

# Existence of extended oriented ion-hydroxide clusters in concentrated aqueous solution

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## Abstract

We probe the local electronic structure at solvated  $\text{Na}^+$  ions in 1 M aqueous NaCl solutions as a function of pH. A dramatic change in the  $\text{Na}^+$  white line intensity in x-ray absorption is observed for high pH values, reflecting a changing local electronic structure at the  $\text{Na}^+$  ions when  $\text{OH}^-$  is present. Given the relative abundance of sodium and hydroxide ions, we conclude that one  $\text{OH}^-$  affects  $2.4 \pm 0.6$   $\text{Na}^+$  ions in an electronically noticeable way at pH 13. From the experimental data we infer that spatially extended clusters or networks incorporating  $\text{Na}^+$  and  $\text{OH}^-$  can exist in the electrolyte solution. The experimental data are complemented by molecular dynamics simulations, which indicate the presence of structured clusters incorporating  $\text{Na}^+$ ,  $\text{OH}^-$ , and solvent molecules.

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For pure water, the existence of hydrogen bond networks and details of the local hydrogen bonding are a matter of current debate[1–4]. Electrostatic interactions in the liquid become even more important when ions are introduced into the solvent. Solvation shells form around the ions and partially shield longer range ion-ion interactions. The influence of ions on hydrogen networks is studied with static and dynamic probes. [2, 5, 6]. Here, we focus on the electronic structure of solvated sodium ions, investigating the structure of aqueous NaCl as a function of pH. Long-range structuring in neat water, albeit invoked numerous times in the literature, most likely does not occur due to the remarkable ability of water molecules to reorient fast in the liquid. In concentrated salt solutions (e.g., NaCl) intermediate size structures can build up as a result of ion-pairing and clustering. An even more interesting situation occurs upon adding a strong base, such as NaOH, since hydroxide ions are not spherically symmetric and can form extended anisotropic networks of ions. This situation, which is explored in the present study, can have important consequences for physical and chemical processes in electrolytes, ranging from binding of ions to proteins to atmospheric reactions in aqueous aerosols.

In Fig.1, near edge x-ray absorption fine structure (NEXAFS) spectra are presented for 1 M aqueous solutions of NaCl at pH 1.9, 7.0, 8.5, 9.9, 11.5, 12.2, and 13.0. The pH was varied by adding concentrated HCl or NaOH solution, resulting in ion concentrations listed in Table. I. The solutions were prepared using deionized water directly before the NEXAFS measurements at the BESSY II beamline U41-PGM. The pH was checked with a pH-meter before and after the measurements. X-ray absorption was monitored via the fluorescence yield measured by a GaAsP photodiode. The liquid was introduced into the He filled experimental chamber as a low pressure jet of approx. 1 mm diameter with a flow rate of 1 l/min. Accordingly, radiation damage or precipitation effects can be excluded as the sample is continuously refreshed.

The absorption intensity shown in Fig. 1 has been normalized to the incident photon flux, keeping the overall experimental geometry exactly the same. As a result, the overall changes in intensity are meaningful. To exclude systematic errors, data have been acquired several times with ascending and descending concentration series, yielding identical results; two datasets for each pH are shown in Fig.1.

The general spectral shape is characterized by four peaks at 1072.8, 1075, 1080, and 1110 eV, denoted A, B, C, and D, respectively.[7, 8]. With the exception of the spectrum at

pH 13.0, only minor changes in the absorption white line intensity as defined by the intensity integral under the peaks A-C are observed. In Table I, we list the ion concentrations in the solution. While at pH 7 only  $\text{Na}^+$  and  $\text{Cl}^-$  ions are present in appreciable concentration in the water, the concentration of  $\text{H}^+$  and  $\text{OH}^-$  increases when going to acidic/basic conditions.

As the Na 1s x-ray absorption edge is well described in a single electron picture and in dipole approximation, the spectra in the region of the peaks A-C reflect the unoccupied density of p-type states locally at the sodium atoms (p-DOS).[9] As a result, the white line intensity above the non-resonant background is proportional to the total number of empty states of p symmetry in the integration interval. Peak D is located at the transition to the extended x-ray absorption fine structure (EXAFS) region in the absorption spectrum, where structural information is convoluted with electronic structure information.[10] In this paper, we focus on the electronic structure information in the NEXAFS region.

