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Probing RbBr solvation in freestanding sub-2 nm water clusters[†]

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Concentration dependent solvation of RbBr in freestanding sub-2 nm water clusters was studied using core level photoelectron spectroscopy with synchrotron radiation. Spectral features recorded from dilute to saturated clusters indicate that either solvent shared or contact ion pairs are present in increasing amount when the concentration exceeds 2 mol/kg. For comparison, spectra from anhydrous RbBr clusters are also presented.

1 Introduction

The molecular level details of how ions and solvent molecules arrange themselves and interact with each other are relevant for many branches of science. Out of a vast number of electrolyte and solvent combinations, the details of alkali halide solvation in water has received probably the most attention. For example, aqueous ions are present in sea salt aerosols emitted from ocean surface with implications for atmospheric chemistry¹. Aqueous ions and ionic interactions play important roles also in biological matter². Questions of water behaviour around solute ions³, interfacial effects⁴ (water/air, water/protein) and ion pairing⁵ are among subjects of interest from these systems.

Several^{6–9} experimental and computational studies demonstrate the surface partitioning or concentration enhancement of heavier halide ions near the aqueous surface in *macroscopic* systems. Whereas F[−] ion prefers to be located in the bulk of the aqueous environment, heavier halides Cl[−], Br[−] and especially I[−] are increasingly driven towards the surface of the liquid in this order. If present in aqueous atmospheric aerosols, such surface enrichment could severely enhance certain environmental chemical reactions¹⁰. Coleman *et al.*⁸ explain the behaviour of Cl[−], Br[−] and I[−] as originating from the more favourable water–water interaction energy when the ions are partially desolvated while F[−] is expelled from the surface due to entropic effects. On the other hand, all the alkali metal cations prefer the bulk due to favourable water–ion interaction energy. Thus, various mechanisms move the ions in different directions depending on the complex interactions among water molecules and ions.

Ion pairing is a phenomenon where ions associate either fully or partially to each other in electrolyte solution. Ion pairs are commonly classified as contact ion pairs (CIP), solvent-shared ions pairs (SIP) or solvent separated ion pairs (2SIP or SSIP). For the first two cases, either no solvent layer or one solvent layer exists between the ions, respectively, whereas in the last case both ions have separate primary hydration shells⁵. The concept of ion pairing has been invoked when deviations of solution properties in moderate concentrations cannot be explained using theories developed for very dilute solutions as discussed in detail by Marcus and Hefter⁵. In general, ion pairing increases as a function of solution concentration and temperature and decreases as a function of solvent relative permittivity (dielectric constant). Studying this phenomenon in nanoscale water clusters provides an interesting comparison as for example the cluster temperature can be severely reduced compared to bulk aqueous system without turning into solid¹¹. Also, the high number of surface molecules in relation to the bulk molecules and the reduced size of the system could alter the solvation dynamics, especially when segregation effects of ions are present.

Here we report on a photoelectron spectroscopic study of RbBr in freestanding water clusters with mean size of 100 molecules/cluster. The concentration was varied systematically over a range covering dilute and concentrated solutions. Core level spectra of Rb⁺ and Br[−] ions as well as valence spectra were measured at each concentration. Together with concentration estimates and chemical shift calculations, the experimental results indicate that the ion pairing increases when the molal concentration is beyond 2 mol/kg. Anhydrous RbBr cluster core level spectra are presented for comparison.

2 Description of the experiment

A beam of water clusters doped with RbBr propagating freely in vacuum was generated using the so-called Exchange Metal Clus-

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ter source (EXMEC)¹². The beam was crossed at a right angle by synchrotron radiation. Kinetic energies of the electrons emitted from the cluster beam were recorded using a hemispherical deflection analyzer installed perpendicular to the cluster and synchrotron radiation beams. The experiment was carried out at the I411 undulator beamline^{13,14} at the 1.5 GeV ring of MAX-lab (MAX IV Laboratory) in Lund, Sweden.

The cluster formation took place in two stages. First, a beam of water clusters was generated by expanding a mixture of water vapor and He into vacuum through a conical nozzle. Water clusters were then doped with RbBr using a pick-up oven located downstream along the water cluster beam path. Further details of the cluster source^{12,15–17} and the cluster formation process^{17,18} can be found elsewhere.

The experiment specific parameters were as follows. The expansion source nozzle diameter was 150 μm and the total opening angle was 20°. The water vapor was generated using an in-vacuum reservoir kept at 77 °C $\pm$ 2 °C while the nozzle temperature was 125 °C $\pm$ 2 °C. Helium backing gas was added for a total stagnation pressure of 1030 mbar $\pm$ 20 mbar as measured by an absolute capacitance manometer. A 500 μm conical skimmer located about 1 cm from the nozzle was used to separate the cluster source and measurement chamber. The 10 mm long pick-up region was defined by the length of the RbBr containing crucible. The crucible temperature was gradually increased in steps between 465 °C and 630 °C in order to change the RbBr vapor pressure and the number of picked up RbBr monomers by the water clusters.

