

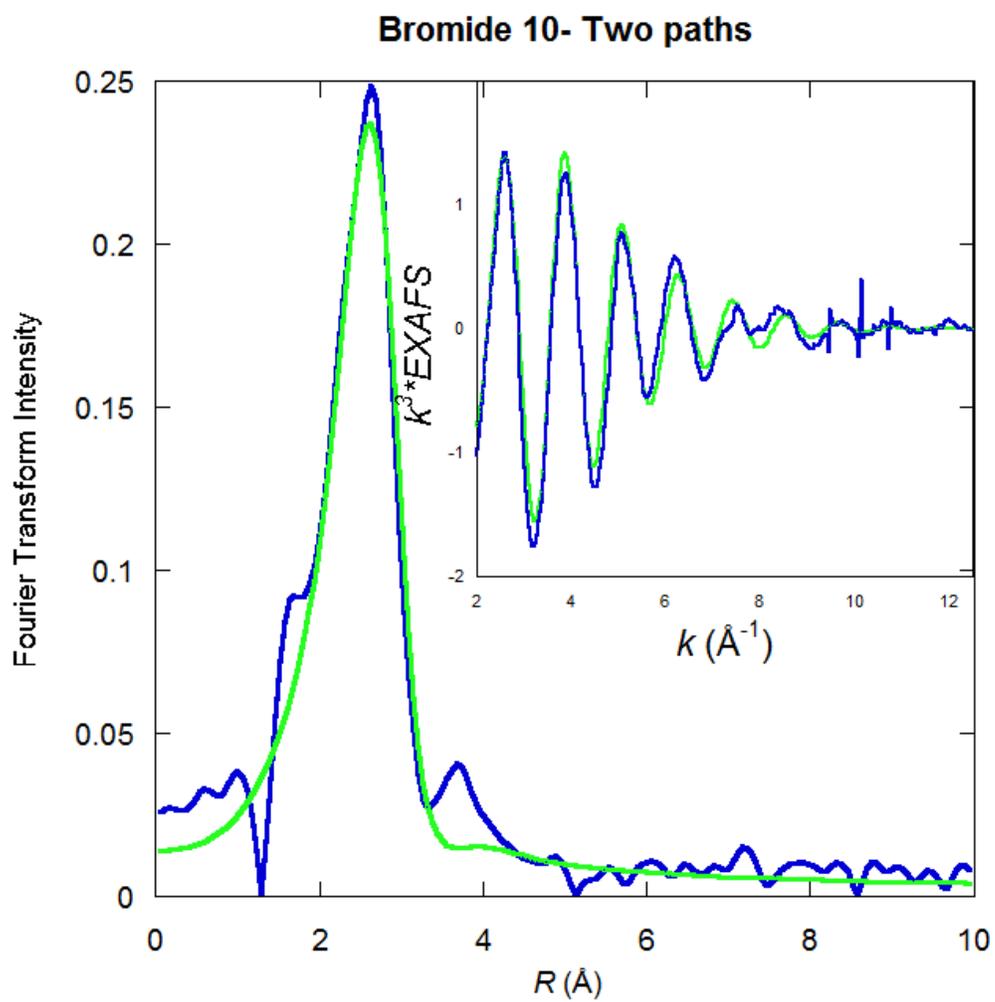


Figure 6: Fourier Tranform and EXAFS data, Bromide coordination number 10. Blue lines indicate experimental data, green lines indicate theoretically reproduced spectra.

