Monte Carlo studies of the structure of dilute aqueous solutions of Li^+, Na^+, K^+, F^-, and Cl^-

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Monte Carlo–Metropolis statistical thermodynamic computer simulations are reported for dilute aqueous solutions of Li^+, Na^+, K^+, F^-, and Cl^-. The calculations are carried out on systems consisting of one ion and 215 water molecules at 25 °C and experimental densities. The condensed phase environment is modeled using periodic boundary conditions. The configurational energies are developed under the assumption of pairwise additivity by means of potential functions representative of nonempirical quantum mechanical calculations of the ion–water and water–water energies. The internal energies, radial distribution functions, and related thermodynamic properties are calculated for each system. The structure of the local solution environment around each dissolved ion is analyzed in terms of quasicomponent distribution functions. The results are compared with analogous calculations on a smaller system to estimate the effect of long-range forces in the ion–water potential function on the calculated results.

I. INTRODUCTION

The particular significance of electrolytes in solution chemistry and the role of ion hydration in diverse chemical and biochemical processes combine to make the structure of dilute aqueous solutions of ions a topic of fundamental scientific interest. Recent progress in molecular quantum mechanics, statistical thermodynamics, and computer technology have made studies at improved levels of rigor possible for these systems.[1] While approximations in the description of the interparticle interactions and in the general treatment of the problem in liquid state theory must still be introduced, a significantly improved theoretical description of the systems can still be obtained. The results of these calculations serve to quantify the structural chemistry of ionic solutions at the molecular level and allow the prevalent qualitative concepts about aqueous hydration to be critically examined.

We report herein Monte Carlo–Metropolis statistical thermodynamic computer simulations for dilute aqueous solutions of Li^+, Na^+, K^+, F^-, and Cl^-. The calculations are carried out on systems consisting of one ion and 215 water molecules at 25 °C and experimental density. The condensed phase environment is modeled using periodic boundary conditions. The configurational energies are developed under the assumption of pairwise additivity by means of potential functions representative of nonempirical quantum mechanical calculations of the ion–water and water–water energies. The internal energies, radial distribution functions, and related thermodynamic properties are calculated for each system. The structure of local solution environment around each dissolved ion is analyzed in terms of quasicomponent distribution functions in a manner consistent with our recent studies on liquid water, hydrophobic hydration, and hydrophilic hydration. This study forms an integral part of an ongoing series of theoretical investigations underway in this laboratory on the nature of aqueous solvation of bimolecular species and solvent effects on biomolecular structure and process.[2–7] Of particular interest in this work are the results on $[Na^+]_{aq}$ and $[K^+]_{aq}$. These ions figure prominently in biomembrane potential phenomena, and their hydration state in aqueous solution is undoubtedly an important factor in ion selectivity and membrane permeability in biological systems.

The background for this project is described in the next section, followed in Sec. III by a detailed description of the calculations carried. The results are presented in Sec. IV and discussed in detail in Sec. V. A summary of the results and discussion is given in Sec. VI.

II. BACKGROUND

The prevalent descriptive picture of ion solvation in aqueous solution stems from the ideas presented by Frank and Wen[8] and Gurney.[9] Here the environment of a dissolved ion is divided into three regions, labeled *A*, *B*, and *C* (cf. Fig. 1 of Ref. 8). In region *A*, solvent water molecules are tightly bound by the strong Coulombic field of the ion, and highly oriented under the influence of the ion–water forces. Region *A* is generally identified with the first hydration shell, composed of dense, electrostricted solvent. Diffraction data have provided some experimental data on this region. Region *C* is bulk water. Region *B* interfaces *A* and *C*. The nature and extent of region *B* is not well understood at this time, although it has been discussed extensively in the interpretation of experimental data on ionic solution in terms of the concepts "structure making" and "structure breaking." Progress in resolving the well known ambiguities[10] arising in the application of these concepts requires further detailed studies on aqueous solvation of ions at the most fundamental theoretical level possible.

Theoretical studies of the aqueous hydration of ions emanate from the papers of Born[11] on the dielectric continuum model and Bernal and Fowler,[12] who introduced discrete molecular approach to the system. The subsequent diverse elaborations of *ad hoc* modelistic approaches to the problem and the current status of experiment data on structure and energetics of ion hydration is available in several recently published books and comprehensive review articles, particularly by Friedman and co-workers.[13] Recently, it has become feasible to treat aqueous solutions using computer simulations

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rigorously based on the statistical thermodynamics of liquids. Liquid state properties can be calculated by numerical integration of the configurational integrals of the system using Monte Carlo methods, or alternatively by molecular dynamics. In computer simulation the structure of the system emerges as a result of theoretical calculation rather than an assumption as in *ad hoc* methods, and the main approximation necessary to treat the system enters at a generally more fundamental level in the theoretical hierarchy, that of intermolecular interactions. An extensive series of papers on the dynamical motion of particles in ionic solution has been reported by Heizinger and co-workers.[14]

Significant advances in the treatment of water and certain aqueous solutions were made possible by the development of potential functions for water–water and ion–water interactions based on nonempirical quantum mechanical calculation by Clementi and co-workers.[15,16] These functions have been subsequently used extensively for studies of the characterization of hydrated ion pairs[17] and hydrated ions[18] in cluster models for the systems, and were used in studies of the energetics of ion hydration based on the supermolecule–continuum model,[19] a hybrid *ad hoc* approach combining the discrete and continuum ideas from the early work on the problem. Gibbs free energies were determined for small ion–water clusters by Mruzik, Abraham, Schreiber, and Pound.[20]

The best of the water–water potentials developed by Clementi and co-workers were used in this laboratory as a basis for fully discrete computer simulation studies of the structure of liquid water,[2,3,7] hydrophobic hydration,[4] and hydrophilic hydration,[5] with the compositional characteristics of the system developed in terms of quasicomponent distribution functions (QCDF)[21] and the examination of supramolecular structures contributing significantly to the ensemble average. The QCDF's have proved to be a well-defined, graphic means of describing the statistical state of a molecular liquid. This approach has recently been extended to general problems in the area of molecular solutions and had recently been used to describe a prototype aqueous hydrophilic hydration problem.[5] Our present aim is to characterize the aqueous hydration of diverse chemical species by means of QCDF calculated from fully *ab initio* statistical thermodynamic computer simulation.