While the white line intensity changes only marginally between pH 1.9 and 12.2, it is drastically reduced when going from the neutral solution to pH 13.0. Between pH 1.9 and 13, the relative concentration of  $\text{Cl}^-$  to  $\text{Na}^+$  changes only marginally while the concentrations of  $\text{H}^+$  and  $\text{OH}^-$  change by orders of magnitude relative to the  $\text{Na}^+$  concentration. Consequently, the observed changes in the NEXAFS spectra at pH 13.0 as compared to less basic pH can only be attributed to the presence of the hydroxide ions. With respect to a quantitative analysis, the observed changes between pH 1.9 and pH 12.2 are too small to be interpreted. (Our estimate of the intensity error which is dominated by potential systematic or non-linear changes in the absorption background is indicated in Fig. 1 by an error bar.) In the following, we focus on the unambiguous effect at pH 13.0.

As a starting point for the discussion of our experimental findings, we employ a local picture of solvated  $\text{Na}^+$  ions. As evident from table I, only one hydroxide ion per 11 sodium ions is present at pH 13.0, while no significant amount of hydroxide or hydronium ions are present at pH 7. Neutral NaCl solutions are typically modeled with approximately sixfold water coordination of the  $\text{Na}^+$  ion.[7, 8, 11]. In the most simplistic scenario, one water molecule may be replaced by a hydroxide anion in a basic solution. In this fractionation model, a sodium ion would thus be either unaffected by the presence of hydroxide ions and still coordinated exclusively with water molecules, or it would have a hydroxide ion in its vicinity such that its electronic structure is influenced as compared to pure water coordination. With increasing  $\text{OH}^-$  to  $\text{Na}^+$  ratio, more  $\text{Na}^+$  ions will be in the affected

fraction; multiple occupancies of  $\text{OH}^-$  next to  $\text{Na}^+$  can in first approximation be excluded on the grounds of the relative concentrations.

On this basis, we would expect the NEXAFS spectrum at pH 13 to be a superposition of two contributions: (i) a "pH 7-like fraction" where the  $\text{Na}^+$  have the same local environment and the same electronic structure as at pH 7. This contribution should have a relative weight of  $10/11 \approx 91\%$ . (ii) an "affected fraction" which is non-pH 7-like and which contains all  $\text{Na}^+$  ions which have a local environments different from  $\text{NaCl}^*\text{aq}$  at pH 7. The relative weight of this contribution should be  $1/11 \approx 9\%$ . This argument is simply based on the relative abundance of  $\text{H}_3\text{O}^+$  or  $\text{OH}^-$  relative to  $\text{Na}^+$  ions as listed in Table I. In this picture, we should be able to subtract 91% of the NEXAFS spectrum at pH 7.0 from the spectrum at pH 13.0. Obviously, we observe a much larger effect in our experiment. In Fig. 2 we demonstrate that we can only subtract 78.5% of the pH 7 NEXAFS spectrum without obtaining an unphysical, negative intensity for the remaining fraction. Without any knowledge or assumptions on the spectral shape of the affected fraction, this implies that *at least* 21.5% of the sodium ions in the solution are affected in their electronic structure by the presence of the hydroxide ions. Note that the existence of a variety of local configurations around the  $\text{Na}^+$  ions in the spatial and temporal ensemble average is taken care of by the fact that we subtract measured data at pH 7, which does reflect such an ensemble average. As we do not know the spectral shape of the affected fraction *a priori*, the number of 21.5% affected  $\text{Na}^+$  ions is a *lower* bound for this value.

The fact that we can only subtract much less of the 'unaffected', pH 7-like intensity from the spectra at basic pH than we would expect from the  $\text{Na}^+$  to  $\text{OH}^-$  concentration ratios according to Table I clearly proves that more than one  $\text{Na}^+$  ion is affected in its local electronic structure by a single  $\text{OH}^-$ . We thus can not maintain a simple, local picture of the interaction of  $\text{OH}^-$  with  $\text{Na}^+$  in the aqueous solution. The *minimum* number  $N_{min}$  of  $\text{Na}^+$  ions that are electronically affected by a *single* hydroxide at pH 13.0 is obtained as