After generation, the clusters passed through a synchrotron radiation beam about 2 cm downstream from the pick-up oven. The emitted photoelectrons were energy analyzed with a Scienta R4000 set to the so-called “magic angle” of 54.7° with respect to the horizontal linear polarization of the synchrotron radiation. Measurements were carried out using a photon energy of 196 eV. The experimental energy resolution was estimated to be 118 meV, including both the photon energy as well as the analyzer energy resolution. Spectra were recorded from binding energy regions covering 6–17 eV (valence), 70–80 eV (Br 3*d*) and 111–123 eV (Rb 3*d*). Calibration of the binding energy scale was done using the molecular water 1*b*₁ adiabatic ionization energy of 12.615 eV¹⁹.

A separate experiment was carried out using the same experimental setup where anhydrous RbBr clusters with variable mean size were generated. Instead of water, argon was used as the initial host cluster for pick-up of RbBr monomers. The experiment details and cluster formation process description have been published earlier in connection to RbCl cluster data¹⁷ which was acquired during the same beamtime. The recorded Rb and Br 3*d* core level photoelectron spectra can be used as a comparison in order to gain more insight into the hydrated clusters.

3 Experimental results

In order to monitor the ionic species in the water clusters, photoelectron spectra (PES) were measured from binding energy regions corresponding to Rb 3*d* and Br 3*d* core levels. The valence region was recorded in order to verify the presence of water

Fig. 1 Valence photoelectron spectra measured using a photon energy of 196 eV. Spectrum labels denote the estimated mean molalities of the clusters. See the text for explanation of the designations. Spectra have been normalized with respect to molecular water signal for easier comparison

molecules in cluster form. A set of spectra from all three regions was recorded for each pick-up oven temperature set point. The spectra are labeled by the estimated molal salt concentration *b* in units of mol/kg which is proportional to the pick-up oven temperature. The details of the concentration estimation are presented in Section 4.

3.1 Valence PES

The valence photoelectron spectra are shown in Fig. 1. The region illustrated covers the outermost valence orbitals of both RbBr and water. The lowest binding energy peaks between 7.6 eV and 10 eV belong to uncondensed RbBr monomer ²P_{3/2} and ²P_{1/2} levels which essentially derive from the Br[−] 4*p* orbital²⁰. The shallow feature denoted by A at the higher binding energy side of the monomer peaks is associated with dimer and higher multimer/cluster species²⁰.

Bands between ~10.4 eV and 13 eV belong to the outermost 1*b*₁ valence orbital of water. Centered at ~11.6 eV, band originating from water clusters is seen while the sharp peaks at 12.615 eV belong to molecular water²¹ present in the cluster beam. The water cluster bands continue towards higher binding energies overlapping with the molecular water peaks. As only the outermost 1*b*₁ band of water clusters was of interest, the rest were not recorded.

The behaviour of RbBr valence band intensity correlates positively with increasing vapor pressure as the pick-up oven temperature rises. At the same time, the water cluster signal decreases indicating a reduced water content in a cluster form as the salt concentration increases.

3.2 RbBr core level PES

Spectra from Rb 3*d* and Br 3*d* core levels are shown in Fig. 2 and Fig. 3, respectively. Again, most of the total signal intensity can be associated with the uncondensed RbBr monomer signal. The remainder of the signal is connected to RbBr embedded in water clusters. This was confirmed during the experiment by diverting

Fig. 2 Photoelectron spectra measured from Rb $3d$ region. The estimated mean molal concentration is indicated for each spectrum. Monomer $3d_{5/2,3/2}^{-1}$ peaks originate from the uncondensed RbBr while peak doublets M_1 and M_2 were used to fit the cluster response (see text for details). The spectra are normalized with respect to the monomer Rb $3d_{3/2}^{-1}$ peak. The topmost spectrum illustrates the Rb $3d$ monomer response

Fig. 3 Photoelectron spectra measured from Br $3d$ region. The estimated mean molal concentration is indicated for each spectrum. Monomer $3d_{5/2,3/2}^{-1}$ peaks originate from the uncondensed RbBr while peak doublet X was used to fit the cluster response (see text for details). The spectra are normalized with respect to the monomer Br $3d_{5/2}^{-1}$ peak. The topmost spectrum illustrates the Br $3d$ monomer response

the water cluster beam before it entered the pick-up oven which resulted in a complete loss of the cluster signal (see the topmost reference spectra in Figs. 2 and 3). The spectra are normalized with respect to the Rb $3d_{3/2}^{-1}$ and Br $3d_{5/2}^{-1}$ monomer peaks for easier visual comparison since these peaks have the least overlap with the cluster response.