This paper describes the extension of our (T, V, N) ensemble computer simulation studies to dilute aqueous solutions of monatomic cations and anions. These systems present special numerical problems in computer simulation due to the long-range nature of the ion–water interaction potential. This can be expected to engender possible convergence problems in the calculations, possible N dependence in the results, and more subtle problems connected with the intrinsically unphysical nature of the periodic boundary conditions. The difficulties notwithstanding, the structure of local solution environment of the ion, dominated by ion–water interactions, is expected to be accessible to study and the calculated QCDF's can provide leading structural data on the statistical state of the system. The presentation of the full statistical analysis of the Monte Carlo realizations and comparison of calculated indices with experimental data whenever possible serves to keep the results presented herein in proper perspective.

III. CALCULATIONS

We treat herein the diffusionally averaged equilibrium structure of the infinitely dilute solution of individual monatomic cations and anions using the Metropolis method for the statistical thermodynamic Monte Carlo computer simulations. The general literature of this type of calculation has been recently reviewed by Barker and Henderson.[22] The specific formulation of the problem and the notation relativant to this study are given in our previous paper on liquid structure.[2,7] Each Monte Carlo calculation involves one ion and 215 water molecules at a temperature of 25 °C and a density computed from the observed partial molar volumes of ion and water. The condensed phase environment is established by face-centered cubic periodic boundary conditions.

The configurational energy of the system is developed under the assumption of pairwise additivity of intermolecular interactions using potential functions representative of *ab initio* quantum mechanical calculations of water–water and ion–water energies. For the water–water interaction we have carried over the potential function developed by Matsuoka, Clementi, and Yoshimine[15] based on moderately large configuration interaction calculations on the water dimer and used in previous studies. A spherical cutoff of 7.75 Å was applied in the calculations of water–water interaction energies from the potential function, consistent with previous use of this function in studies of $[H_2O]_l$. For the ion–water interactions, the analytical potential functions representative of extended basis set Hartree–Fock molecular orbital calculations, developed by Kistenmacher, Popkie, and Cleminit,[16] were used; ion–water correlation effects as discussed by Clementi *et al.*[17] are expected to be negligible. Three-body effects have been estimated to contribute ~12% error in these functions.[23,23(a)] The ion–water interaction energies were computed in the computer simulation under the minimum image convention.

The quantities calculated in computer simulation can be conveniently considered in two classes, structural and energetic. The energetic quantities are defined in the thermocycle presented previously as Fig. 2 in Ref. 4. The quantities denoted are $\overline{U}_S$, the calculated partial molar internal energy of transfer of the ion into water, and $\overline{U}_{S'}$ and $\overline{U}_{\rm rel}$, the solute–solvent and solvent relaxation contributions to $\overline{U}_S$. The value used for the total internal energy of 125 water molecules $\overline{U}_W$ is -1082.28 kcal based on our longest calculation[7] on the MCY water at 25 °C (uncorrected for the kinetic contribution).

The further analysis of the composition of the system in terms of energetic quantities is developed in terms of quasicomponent distribution functions (QCDF). The QCDF for binding energy $x_B(\nu)$ gives the distribution of energetic environments for each of the types of particles in the system. The corresponding quantity $x_P(\epsilon)$ gives the distribution of pair energies in the system.

TABLE I. Characteristic parameters of the Monte Carlo calculations.

	$\overline{V}_I$ (ml/mol)[a]	$R_{\rm insc}$ (Å)	Discarded	Used
Li^+	−5.88	10.432	1075 K	1000 K
Na^+	−6.21	10.432	900 K	1000 K
K^+	4.02	10.441	950 K	850 K
F^-	−6.10	10.432	1500 K	1000 K
Cl^-	12.83	10.449	1150 K	1000 K

[a] Reference 27.

The indices of structure in the systems under consideration here are $g_{IW}(R)$ and $g_{WW}(R)$, the ion–water and water–water radial distributions, respectively, and several structural QCDF indices of the composition of the system. Defining coordination number K as the number of particles within a radius R_M of a reference particle in a given configuration of the system, the QCDF $x_C(K)$ gives the distribution of coordination numbers in the statistical state of the system. Another useful structural QCDF is $x_D(\theta)$, the distribution of ion–dipole orientations for solvent water molecules in the first hydration shell of an ion; here θ is the angle between the dipole vector of the water molecule and the ion–water position vector. The structural effects of the ion on solvent water can be developed in terms of difference distribution functions, i.e., the difference between the calculated energetic and structural indices for the aqueous solution and the corresponding system of pure water.

Finally, it is possible to extract from the realization certain molecular structures which on the basis of the frequency of appearence in the Metropolis realization can be ascertained to make significant contributions. Of course, no single structure contributes that strongly to the ensemble average, so these "significant" structures must be viewed with caution as representative of the system. Nevertheless, they are quite useful to have available when considered in perspective, and are presented herein for selected cases.