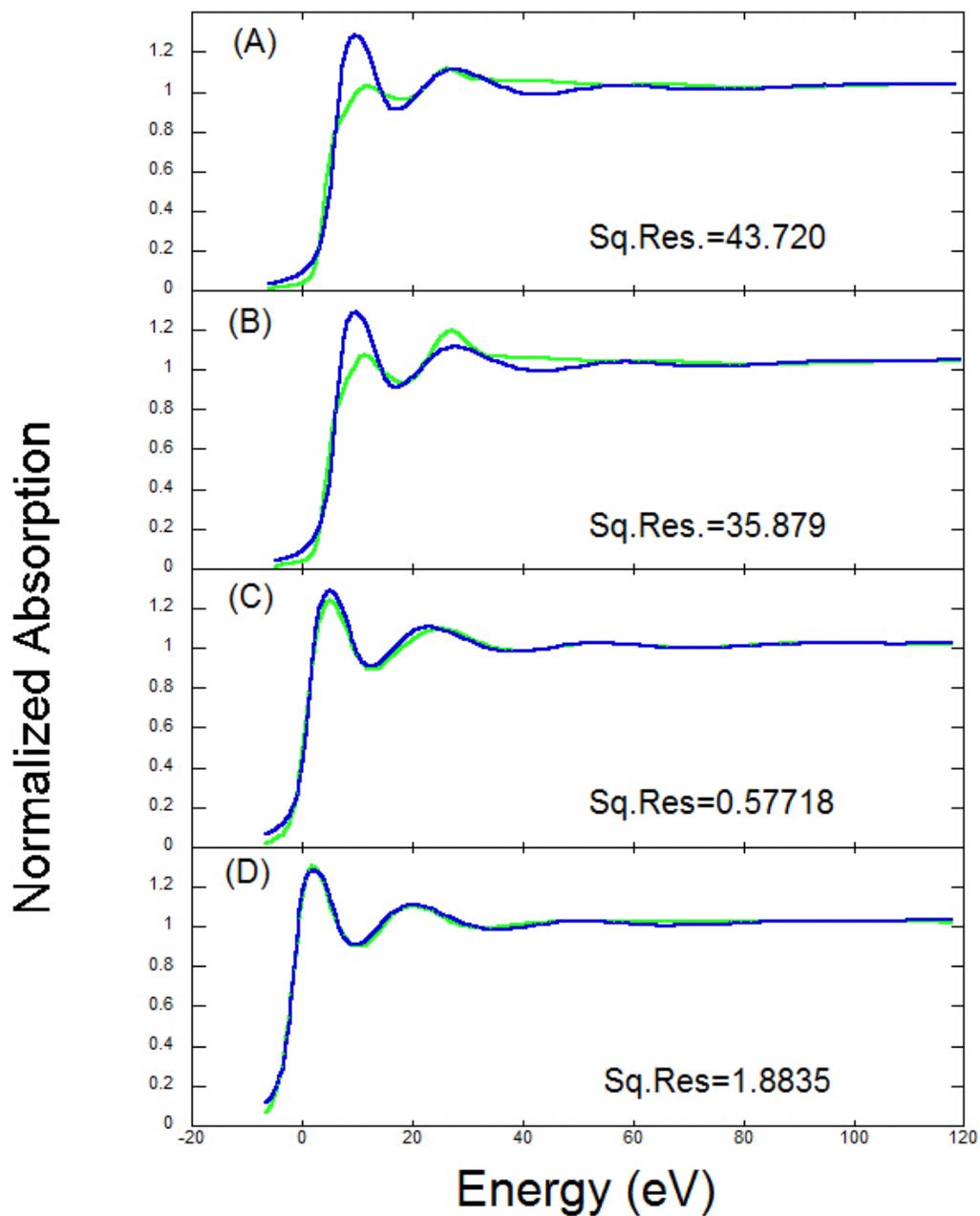


Figure 7: XANES data and MXAN fits for Iodide. Blue lines indicate experimental data, green lines indicate theoretically reproduced spectra. (A): coordination number= 4, (B) coordination number= 6, (C) coordination number= 8, (D) coordination number= 10.