$$N_{min} = \frac{[\text{Na}^+]}{[\text{OH}^-]} \times (1 - f)$$

, where  $f=0.785$  is the fraction determined by the subtraction procedure above. The minimum number of sodium ions affected by a single hydroxide ion determined in this way is  $N_{min} = 2.4 \pm 0.6$ . The relative error of 25 % for this value is dominated by the intensity uncertainty as indicated by the error bar in Fig. 1. For the basic pH region, therefore, the

simple picture of  $\text{Na}^+$  ions which are isolated by their solvation shells and interact only weakly by long range electrostatic forces does not. At pH 13, an  $\text{OH}^-$  ion interacts with more than one  $\text{Na}^+$  such that it manifests itself in the local electronic states at the  $\text{Na}^+$  site, and such changes - certainly when they are as big as observed here - are generally discussed as the formation of strong interactions (or even bonds) between atoms. For pH 13.0, our data prove that one  $\text{OH}^-$  interacts on average with at least  $2.4 \pm 0.6$  or more  $\text{Na}^+$  ions in the spatio-temporal ensemble average. This requires a clustering of  $\text{Na}^+$  around each  $\text{OH}^-$ . Our data are also compatible with the possible existence of extended, percolated  $\text{Na}^+$ - $\text{OH}^-$  networks in the electrolyte at each moment in time.

To the best of our knowledge no other experimental data exist that would allow to draw conclusions about the existence of extended clusters or possibly networks as described here. There are, however, several studies that are primarily concerned with hydrogen-bonded networks in electrolytes, which relate to some extent to the situation presented here. Structural studies by neutron scattering of aqueous NaOH solutions at 2 and 18.5 M complemented by Car-Parinello-type molecular dynamics simulations report a concentration dependent number of water molecules in the  $\text{OH}^-$  hydration shell and the existence of ion pairing at high ion concentrations.[12, 13] Dynamical studies of the reorientation time of water molecules in bulk water vs. water molecules in the first solvation shell of various ions show that the dynamics outside the first solvation shell is practically unaffected by the presence of ions.[2, 14] These results are not in contradiction with the presence of spatially extended  $\text{Na}^+$   $\text{OH}^-$  clusters, which could be envisioned to be embedded in a mainly unaffected matrix of hydrogen bonded water molecules. Monte Carlo simulations for aqueous NaCl solutions (not as a function of pH) have found evidence for the formation of large clusters. Ion pairs, triplets, and larger clusters associated with a dozen or more solvent molecules were predicted.[15]. Again, the role of pH and, in particular, of  $\text{OH}^-$  has so far not been investigated.

To this end, we have additionally carried out molecular dynamics simulations of a system consisting of 110 water molecules with 11  $\text{Na}^+$ , 10  $\text{Cl}^-$ , and 1  $\text{OH}^-$  ion, which corresponds to a 5 M concentration of NaCl at pH 13.5. The salt concentration of 5 M was chosen to keep the total number of water molecules small enough for the system to be accessible for all applied computational methods, while retaining the effective relative abundances between ions. A polarizable force field for water and ions was employed, with a slightly expanded (by

less than 10 %) van der Waals radius of hydroxide in order to avoid the so called polarization catastrophe [16–18]. Moreover, we verified the classical force field against ab initio molecular dynamics employing a BLYP functional for the same system. Within the ab initio approach only short trajectories (several picoseconds) are computationally feasible. These confirmed semi-quantitatively the conclusions obtained from statistically converged classical molecular dynamics simulations.

A bulk system was modeled applying 3D periodic boundary conditions and the Ewald summation method was employed to account for long range electrostatic interactions. After a sufficiently long equilibration within the (N,p,T) ensemble, the ensemble was changed to (N,V,T) at  $T = 300$  K and a 2 ns trajectory was collected and analyzed. Simulations were performed using the Amber 8 program package.[19] In Fig. 3 the resulting radial distribution functions are presented. For distances below 6 Å a strong difference between hydroxide oxygen-sodium and chloride-sodium distributions can be seen. The first peak for both curves corresponds to a contact ion pair. Such a pair is formed in both cases with the peak being stronger and the anion-cation distance being shorter for hydroxide compared to chloride (2.5 Å vs 2.8 Å). Then, at the distance of about 4 Å there is a peak on the first curve corresponding to a second sodium cation in the vicinity of hydroxide and at 4.6 Å there is another peak correlating with a third sodium cation. The integrated distribution shows that there are on average 3 sodium cations within 6 Å from hydroxide oxygen. On the  $\text{Cl}^- - \text{Na}^+$  curve there is no peak around 4 Å. Instead there is a single peak at 5 Å, due to which the number of neighboring cations also reaches 3 at 6 Å.