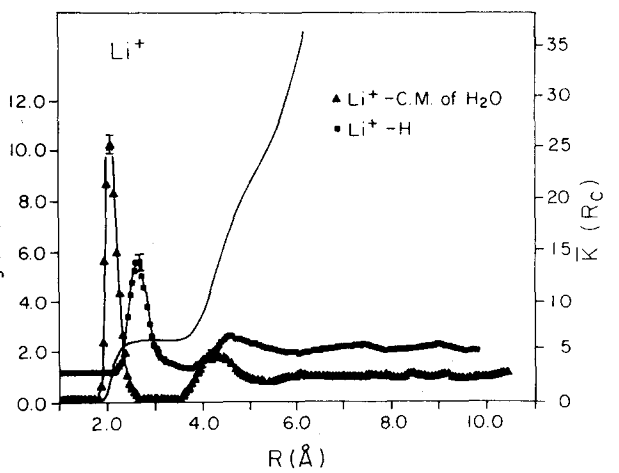

FIG. 1. Calculated Li^+–water center-of-mass (triangles) and Li^+–hydrogen (squares) radial distribution functions and running coordination numbers (full line) for $[Li^+]_{aq}$ at 25 °C. The curve $g_{IH}(R)$ is shifted upwards one unit on the abscissa for legibility.

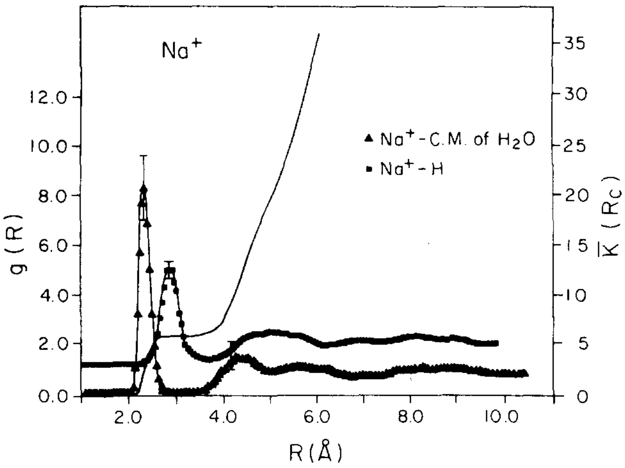

FIG. 2. Calculated Na^+–water center-of-mass (triangles) and Na^+–hydrogen (squares) radial distribution functions and running coordination numbers (full line) for $[Na^+]_{aq}$ at 25 °C. The curve $q_{1H}(R)$ is shifted upwards one unit on the abscissa for legibility.

IV. RESULTS

For each system, a starting configuration was obtained based on our earlier runs on 125 particles and equilibrated through ~1000 K configurations. Ensemble averages of all calculated properties were formed over the next ~1000 K configurations; the actual numbers used are noted in Table I. Convergence criteria and error bounds were determined from control functions taken at 50 or 100 K intervals in the calculations. The partial molar internal energies of transfer and all related quantities are collected in Table II.

The calculated radial distribution functions are given in Figs. 1–5. There is one figure for each ion containing both the ion–water center-of-mass function $g_{IW}(R)$ and the ion–hydrogen $g_{IH}(R)$ in each case. Figures 1–5 also contain the running coordination number $\overline{K}(R)$, the average number of solvent waters in a sphere of radius R around the ion, as a function of R. The ion–oxygen radial distribution function is essentially indistinguishable from the ion–water function since the center of mass of water and the oxygen atom nearly coincide. In each case there are well developed first and second peaks in the distribution, corresponding to the first and second hydration shells. Significant structure beyond

TABLE II. Energetic contributions to the ionic solvation.

	$\overline{U}_s$	$\overline{U}_{s'}$	$\overline{U}_{\rm rel}$	$\overline{U}_S$ (exp)[b]
Li^+	−188.3	−301.0	112.7	−129.1
Na^+	−180.3	−252.3	72.0	−103.0
K^+	−110.0	−178.8	68.4	−82.8
F^-	−142.7	−222.9	80.2	−97.2
Cl^-	−134.1	−150.7	16.6	−79.7

[a] All values are in kcal/mol.
[b] Reference 28, corrected by $P\Delta V$.

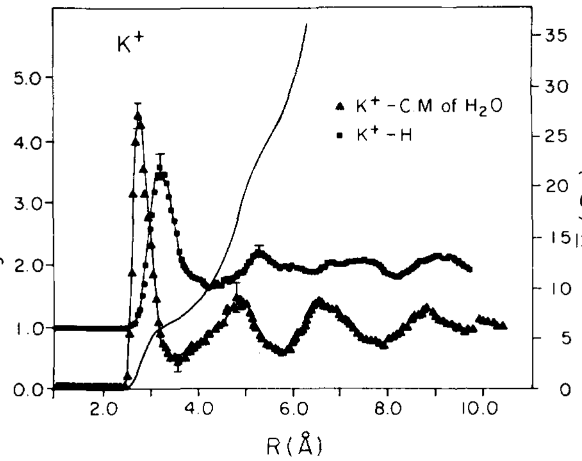

FIG. 3. Calculated K^+–water center-of-mass (triangles) and K^+–hydrogen (squares) radial distribution functions and running coordination numbers (full line) for $[K^+]_{aq}$ at 25 °C. The curve $g_{IH}(R)$ is shifted upwards one unit on the abscissa for legibility.

this is indicated for the larger ions, but as discussed below is expected to be sensitive to the boundary conditions.

