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The hydration number of Na^+ in liquid water

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An ‘ab initio’ molecular dynamics simulation of a Na^+ ion in aqueous solution is presented and discussed. The calculation treats a Na^+ ion and 32 water molecules with periodic boundary conditions on a cubic volume determined by an estimate of zero partial molar volume for this solute in water at normal density and at a temperature of 344 ± 24 K. Analysis of the last half of the 12 ps trajectory shows 4.6 water molecules occupying the inner hydration shell of the Na^+ ion on average, with 5 being the most probable occupancy. The self-diffusion coefficient observed for the Na^+ is $1.0 \times 10^{-5} \text{ cm}^2/\text{s}$. The quasi-chemical theory of solutions provides the framework for two more calculations. First a complementary calculation, based on electronic structure results for ion-water clusters and a dielectric continuum model of outer sphere hydration contributions, predicts an average hydration shell occupancy of 4.0. This underestimate is attributed to the harmonic approximation for the clusters in conjunction with the approximate dielectric continuum model treatment of outer sphere contributions. Finally, a maximum entropy fitting of inner sphere occupancies that leads to insensitive composite free energy approximations suggests a value in the neighborhood of -68 kcal/mol for the hydration free energy of $\text{Na}^+(\text{aq})$ under these conditions with no contribution supplied for packing or van der Waals interactions.

keywords: ab initio molecular dynamics, dielectric continuum, electronic structure, hydration, information theory, quasi-chemical theory, sodium ion

I. INTRODUCTION

Solvation of simple ions in aqueous solution is not yet fully understood despite its fundamental importance to chemical and biological processes. For example, disagreement persists regarding the hydration number of the Na^+ ion in liquid water. A pertinent problem of current interest centers on the selectivity of biological ion channels; it seems clear that the selective transport of K^+ relative to Na^+ ions in potassium channels[1, 2, 3] depends on details of the ion hydration that might differ for K^+ relative to Na^+ .

Experimental efforts to define the hydration structure of $\text{Na}^+(\text{aq})$ using diffraction[4, 5] and spectroscopic[6] methods produce a hydration number ranging between four and six[7]. Simulations have obtained a range of values, but most predict six water molecules in the inner hydration sphere of the Na^+ ion[8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19]. An ‘ab initio’ molecular dynamics simulation produced five inner shell water molecules neighboring $\text{Na}^+(\text{aq})$ [20].

An important limitation of theoretical studies of ion hydration concerns the sufficiency of model force fields used in classical statistical mechanical calculations. In the most customary approaches, interatomic force fields used in theories or simulations derive from empirical fits of a parameterized model to a variety of experimental data. ‘Ab initio’ molecular dynamics avoids this intermediate modeling step by approximate solution of the electronic Schrödinger equation for each configuration of the nuclei[21, 22]. This technique thus goes significantly beyond conventional simulations regarding the accuracy of the force fields. It also augments theories built more directly on electronic structure studies of ion-water complexes by adopting approx-

imate descriptions of the solution environment of those complexes[23, 24, 25, 26, 27, 28].

Relative to conventional simulations, ‘ab initio’ molecular dynamics simulations also have some important limitations due to the high computational demand. Applications of the method have been restricted to small systems simulated for short times. For example, an ‘ab initio’ molecular dynamics study[20] of the $\text{Na}^+(\text{aq})$ ion comparable to the present work obtained a thermal trajectory lasting 3 ps after minimal thermal aging. The present work, though still limited to relatively small systems, pushes such calculations to longer times that might permit more precise determination for $\text{Na}^+(\text{aq})$ of primitive hydration properties. The analysis here utilizes the last half of a 12 ps thermal trajectory. The quasi-chemical theory[23, 24, 25, 26, 27] and separate electronic structure calculations on $\text{Na}(\text{H}_2\text{O})_n^+$ complexes assist in this analysis.