In Fig. 4 we present projected density plots for atoms and ions around the hydroxide for two different isovalues. For sodium cations, three regions around  $\text{OH}^-$  can be identified. The first density maximum of sodium (M1), located 2.5 Å from the oxygen atom opposite to the hydrogen of  $\text{OH}^-$  can be interpreted as a contact ion pair. The second sodium maximum (M2) appears on the hydrogen side of hydroxide, while the third one (M3) is on the oxygen side behind the first maximum. The latter two maxima, roughly corresponding to the second and third sodium cation, represent solvent-separated ion pairs, which is evident from the overlap of the the sodium and water isosurfaces in Fig. 4. A plot for an increased density isovalue (Fig. 2b) visualizes the delocalization of the densities. The three sodium cations can now be seen to form a structured cluster around  $\text{OH}^-$  whereas more distant cations are homogeneously spread around hydroxide.

Molecular dynamics simulations allow us to conclude that ordered local structures of the hydroxide anion and, on average, approximately three sodium cations in the vicinity of  $\text{OH}^-$  exist in the simulated mixed solution, similarly as in pure concentrated NaOH aqueous solutions.[20] One cation forms a contact ion pair and at least the two next nearest sodium ions are interacting with the hydroxide ion as solvent separated ion pairs.

While the molecular dynamics simulation represents the  $\text{Na}^+ / \text{OH}^- / \text{Cl}^-$  ratios of our experiment correctly, it overestimates the ion concentrations relative to the solvent by a factor of five. At 1 M concentration one might thus expect a generally reduced number of contact ion pairs. However, theoretical results for NaCl solutions [21] show that going from 4.4 M to  $\approx 1$  M concentration the average number of water molecules in the first solvation sphere for  $\text{Na}^+$  increases only by 5% and the structure of  $\text{Na}^+ \text{-Cl}^-$  radial distribution is largely unaffected. For NaOH in aqueous solution it was reported that the changes in the coordination number of Na-OH with concentration are small in this range.[20] We thus expect our theoretical results to approximate the experimental situation well.

The results from the molecular dynamics simulation, namely that on average three sodium cations are found within a 6 Å sphere around a  $\text{OH}^-$  ion and that one of them is forming a contact ion pair, are in good agreement with our experimental observation that a single  $\text{OH}^-$  affects  $2.4 \pm 0.6$  with respect to their electronic structure. In the light of the theoretical findings, we expect the sodium ion forming a contact ion pair (M1 in Fig. 4) to have a strongly altered electronic structure as compared to a purely water coordinated  $\text{Na}^+$ , while the sodium ions M2 and M3 in solvent-separated ion pairs can be expected to be affected to a lesser degree. Concerning extended ion organization in solution, MD simulations show a remarkable ability of  $\text{OH}^-$  to form oriented, roughly collinear anion-cation structures. This distinguishes the present system from simple salt solutions (such as aqueous NaCl), where spherical ions at best pair to form on average isotropic clusters at high concentrations. A quantitative characterization of the spatial extent of the ion chains in the present system, as well as their possible networking and dynamics of formation, will be a subject of future studies.

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	$[\text{Na}^+]-1$	$[\text{Cl}^-]-1$	$[\text{H}^+]$	$[\text{OH}^-]$
pH 1.9	0	$1 \times 10^{-1}$	$1.26 \times 10^{-2}$	$7.94 \times 10^{-13}$
pH 7.0	0	0	$1 \times 10^{-7}$	$1.0 \times 10^{-7}$
pH 8.5	$3.16 \times 10^{-6}$	0	$3.16 \times 10^{-9}$	$3.16 \times 10^{-6}$
pH 9.9	$1 \times 10^{-4}$	0	$1.26 \times 10^{-10}$	$7.94 \times 10^{-5}$
pH 11.5	$1 \times 10^{-3}$	0	$3.16 \times 10^{-12}$	$3.16 \times 10^{-3}$
pH 12.2	$1 \times 10^{-2}$	0	$6.31 \times 10^{-13}$	$1.58 \times 10^{-2}$
pH 13.0	$1 \times 10^{-1}$	0	$1 \times 10^{-13}$	$1 \times 10^{-1}$