A theoretical analysis of composition is developed in terms of the various structural and energetic QCDF's. The coordination number QCDF's are given for cations in Fig. 6 and for anions in Fig. 7. The definition of coordination number in each case is based on an R_M value determined from the first minimum in the calculated radial distribution function. Additional structural characteristics are displayed in the QCDF for the water dipole orientations, given in Figs. 8 and 9 for cations and anions, respectively. Here $x_D(\theta)$ is displayed in two forms, unnormalized and normalized with respect to the volume element

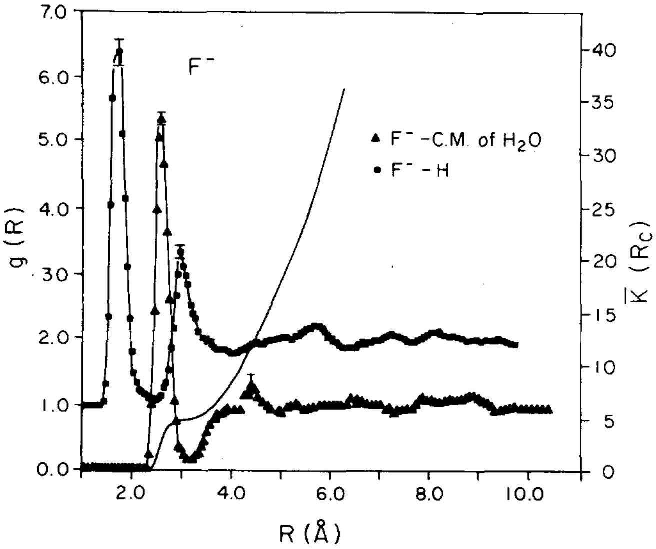

FIG. 4. Calculated F^-–water center-of-mass (triangles) and F^-–hydrogen (squares) radial distribution functions and running coordination numbers (full line) for $[F^-]_{aq}$ at 25 °C. The curve $g_{IH}(R)$ is shifted upwards one unit on the abscissa for legibility.

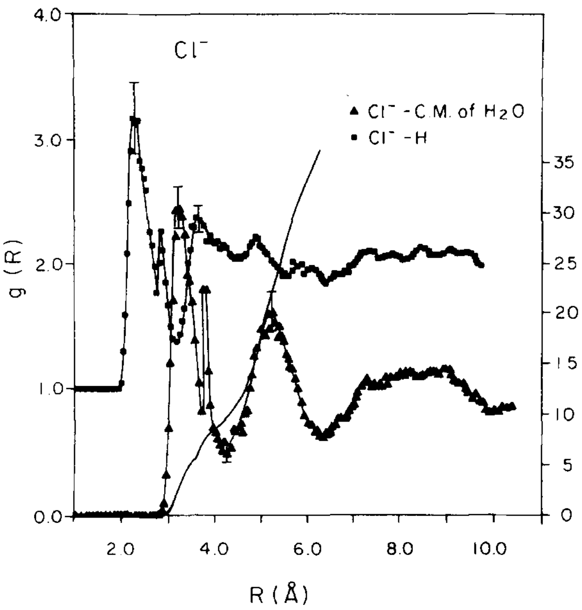

FIG. 5. Calculated Cl^-–water center-of-mass (triangles) and Cl^-–hydrogen (squares) radial distribution functions and running coordination numbers (full line) for $[Cl^-]_{aq}$ at 25 °C. The curve $g_{IH}(R)$ is shifted upwards one unit on the abscissa for legibility.

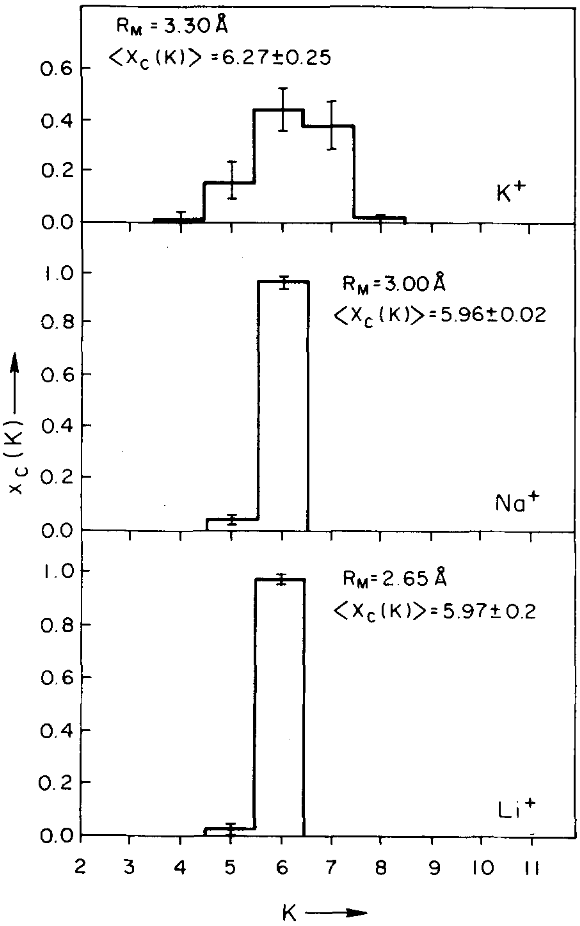

FIG. 6. Calculated quasicomponent distribution functions $x_C(K)$ vs coordination number K for $[Li^+]_{aq}$, $[Na^+]_{aq}$, and $[K^+]_{aq}$ at 25 °C.

