Comprehensive structural modelling of aqueous solutions using neutron diffraction and X-ray absorption spectroscopy

D.T. Bowron
Science and Technology Facilities Council, ISIS Facility, Rutherford Appleton Laboratory, Chilton, Didcot, Oxfordshire, OX11 0QX, UK
E-mail: daniel.bowron@stfc.ac.uk

Abstract. The ability to combine the complementary characteristics of experimental probes is often highly advantageous for advancing our understanding of the physical and chemical properties of structurally disordered systems such as aqueous solutions. Two techniques that have been very influential in this field are neutron diffraction with isotopic substitution and Extended X-ray Absorption Fine Structure (EXAFS) spectroscopy. By taking advantage of the recent significant developments in computational power and associated analytical methods, it is now possible to produce comprehensive three dimensional atomistic models of these systems that are consistent with both sets of experimental data. One such method is Empirical Potential Structure Refinement, and this study will illustrate its capabilities in an investigation of a 1:500 aqueous solution of rubidium bromide in water. Hydrogen-deuterium isotopic substitution is used to probe the details of the structural correlations between the solvent water molecules, and Rb and Br K-edge EXAFS is used to validate the structural aspects of the incorporation of the solute ions into the bulk solvent matrix. The resulting model allows an estimate to be made of the extent of ion pairing that occurs in the dilute solution.

1. Introduction

Investigating the structure of inherently disordered multi-component liquids and glasses is a major challenge because information about the interactions between specific atomic species is often lost in the highly averaged nature of the experimentally accessible correlation functions. For example, in a binary system containing atoms of type A and B, three pair correlation functions are required to fully characterise the interactions, AA, AB (= BA) and BB. If a single diffraction experiment is performed to probe the structure of the system, it can only provide access to a weighted sum of these correlations, and if the interactions occur over similar interatomic distance ranges, it is often not possible to reliably estimate their form. Naturally, this issue only becomes more difficult with increasing numbers of component species, n, and scales as n(n + 1)/2.

Fortunately, with the advent of modern neutron and X-ray experimental facilities, several experimental techniques now allow us address this challenge, though in most cases no single method is sufficient to entirely separate all the correlations of interest. Two of the most useful methods are neutron scattering with isotopic substitution and Extended X-ray Absorption Fine Structure (EXAFS) spectroscopy. The first of these techniques takes advantage of the fact that
for several elements in the periodic table, isotopes exist that possess different neutron scattering properties. By performing a series of measurements on isotopically distinct samples that are chemically identical, it is possible to extract information on specific atomic pair distribution functions [1, 2]. With regards to structural studies of ion hydration, the isotopic substitution method can in some cases provide direct information for a range of elements [2], however this can only be performed at relatively high solute concentrations. For dilute solutions, the most informative isotopic substitution measurements make use of the differing neutron scattering properties of hydrogen and deuterium to probe the structure of the solvent water itself [1]. In these systems, to study ion hydration, EXAFS spectroscopy is the structural probe of choice. Due to the intrinsic chemical specificity and short range sensitivity of this technique, this method directly measures a less complex structural correlation function, where only atomic correlations involving the photo excited constituent element contribute to the measured signal.

Taken together, these two techniques provide highly complementary structural information. Neutron scattering measures the bulk average structure of the solutions, whilst EXAFS spectroscopy provides detailed insight into the local environment of the photo-excited atomic sites. The outstanding challenge for the solution chemist or physicist is then the question of how best to combine the insight gained from these two experimental methods into a single coherent picture of the overall structure of the solution. Here we can now take advantage of the major developments in modern atomistic simulation methods. The underlying principle that will be presented in this study is based on the idea that from a simulated set of atomic coordinates, it is possible to calculate neutron (or X-ray) scattering patterns and EXAFS spectra. These functions can then be compared with measured experimental data and if a suitable feedback mechanism is applied, the model potentials that drive the simulation can be perturbed to bring the simulated and measured data into agreement. The final result is the production of a three dimensional atomistic model that provides an informed estimate of the actual structure of the real solutions, and that can be interrogated for any desired information.

To illustrate the potential of this hybrid analytical technique for the study of aqueous solutions, an investigation of a dilute solution of rubidium bromide in water has been undertaken. The concentration of the investigated solution corresponds to $1 \text{Rb}^+ : 1 \text{Br}^- : 500$ water molecules. Neutron scattering with H/D isotopic substitution is used to probe the structure of the solvent, whilst Rb and Br K-edge EXAFS spectroscopy is used to provide insight into the cation and anion hydration environments. Empirical Potential Structure Refinement [3, 4] is then used to combine the experimental information into the production of a comprehensive atomistic structural model.

