Monte Carlo Simulations with an Improved Potential Function for Cu(II)-Water Including Neighbour Ligand Corrections

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Monte Carlo simulations for a Cu^{2+} ion in infinitely dilute aqueous solution were performed on the basis of a simple pair potential function leading to a first-shell coordination number of 8, in contrast to experimental data. A simple method was introduced therefore, which allows the direct construction of a pair potential containing the most relevant 3-body interactions by means of a correction for the nearest neighbour ligands in the ion's first hydration shell. This procedure leads to much improved results, without significant increase in computational effort during potential construction and simulation.

1. Introduction

Although the importance of 3-body terms for the accurate description of intermolecular interactions in condensed systems is well-known [1–5], most of Monte Carlo and molecular dynamics simulations of aqueous salt solutions have been performed assuming additivity of pair potentials [6–11]. For monovalent and some divalent metal ions, most of the structural data obtained appeared to be correct, except for minor deviations from experimental structural details [6, 9, 12]. When, however, water is strongly bound to divalent ions at comparatively short distances, the neglected 3-body terms become significant enough to alter crucial structural data such as the first-shell coordination number. For example, inclusion of 3-body effects was needed to correct the hydration number 6 as predicted for Be^{2+} by the pair potential function, to 4 [5].

Simulations of aqueous solutions of some transition metal ions as Ni^{2+} [13] or Fe^{2+} [14] also produced overestimated coordination numbers. For Cu^{2+}, ab initio studies of successive hydration [15, 16] led to the conclusion that 3-body or even higher-order terms should be of major importance to describe this ion in solution correctly. In our work, we therefore performed a simulation for Cu^{2+} in water first on the basis of an improved conventional pair potential. When it became clear that pairwise addition of interactions leads to wrong structural data, we investigated a simple way to construct a potential function taking into account at least the main contributions of 3-body effects by a "nearest-neighbour-ligand correction".

2. Monte Carlo Simulation with Conventional Pair Potential

2.1. *The Pair Potential*

After some initial MC simulations, using a recently developed pair potential function for Cu^{2+}/H_2O [17], it became clear, that the ECP-DZP basis set [18] used for the evaluation of the corresponding energy surface allowed too large charge-transfer effects and gave partially erroneous energies at larger ion-water distances, leading to artifacts in the simulation. Therefore, new ab initio calculations for the energy surface were performed using the modified basis set for Cu from [19]. For water, the same ECP-DZP basis set [20, 21] as in [17] was used again, but polarization functions on hydrogen were removed. A total of 510 energy surface points were evaluated and fitted to a functional of the form

$$\Delta E = \sum_i \frac{q_{Cu}\, q_i}{r} + A_1 r^{-3} + A_2 r^{-4} + A_2 \exp(A_4 r),$$

i: atoms in H_2O, r: Cu^{2+}–O distance,

using the same method as in [17]. The global minimum of the potential surface was found to be −83.4

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Table 1. Final optimized parameters for the conventional pair potential.

Atom	q_i (a.u.)	A_1 ($Å^{+3}$ kcal/mole)	A_2 ($Å^{+4}$ kcal/mole)	A_3 (kcal/mole)	A_4 ($Å^{-1}$)
O	−0.742	523.62	−2128.0	106840.0	−3.8096
H	+0.371	−100.42	122.38	564.59	−2.1576

kcal/mole at a Cu^{2+}–O distance of 1.92 Å in dipole-oriented C_{2v} geometry. The final parameters of the function are given in Table 1. The standard deviation of the fitted function values from SCF calculated data was 3.7%.

2.2 Monte Carlo Simulation

A Monte Carlo simulation was carried out with this potential function, for infinitely dilute solution conditions represented by 1 Cu^{2+} ion and 200 water molecules in the periodic box, at a temperature of 20.0 °C. The Metropolis algorithm [22] was applied. For water-water interaction, the MCY [23] potential was used. The edge length D of the box was 18.143 Å, corresponding to the density of pure water, and a spherical cut-off for experimental terms of $D/2$ was employed. The starting configuration was obtained by random generation. After 1 million configurations, the system had reached energetic equilibrium, and a further million configurations were generated for the evaluation of radial distribution functions and other statistical data.