With increasing salt concentration, the core level cluster response experiences relatively subtle changes which are hard to discern without further analysis. For this reason, the spectra were analyzed using Igor Pro 7 by Wavemetrics together with a least-

squares spectrum fitting package SPANCF^{22,23}. For both Rb and Br $3d$, the pure monomer spectra were fitted using two Voigt profile peaks corresponding to the $j = 5/2$ and $j = 3/2$ spin-orbit split components of the final ionized state. From these fits, the intensity ratios, spin-orbit splitting and Lorentzian widths were used to fit the cluster spectra. Gaussian widths, absolute intensity and absolute energy positions were left as parameters to be optimized by the least-squares algorithm. The Gaussian widths of a given $j = 5/2$ and $j = 3/2$ doublet were linked to have the same value to be optimized. Two peak doublets (labeled M_1 and M_2) for Rb

and one doublet (labeled X) for Br were used. The results are shown in Figs. 2 and 3. The overall fit curve is given by the black continuous curve.

At the most dilute concentrations the Rb $3d$ cluster response displays essentially only one spin-orbit split peak doublet M_1 . With increasing concentration a second peak doublet M_2 arises (see Fig. S1 in Electronic Supplementary Material). This is justified by the fact that the intensity ratio of the spin-orbit components does not change with increasing concentration. We see however that the intensity ratio of peak maxima located at around 115.1 eV and 116.6 eV in the original data changes which points to at least two partially overlapping doublets. We also see that the monomer Rb $3d_{5/2}$ component increases in intensity with respect to monomer Rb $3d_{3/2}$ component at higher concentrations, which indicates presence of an additional overlapping feature. The Gaussian full width at half maximum (FWHM) for M_1 stays constant at around 640 meV until 5.4 mol/kg spectrum. In two of the highest concentration spectra the FWHM monotonously increases up to 1000 meV. The Gaussian FWHM of the second peak doublet M_2 increases over the whole concentration range from 650 meV to 1200 meV monotonously until 5.4 mol/kg spectrum. In the highest concentration spectra, the width of M_2 decreases first to 1100 meV (13 mol/kg spectrum) and then to 830 meV (21 mol/kg spectrum). For comparison, the Gaussian FWHM of the monomer varied between 520 meV and 550 meV depending on the pick-up oven temperature. A more detailed analysis of the chemical shifts and relative intensities of M_1 and M_2 is given later.

Analysis of the Br $3d$ cluster response was not as straight forward. This was mainly due to the heavily overlapping peaks between the cluster and monomer response. Also, any chemical shifts that there might be occur in a narrow binding energy range making the chemical resolution somewhat limited. For this reason, the spectra could be fitted using either one or more peak doublets producing equally good fits. However, when using more than one peak doublet the uncertainty related to physically meaningful fitting results increases. The use of only one peak doublet denoted by X aims at reproducing the overall cluster response while acknowledging that there might be more than one underlying chemical state. Further evidence for this is the decreasing Gaussian FWHM of the peak doublet from about 800 meV to 550 meV as the salt concentration increases. The Gaussian FWHM of the Br $3d$ monomer response was about 440 meV. Also, the chemical shift is inversely proportional to the salt concentration decreasing from around +1.1 eV to +0.7 eV in comparison to the RbBr monomer peaks.

3.3 Anhydrous RbBr clusters

As a reference for the highest concentration spectra, Fig. 4 illustrates Rb $3d$ (upper panel) and Br $3d$ (lower panel) photoelectron spectra measured from anhydrous $(\text{RbBr})_k$ clusters with varying estimated mean size k indicated. These are later used when assigning and evaluating features in the hydrated salt spectra. A comparison of some of the anhydrous cluster spectra with some of the hydrated cluster spectra is included in Fig. S2 of the Electronic Supplementary Material. The overall Rb $3d$ spectrum consist of

the strong monomer signal and the slightly overlapping cluster response. The details of the cluster response are qualitatively similar to those of anhydrous RbCl, CsCl and CsBr clusters^{17,24} and will not be analyzed here in detail.

Briefly, the Rb $3d$ cluster response from RbBr clusters can be broken down to four contributions originating from four different coordination sites in the cluster. As RbBr clusters tend to form a NaCl lattice, ions residing in corner, edge, face and bulk sites of the cluster have coordination numbers 3, 4, 5 and 6, respectively. The observed chemical shift in comparison to the monomer signal depends strongly on the nearest neighbour coordination and thus the individual site contributions can be resolved from the spectra. As the mean cluster size changes, the relative proportions of each site change, thus explaining the changing outlook of the whole cluster response. With larger clusters the second and higher coordination shells differ from each other giving rise to an effective "blurring" of the individual site responses due to small chemical shifts upon the shifts caused by the first shell coordination. There is also a small shift of the site responses as a function of cluster size but the approximate positions of the different coordination sites stay constant and are indicated in the figure. These will be later compared to the peak positions from the hydrated cluster. For further details, the reader is referred to previous publications^{17,24}.