TABLE I: Calculated concentration of ions in the solutions at the measured pH, assuming the change of the water concentration is negligible, i.e.  $[\text{H}_2\text{O}] \approx 55.4 \text{ M}$ . All concentration units are Molar. For  $\text{Na}^+$  and  $\text{Cl}^-$ , the deviation from 1 M is tabulated.

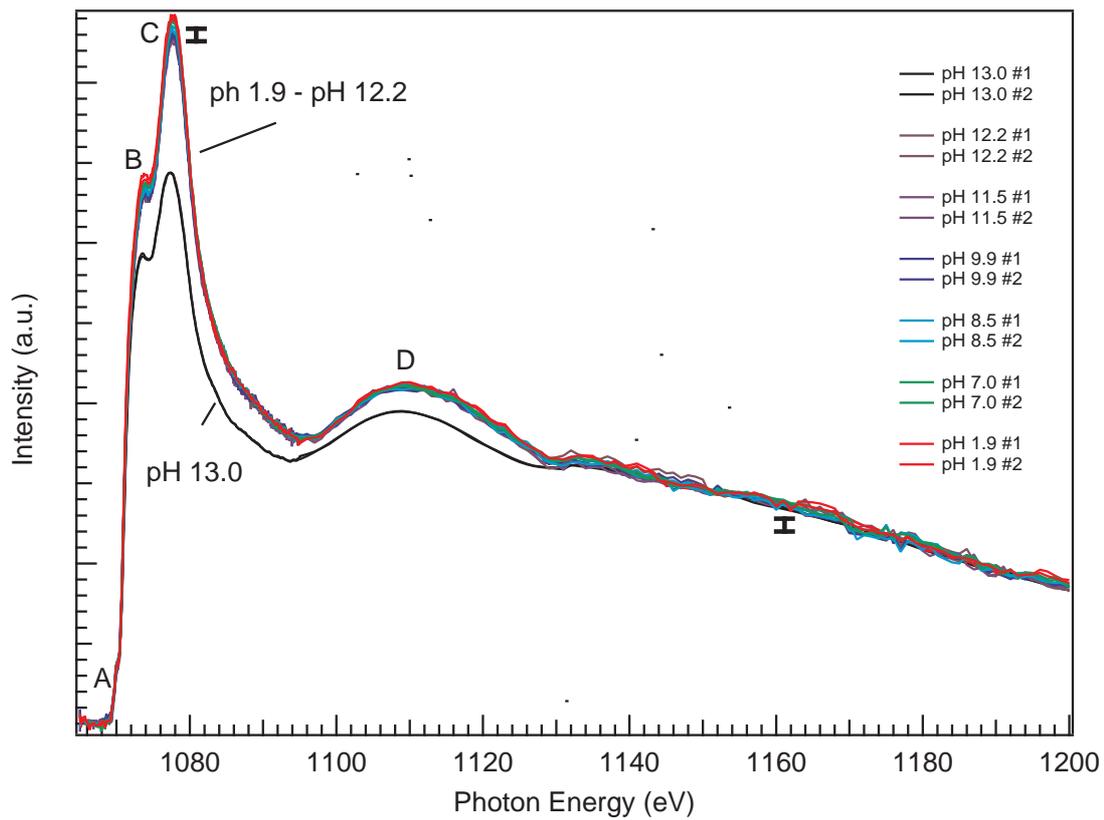


FIG. 1: Na K-edge FY-XANES spectra for approx. 1 M NaCl solutions recorded at different pH values. Exact concentrations are listed in Table I