3. Results

The radial distribution functions (RDF) $g_{\alpha\beta}(r)$ for copper-oxygen and copper-hydrogen are shown in Fig. 1, together with the corresponding running integration numbers. In the Cu^{2+}–O RDF, the first peak is centered at 2.10 Å, 0.18 Å beyond the minimum of the SCF Cu^{2+}-water potential. Clearly separated, a second hydration sphere appears in the region between 3.4 and 5.0 Å. The average coordination number for the first hydration shell results as 8, in contrast to the value 6 expected from experimental data [24]. This overestimation was not very surprising, considering the copper/water stabilization energy of −83 kcal/mole, the shape of the energy surface of this system and the investigations concerning non-additivity of ion-ligand interactions in $Cu^{2+}(H_2O)_n$ based on ab initio calculations [15, 16, 25]. Water-water repulsion alone is apparently not sufficient to prevent accumulation of a larger number of water molecules in the first hydration sphere of Cu^{2+} ion, even at the price of a moderate enlargement of the Cu^{2+}–O distance. It was obvious, therefore, that 3-body effects had to be taken into account for further simulation work.

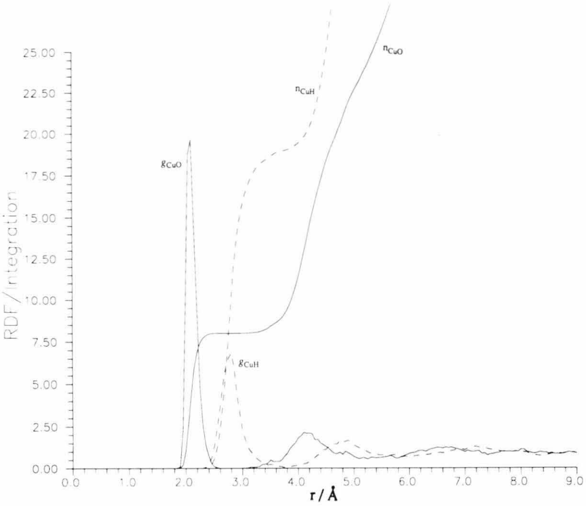

Fig. 1. Copper-oxygen and copper-hydrogen radial distribution functions $g_{\alpha\beta}(r)$ and running integration numbers $n_{\alpha\beta}$ obtained by pair potential.

The second hydration shell contains about 16 water molecules. Since this value should strongly depend on the structure of the first hydration sphere, it should also not be considered too reliable.

Evaluation of a potential function taking into account 3-body effects exactly implies – besides the evaluation of the "conventional" pair potential function – the performance of a large number of SCF calculations on $H_2O \cdots Cu^{2+} \cdots H_2O$ and $H_2O \cdots H_2O$ with wide variations of distances and angles, followed by a fitting of these data to a separate correction function. Although the first part of these efforts had already been performed (i.e. the pair potential evaluation), it seemed worthwhile to investigate the possibility of a different approach, allowing to obtain an improved ion-ligand function in one step by a less computer-intensive way. Such a function should also fulfill the requirements not to increase significantly the time needed for energy computations during statistical simulations. These considerations were finally realized in a correction algorithm outlined in the following Section 4.

4. Nearest Neighbour Ligand Correction

4.1. Principles

(a) Instead of SCF calculations on a metal ion/water energy surface, points are evaluated for the energy surface of a water molecule in the field of a fixed M^{2+}–H_2O system, where the water molecule attached to the metal ion is kept at the equilibrium distance evaluated for the $M^{2+}(H_2O)_n$ cluster in ab initio calculations (2.0 Å for Cu^{2+}, dipole-oriented C_{2v} geometry). The Cu^{2+}–O distance of the second water molecule and its orientation are varied. Different directions of approach are chosen to ensure a wide enough spectrum of O/Cu/O angle variation from 180° to 30°.

(b) Fitting of the resulting SCF interaction energies is performed to a potential function of the type

$$\Delta E = \sum_i \frac{q_{Cu} q_i}{r} + A_1 r^{-3} + A_2 r^{-4} + A_3 \exp(A_4 r) + \mathrm{NNLC},$$

$$\mathrm{NNLC} = \sum_N (\mathrm{CL} - r)^2 A_5 \exp(A_6 R),$$

r: Cu^{2+}–O distance, R: O–O distance,
NNLC: Nearest Neighbour Ligand Correction,
i: atoms in H_2O,
N: number of neighbour ligands within a selected spherical area.