The Br $3d$ response from anhydrous RbBr clusters is qualitatively similar than that found from anhydrous CsBr clusters²⁴. It can be modelled using two peak doublets overlapping with the monomer signal. The origin of the first peak doublet and the visible $j = 5/2$ peak of it denoted by X_1 is still unknown as discussed previously²⁴. It can be observed only in the spectra corresponding to the smallest RbBr clusters. The larger average size RbBr spectra can be fitted with single peak doublet of which the visible $j = 3/2$ component is denoted by X_2 .

4 Cluster composition model

Before discussing the origin and significance of the spectral features presented, it is advantageous to first define the parameters such as the mean cluster size and the salt concentration in the studied clusters more clearly. First, the mean water cluster size is deduced based on spectroscopic data. The amount of salt is then estimated by modelling the pick-up process.

4.1 Estimating water cluster size

There are different ways to estimate the mean cluster size of the initial water cluster size distribution as generated by the supersonic expansion. One of these is based on the scaling parameter approach introduced by Hagena¹⁸ but cannot be used in the present experiment due to the presence of a carrier gas.

A second method to estimate the water cluster size as described by Barth *et al.*²¹ relies on the experimentally derived relation between the valence ionization potential of water clusters and water molecules. The mean water cluster size $\langle n \rangle$ is given by

$$\langle n \rangle = \left(\frac{\Delta G}{\Delta G - \Delta E} \right)^3, \quad (1)$$

Fig. 4 (Upper panel) Rb 3d PES from anhydrous $(\text{RbBr})_k$ clusters with estimated mean cluster size ranging from $k = 14$ to 100. The Rb 3d cluster response can be fitted with 4 doublets, each corresponding to different coordination site for the Rb^+ ion. Approximate $j = 5/2$ peak positions are indicated by the dashed lines. The spectra have been normalized with respect to the $j = 3/2$ component of the monomer signal. (Lower panel) Corresponding Br 3d PES have less cluster features which can be fitted using two peak doublets with X_1 and X_2 denoting the approximate $j = 5/2$ and $j = 3/2$ peak positions of the first and second doublet structure, respectively. Other peaks overlap with the monomer signal

where $\Delta G = 1.4\text{ eV}$ is the Gibbs energy of solvation of a positive charge into a dielectric medium and $\Delta E = E_m - E_c$ is the binding energy difference between the water molecule and water cluster $1b_1$ bands, respectively. This approach can be used even when carrier gas is present in the expansion but due to the cubic dependence the cluster size estimate is very sensitive to ΔE .

The outermost valence band of a water molecule was fitted using peaks derived from a higher resolution spectrum (not shown) as a template. The water cluster response was fitted using two symmetric Gaussian peaks with their weighted average giving the E_c . The size estimation should be done for pure water clusters without any adsorbed species but as such spectra were not measured during the experiment, the lowest concentration spectrum was used for the size estimation. We thus get $\langle n \rangle \approx 100 \pm 50$ ($\Delta E = 1.1\text{ eV}$) when taking into account the uncertainty in the bind-

ing energy determination. In the estimated size range, it has been observed experimentally²⁵ that the water cluster size distribution can be described by an exponential or log-normal distribution.

The corresponding diameter d of the water clusters can be calculated from

$$d = 2r_{ws}n^{1/3}, \quad (2)$$

where $r_{ws} = 1.97\text{ \AA}$ is the water molecule Wigner-Seitz radius calculated from

$$r_{ws} = \left(\frac{3M}{4\pi\rho N_A} \right)^{1/3}, \quad (3)$$

where $\rho = 940\text{ kg m}^{-3}$ is the density of solid amorphous water²⁶, M is the molar mass of water and N_A is the Avogadro constant. With $\langle n \rangle = 100 \pm 50$, the diameter of the mean water cluster size is $(1.8 \pm 0.4)\text{ nm}$.

4.2 Estimating salt concentration

If the number of RbBr monomers picked up by the water cluster k along a path length L through the pick-up oven is small (of the order of unity), it can be estimated using²⁷

$$k = n_g \sigma_p L = \frac{p}{k_B T} \sigma_p L, \quad (4)$$

where n_g is the number density of the dopant species (having vapor pressure p at temperature T), k_B is the Boltzmann constant and σ_p is the effective pick-up cross-section. Lengyel *et al.*²⁷ found for water clusters with $\langle n \rangle = 260$ that the pick-up cross-section σ_p for all the studied dopant molecules is always larger than the geometric cross-section $\sigma_g = \pi r_n^2$, where r_n is the cluster radius. Measurements indicated for example for the pick-up of water molecules on water cluster $\sigma_p/\sigma_g = 2.5$ and for HBr, $\sigma_p/\sigma_g = 1.4$. In general, the pick-up cross section depends on the interaction potential between the cluster and the molecule, the mass of the molecule and the relative velocity between the two²⁷.