2. Experiment

2.1. Neutron Scattering

To probe the bulk structure of the $\text{RbBr}$ solution, a series of three neutron scattering measurements have been performed on isotopically distinct but chemically identical samples prepared in $\text{H}_2\text{O}$, $\text{D}_2\text{O}$ and an isotopic null mixture of the two, in the proportion $(\text{H}_2\text{O})_{0.64}(\text{D}_2\text{O})_{0.36}$. All measurements were made at room temperature (298K) using the Near and InterMediate Range Order Diffractometer (NIMROD), on the second target station of the ISIS spallation neutron source, UK. During the measurements, the solutions were contained in null scattering Ti$_{0.68}$Zr$_{0.32}$ alloy cells of 1mm wall thickness and internal dimensions of 1mm thickness x 35mm width x 35mm height. The data were corrected for cell and instrument backgrounds, absorption and multiple scattering, and were normalized to absolute units using the scattering from a vanadium standard [5]. The contributions from the inelastic scattering from light hydrogen were subtracted using the methods outlined in Soper and Luzar [6].

Each experiment measures the isotopically weighted total structure factor, $F(Q)$, which is
defined as
\[
F(Q) = \sum_{\alpha \leq \beta} (2 - \delta_{\alpha\beta})c_\alpha c_\beta b_\alpha b_\beta [S_{\alpha\beta}(Q) - 1]
\] (1)

where \(c_\alpha\), \(c_\beta\) and \(b_\alpha\), \(b_\beta\) are the concentrations and neutron scattering lengths of each of the atom types in the solution. \(S_{\alpha\beta}(Q)\) is the partial structure factor for correlations between atoms of type \(\alpha\) and \(\beta\) and to avoid double counting the like-atom correlations \(\delta_{\alpha\beta}\) is the Kronecker \(\delta\) function. \(Q\) is the magnitude of the momentum transfer vector of the scattering process and is related to the incident neutron wavelength, \(\lambda\), and scattering angle, \(2\theta\), by
\[
Q = \frac{4\pi}{\lambda} \sin \theta
\] (2)
The total structure factor and partial structure factors are related to the total and partial pair distribution functions, \(g(r)\) and \(g_{\alpha\beta}(r)\), by Fourier transform, weighted by the atomic density of the system, \(\rho\),
\[
g_{\alpha\beta}(r) - 1 = \frac{1}{(2\pi)^3 \rho} \int_0^{\infty} 4\pi Q^2 [S_{\alpha\beta}(Q) - 1] \frac{\sin(Qr)}{Qr} dQ
\] (3)
The neutron scattering lengths of \(\text{Rb}\), \(\text{Br}\), \(\text{H}\), \(\text{D}\) and \(\text{O}\) are 7.08, 7.81, -3.74, 6.67 and 5.81fm respectively. Taking these values into consideration along with the known concentrations of the four atomic sites in the solution, Table 1 gives the relative contributions of the 10 partial structure factors to the measured total structure factors of each of the isotopic solutions.

| Correlation          | \(\text{H}_2\text{O}\) | \(\text{D}_2\text{O}\) | \(\text{H}_2\text{O}_{0.64}\text{D}_2\text{O}_{0.36}\) |
|----------------------|-------------------------|-------------------------|--------------------------------------------------|
| \(\text{Rb} - \text{Rb}\) | 0.00                    | 0.00                    | 0.00                                             |
| \(\text{Rb} - \text{Br}\) | 0.00                    | 0.00                    | 0.00                                             |
| \(\text{Rb} - \text{O}_{\text{water}}\) | 0.09                    | 0.04                    | 0.48                                             |
| \(\text{Rb} - \text{H}_{\text{water}}\) | 0.12                    | 0.10                    | 0.00                                             |
| \(\text{Br} - \text{Br}\) | 0.00                    | 0.00                    | 0.00                                             |
| \(\text{Br} - \text{O}_{\text{water}}\) | 0.09                    | 0.04                    | 0.46                                             |
| \(\text{Br} - \text{H}_{\text{water}}\) | 0.11                    | 0.10                    | 0.00                                             |
| \(\text{O}_{\text{water}} - \text{O}_{\text{water}}\) | 19.01                   | 9.16                    | 98.47                                            |
| \(\text{O}_{\text{water}} - \text{H}_{\text{water}}\) | 49.00                   | 42.12                   | 0.58                                             |
| \(\text{H}_{\text{water}} - \text{H}_{\text{water}}\) | 31.57                   | 48.43                   | 0.00                                             |

Table 1. Relative percentage weights (to 2 decimal places) of the ten partial structure factors that characterise the 1:500 solutions of \(\text{RbBr}\) in water.