The first part of this function is identical to the form of the conventional pair potential previously used for Cu^{2+}–H_2O. The second term (NNLC) corresponds to a "Nearest Neighbour Ligand Correction" and is related to the distance of the oxygens of the fixed water in Cu^{2+}–H_2O and the moved water molecule. N is the number of nearest neighbour ligands determined by a search algorithm in the simulation which evaluates number and position of other water molecules fulfilling the condition $2.0\ \text{Å} < R_{Cu-O} < 2.2\ \text{Å}$. These narrow limits around the peak of the first-hydration-shell obtained by the pair potential have to be set, as the fitted function will be applicable only when the second water molecule is located at, or near the distance it had in the SCF calculations.

The cut-off limit CL allows to invoke the NNL correction during the simulation only if an ion-water energy is evaluated for an ion-oxygen distance below this limit, and hence strongly reduces the computational effort. The factor $(\mathrm{CL} - r)^2$ guarantees that the potential function is steady at the point of the cut-off limit. The choice of CL is made within the fitting procedure as to lead to the smallest standard deviation.

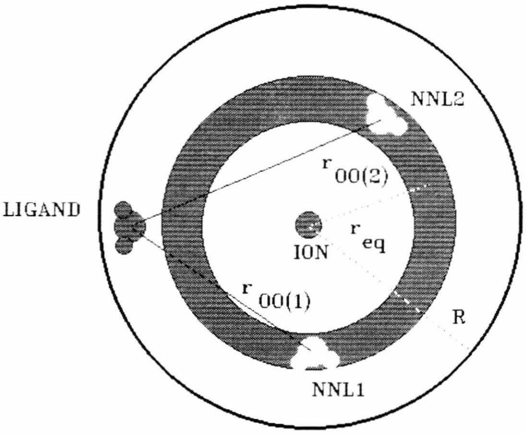

Fig. 2. Schematic illustration of correction method for ion-water potential.

Figure 2 illustrates the use of the NNL correction during a simulation. The large sphere indicates the area where the correction is effective for the water molecule whose interaction with the central ion is under consideration. The two inner sphere limits mark the area where nearest neighbour ligands are searched and included in the correction of the interaction energy.

At this point, a principle error inherent to the present correction algorithm should be mentioned: a pair potential derived this way automatically takes into account the repulsion of 2 water ligands; in the simulation, this water-water repulsion is included once more via the water-water pair potential. In principle, the latter contribution should be subtracted therefore. Omission of this step seems to be acceptable, however, as the NNL correction function contributes very little when the O/Cu/O angle is large (i.e. large R_{OO}), so that the strong ligand-ligand repulsion for this configuration with opposite ligand dipole moments is taken into account correctly by the water-water potential. On the other hand, when the O/Cu/O angle becomes smaller (<90°), a smaller contribution arises from the water-water term (partially H-bond stabilized conformations), whereas the NNL correction energy becomes large. Thus the resulting values seem to be sufficiently accurate for the purposes of the simulation.

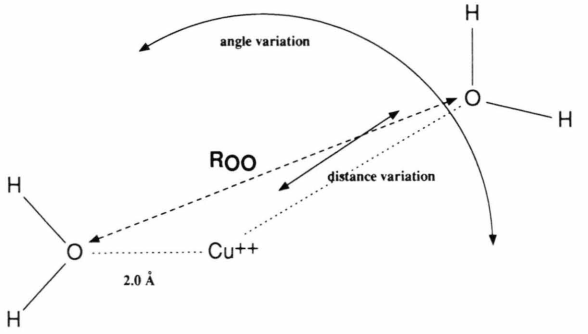

Fig. 3. Geometrical variations in SCF calculations on the $Cu^{2+} \cdots H_2O \cdots H_2O$ energy surface.

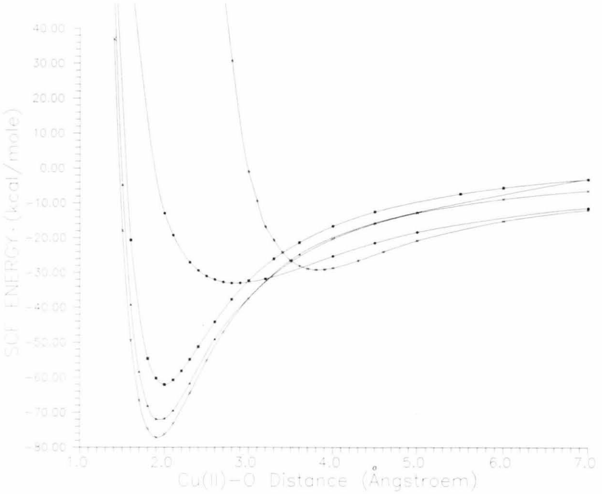

Fig. 4. Dependence of stabilization energy and location of local minima on the angle $H_2O–Cu^{2+}–H_2O$. ∗ 45°; ● 60°; ■ 30°; ▲ 120°; × 180°.