II. METHODS

The system consisted of one Na^+ ion and 32 water molecules in a cubic box with edge 9.86518 Å and periodic boundary conditions. The dimensions of the box correspond to a water density of 1 g/cm^3 and zero partial molar volume for the solute. Initial conditions were obtained as in an earlier ‘ab initio’ molecular dynamics simulation on $\text{Li}^+(\text{aq})$ [23]. In that earlier work, an optimized structure for the inner sphere $\text{Li}(\text{H}_2\text{O})_6^+$ complex was equilibrated with 26 water molecules under conventional simulation conditions for liquid water, utilizing a current model force field and assuming a partial molar volume of zero. In the present calculation, the same pre-equilibrated system was used as an initial configuration

for the ‘ab initio’ molecular dynamics except that an optimized structure for the inner sphere $\text{Na}(\text{H}_2\text{O})_6^+$ complex replaced the hexa-coordinated Li^+ structure. Constant pressure or constant water activity simulations, defined by intensive rather than extensive variables, probably would produce a more useful characterization of the solvent thermodynamic state for these small systems, but those alternatives are currently impractical.

Molecular dynamics calculations based upon a gradient-corrected electron density functional description of the electronic structure and interatomic forces were carried out on this $\text{Na}^+(\text{aq})$ system utilizing the VASP program[29]. The ions were represented by ultrasoft pseudopotentials[30] and a kinetic energy cutoff of 31.5 Rydberg limited the plane wave basis expansions of the valence electronic wave functions. The equations of motion were integrated in time steps of 1 fs, which is small enough to sample the lowest vibrational frequency of water. A thermostat constrained the system temperature to 300 K during the first 4.3 ps of simulation time. After removing the thermostat, the temperature rose slightly and then leveled off by 6 ps to an average of 344 ± 24 K. During the simulation, the initial $n=6$ hydration structure relaxed into $n=4$ and $n=5$ alternatives, such as those shown in Fig. 1. All analyses reported here rely on the trajectory generated subsequent to the 6 ps of aging with the system at a temperature elevated from room temperature.

III. RESULTS

The ion-oxygen radial distribution function is shown in Fig. 2. The first maximum occurs at a radius of 2.35 Å from the Na^+ ion and the minimum at radius 3.12 Å demarcates the boundary of the first and innermost hydration shell. An average of $\langle n \rangle = 4.6$ water molecules occupy the inner hydration shell. Fig. 3 tracks the instantaneous number of water oxygen atoms found within the first hydration shell of the Na^+ , defined by radius $r \leq 3.12$ Å for the upper panel. The fractions x_4 and x_5 of four-coordinate and five-coordinate hydration structures, respectively, constitute $x_4=40\%$ and $x_5=56\%$ of the last 6 ps of the simulation. Structures in which the Na^+ ion acquires six innershell water molecules occur with a 4% frequency, while structures with three and seven innershell water molecules occur less than 1% of the time. Analysis of the mean-square displacement of the Na^+ ion (Fig. 4) produces a self-diffusion constant of $1.0 \times 10^{-5} \text{ cm}^2/\text{s}$, which agrees reasonably well with an experimental result of $1.33 \times 10^{-5} \text{ cm}^2/\text{s}$ [31].

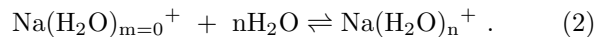
These results correspond coarsely with an ‘ab initio’ molecular dynamics calculation on this system carried-out independently[20]. The most probable inner shell occupancy found there was also five, but the probabilities of $n=4$ and $n=6$ were reversed from what we find here. This difference may be associated with the lower temperature used in Ref [20].

One motivation for this study arises from the quasi-chemical theory of solutions. According to this formulation, x_0 contributes a ‘chemical’ contribution to $\mu_{\text{Na}^+}^{\text{ex}}$, the excess chemical potential or absolute hydration free energy of the ion in liquid water[27],

$$\beta \mu_{\text{Na}^+}^{\text{ex}} = \ln x_0 - \ln \left[\left\langle e^{-\beta \Delta U} \prod_j (1 - b_{\text{Na}^+j}) \right\rangle_0 \right]. \quad (1)$$

Here the inner shell is defined by specifying a function b_{Na^+j} that is equal to one (1) when solvent molecule j is inside the defined inner shell and zero (0) otherwise; ΔU is the interaction energy of the solvent with the solute Na^+ that is treated as a test particle, $\beta^{-1} = k_B T$, and the subscript zero associated with $\langle \dots \rangle_0$ indicates a test particle average [27]. The second term on the right-hand side of Eq. (1) is the excess chemical potential of the solute lacking inner shell solvent molecules whereas the first term is the free energy of allowing solvent molecules to occupy the inner shell. The validity of Eq. (1) has been established elsewhere[27]. The second term on the right of Eq. 1 is the outer sphere contribution to the excess chemical potential in contrast to the first or chemical term.