When the number of picked up monomers increases beyond unity, each pick-up event alters the likelihood of the next event and the requirement of independence of each event from each other is no longer valid. Pick-up cross section variations can occur due to momentum transfer from the monomer to the host cluster which alters the relative speed of the cluster and picked up species, and due to accommodation of additional species (increased size, interaction potential changes) and possible evaporative cooling (decreased size, interaction potential changes). To what extent these mechanisms contribute (if at all) depends on the details of the experiment. Furthermore, the simple formula (4) does not give any estimate of the terminal number of water molecules present in the cluster at the moment of ionization.

In order to take the above mentioned effects into account, the number of picked up monomers was calculated using an iterative process fundamentally similar to the one described in Ref.¹⁷. Modifications (as described below) were made in order to account for the present cluster beam composition and experimental conditions.

Firstly, the speed of the water cluster beam v_c was calculated

assuming an ideal mixture of He and H₂O using^{28–30}

$$v_c = \sqrt{\frac{2k_B T_n}{\bar{m}} \frac{\bar{\gamma}}{\bar{\gamma} - 1}}, \quad (5)$$

where T_n is the nozzle temperature, $\bar{m} = x_1 m_1 + x_2 m_2$ is the molecular mass of the He/H₂O mixture weighted by the mole fractions x_i of the component gases, and $\bar{\gamma} = \bar{C}_p / \bar{C}_v$ is the weighted specific heat ratio for the mixture where $\bar{C}_p$ is the (weighted) isobaric heat capacity and $\bar{C}_v$ is the (weighted) isochoric heat capacity. The weighed values were calculated as $\bar{C}_p = x_1 C_p^1 + x_2 C_p^2$, where C_p^1 and C_p^2 are the isobaric specific heat capacities of species 1 and 2, respectively. The value of $\bar{C}_v$ was calculated similarly. The following heat capacity values for water and He at 100 °C and 1 bar were used³¹ (in units of J/(mol·K)): $C_p^{\text{H}_2\text{O}} = 37.4105$, $C_v^{\text{H}_2\text{O}} = 27.9867$, $C_p^{\text{He}} = 20.7895$ and $C_v^{\text{He}} = 12.4761$. With the present experimental conditions, the initial water cluster beam speed (before any pick-up) was calculated to be about 1465 m/s which seems reasonable reflecting on previous measured values²⁷.

The distance the water cluster travels into the RbBr vapor filled oven until a pick-up event occurs was calculated as the mean free path ℓ of the cluster

$$\ell = \frac{k_B T}{\sigma_p p} \frac{v_c}{\langle v_r \rangle}, \quad (6)$$

where p is the vapor pressure of RbBr³², T is the pick-up oven temperature and

$$\langle v_r \rangle = \sqrt{v_c^2 + \langle v_m \rangle^2} = \left(v_c^2 + \frac{8k_B T}{\pi m_m} \right)^{1/2} \quad (7)$$

is the mean relative speed between the cluster beam and the RbBr monomer (with mass m_m) having a Maxwellian speed distribution. Instead of using a constant pick-up cross section as in Eq. (4), it was recalculated after each pick-up event from $\sigma_p = f \sigma_g$, where $f = 2.5 \pm 0.5$ is the cross section correction factor. There is no standard and easy way for calculating the geometric cross section σ_g of a cluster consisting of several species, in this case water molecules and two types of ions. One way to model such mixed cluster is to assume it has an overall spherical shape and that the species can be treated as hard spheres packed in a certain geometric configuration. With these assumptions, the geometric cross section σ_g of the cluster can be calculated from

$$\sigma_g = \pi \left(\frac{r_{ws} n + (r_+ + r_-) k}{n + 2k} \right)^2 (n + 2k)^{2/3}, \quad (8)$$

where r_{ws} is the van der Waals radius of water as before, $r_+ = 1.52 \text{ \AA}$ and $r_- = 1.96 \text{ \AA}$ are the effective ionic radii³³ of Rb⁺ and Br[−] ions, respectively, n is the number of water molecules left in the cluster and k is the number of picked up RbBr monomers.