It can immediately be seen that at the measured concentration of 1 \(\text{RbBr}\) to 500 water molecules, the neutron scattering experiments are dominated by the correlations between the oxygen and hydrogen sites of the water molecules. By linear combination of these three measurements, it is possible to cleanly extract the \(S_{\text{H}_{\text{water}}\text{H}_{\text{water}}}(Q)\) partial structure factor, and obtain good estimates of \(S_{\text{O}_{\text{water}}\text{H}_{\text{water}}}(Q)\) and \(S_{\text{O}_{\text{water}}\text{O}_{\text{water}}}(Q)\) [7]. However, the ion hydration partial correlation functions are largely undefined.

2.2. EXAFS
To obtain information on the structural aspects of \(\text{Rb}^+\) and \(\text{Br}^-\) hydration, EXAFS measurements were made at room temperature on solutions prepared in \(\text{H}_2\text{O}\) at a concentration of 1 \(\text{RbBr} : 500\) water molecules. The spectra were collected using the general purpose X-ray
absorption spectroscopy beamline, BM29, of the European Synchrotron Radiation Facility in Grenoble, France. Measurements were made at the Rb and Br K-edges, at 15.200keV and 13.474keV respectively. At the time of the measurements the spectrometer was operating with Si(311) crystals in the monochromator, detuned to 70% of peak intensity for harmonic suppression. The synchrotron was operating at a ring current and electron energy of 200mA and 6GeV, in a 2/3 fill operating mode. The absorption coefficient of the sample was measured in transmission mode using ion chambers filled with Ar/He gas mixtures optimized to give 30% and 70% absorption of the incident and transmitted beam. The data were reduced for structural analysis using the Athena package [8].

3. Data Modelling

To extract the structural information from the experimental data, the technique of Empirical Potential Structure Refinement [3, 4] has been used to build a three dimensional model of the solution. The technique is based upon a classical Monte Carlo simulation of the system, which is initially equilibrated using standard Lennard-Jones plus charges reference potentials, see Table 2.

| Atom     | $\epsilon$  | $\sigma$ | $q$   | Mass |
|----------|--------------|----------|-------|------|
| Rb       | 0.125        | 3.790    | +1.0000 | 85   |
| Br       | 0.566        | 4.465    | -1.0000 | 80   |
| $O_{\text{water}}$ | 0.650 | 3.166    | -0.8476 | 16   |
| $H_{\text{water}}$ | 0.000 | 0.000    | +0.4238 | 2    |

Table 2. Lennard-Jones ($\epsilon, \sigma$), charge ($q$) and atomic mass parameters used to seed the simulation of the 1 : 500 solutions of $RbBr$ in water. Within the EPSR simulation the $\epsilon$ and $\sigma$ parameters are combined using the Lorentz-Berthelot mixing rules: $\epsilon_{\alpha\beta} = (\epsilon_{\alpha}\epsilon_{\beta})^{1/2}$ and $\sigma_{\alpha\beta} = 1/2(\sigma_{\alpha} + \sigma_{\beta})$.

The model consists of 5 $Rb^+$ and 5 $Br^-$ ions in a cubic box of side length 42.19Å containing 2500 SPC/E water molecules [9]. After the system equilibrates under the reference potentials, structural difference functions are calculated between the model derived, and the experimentally measured, neutron structure factors. These are then used to generate a perturbation function $U_{\alpha\beta}^{EP}(r)$ that is added to the reference potential.

$$U_{\alpha\beta}(r) = 4\epsilon_{\alpha\beta} \left[ \left( \frac{\sigma_{\alpha\beta}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{\alpha\beta}}{r_{ij}} \right)^{6} \right] + \frac{q_{\alpha}q_{\beta}}{4\pi\epsilon_0 r_{ij}} + U_{\alpha\beta}^{EP}(r)$$

(4)

Over a series of iterative cycles this procedure operates to bring the structural configurations captured in the model, into agreement with the functions derived from the neutron scattering data. Once the structure factors calculated from the model and the experimental data agree, the model ceases to evolve. At this point, the Monte Carlo procedure is continued and structural information is accumulated in the form of ensemble averages.

