The Cu^+–H_2O Interaction Potential and its Application to the Study of $[Cu(H_2O)_n]^+$ Clusters at Different Temperatures

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An analytical pair potential for the interaction of Cu^+ ion with H_2O has been obtained by fitting to quantum-mechanically calculated energies of the monohydrate Cu^+–H_2O. This analytical potential and Clementi's MCY potential for the H_2O–H_2O interaction have been used in the pairwise approximation to study $[Cu(H_2O)_n]^+$ clusters, with $n = 6, 8, 10, 15$ and 20. This study has been performed at $T = 0$ K by energy minimization and at $T = 50, 298$ and 500 K using Monte Carlo techniques, in order to assess the effect of thermal motion. A detailed analysis of the interaction energies, the resulting radial distribution functions and the corresponding running coordination number leads to the prediction of a coordination number of six for the first hydration shell of the Cu^+ ion. In this first shell the water molecules have an octahedral structure, which is slightly distorted when the temperature is increased. The reliability of these results and their validity at infinite dilution are discussed.

1. Introduction

Transition metals are essential elements in many biological systems where they normally exist as ionic aqueous solutions. Of the different types of reactions in which transition metals take part, we single out redox reactions, the kinetics and thermodynamics of which are fundamentally dependent on the characteristics of the solvation shells.

Accurate experimental studies of the coordination numbers of several transition metals in crystals of ionic hydrated salts have been published.[1] The corresponding experimental studies in solution are difficult and the results are frequently controversial as it has been found that the coordination number may vary with experimental conditions.[1,2] Although coordination complexes of Cu^+ ion have been studied in the gas phase,[3] no experimental data are available for Cu^+ in aqueous solution, as its lifetime is less than 1 s.[4] It is in such cases that theoretical calculations of the type discussed in this work are invaluable.

The main purpose of this work is the theoretical study of the structural and energetic features of the hydrates of Cu^+ in aqueous solution. In order to obtain an insight into the nature of the solvated ion, Monte Carlo simulations of several $[Cu(H_2O)_n]^+$ ($n = 6, 8, 10, 15, 20$) clusters were performed. The choice of this statistical method is justified by two different arguments. First, the complexity of the systems we intend to study is such that a complete quantum-mechanical calculation is not feasible at the present time. If this was attempted, only a small number of water molecules could be considered,

and their arrangement around the central metal would have to be predefined. The second basic argument depends on the inability of conventional quantum-mechanical models to describe temperature effects on the structure and properties of hydration shells. With the Monte Carlo method, several thermodynamic properties of the solution may be calculated simultaneously. However, knowledge of the interaction potentials for metal ion–water and water–water is required. For the potential of the H$_2$O–H$_2$O system, the analytical function proposed by Clementi and co-workers (the MCY potential)[5] has been shown to be efficient in several studies of systems similar to ours.[6] On the other hand, knowledge regarding the interaction potentials of the transition-metal ions is as yet very sparse. It is thus crucial for the purpose of the present work that a good-quality potential for the system Cu$^+$-H$_2$O be determined.

In this paper, an interaction potential is assumed in the form of an analytical function with adjustable parameters. These, in turn, are to be determined by fitting to quantum-mechanical interaction energies. The actual shape of the potential function and the quantum model used in the auxiliary calculations are discussed in the following section. Finally, the application of the potential generated to the study of [Cu(H$_2$O)$_n$]$^+$ clusters is presented in the last section.

2. Analytical Representation of the Interaction Potential for the Cu$^+$–H$_2$O System

2.1. Method

The most general form of the interaction energy of an ensemble of N mutually interacting particles may be written as a sum of 2, 3, ... N-body interactions. For simplicity, however, in most applications of the type we are interested in here, three-body interactions and beyond are disregarded[6,7] and we are thus left with

$$V = \sum_{i>j} V(i, j). \tag{1}$$

Depending on the particular chemical system and on the problem of interest, different analytical functions have been suggested to represent the two-body interactions. The choice of the functional form and of the parameters therein is not straightforward and depends on the amount of experimental (or theoretical) information available.