The utility of this quasi-chemical formulation is the suggestion[32] of more detailed study of the x_n , the fractions of n -coordinate hydration structures found in solution, on the basis of the equilibria forming inner shell complexes of different aggregation number:



Utilizing the chemical equilibrium ratios

$$K_n = \frac{\rho_{\text{Na}(\text{H}_2\text{O})_n^+}}{\rho_{\text{H}_2\text{O}}^n \rho_{\text{Na}(\text{H}_2\text{O})_{m=0}^+}}, \quad (3)$$

the normalized x_n can be expressed as

$$x_n = \frac{K_n \rho_{\text{H}_2\text{O}}^n}{\sum_{m \geq 0} K_m \rho_{\text{H}_2\text{O}}^m}. \quad (4)$$

The ρ_σ are the number densities and, in particular, $\rho_{\text{H}_2\text{O}}$ is the molecule number density of liquid water. If the medium external to the clusters is neglected, the equilibrium ratios, denoted as $K_n^{(0)}$, can be obtained from electronic structure calculations on the complexes, assuming for the thermal motion of the atoms the harmonic approximation evaluated at the calculated minimum energy configuration. Finally utilization of a dielectric continuum approximation for the outer sphere contributions to the chemical potential gives a natural, though approximate, quasi-chemical model[23, 24, 25, 26, 27, 28].

For the present problem, the quasi-chemical approximation was implemented following precisely the procedures of the earlier study of $\text{Li}^+(\text{aq})$ [23], except that the sodium ion cavity radius for the dielectric model calculation was assigned as $R_{\text{Na}^+} = 3.1$ Å, the distance of

the first minimum of the radial distribution function of Fig. 2. The temperature and density used were 344 K and 1.0 g/cm³ and the value of the bulk dielectric constant was 65.3[34].

Results of the calculations are summarized in Fig. 5. The electronic structure results are consonant with those found previously for the Li⁺ ion. The n=4 inner sphere gas-phase complex has the lowest free energy. Although outer sphere placements are obtained for additional water molecules in the minimum energy structures of larger clusters, attention is, nevertheless, here restricted to inner sphere structures. The mean occupation number predicted by this quasi-chemical model is $\langle n \rangle = 4.0$; the computed absolute hydration free energy of the Na⁺ ion under these conditions is -103 kcal/mol, not including any repulsive force (packing) contributions. An experimental value for Na⁺ ion in liquid water at room temperature is -87 kcal/mol[35].

Because of the significance of x_0 [Eq. 1], we fitted several model distributions $\{x_n\}$ based on different ideas to the ‘ab initio’ molecular dynamics results. The varying success of those models in inferring x_0 was enlightening. An instructive selection of those models is shown in Fig. 6 and we describe those results here.

First, we note that though the preceding quasi-chemical approximation does not agree closely with the ‘ab initio’ molecular dynamics simulation, the populations obtained from the quasi-chemical approximation, \hat{x}_n , can serve as a default model for a maximum entropy inference of x_n [32]. In this approach we model

$$\ln x_j = \ln \hat{x}_j - \lambda_0 - j\lambda_1 - j(j-1)\lambda_2/2 - \dots, \quad (5)$$

with Lagrange multipliers λ_k adjusted to conform to available moment information

$$\left\langle \binom{n}{j} \right\rangle = \sum_k x_k \binom{k}{j} \quad (6)$$

for $j = 0, 1, 2, \dots$. In view of the limited data available, use of more than two moments produced operationally ill-posed fitting problems.