A certain amount of collision energy is released upon the pick-up of RbBr by the water cluster. The monomers carry energy stored in their translational, vibrational and rotational degrees of freedom which is equilibrated with the (cold) water cluster at 50 – 100 K¹¹ upon pick-up. As the temperature is relatively high in the oven, the energy contained in the rotational and vibrational

degrees of freedom can be approximated by $k_B T$, each. Translation gives additional $\frac{3}{2} k_B T$. The collision energy averaged over all angles is then³⁴

$$\langle E_{\text{col}} \rangle = \frac{7}{2} k_B T + \frac{1}{2} \frac{m_m m_c}{m_m + m_c} |\mathbf{v}_c|^2,$$

where m_m and m_c are the masses of the monomer and cluster, respectively, $\mathbf{v}_c$ is the velocity of the cluster beam and T is the pick-up oven temperature (RbBr vapor assumed to be in thermal equilibrium with the oven).

Upon monomer capture, the momentum of the water cluster changes. Momentum conservation was included only in the direction of the cluster beam and the cluster speed after each pick-up event v_f was calculated as

$$v_f = \frac{m_i}{m_f} v_i, \quad (9)$$

where v_i is the speed of the cluster before pick-up and m_i and m_f are the masses of the cluster before and after the pick-up, respectively.

After each pick-up, the RbBr monomer is assumed to be dissolved by the water cluster. Dissolution of alkali halides can be either exothermic or endothermic depending on the salt. For RbBr it is an endothermic process with enthalpy of solvation at room temperature being 21.88 kJ/mol (0.23 eV/monomer)³¹. In the model calculation, it was assumed that the collision energy is used for evaporating water molecules from the cluster after subtracting the energy required to dissolve the RbBr monomer. The binding energy of water molecule to the cluster was assumed to be 480 meV²⁵ which is close to the value that can be calculated from the enthalpy of vaporization for bulk water.

The energetic considerations of the presented model can be regarded as sensible when the ions can be completely hydrated, *i.e.* there are enough water molecules to form at least the first solvation shell. Once the number of water molecules drops below the usually required³⁵ 6–7 per Rb⁺ and Br[−] ion, it becomes increasingly more likely that contact ion pairs are formed and crystallization of RbBr commences. At exactly which point this happens in the low nanometer size system is not known and was left out of the model. Also, any energy which might be associated with the crystallization was not included in the evaluation.

The estimated mean number of picked up monomers $\langle k \rangle$, the number of water molecules n in the cluster after pick-up and the water molecules per ion ratio $\langle h \rangle$ is tabulated in Table 1 together with the calculated molal concentration b . The number of itinerant water molecules n_i gives the amount of water molecules not associated to any ion when assuming that each has a hydration number of 6. This is equivalent to assuming a formation of SSIPs upon RbBr solvation. The uncertainty range in the molal concentration was calculated by varying the pick-up cross section correction factor f between 2.0 and 3.0, and taking into account the RbBr vapor pressure uncertainty of 30 %³². These two factors were seen to have the largest effect on the simulation results.

In the lowest concentration conditions, the mean free path of the water clusters ℓ is much longer than the effective length of the pick-up region L . As the pick-up process is stochastic in nature,

Table 1 Parameters and results of the pick-up process simulation. Pick-up oven temperature T , RbBr vapor pressure p , estimated mean number of picked up RbBr monomers $\langle k \rangle$, number of water molecules in the cluster after pick-up n , number of itinerant water molecules n_i , water molecules per ion $\langle h \rangle$ and calculated molal concentration b

T (°C)	p (mbar)	$\langle k \rangle$	n	n_i	$\langle h \rangle$	b (mol/kg)
465	$1.20 \cdot 10^{-4}$	1	111	99	> 50	0.5 (0.4 – 0.6)
485	$2.85 \cdot 10^{-4}$	1	111	99	> 50	0.5 (0.4 – 0.6)
521	$1.21 \cdot 10^{-3}$	1	100	88	50	0.6 (0.4 – 0.8)
556	$4.35 \cdot 10^{-3}$	3	91	55	15	1.8 (1.2 – 2.5)
588	$1.27 \cdot 10^{-2}$	8	82	-	5.1	5.4 (2.5 – 8.5)
616	$3.05 \cdot 10^{-2}$	18	74	-	2.0	13 (6.9 – 23)
628	$4.36 \cdot 10^{-2}$	26	70	-	1.3	21 (10 – 40)

there is still a finite probability $P \propto (L/\ell)\sigma_p$ that a cluster captures one monomer. Assuming that the water cluster size distribution is log-normal with full width at half maximum equal to the mode of the distribution ($\langle n \rangle = 100$), the water cluster size mostly present in the beam with single monomer captured is 111. The first three conditions reflect a very dilute system where mostly a single monomer resides in the water cluster and plenty of water molecules per ion are present. In these conditions the mean water cluster size defines the lowest molal concentration reachable.