4. Results

Figure 1 shows the experimentally measured $F(Q)$ for the three isotopic solutions and the corresponding fits and fit residuals of the EPSR model. As indicated in Table 1, this data
strongly constrains the structural correlations between the water molecules in the model, and the associated pair distribution functions, \( g_{O\text{-water}O\text{-water}}(r) \), \( g_{O\text{-water}H\text{-water}}(r) \) and \( g_{H\text{-water}H\text{-water}}(r) \) are shown in Figure 2. As expected, these functions are highly comparable with those of the pure liquid [10]. The integral of the first peak of \( g_{O\text{-water}O\text{-water}}(r) \), in the distance range from 2.3Å-3.3Å, tells us that on average each water molecule has \( \sim 4.4 \) neighbours which is highly comparable with the value of \( \sim 4.3 \) that is found for the pure liquid in the same range. The presence of the 1 part in 500 of RbBr therefore does not appear to significantly affect the bulk tetrahedral network of water hydrogen bonds. This is confirmed by the integral of the first peak in \( g_{O\text{-water}H\text{-water}}(r) \), to the first minimum at 2.5 Å, that tells us that each water molecule donates and accepts two hydrogen bonds to and from its neighbourhoods.

As the neutron scattering data provide minimal constraints upon the structural correlations involving the ions in solution, the \( g_{RbO\text{-water}}(r) \), \( g_{RbH\text{-water}}(r) \), \( g_{BrO\text{-water}}(r) \) and \( g_{BrH\text{-water}}(r) \) correlation functions are only constrained by the Lennard-Jones plus charge reference potentials used to seed the ion interactions. To evaluate the quality of these reference potentials it is necessary to compare a calculated structural quantity with an experimental function that is more strongly weighted to the interactions involving the ions. It is for this purpose that the EXAFS data were collected. Small deviations from the optimal Lennard-Jones parameters have been found to have a marked effect upon the ability of the simulations to generate local structure configurations about the photo-absorbing atoms, that are consistent with the experimental spectroscopy data [11].

With the development of modern codes that facilitate the calculation of EXAFS spectra, it has become a simple procedure to calculate the EXAFS from an atomistic structural model.
Figure 2. Intermolecular $O_{\text{water}} - O_{\text{water}}$, $O_{\text{water}} - H_{\text{water}}$, and $H_{\text{water}} - H_{\text{water}}$ pair distribution functions for a 1:500 solution of $RbBr$ in water.

[11, 12, 13]. These algorithms only require the relative coordinates of the atoms in the local vicinity of the photoabsorbing atomic sites, from which they calculate the scattering potentials and scattering paths that give rise to the spectral signals. A particular advantage of this method for the study of liquids and highly disordered materials is that the computer simulation provides a natural means to perform the appropriate ensemble averaging of the EXAFS signal contributions [14]. In this study the FEFF 8 code [15] has been used to perform the calculation of the EXAFS spectra from each of the $Rb$ and $Br$ sites in the model. Each calculation is performed for a static cluster of atomic coordinates extracted from the model, and averaged over many hundreds of configurations generated during the EPSR ensemble averaging procedure. For both the $Rb$ and $Br$ photoabsorbing sites, the extracted clusters had a radius of 5.0 Å, centered on the ion site. During the initial optimization of the EXAFS signal calculations it was found that due to the high degree of inherent structural disorder, it was only necessary to calculate the multiple scattering paths up to 4 legs. An advantage of the FEFF 8 code is its ability to estimate the spectral amplitude reduction factor $S^2_0$, which leaves only the offset of the energy scale as a free parameter in the signal calculation. This is selected to provide the optimum phasing between the experimental data and the theoretical model.