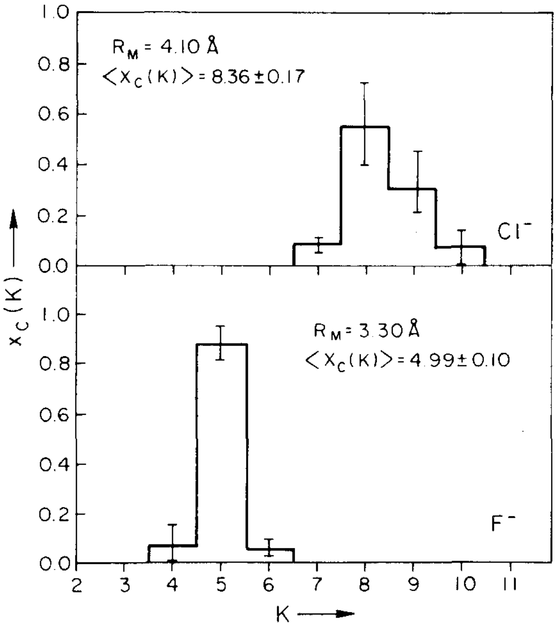

FIG. 7. Calculated quasicomponent distribution functions $x_C(K)$ vs coordination number K for $[F^-]_{aq}$ and $[Cl^-]_{aq}$ at 25 °C.

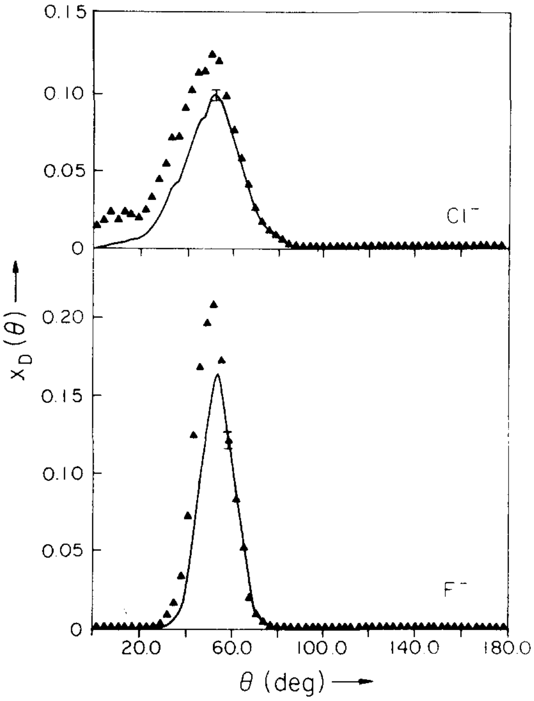

FIG. 9. Calculated quasicomponent distribution functions $x_D(\theta)$ vs dipole angle for $[F^-]_{aq}$ and $[Cl^-]_{aq}$ at 25 °C. The full line represents $x_D(\theta)$, and the triangles represent $x_D(\theta)/\sin\theta$.

corresponding to the coordinate θ, i.e., $\sin\theta$. The unnormalized form shows the raw distribution of dipole angles and the normalized form defines the deviation from a uniform random distribution of dipole orientation angles. The latter quantity is defined analogously to the radial distribution functions in Figs. 1–5.

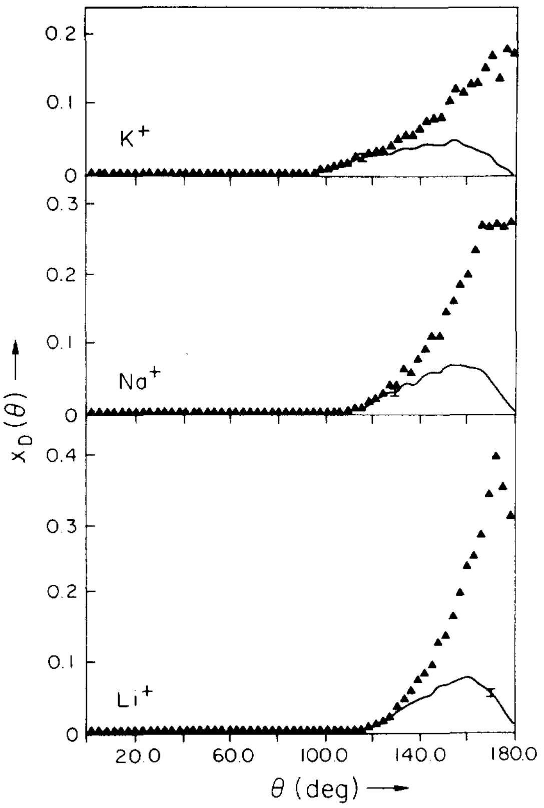

FIG. 8. Calculated quasicomponent distribution functions $x_D(\theta)$ vs dipole angle θ for $[Li^+]_{aq}$, $[Na^+]_{aq}$, and $[K^+]_{aq}$ at 25 °C. The full line represents $x_D(\theta)$, and the triangles represent $x_D(\theta)/\sin\theta$.

The energetic QCDF's are represented here by $x_B(\nu)$, the distribution of ion–water binding energies. The results on $x_B(\nu)$ are given in Fig. 10 for cations and in Fig. 11 for anions. Stereographic views of significant structures from $[K^+]_{aq}$ and $[F^-]_{aq}$ are included in Figs. 12 and 13, respectively; these are representative of the results for other systems.