One difficulty with this specific approach is that the ‘ab initio’ molecular dynamics produced $x_7 > 0$ in contrast to the electronic structure methods that found no minimum energy hepta-coordinated inner-sphere clusters. Since the observed x_7 is likely to be relatively less accurate and is furthest away from the desired $n=0$ element, we excluded $n=7$ configurations of the ‘ab initio’ molecular dynamics, renormalized the probabilities x_n , and recalculated the moments. As the upper panel in Fig. 6 shows, this simple maximum entropy model is qualitatively satisfactory although not quantitatively convincing. The fitted model significantly disagrees with the observed x_3 . The chemical contribution suggested by Fig. 6 is approximately -70 kcal/mol. Using the Born formula, $-q^2(1 - 1/\epsilon)/2R$ with $R=3.12$ Å, to estimate the outer sphere contributions represented by the last term in Eq. 1, then the net absolute hydration free energy falls

in the neighborhood of -115 kcal/mol. Since experimental values for the absolute hydration free energy at room temperature center around -90 kcal/mol, this comparison shows that the present free energy results are not to be interpreted quantitatively, but rather as indicative of the present state of the theory.

A second approach focused on testing a default model that supplies a nonzero \hat{x}_7 ; we used the Gibbs default model $\hat{x}_n \propto 1/n!$ that would give the correct answer for an ideal gas ‘solvent.’ This model has the additional and heuristic advantage of being significantly broader. Our experience has been that these maximum entropy fitting procedures work better when the default model is broader than the distribution sought. The results, illustrated in the middle panel of Fig. 6, show an improved fit. Here the chemical contribution to the free energy is -23 kcal/mol, yielding a net absolute hydration free energy of -68 kcal/mol when the same Born formula is used to estimate the outer sphere contributions.

A third fitting possibility was based on a suggestion from a previous ‘ab initio’ molecular dynamics calculation on K⁺(aq): that the innermost *four* water molecules have a special status[36]. In fact, the quasi-chemical approximation above and the fitting of the upper panel of Fig. 6 suggests also that the x_n results for $n \leq 4$ and for $n \geq 5$ display different behaviors. The radial distribution function of Fig. 2, somewhat better resolved than heretofore, is relevant to this issue and, in contrast, doesn’t directly support a hypothesis of two populations of water molecules in the inner shell. Nevertheless, that $g(r)$ does not rule out the possibility that the structures might become more flexible as the inner shell nears maximum capacity with lower incremental binding energies.

To clarify these possibilities, we reduced the radius defining the inner sphere to $R=2.68$ Å, for which $\langle n \rangle$ is close to 4 (see bottom panel of Fig. 2) and reanalysed the ‘ab initio’ molecular dynamics trajectory to extract the appropriate alternative moment information. Again using the Gibbs default model, we obtained the results shown in the lowest panel of Fig. 6. The inferred chemical contribution is $RT \ln x_0 \approx -13$ kcal/mol. Using again the Born approximation for the outer sphere contribution, this time with $R=2.68$ Å, we obtain an absolute hydration free energy estimate of -65 kcal/mol.

The insensitivity of these latter results to choice of inner sphere radius deserves emphasis and further discussion. From a formal point of view, the inner sphere radius R serves only a bookkeeping role; the left side of Eq. 1 should be strictly unaffected by changes in R . Nevertheless, the terms on the right side of that equation are individually affected by changes in R . Thus, we might take the insensitivity of the sum of those individual terms as an indication that the inevitable approximations are reasonably balanced. Values of R for which the sum Eq. 1 is insensitive are pragmatic values given the approximations made. Fig. 7 illustrates these points and establishes the pragmatic value $R \approx 3.06$ Å for the current application. The similarity of this value with the radius of the inner

shell suggested by Fig. 2 (3.12Å) is encouraging. The value -68 kcal/mol is then suggested for the hydration free energy in the absence of any account of packing or van der Waals interactions.

IV. CONCLUSIONS

The ‘ab initio’ molecular dynamics simulation predicts the most probable occupancy of the inner shell of $\text{Na}^+(\text{aq})$ to be 5 and the mean occupancy to be 4.6 water molecules at infinite dilution, $T=344$ K, and a nominal water density of 1 g/cm^3 . The simulation produces both a satisfactory Na-O radial distribution function and self-diffusion coefficient for Na^+ , but these satisfactory results required more care with thermalization and averaging time than is most common with these demanding calculations. Recently, this point has been separately emphasized in the context of ‘ab initio’ simulation of water[38].