Figure 3 shows the comparison between the $Rb$ and $Br$ K-edge EXAFS spectra calculated from the EPSR model, and the experimental data. The signal envelope and frequency allow us to be reasonably confident that the generated EPSR model appropriately captures the structural environment of the cations and anions in the solution. Figure 4 then shows the partial distribution functions that correspond to the cation and anion interactions with the water oxygen and hydrogen sites in their local vicinity.
As expected, the Rb\(^+\) cation is most closely coordinated by water oxygen atoms at a first neighbour distance of \(\sim 2.9\) Å. The integral of the first peak of \(g_{RbO_{water}(r)}\) tells us that on average each Rb\(^+\) has \(\sim 6.3\) water oxygens in its first hydration shell, when integrated to the first minimum at a distance of \(3.75\) Å. In accordance with its negative charge, each Br\(^-\) anion is directly hydrated via the hydrogen atoms of the solvent water molecules, at a distance of \(\sim 2.3\) Å. This positions the oxygen atoms of the first shell hydration water at \(\sim 3.3\) Å. Integrating the first peak in \(g_{BrH_{water}(r)}\) to a distance of \(\sim 3.1\) Å indicates that this ion also has a first hydration shell coordination number of \(\sim 6\) water hydrogens, or \(\sim 6.3\) water oxygens on integrating the corresponding feature in \(g_{BrO_{water}(r)}\).

5. Discussion

The aim of this study was not simply to develop new understanding of the hydration structure of the Rb\(^+\) and Br\(^-\) aqua ions, but rather to demonstrate that a combination of neutron scattering and EXAFS spectroscopy can now be used to refine the potentials used in classical atomistic simulations. These refined potentials are used to drive the configurations of atomic coordinates into simulataneous agreement with bulk and local structure information. In this example, the concentration of RbBr in the solution was far too low to enable the neutron scattering technique to provide any constraints on how the ions were incorporated into the bulk solvent network, and
Figure 4. EPSR derived ion-water pair distribution functions for a 1 : 500 solution of $RbBr$ in water, that correspond to the calculated EXAFS signals shown in Figure 3.

| Ion  | Ion-O$_{water}$ distance (Å) | Hydration number ($N_{O_{water}}$) | Concentration (mole dm$^{-3}$) | Technique      | Reference |
|------|------------------------------|-----------------------------------|-------------------------------|----------------|-----------|
| $Rb^+$ | 3.05                         | 6.9                               | 4.0                           | AXS            | [16]      |
| $Rb^+$ | 2.9                          | -                                 | 0.9                           | EXAFS          | [17]      |
| $Rb^+$ | 2.99                         | 8                                 | 1.5                           | EXAFS          | [18]      |
| $Rb^+$ | 2.96                         | 8                                 | 3.0                           | EXAFS          | [18]      |
| $Rb^+$ | 2.9                          | 6.3                               | 0.11                          | ND+EXAFS       | This work |
| $Br^-$ | 3.19                         | 6                                 | 0.1                           | EXAFS          | [19]      |
| $Br^-$ | 3.35                         | 7.4                               | 3.1                           | AXS            | [20]      |
| $Br^-$ | 3.4                          | 6.9                               | 0.02                          | EXAFS          | [21]      |
| $Br^-$ | 3.4                          | 6.9                               | 0.2                           | AXS            | [16]      |
| $Br^-$ | 3.4                          | -                                 | 0.92                          | EXAFS          | [17]      |
| $Br^-$ | 3.3                          | 6.3                               | 0.11                          | ND+EXAFS       | This work |

Table 3. Comparison of the structural parameters for $Rb^+$ and $Br^-$ hydration shells obtained in a selection of recent studies. The abbreviation AXS refers to Anomalous X-ray Scattering, EXAFS to Extended X-ray Absorption Fine Structure spectroscopy and ND to Neutron Scattering.
hence demonstrates the value of X-ray absorption spectroscopy to establish the veracity of the potentials used within the model.

To see how the results obtained in this study compare with other recent investigations of Rb\(^+\) and Br\(^-\) hydration, the relevant values for shell radius and hydration number are tabulated in Table 3. We can thus see that this hybrid method combining neutron scattering, EXAFS spectroscopy and computer simulation gives a consistent determination of the ion-O\(_\text{water}^{-}\) distances. Some variation is found in the hydration numbers between the various studies, though it is reasonable to consider this hybrid method to be more reliable on this issue. This is because the simulation is constrained to be consistent with the known bulk atomic density of the solution and with the detailed structure of the solvent water itself, that is strongly constrained by the neutron scattering data.

In many cases the greatest strength of this hybrid analytical approach based on atomistic computer simulation, is the access that the ensemble average atomic configurations give to the partial radial distribution functions. By estimating their functional forms over an extended length scale, generally reliable to half the simulation box size, the information content that can be extracted from experimental data is much greater than simply the average distances and first shell coordination numbers that so often are the limit of traditional studies. The three dimensional models allow for the calculation of bond angle distribution functions, coordination number histograms, molecular centres distribution functions, molecular orientation correlation functions and any other parameters that can be derived from the atomic coordinates.