V. DISCUSSION

The following topics are discussed in this section: (a) the calculated ion–water energetics, (b) the ion–water

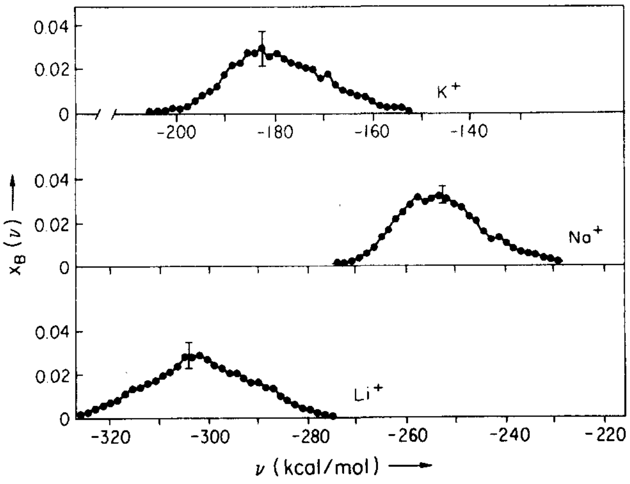

FIG. 10. Calculated quasicomponent distribution functions $x_B(\nu)$ vs binding energy ν for $[Li^+]_{aq}$, $[Na^+]_{aq}$, and $[K^+]_{aq}$ at 25 °C.

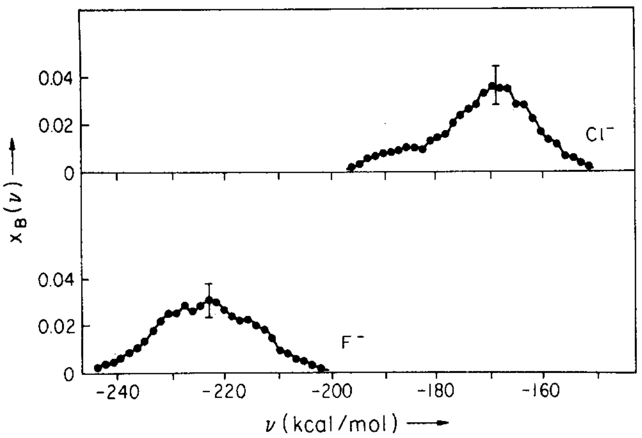

FIG. 11. Calculated quasicomponent distribution functions $x_B(\nu)$ vs binding energy ν for $[F^-]_{aq}$ and $[Cl^-]_{aq}$ at 25 °C.

radial distribution functions and the extent to which these are reasonable in light of available experimental data, (c) the prevalent geometrical dispositions of water molecules around ions in aqueous solutions, and (d) the structure of water in ionic solutions compared to that in pure water.

The central calculated energetic quantity is $\bar{U}_s$, the partial molar internal energy of transfer of an ion from vacuum to water. The corresponding enthalpy data is available for comparison and the calculated quantities in this as well as the previous calculations from diverse origins remain considerably lower than the best experimental estimates. This discrepancy has been pointed out and discussed also by Mruzik *et al.*[20] The interaction energy of the ions with distant water molecules is certainly overestimated, since the dipole moment of the water monomer in with the corresponding basis set is 18% too large.[24] (Waters farther than 7.75 Å from the ion—the radius of the inscribed sphere of the unit cell for the $N=125$ calculations—contribute 35–45 kcal/mol to $\bar{U}_{S'}$, depending on the ion.) Based on the results of Jorgensen,[25] it is likely that some systematic scaling of the ion–water potentials could result in better agreement on energetics with no degradation in the quality of the structural information. A full treatment of this aspect is a subject for future research investigations.

Full resolution of these questions must necessarily await more refined calculations, where problems due to three-body effects, N dependence, boundary conditions, and extrapolation to the ∞-system limit are definitely dealt with. For the present, an extrapolation of $\bar{U}_{S'}$ to the ∞-system limit based on a Born-type correction term for the worst case $[Li^+]_{aq}$ provisionally indicates a ~4% error from this effect. A comparison of mean energies computed here on $N=216$ with analogous calculations with $N=125$ shows an N dependence of ~15% in the energetic results. The trends in $\bar{U}_S$, i.e., $[Li^+]_{aq} < [Na^+]_{aq} < [K^+]_{aq}$ and $[F^-]_{aq} < [Cl^-]_{aq}$, are well reproduced.

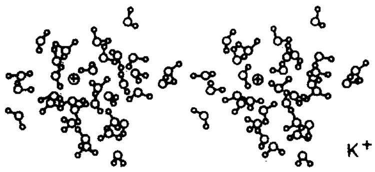

FIG. 12. Stereographic view of a molecular structure contributing to the statistical state of $[K^+]_{aq}$ at 25 °C.

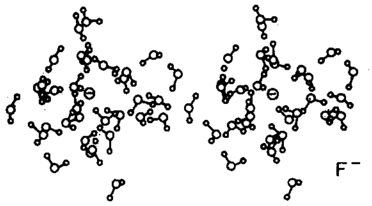

FIG. 13. Stereographic view of a molecular structure contributing to the statistical state of $[F^-]_{aq}$ at 25 °C.

The $\bar{U}_S$ terms are decomposed in Table II into direct ion–water contribution $\bar{U}_{S'}$ and a water relaxation term $\bar{U}_{\mathrm{rel}}$. The water relaxation term is ~30% of $\bar{U}_S$ in magnitude, except for the $[Cl^-]_{aq}$ system where the percentage drops to 11%. The water relaxation term is opposite in sign to $\bar{U}_{S'}$, indicative that water–ion interactions are formed at the expense of the water–water interactions as expected.