The complementary calculation framed in terms of quasi-chemical theory based on electronic structure results for ion-water clusters, the harmonic approximation for cluster motion, and a dielectric continuum model for outer sphere contributions underestimates the inner shell water molecule occupancies for Na^+ in liquid water. Maximum entropy fitting of the inner shell occupancy distribution shows that the ion-water cluster results yield a distribution significantly narrower than that

obtained from the simulations. For this reason, naive inference of the absolute hydration free energy of $\text{Na}^+(\text{aq})$ based on the cluster electronic structure results and utilizing information gleaned from the ‘ab initio’ molecular dynamics was unsuccessful. The electronic structure calculations found minimum energy $\text{Na}(\text{H}_2\text{O})_7^+$ clusters only with obvious outer sphere placements of some water molecules though hepta-coordinate inner sphere clusters were observed in the ‘ab initio’ molecular dynamics with the most natural cluster definition. These results suggest that the anharmonicities and large amplitude motion are serious concerns, particularly for the larger clusters, and that the approximate theory utilized for outer sphere contributions must treat cluster conformations differently from minimum energy structures of the isolated clusters.

Abandonment of the cluster electronic structure results in favor of a broader default model improved the modeling of the x_n distribution on the basis of the information extracted from the simulation. A sequence of more aggressive fits eventually suggested the value -68 kcal/mol for the hydration free energy at this somewhat elevated temperature on the basis of the quasi-chemical perspective of inner sphere occupancies but in the absence of any account of packing or van der Waals interactions.

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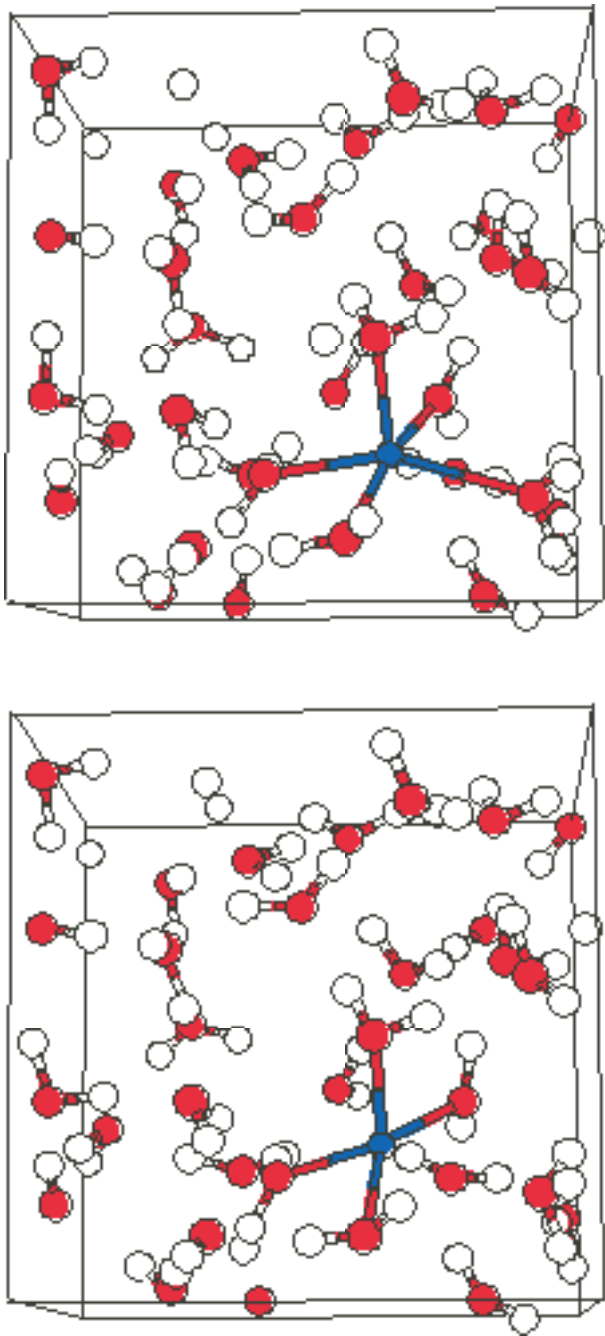


FIG. 1: Structures from ‘ab initio’ molecular dynamics calculations. In the top panel, the Na^+ ion has five (5) inner shell water molecule neighbors. The bottom panel shows the four-coordinate structure produced 70 fs later. The bonds identify water oxygen atoms within 3.1 Å of the Na^+ ion. The hydrogen, sodium, and oxygen atoms are shown as open, black, and gray circles, respectively.