Table 2. Final optimized parameters for the corrected pair potential.

Atom	q_i (a.u.)	A_1 ($Å^{+3}$ kcal/mole)	A_2 ($Å^{+4}$ kcal/mole)	A_3 (kcal/mole)	A_4 ($Å^{-1}$)
O	−0.742	1345.49	−3374.29	160739.47	−4.0515
H	+0.371	−724.32	611.877	987.0948	−1.5334
for NNLC:		A_5 (kcal/mole)	A_6 ($Å^{-1}$)		
		597.2487	−1.8424		

4.2. Corrected Pair Potential

A total of 287 points of the energy surface were calculated using the same basis set as before, by the LCAO-MO-UHF method. Variations of position and orientation of the water molecule followed the previously outlined procedure ($Cu^{2+}–O$ distance varying from 1.3 to 8.0 Å, O/Cu/O angle from 30° to 180°, as illustrated in Figure 3).

The global minimum of the potential surface was found to be −76.6 kcal/mole at a $Cu^{2+}–O$ distance of 1.90 Å and O/Cu/O angle of 180°. In Fig. 4, the dependence of stabilization energy and location of local minima on the angle between the two water molecules is illustrated. This figure clearly demonstrates that angles around and below 90° induce considerable changes in the shape of the potential function.

The best fitting results to the functional form given above resulted for a cut-off limit CL = 4.0 Å. In Fig. 5, the SCF energies obtained from quantum chemical calculations (ΔE_{SCF}) are plotted versus those obtained by this function (ΔE_{FIT}), with its final parameters given in Table 2.

The optimized function parameters were tested by the Beveridge procedure [26], and constant standard deviations were obtained. Investigation of the behaviour of the potential function without adding the NNL correction showed that the shape of the function for various approaches of a water molecule to the metal ion is very similar to that obtained with the conventional pair potential, with minor flattenings in the short-range area.

5. Monte Carlo Simulation with Corrected Pair Potential

The same system of $1\,Cu^{2+}/200\,H_2O$ was simulated under conditions identical to those in Section 2, but with the new potential function including the NNL correction term. The limits for the spherical section where nearest neighbour ligands were considered was confined to 2.0–2.2 Å, for reasons mentioned above and as a result of an extended variation of these parameters in the Zn^{2+}/H_2O system [27]. After equilibration (1 million configurations) sampling from further 2 million configurations was performed. The average number of "nearest neighbour ligands" found within the selected limits was 0.71, corresponding to an average energy correction term of 6.1 kcal/mole.

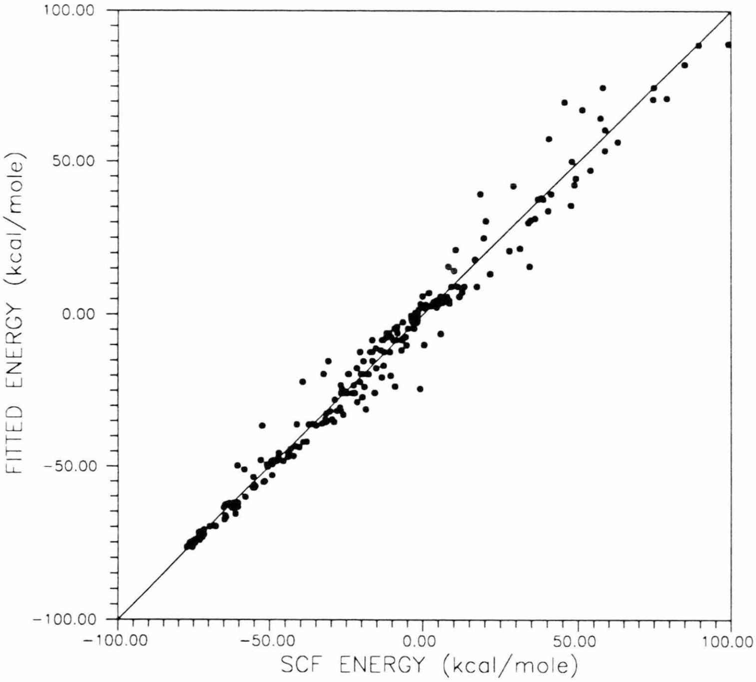

Fig. 5. Comparison of the stabilization energies from ab initio calculations (ΔE_{SCF}), and fitted energies (ΔE_{FIT}) with the final fitting parameters given in Table 2.