The distributions of the ion binding energies (Figs. 10 and 11) $x_B(\nu)$ are all unimodal. Their maxima are shifted to more negative values compared to the earlier, $N=125$ results, reflecting the interaction of ions with the added water molecules. The distribution of the pair energies between the ions and waters in the first solvation shell have also been computed. These curves (not shown here) are also all unimodal, with peaks at −31, −27, −17, −22, and −11 kcal/mol and values in the intervals (−35, −14), (−33, −10), (−18, 3), (−23, −11), and (−13, −4) kcal/mol for the ions Li⁺, Na⁺, K⁺, F⁻, and Cl⁻, respectively.

A comparison of the calculated ion–water radial distribution functions with related experimentally determined quantities may be developed in terms of effective ionic radii, hydration numbers, and in the case of $[Cl^-]_{aq}$ the extent of direct correspondence with an observed $g_{I-H_2O}(R)$ obtained by a new methodology. Values for the effective radius of an ion in solution can be determined from the position of the first maximum in $g_{IW}(R)$ minus the effective water radius $r_W = 1.38$ Å. The values thus obtained are collected alongside the corresponding crystal radii for each ion in Table III. The

TABLE III. Ionic radii and related quantities.

	Li^+	Na^+	K^+	F^-	Cl^-
$g_{IW}(R)$, max	2.10	2.35	2.71	2.60	3.25
r_I^{eff}, soln	0.72	0.97	1.33	1.22	1.87
r_I, xtal[b]	0.60	0.95	1.33	1.38	1.81
r_I, xtal[c]	0.82	1.17	1.44	1.16	1.64

[a] All distances are in Å.
[b] Reference 29.
[c] Reference 30.

TABLE IV. Calculated and experimentally determined hydration numbers and related quantities.

	Li^+	Na^+	K^+	F^-	Cl^-
This work	5.97 ± 0.02	5.96 ± 0.02	6.27 ± 0.25	4.09 ± 0.10	8.36 ± 0.17
(R_M	2.65	3.0	3.3	3.3	4.10)
x-ray	4 and 6[b]	4[c]	6[c]	4.5[d]	8 – 8.2[e]
Part. Mol. V.[f]	4.9	6.8	7.7	5.1	6.1
Clementi, *MC*[g]	5.0	5.4	6.8	5.0	5.6
(R_M, Clementi	2.28	2.59	3.27	1.99	2.85)
Heizinger, MD[h]	5.7	6.6 and 7.3	—	6.3	7.4

[a] All distances are in Å.
[b] Reference 31.
[c] Reference 32.
[d] Reference 33.
[e] Reference 34.
[f] Reference 35.
[g] Reference 18.
[h] Reference 14.

correspondence is generally quite close, indicating that the simulations are providing reasonable values for the dimensions of the first hydration shells of the ions.

The calculated values for hydration numbers from this work together with values reported in other relevant experimental and theoretical studies are collected in Table IV. The experimental data are taken from diverse sources of x-ray data and the determinations are based on observed partial molar volumes. The values obtained from our calculations are generally within one molecule of the experimental values. We consider this reasonable agreement considering that there remain fine differences in the definition of experimental and theoretical hydration numbers. The comparison with the $N = 125$ results shows the rather similar behavior of the smaller systems, with the possible exception of $[Li^+]_{aq}$, where the coordination number 5 was dominating the smaller system instead of the present 6. This latter value agrees with the recent finding of Enderby and Neilson.[26(a)] The values reported by Clementi and Barsotti[18] on ion–water clusters are slightly different from our values, giving an idea of the sensitivity of the results to the choice of R_M and to the boundary conditions. The resolution of the hydration numbers into contributions from the various coordination numbers shows the distribution of coordination numbers to be wider for the larger ions as expected.

The direct comparison of the calculated radial distribution function with experiment has until recently been hindered by difficulties in extracting the ion–water contributions from the measured total diffraction pattern. Recently, Enderby and co-workers[26] have developed a neutron first order difference method which allows detailed ion–water conformations to be obtained directly and without recourse to modeling techniques. A detailed comparison of our calculated results and the experimentally derived data as reported by Enderby is possible for the $[Cl^-]_{aq}$ system only, and is presented on Fig. 14. The calculated and observed positions of the extrema in the combined radial distribution function of hydrogen and oxygen $g_{I-H,O}(R)$ are seen to be within 0.1 Å, indicating quite satisfactory accord between theory and experiment. The combined radial distribution function is an ion–atom distribution, considering the H and O atoms as independent atoms.

The calculated results on $x_D(\theta)$ for cations and anions in aqueous solution provide a basis for the discussion of ion–water orientation and orientational distributions for cations. The average of the dipole angle θ is 140°–160°, which serves to orient a water lone pair essentially in the direction of the ion. This is on initial consideration a curious point since $\theta = 180°$, corresponding to the optimal ion–dipole interaction is a minimum energy in the cation water potential function. However, in studying structural orientation in the statistical mechanical context, it should be noted that there are both probabilistic and energetic factors to consider, and that the most favorable orientation energetically may not be the most probable, particularly when it is associated with a relatively small region of configuration space. This circumstance is expressed quantitatively by a comparison of $x_D(\theta)$ and $x_D(\theta)/\sin\theta$, the latter quantity being normalized by the volume element of the configuration space with respect to the orientational coordinate. The normalized quantity is thus proportional to the frequency of observing