At higher pick-up oven temperatures, even the average size water cluster has the possibility to collect multiple RbBr monomers. Thus, the spectra measured at $b = 1.8 - 5.4$ mol/kg correspond to intermediate concentration before gradual saturation of the water cluster. The last two or three most concentrated conditions reflect quite likely a saturated or supersaturated state based on the comparison to the molal concentration of 5.45 mol/kg of a saturated aqueous RbBr solution at 0 °C³¹. In the last two conditions the average number of water molecules per ion is so low that significant ion association is likely to occur.

5 Discussion

Turning back to the experimental results we can compare the just derived salt concentrations to the spectral characteristics. As mentioned in the introduction, ion pairing has been observed to increase as a function of concentration in bulk aqueous solutions. A bulk RbBr solution study³⁶ using EXAFS indicated that some CIP formation was evident starting from 4 mol/kg solution with linear dependence on the concentration. Extrapolation to lower concentrations suggested that no ion pairs should be present below 2 mol/kg. In 6 mol/kg solution the average CIP coordination was found^{36,37} to be around 0.8 meaning that, on average, only simple ion pairs are formed. In saturated solution ($b = 7.02$ mol/kg) the average CIP coordination increased to 1.8 indicating the presence of not only ion pairs but small ion clusters.

The present experimental results cover a wide range of concentrations. In the most dilute conditions only a single RbBr monomer resides in the water cluster while in the most concentrated solution for every ion there is on average 1.3 water molecules. Starting from the former case, the fact that the water cluster valence band intensity in Fig. 1 shows only slight decrease in the first three concentration points indicates that the water cluster beam is relatively unaffected by the pick-up process. The simulations suggest only a single monomer is captured which is not able to cause large amount of water evaporation from the

Fig. 5 Chemical shifts of the hydrated cluster response peak doublets M_1 (green), M_2 (blue) and X (purple) as a function of salt concentration. The dashed red lines between -1.1 eV and -2.8 eV indicate the chemical shifts of 3–6 fold coordinated Rb^+ ions in anhydrous RbBr clusters for comparison. The dot-dashed red line at $+0.65$ eV is the approximate chemical shift of the Br $3d$ cluster response in the larger anhydrous RbBr clusters

water cluster.

The Rb $3d$ core level in the dilute concentrations displays mostly the doublet structure M_1 , corresponding to single chemical state. This is logical if the Rb^+ ion resides predominantly in the bulk of the cluster as has been observed in the case of aqueous RbBr solutions⁶. One can also compare the chemical shift value of M_1 to other shift values recorded for Rb^+ ion in various environments. Figure 5 shows the chemical shifts derived from the present data for doublets M_1 , M_2 and X , but also includes the approximate chemical shifts of the various coordination sites as obtained from the anhydrous RbBr clusters (see Fig. 4) denoted by horizontal dashed and dot-dashed lines. We thus see that the M_1 shift occurs in the middle of the 5 and 6 coordinated Rb^+ and stays relatively constant as the concentration increases. Although one can fit two closely separated Voigt profiles (corresponding to two chemical states) using only a single, wider Voigt profile, we have no reason to suspect the presence of more than a single chemical state as the width of M_1 peaks are very close to the monomer peak widths (see section 3).

Corresponding Br $3d$ spectra in the dilute conditions tell a different story however. The cluster response peaks X are twice as wide as the monomer peaks which could be indicative of two (or more) chemical states. One possibility based on earlier literature^{6,8} is that the Br^- is present either in the surface of the water

Fig. 6 Relative fractions of Rb 3d responses M₁ (green) and M₂ (blue) as derived from the peak areas. A constant ± 5 percentage point uncertainty was assumed

cluster (less coordinated state) or in the subsurface or bulk layers (more coordinated state) while the Rb⁺ is located preferentially in the bulk of the cluster. The RbBr would thus exist as a solvent-separated ion pair (SSIP) in these dilute concentrations.

With increasing concentration, peak doublet M₂ in Rb 3d becomes more pronounced. Based on bulk solution studies^{36,37} and composition analysis one arrives at a conclusion that M₂ originates from increasing SIP and CIP formation within the water cluster. At the highest concentrations and upon re-crystallization, M₂ and M₁ represent the 3–4 and the 5–6 coordinated sites, respectively. According to Table 1, the estimated mean number of RbBr monomers in the final spectrum was 26. Comparing this “wet” cluster spectrum with the anhydrous RbBr cluster spectrum with estimated mean cluster size of 24 monomers, the latter shows more fine structure. The presence of water could hamper the chemical resolution in the “wet” spectrum as the structure is more amorphous compared to highly ordered crystal without water. With increasing concentration, the chemical shift of peak doublet X from Br[−] becomes almost identical with that recorded from anhydrous clusters as seen from Fig. 5. We regard this as an additional sign of ion pairing and/or crystallization.