For the pair Cu$^+$-H$_2$O, four different analytical functions are considered:

$$
\begin{aligned}
V_1 = {} & c_1[q_M q_O/r_A + q_M q_H(1/r_B + 1/r_C)] \\
& + c_2[1/r_A^3 - 1/2(1/r_B^3 + 1/r_C^3)] + c_3/r_A^{12} + c_4(1/r_B^{12} + 1/r_C^{12}) \\[4pt]
V_2 = {} & c_1[q_M q_O/r_A + q_M q_H(1/r_B + 1/r_C)] \\
& + c_3/r_A^{12} + c_4(1/r_B^{12} + 1/r_C^{12}) - c_5/r_A^6 - c_6(1/r_B^6 + 1/r_C^6) \\[4pt]
V_3 = {} & c_1[q_M q_O/r_A + q_M q_H(1/r_B + 1/r_C)] \\
& + c_2[1/r_A^3 - 1/2(1/r_B^3 + 1/r_C^3)] + c_3/r_A^{12} \\
& + c_4(1/r_B^{12} + 1/r_C^{112}) - c_5/r_A^6 - c_6(1/r_B^6 + 1/r_C^6) \\[4pt]
V_4 = {} & c_1[q_M q_O/r_A + q_M q_H(1/r_B + 1/r_C)] \\
& + c_2[1/r_A^3 - 1/2(1/r_B^3 + 1/r_C^3)] + c_3/r_A^{12} \\
& + c_4(1/r_B^{12} + 1/r_C^{12}) - c_5/r_A^6 - c_6(1/r_B^6 + 1/r_C^6) + c_7[1/r_A^2 - 1/2(1/r_B^2 + 1/r_C^2)] \\
& + c_8/r_A^4 + c_9(1/r_B^4 + 1/r_C^4) + c_{10}/r_A^5 + c_{11}(1/r_B^5 + 1/r_C^5)
\end{aligned}
\tag{2}
$$

where $q_M(=1)$, q_O $(=-0.6836)$ and q_H $(=0.3418)$ are atomic charges; r_A, r_B and r_C are the internuclear distances copper–oxygen and copper to both hydrogen atoms; and c_p

$(p = 1, 2, \ldots, 11)$ are the fitting parameters. In this equation the interaction energies V_1, V_2, V_3 and V_4 are expressed in hartree when the distances r_A, r_B and r_C are in bohr. It should be noticed that functional V_1 contains terms in r^{-12}, r^{-3} and r^{-1}; V_2 terms in r^{-12}, r^{-6} and r^{-1}; V_3 terms in r^{-12}, r^{-6}, r^{-3} and r^{-1}; finally V_4 contains all the terms in r^{-n} with $n = 1$ to 6 and a term in r^{-12}. No direct physical meaning may be attached to the parameters of these terms. These functional forms were inspired in earlier work on other hydrated metalic ions,[6] including those of transition metals Zn^{2+},[6(a)] Fe^{2+},[8] Fe^{+}[9] and Fe^{0}.[9] It should be stressed that all four functions have the appropriate asymptotic behaviour.

To calculate the coefficients c_p we need the interaction energy,

$$E_{int}(Cu^+-H_2O) = E(Cu^+-H_2O) - E(Cu^+) - E(H_2O) \tag{3}$$

in a set of N points thought to give a good description of the potential-energy surface. This being known, a minimization procedure for the quadratic error

$$\Delta = 1/N \sum_{k=1}^{N} w_k [E_{int}(r_A^k, r_B^k, r_C^k) - V(r_A^k, r_B^k, r_C^k; c_p)]^2 \tag{4}$$

will produce the desired coefficients. The set of weights (w_k) is chosen so that the more attractive parts of the potential curve are given greater importance in the adjustment. The attractive region of the potential thus obtained will be most accurately described because water molecules in this region make the major contribution to the calculated thermodynamic properties.

In this work all quantum energies, for Cu^+, H_2O and for the complex Cu^+-H_2O have been calculated by the method of pseudo-potentials developed by Barthelat and co-workers[10] using the program PSHONDO.[11] The use of this method is justified by the difficulty in performing the explicit all-electron calculation for a system like Cu^+-H_2O. Some remarks should be made about this method, especially concerning its application to the chemical species of interest in the present work.