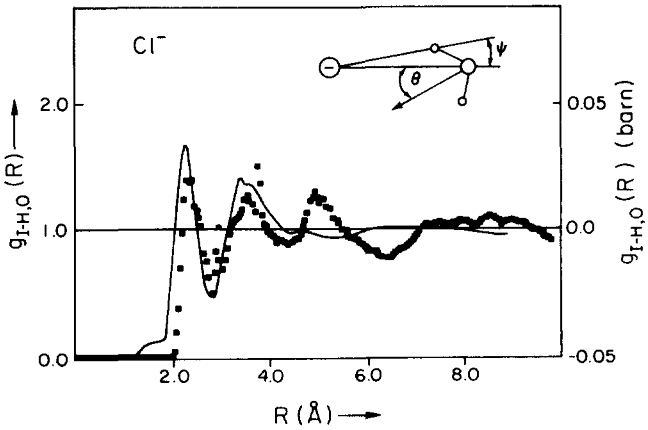

FIG. 14. Comparison of the computed composite radial distribution function $g_{I-H,O}(R)$ with the experimental data on the $[Cl^-]_{aq}$ system.

TABLE V. Calculated extrema of $g_{wW}(R)$ and x_C (4) for pure water and solvent water beyond the A region in ionic solutions.

	R_{max}	$g_{ww}(R)_{max}$	R_{min}	$g_{ww}(R)_{min}$	$x_C(4)$
H_2O[b]	2.85	2.592	3.40	0.976	0.443
		2.665		0.917	0.474
Li^+	2.80	2.535 ± 0.022	3.50	0.985 ± 0.015	0.426 ± 0.007
Na^+	2.80	2.616 ± 0.075	3.40	0.933 ± 0.021	0.455 ± 0.012
K^+	2.85	2.581 ± 0.032	3.50	0.963 ± 0.020	0.442 ± 0.008
F^-	2.80	2.539 ± 0.021	3.50	0.989 ± 0.027	0.431 ± 0.010
Cl^-	2.85	2.595 ± 0.030	3.45	0.965 ± 0.013	0.441 ± 0.005

[a] All distances are in Å. [b] Reference 7.

an ion–dipole angle per unit volume of configuration space. When the curves of $x_D(\theta)$ and $x_D(\theta)/\sin\theta$ are similar in shape, the energetic factor can be considered dominant, and when these distributions turn out to have different shapes the probabilistic factor is responsible. For the cation–water results, the geometry is thus clearly due to probabilistic factors, i.e., to the fact that there are statistically more probabilities for obtuse geometries and *not* due to any energetic preference of ion-lone-pair interactions. For anions, $x_D(\theta)$ and $x_D(\theta)/\sin\theta$ essentially coincide with the averages falling around 55° leading clearly to an interpretation of anion–water orientations in terms of hydrogen bonding rather than anion–dipole forces.

Further quantitative comparison with experiment is possible using the data and analysis scheme recently reported by Enderby.[26] The hydrogen–Cl^-–oxygen angle ψ (shown on the inset of Fig. 14) is reported to fall in the ranges (0°, 0°) and (0°, 20°) depending on the counterion. The relation between the angles θ and ψ (see the inset of Fig. 14) is

$$\theta(\psi) = \measuredangle\mathrm{HOH}/2 - [180 - \psi - \sin^{-1}(\sin d_{IO}/d_{HO})] ,$$

where $\measuredangle$HOH is the water angle, and d_{IO} and d_{IH} are the ion–oxygen and ion–hydrogen distances, respectively. This expression assigns two possible θ values for each ψ except at the largest possible ψ, i.e., $\psi_{max} = \sin^{-1}(d_{HO}/d_{IO})$. Using the smallest Cl^-–oxygen distance that was sampled by the calculation (2.9 Å), it yields $\psi_{max} = 19°$, in good agreement with the range (0°, 20°) obtained from the experiment. The value $\psi = 0°$ corresponds to $\theta = 54°$ or $\theta = 126°$. Our distribution is found to peak around 54°, which is in accord with the experimental results using Li^+ as a counterion where only this value is reported to occur.

We turn now to the effect of the dissolved ion on the solvent water structure. In the first solvation shell of the ion, the structure of water is clearly dominated by ion–water forces and it can be identified with the Frank and Wen A region. The remainder of waters in our calculations must be counted as B region. The following analysis is based on all waters beyond the A region and within the inscribed sphere tangent to the sides of the system box. Within this region, it is possible to examine structuration effects by comparing calculated $g_{WW}(R)$ and $x_C(K)$ values with the corresponding results for pure water. This information has been calculated and is presented in Table V.

The main features of the analysis of solvent structuration effects emerge from a consideration of $g_{WW}(R)_{max}$, the amplitude of the B-region water center-of-mass radial distribution function at the position of the first maximum, and $g_{WW}(R)_{min}$, the analogous quantity referring to the first minimum in the radial distribution function and the structural QCDF index $x_C(K)$ for $K = 4$. Comparing the values for each ion with those for pure water, there is evidence for reduced structure in all cases except $[Na^+]_{aq}$, for which there is no statistically significant difference with respect to pure water. The reduction in structure is the most pronounced for the two smallest ions: Li^+ and F^-. This is generally consistent with the prevalent idea that region B is structure breaking. We are currently considering further the more general question of defining a structure making–structure breaking index in terms of molecular distribution functions and computer simulation results. A point of view on this, including consideration on hydrophobic solutes as well as ions, is described in a recent paper.[36]

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