Table 3. Characteristic values for the radial distribution functions $g_{\alpha\beta}(r)$ [a] obtained by the corrected pair potential.

α	β	r_{M1}	r_{m1}	$n_{\alpha\beta}(r_{m1})$	r_{M2}	r_{m2}	$n_{\alpha\beta}(r_{m2})$
Cu	O	1.95	2.25	6.0	3.90	5.55	25.0
Cu	H	2.65	3.00	12.3	4.65	5.75	48.0
O	O	2.85	3.55	5.8	4.25	5.50	17.0
O	H	1.95	2.55	2.0	3.35	4.80	27.9

[a] r_{Mi} and r_{mi} are the distances in Å for the ith maxima and minima of $g_{\alpha\beta}(r)$, respectively. – $n_{\alpha\beta}(r_{m1})$ and $n_{\alpha\beta}(r_{m2})$ are the average coordination numbers for the first and second hydration shell, respectively.

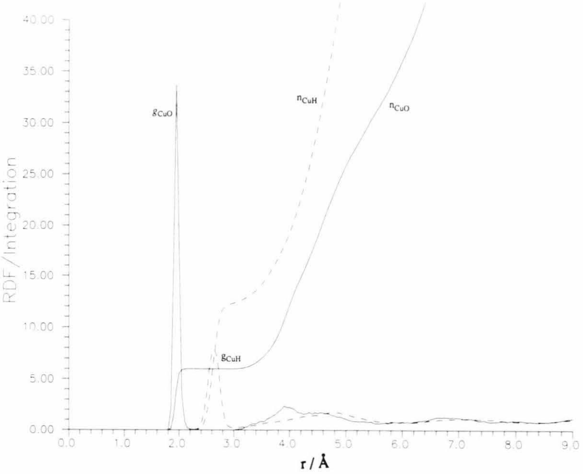

Fig. 6. Copper-oxygen and copper-hydrogen radial distribution functions $g_{\alpha\beta}(r)$ and running integration numbers $n_{\alpha\beta}$ obtained by corrected pair potential.

The same radial distribution functions $g_{\alpha\beta}(r)$ as before, including their integration, are displayed in Figure 6. In Table 3 some of the characteristic values for these RDFs are listed. The most important change observed is the average coordination number of six for the first hydration shell of Cu^{2+}, which agrees with experimental findings [24] and theoretical predictions [15, 25]. The first Cu–O peak is centered at 1.95 Å, almost coinciding with the experimental value for the equatorial Cu–O distance obtained by X-ray diffraction studies of aqueous solutions of $CuSO_4$ (1.94 Å) [24]. The difference between this value and the location of the global minimum in the potential function is also much less pronounced than in the simulation with conventional pair potential. The peak is extremely sharp (and accordingly high), virtually all water molecules are located within 0.4 Å distance variation. The first Cu^{2+}–H peak appears at 2.65 Å containing all 12 hydrogens belonging to the 6 oxygens found in the first peak of $g_{CuO}(r)$. The distance between this peak and the first Cu–O peak confirms dipole orientation for all water molecules of the first hydration shell.

Analysis of coordination number distribution in this first hydration shell revealed exclusivity of the coordination number 6.

The second hydration shell is much less well-defined, and its limit more difficult to determine than in the simulation with conventional pair potential. It contains about 25 water molecules, if integration is performed up to the value of $r_{\mathrm{mi}} = 5.5$ Å. If the value of r_{mi} is taken at 4.25 or 4.50 Å (where small local minima appear), 9 or 12 water molecules are found, respectively.

6. Conclusions

The nearest-neighbour-ligand correction method presented and applied in this work appears as a simple and economic tool for the development of a pair potential function for ion-ligand systems, where at least an approximate consideration of 3-body contributions is needed for obtaining correct structural data in statistical simulations of the condensed phase.

Besides the advantage to obtain a potential function from one single series of SCF calculations followed by a simultaneous fitting procedure for pair potential and correction term, its demand in computing time during the simulation is only marginal (0.1% of total time in the present case, and 0.3% in the case of a 1 M $ZnCl_2$ solution [27]). These advantages might compensate for the inevitable loss of accuracy compared to a full, exact consideration of 3-body contributions.