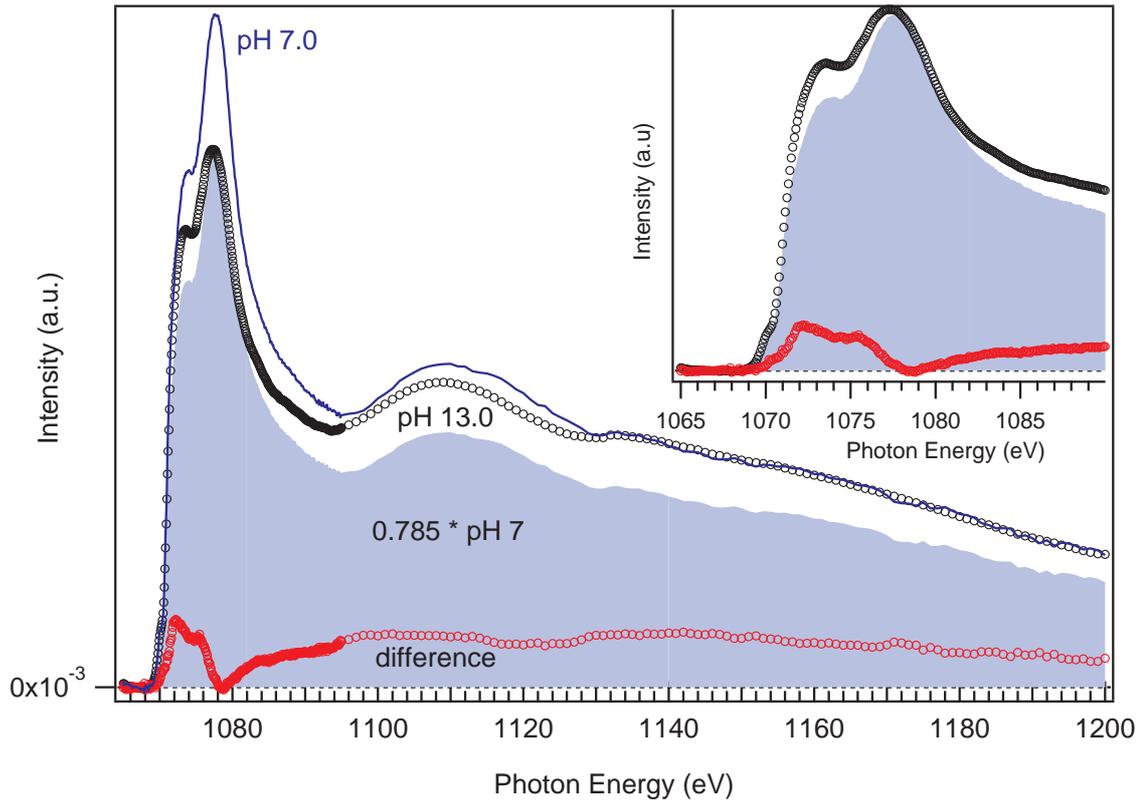


FIG. 2: At most 78.5% of the pH 7.0 NEXAFS spectrum (blue line) can be subtracted from the pH 13.0 NEXAFS spectrum (black markers) while keeping the difference (red markers) non-negative. A magnification of the immediate near edge region is shown in the inset.