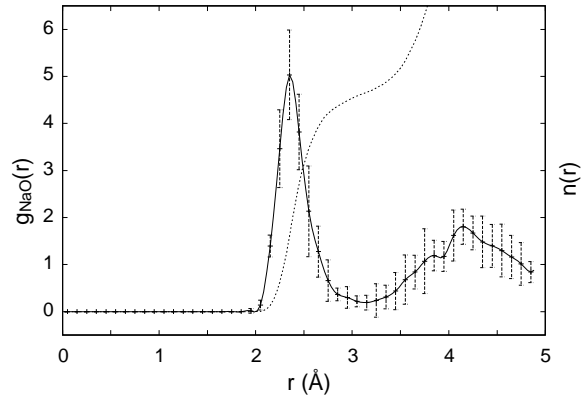


FIG. 2: Radial distribution function $g_{\text{NaO}}(r)$ and number $n(r)$ of oxygen atoms neighboring the Na^+ ion. Error estimates of $\pm 2\sigma$ are also plotted for the radial distribution function. σ was estimated by dividing the observed trajectory into four blocks of approximate duration 1.5 ps; those blocks were assumed to provide independent observations. The first minimum in the $g(r)$ function is at $r=3.12$ Å where $g(r)$ falls to 0.2. Here an average of 4.6 oxygen atoms surround the Na^+ ion.

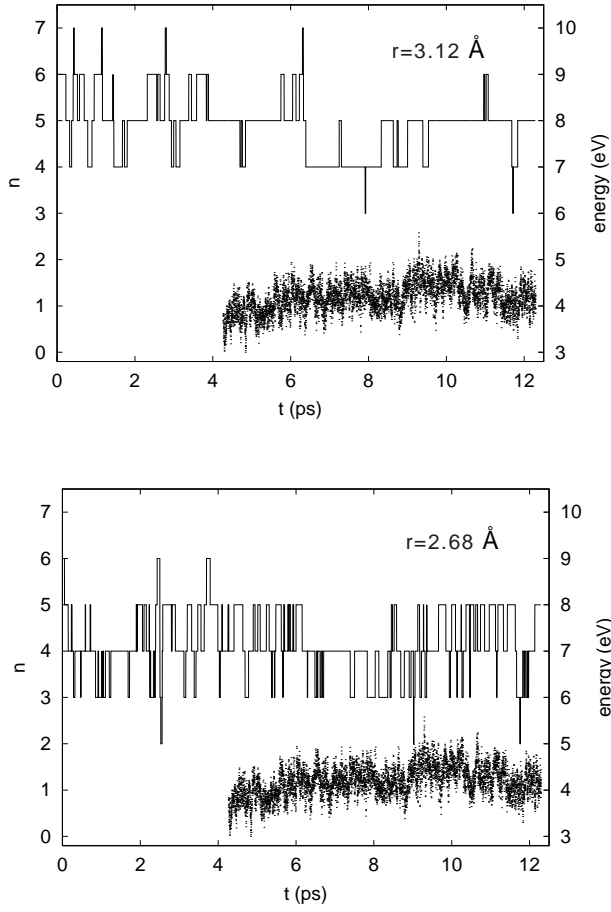


FIG. 3: The solid line in the upper plot depicts the number of oxygen atoms within a radius of 3.12 \AA from the Na^+ at each configuration in the molecular dynamics simulation. A radius of 2.68 \AA defines the nearest oxygen neighbors in the lower plot. The dashed lines show the kinetic energy per atom during the simulation, plotted after removal of the 300 K thermostat at 4.3 ps. The axis on the right refers to the kinetic energy values. In the upper plot, an average of 4.6 water molecules surround the Na^+ ion, while an average of 4.0 water molecules surround the ion in the lower plot.