Figure 6 displays the fraction of cluster signal originating from either M₁ or M₂ in Rb 3d region. The 0.5 mol/kg data point is an average of the two available ones (see Table 1). Below 1.8 mol/kg the fraction of M₂ stays relatively constant at around 10%. Beyond this concentration, it increases to 35–40% of the total cluster response indicating increased ion pair formation. Indeed, two of the highest concentration spectra are qualitatively identical to the anhydrous cluster spectra. As a reference, the expected area ratio for spectral features similar to M₁ and M₂ in anhydrous RbBr clusters with NaCl structure and mean size of 22 monomers is approximately 40:60 (M₁:M₂)^{17,24}.

In order to gain more information about the observed chemical shifts and assignment of different spectral features, we performed a small set of quantum chemical calculations using the Orca software³⁸. The calculations included estimations of core shell binding energy shifts between RbBr monomer and RbBr-(H₂O)_n clusters. The simulations were done by surrounding the RbBr

monomer with *n* randomly oriented H₂O molecules. The system was then optimized using DFT with B3LYP^{39,40} functional and def2-TZVP^{41,42} basis sets utilizing RIJCOSX⁴³ method for two-electron Coulomb integrals. Binding energy shifts were calculated using Hartree-Fock method with the same basis set from the optimized structures using the relaxation potential model (RPM) (see, e.g. Refs.^{17,44,45} and references therein). In RPM, the shift is taken as the difference in the potentials between the bare monomer potential and the potential of the monomer surrounded by H₂O molecules with an additional factor that accounts for relaxation of the wave function in the ionic state. Further details about RPM can be found from Refs.^{17,44,45}.

The simulated RbBr-(H₂O)_n clusters consisted of one RbBr monomer surrounded by 10, 20 or 30 water molecules. The concentrations thus varied between 1.9 mol/kg and 5.5 mol/kg. In all calculation runs the Br[−] ion assumed a position located on the surface of the cluster while the Rb⁺ ion surrounded itself with more water molecules inside the cluster. Averaged over all concentrations, the chemical shift for the Br[−] ion was $(+1.4 \pm 0.4)$ eV and (-2.2 ± 0.3) eV for the Rb⁺ ion. With changing concentration the shift values varied but not in a monotonous way. The Rb–Br separation monotonously increased from 4.5 Å to 8.4 Å with increasing system size which can be compared to the calculated gas phase monomer value of 3.1 Å. Noteworthy is that even though the separation between ions increased with increasing cluster size, the chemical shift did not change monotonously.

Comparison chemical shift calculations were also performed where only either Rb⁺ or Br[−] ion was placed together with 10 water molecules. The missing counter ion resulted in a sign change of the chemical shift (with respect to RbBr monomer) with -2.0 eV for Br[−] and $+1.2$ eV for Rb⁺. It is thus expected that changes in the stoichiometric ratio of ions would be reflected in the chemical shift values.

The present chemical shift calculations are in tentative agreement with the experimental results. We could not however confirm the origin of the spectral features M₁ and M₂. As the modeled clusters were smaller than those estimated to be present in the experiment, cluster size effects on chemical shifts are likely to be present.

6 Conclusions

In the present work, solvation of RbBr in water clusters was studied as a function of RbBr concentration using photoelectron spectroscopy and small set of quantum chemical simulations. The calculations suggest that the spectral features seen in the dilute concentration (< 1.8 mol/kg) belong to solvated RbBr with the Br[−] being closer to the surface layer. At higher concentration (≥ 1.8 mol/kg) we interpret the appearance of a second spectral feature in Rb 3d spectrum as indicating the onset of ion pairing. Based on recent results (see Refs.^{37,46} and references therein) concerning Rb halide solvation in bulk water, we may speculate that the formed ion pairs are mostly of the CIP type rather than SIP or SSIP due to the low charge density of the related monovalent ions (Rb⁺ and Br[−]). Direct experimental or computational evidence in the present case is however lacking. Pinpointing the saturation concentration is not possible due to limited number of

concentration data points but is expected to happen somewhere at or beyond 5.4 mol/kg.

Overall, we see no clear evidence of solvation behaviour which would differ drastically from bulk solution results^{31,36,37}. This even though water clusters quite likely present a different type of environment for the salt ions in terms of *e.g.* temperature and structure¹¹. We cannot however rule out the possibility that such differences arise as models and assumptions used to describe for example the pick-up process, solvation and different spectral features are refined. This presents a considerable quantum chemical and experimental problem for the future.

The work demonstrated that information about the solubility of an alkali halide compound into freestanding sub-2 nm water clusters can be obtained. This opens up new possibilities for studies requiring nanoscale matter such as atmospheric ultrafine particle research. Although the present alkali halide sample (RbBr) has no direct environmental significance, extension of the research into properties of more relevant compounds (such as NaCl, KCl, *etc.*) is straight forward.

Conflicts of interest

There are no conflicts of interest to declare.

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