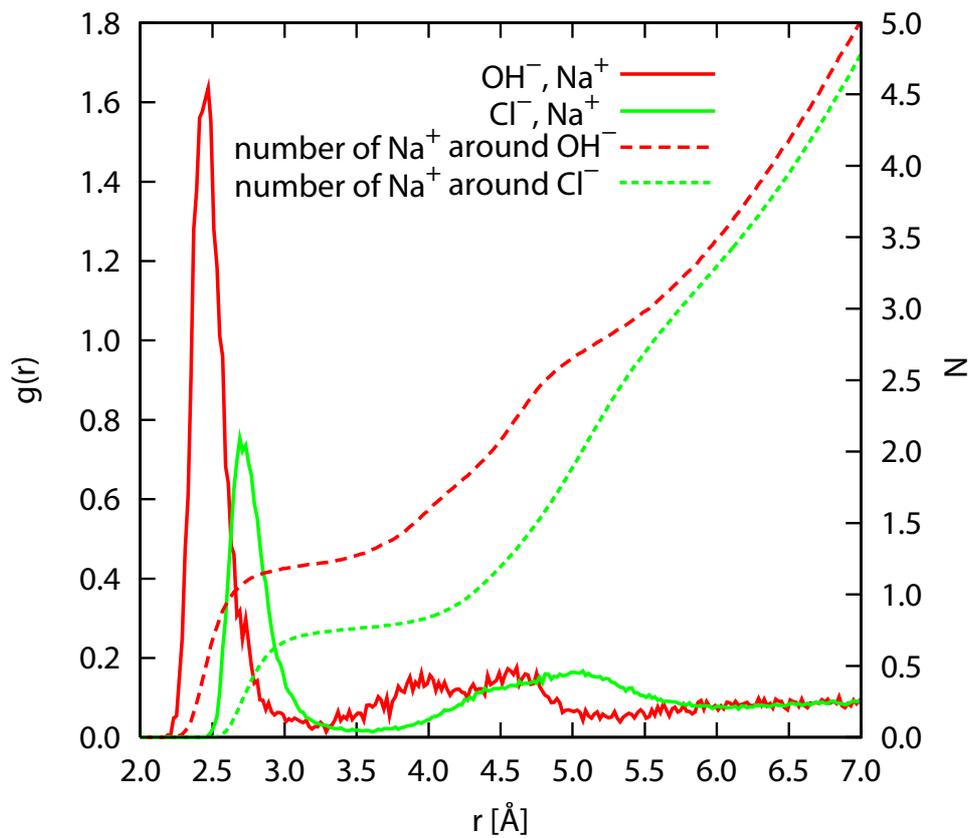


FIG. 3: Hydroxide oxygen-sodium and chloride-sodium radial distribution functions and the corresponding integrated curves, which give the number of cations within a given distance from the anion.

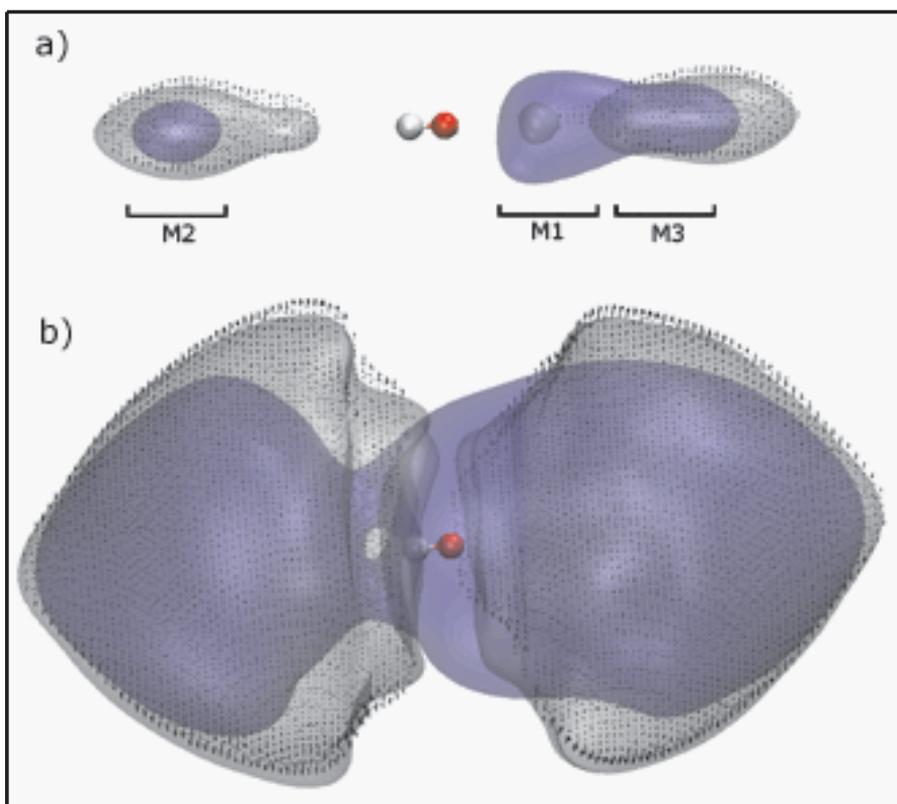


FIG. 4: Isosurfaces of sodium and water densities around a hydroxide anion for (a) density isovalues of 1.9 for water and 4.2 for sodium and (b) density isovalues of 4.0 for water and 6.0 for sodium. Color coding: red oxygen, white hydrogen, blue sodium, gray water oxygen, and black dots water hydrogen. The first three maxima ( $M1$ ,  $M2$ ,  $M3$ ) for sodium are shown in (a)