The results obtained by this method for a copper ion in water are in full agreement with experimental data for the first hydration shell of this ion. This fact also appears to favour the idea that inclusion of 3-body terms guarantees a satisfactory description of the hydrated copper ion's structure, as suggested by Cordeiro [15], in contrast to Curtiss, who assumed a slow convergence of *n*-body contributions and thus significant influence of higher terms [16]. For a final decision in this matter and control of the method presented here, further simulations of copper salt solutions and comparison with exact 3-body corrections will be performed.

Acknowledgement

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[1] E. Clementi, H. Kistenmacher, W. Kotos, and S. Romano, Theoret. Chim. Acta **55,** 257 (1980).
[2] O. Blake, O. Novaro, A. Leś, and S. Rybak, J. Chem. Phys. **76(11),** 5405 (1982).
[3] T. P. Lybrand and P. A. Kollman, J. Chem. Phys. **83,** 2923 (1985).
[4] L. A. Curtiss, J. W. Halley, J. Hautman, and A. Rahman, J. Chem. Phys. **86(4),** 2319 (1987).
[5] M. M. Probst, E. Spohr, and K. Heinzinger, Chem. Phys. Lett. **165,** 405 (1989).
[6] J. P. Limtrakul, M. M. Probst, and B. M. Rode, J. Mol. Structure (Theochem.) **121,** 23 (1985).
[7] M. M. Probst, T. Radnai, K. Heinzinger, P. Bopp, and B. M. Rode, J. Phys. Chem. **89(5),** 753 (1984).
[8] P. Bopp, I. Okada, H. Ohtaki, and K. Heinzinger, Z. Naturforsch. **40a,** 116 (1985).
[9] E. Spohr, G. Pàlinkàs,. K. Heinzinger, P. Bopp, and M. M. Probst, J. Phys. Chem. **92,** 6754 (1988).
[10] W. Dietz, W. O. Riede, and K. Heinzinger, Z. Naturforsch. **37a,** 1038 (1982).
[11] T. Yamaguchi, H. Ohtaki, E. Spohr, G. Pàlinkàs, K. Heinzinger, and M. M.Probst, Z. Naturforsch. **41a,** 1175 (1986).
[12] M. Mezei and D. L. Beveridge, J. Chem. Phys. **74(12),** 6902 (1980).
[13] D. G. Bounds, Mol. Phys. **54,** 1335 (1985).
[14] A. G. Lafont, J. M. Lluch, A. Oliva, and J. Bertràn, Chem. Phys. **111,** 241 (1987).
[15] M. N. D. S. Cordeiro, J .A. N. F. Gomes, A. G. Lafont, J. M. Lluch, and J. Bertràn, Chem. Phys. **141,** 379 (1990).
[16] L. A. Curtiss and R. Jurgens, J. Phys. Chem. **94(14),** 5509 (1990).
[17] S. Islam, E. H. S. Anwander, M. M. Probst, and B. M. Rode, Z. Naturforsch. **45a,** 184 (1990).
[18] P. J. Hay and W. R. Wadt, J. Chem. Phys. **82,** 270 (1970).
[19] R. T. Krömer, Y. Michopoulos, and B. M. Rode, Z. Naturforsch. **45a,** 1303 (1990).
[20] W. J. Stevens, H. Basch, and M. Kraus, J. Chem. Phys. **81,** 6026 (1984).
[21] T. H. Dunning, J. Chem. Phys. **53,** 2823 (1970).
[24] H. Ohtaki, T. Yamaguchi, and M. Maeda, Bull. Chem. Soc. Japan **49,** 701 (1976). – H. Ohtaki, T. Yamaguchi, and M. Maeda, The Structures of Hydrated Divalent Transition-Metal Ions in Solution, Pergamon Press, Oxford 1977. – H. Ohtaki and M. Maeda, Bull. Chem. Soc. Japan **47,** 2197 (1974).
[25] H. Veillard, J. Demuynck, and A. Veillard, Chem. Phys. Lett. **33(2),** 221 (1975). – H. Veillard, J. Amer. Chem. Soc. **99(22),** 7194 (1977).
[26] S. Swaminathan, R. J. Whitehead, E. Guth, and D. L. Beveridge, J. Amer. Chem. Soc. **99,** 7817 (1977).
[27] B. M. Rode and Y. Yongyai, in preparation.