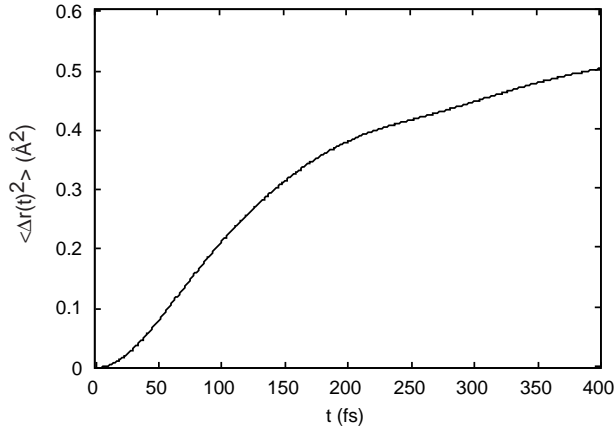


FIG. 4: Mean-square displacement of the Na^+ ion plotted with respect to the time interval analyzed. Analysis of the slope from 200-400 ps gives a diffusion constant of $1.0 \times 10^{-5} \text{ cm}^2/\text{s}$.

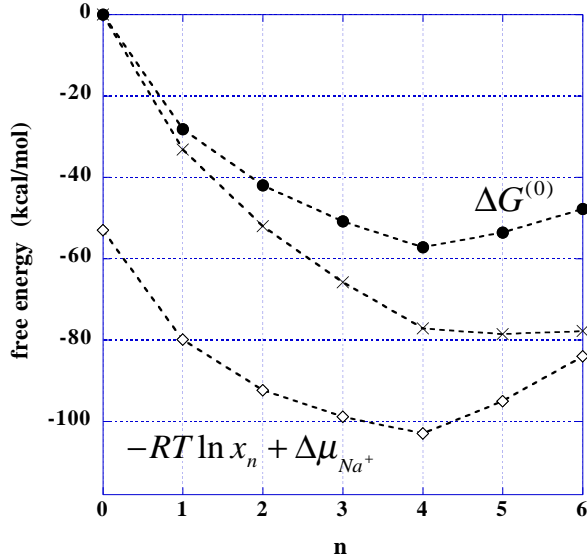


FIG. 5: Free energies for Na^+ ion hydration in liquid water as a function of the number of inner shell water neighbors at $T=344 \text{ K}$ and $\rho_{\text{H}_2\text{O}}=1 \text{ g/cm}^3$. The lowest results (open diamonds) show quasi-chemical approximate values for the liquid, labelled according to the quasi-chemical interpretation. This graph indicates that the $n=4$ inner sphere structure is most probable under these conditions. The radius used for the Na^+ ion here is 3.1 \AA , though a substantial reduction of this value produced only a minor change in the inferred absolute hydration free energy; otherwise the procedure is the same as in previous reports[23, 27]. The absolute hydration free energy predicted here is -103 kcal/mol . The results marked $\Delta G^{(0)}$ (filled circles) are the free energies predicted for the reaction $\text{Na}^+ + n \text{ H}_2\text{O}$ in an ideal gas at $p = 1 \text{ atm} \equiv \bar{p}$ and $T=344 \text{ K}$. The minimum value is at $n=4$. The middle graph (crosses) add to the ideal gas results the ‘replacement’ contribution reflecting the formal density of the water molecules $-nRT \ln [RT\rho_{\text{H}_2\text{O}}/\bar{p}] = -n * 5.03 \text{ kcal/mol}$ with $T=344 \text{ K}$, and $\rho_{\text{H}_2\text{O}} = 1 \text{ g/cm}^3$.