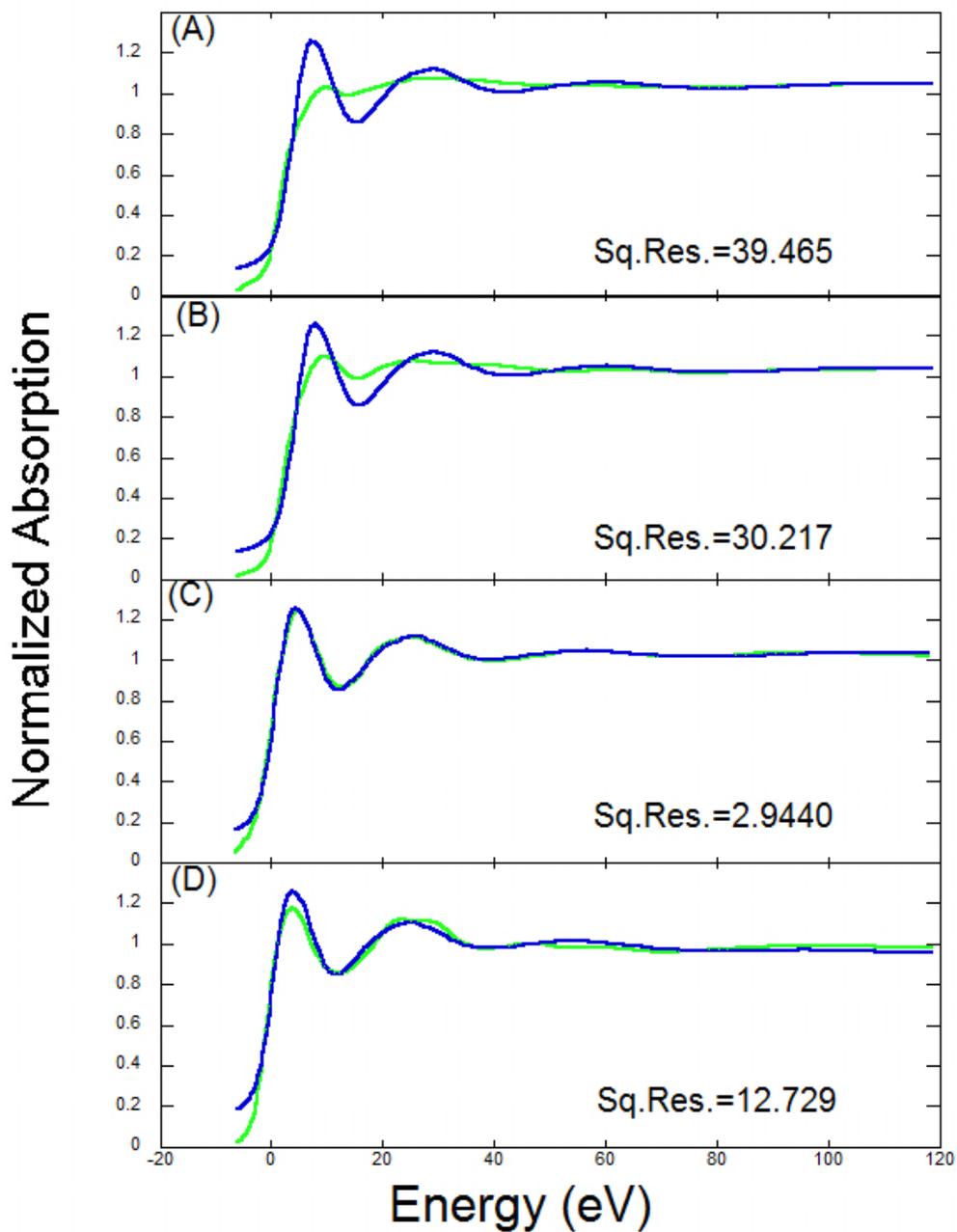


Figure 8: XANES data and MXAN fits for Bromide. Blue lines indicate experimental data, green lines indicate theoretically reproduced spectra. (A) coordination number= 4, (B) coordination number= 6, (C) coordination number= 8, (D) coordination number= 10

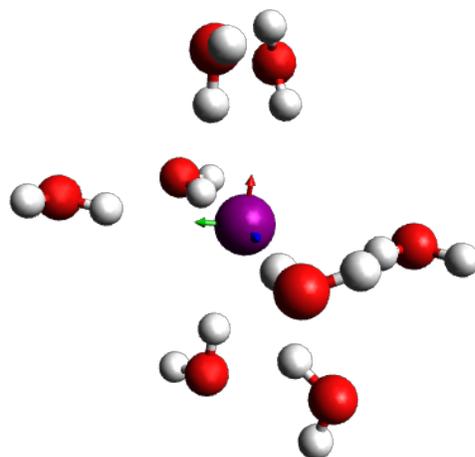


Figure 9: Model of Iodide coordination number= 8.

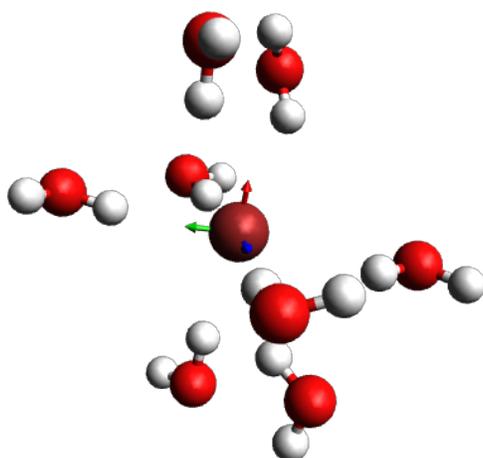


Figure 10: Model of Bromide coordination number= 8.