For aqueous electrolyte systems, the atomistic model allows us to estimate the extent of ion-pairing that is often a critical consideration in their solution chemistry, this can be seen in Figure 5. These functions are almost always inaccessible to direct probes of solution structure, due to their very small contribution to the overall measured signals. At the dilute concentration of the RbBr solution studied here, unlike ion pairing was found to occur at a low level with the shortest Rb\(^+\)–Br\(^-\) interactions taking place at a mean distance of 3.3Å and with an average coordination number of \(\sim 0.6\), on integration of the peak to a distance of 4.0Å. Like-ion correlations all occur on length scales greater than \(\sim 4\)Å for Rb\(^+\) and \(\sim 8\)Å for Br\(^-\) and indicate that in this system, these are always mediated by at least one shell of hydration water.

6. Conclusion

This study was designed to illustrate the significant benefits of applying a comprehensive experimental and computational approach to common structural problems in aqueous solution chemistry. Neutron diffraction with H/D isotopic substitution has been used to provide extensive constraints on the structure of the bulk solvent medium. These constraints were then used to generate an experimentally consistent atomistic structural model using the Empirical Potential Structure Refinement method. To validate the accuracy of the cation and anion hydration environments generated in the model of the dilute solution, use was made of EXAFS spectroscopy data. The final result was the production of an accurate bulk and local structure model. This was then used to estimate the experimentally inaccessible extent of ion-pairing that is expected to occur within a dilute solution of 1:500 RbBr in water.

References

[1] Finney J L and Soper A K 1994 Chem. Soc. Revs. 23 1–10
[2] Enderby J E 1995 Chem. Soc. Revs. 24 159–168
[3] Soper A K 1996 Chem. Phys. 202 295–306
[4] Soper A K 2005 Phys. Rev. B 72 104204
[5] Soper A K, Howells W S and Hannon A C 1989 ATLAS Analysis of Time-of-Flight Diffraction Data from Liquid and Amorphous Samples vol RAL-89-046 (Oxfordshire, UK: Rutherford Appleton Laboratory Report)
[6] Soper A K and Luzar A 1992 J. Chem. Phys. 97 1320–1331
**Figure 5.** EPSR derived ion-ion pair distribution functions for a 1 : 500 solution of $RbBr$ in water. The noise in these functions is the result of the limited sampling of the correlations due to the dilute nature of the solutions. As the strength of these correlations in either the neutron scattering data or the EXAFS data is very low, these functions are purely an estimation obtained from the atomistic model.

[7] Bowron D T, Soper A K and Finney J L 1998 *J. Phys. Chem.* 102 3551–3563
[8] Ravel B and Newville M 2005 *J. Synchrotron Rad.* 12 537–541
[9] Berendsen H J C, Grigera J R and Straatsma T P 1987 *J. Phys. Chem.* 91 6269–6271
[10] Soper A K 2000 *Chem. Phys.* 258 121–137
[11] Bowron D T and Díaz-Moreno S 2007 *J. Phys. Chem. B* 111 11393–11399
[12] Bowron D T 2008 *Mat. Sci. Eng. B* 149 166–170
[13] Bowron D T 2008 *Pure App. Chem.* 80 1211–1227
[14] Filipponi A 2001 *J. Phys.: Condens. Matter* 13 R23–R60
[15] Ankudinov A L, Ravel B, Rehr J J and Conradson S D 1998 *Phys. Rev. B* 58 7565–7576
[16] Ramos S, Barnes A C, Neilson G W and Capitán M J 2000 *Chem. Phys.* 258 171–180
[17] Filipponi A, De-Panfilis S, Oliva C, Ricci M A, D’Angelo P and Bowron D T 2003 *Phys. Rev. Lett.* 91 165505
[18] D’Angelo P and Persson I 2004 *Inorg. Chem.* 43 3543–3549
[19] Tanida H, Sakano H and Watanabe I 1994 *J. Chem. Soc. Dalton Trans.* 2321–2326
[20] Beudert R, Bertagnolli H and Zeller M 1997 *J. Chem. Phys.* 106 8841–8848
[21] Wallen S L, Palmer B J, Pfund D M, Fulton J L, Newville M, Ma Y and Stern E A 1997 *J. Phys. Chem. A* 101 9632–9640
[22] Ferlat G, Miguel A S, Jal J F, Soetens J C, Bopp P A, Daniel I, Guiot S, Hazemann J L and Argoud R 2001 *Phys. Rev. B* 63 134202