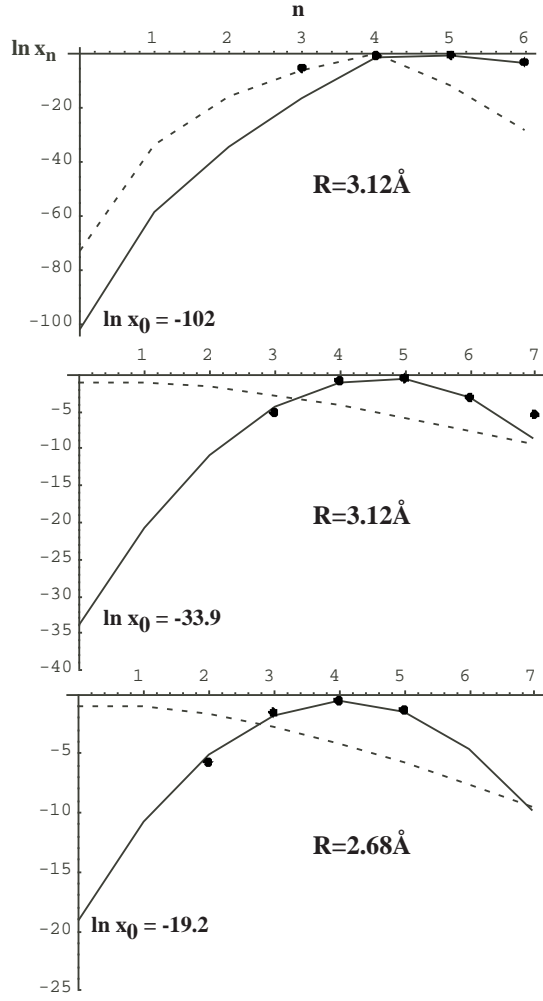


FIG. 6: Results for the inference of x_0 from ‘ab initio’ molecular dynamics information. The solid points represent the information extracted from the molecular dynamics simulation, the dotted lines are the default models, and the solid lines show the fit achieved by the information theory approach. In the top panel, the hepta-occupancy was excluded, the probabilities were renormalized on this condition, and the quasi-chemical default model was used together with the moments $\langle n \rangle = 4.633$ and $\langle n(n-1)/2 \rangle = 8.577$. In the middle panel, all x_n observed in the simulation were included, $\langle n \rangle = 4.642$ and $\langle n(n-1)/2 \rangle = 8.624$, and the ideal gas (or Gibbs default) model was used along with the same moments as above. The bottom panel shows the results using the inner sphere radius $R = 2.68 \text{ \AA}$ and the moments $\langle n \rangle = 4.046$, and $\langle n(n-1)/2 \rangle = 6.393$ with the Gibbs default model.

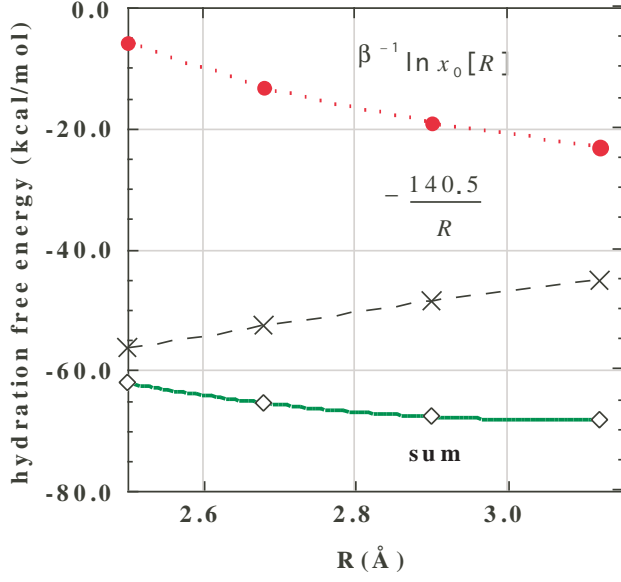


FIG. 7: Variation of hydration free energy contributions with changes in radius R defining the inner sphere. The upper curve is the chemical contribution obtained with an information theory fit using a Gibbs default. The middle curve is the outer sphere contribution approximated by the Born formula for a spherical ion with unit charge at its center. The bottom curve is the sum of the other two. The slope of the bottom curve is zero at $R \approx 3.06 \text{ \AA}$. As discussed in the text, this value identifies a R -region for which the approximations used are pragmatically balanced. The curve takes the value -68 kcal/mol in that region.