(i) The quality of the results depends clearly on the number and shape of the valence basis functions used and on the parametrization of the pseudo-potentials. The pseudo-potentials and the basis set were taken from Barthelat and co-workers,[10] with a double-zeta contraction on $2s$ and $2p$ for O, and $3d$ and $4s$ functions for Cu^0; Cu^+ has not, to our knowledge, been studied and the parameters of Cu^0 were used instead. This may be justified by analogy with the findings of Ortega-Blake and Barthelat[12] on calcium and magnesium.

(ii) Concerning electron correlation, the method used here suffers from the same shortcomings as the Hartree–Fock method. The motion of the valence electrons is studied under the field created by atomic cores assumed to be frozen. However, the distortion of the core induced by the outer electrons may be very important and have a large energy contribution. This was disregarded as it has been shown to be relevant only in Group I, II and VIII atoms;[13] however, modified calculations to take into account core polarization and correlation are envisaged for a later stage.

2.2. Results

The quantum-mechanical interaction energies of the system Cu^+-H_2O were computed for 11 orientations of the water molecule (fig. 1) and for several distances r_{Cu^+-O} in a total of 133 calculations. The geometry of the water molecule was fixed at the experimental[14] values of $r_{OH} = 0.9572$ Å and $\angle HOH = 104.5°$. The calculated potential energies for the Cu^+-H_2O interaction are plotted in fig. 2 and 3.

This interaction energy may be interpreted as the result of the balance between the attraction Cu^+-O (except for very short distances) and the repulsion Cu^+-H. Configuration $\alpha = 0°$ is thus expected to be the most stable and that for $\alpha = 180°$ the most
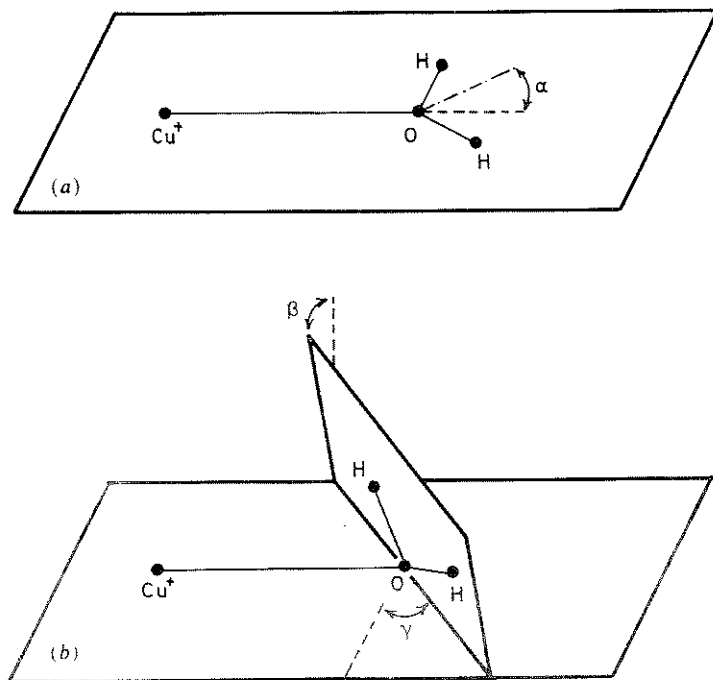
Fig. 1. Schematic representation of the 11 orientations of the water molecule that are considered in the quantum calculations. Five planar configurations with α (*a*) equal to 0, 45, 90, 135 and 180 °. The six non-planar configurations are constructed, from a configuration in which the water molecule is in a plane perpendicular to the plane containing the Cu⁺ ion, by successive rotations by angles β and γ, defined as shown in (*b*), with $(\beta, \gamma) = (0, 0), (45, 0), (-45, 0), (0, 45), (45, 45)$ and $(-45, 45)$.

unstable, with the other in between. This is clearly shown in fig. 2 and 3, the energy minimum of -166.35 kJ mol^{-1} ($-0.063\,36$ hartree) being found for the planar conformation with $\alpha = 0$ ° at a Cu⁺-O distance of 2.05 Å.

The fitting of functionals V_1, V_2, V_3 and V_4 in eqn (2) to the calculated interaction energies in fig. 2 and 3, was made with a weight $w_k = 3$ for points of energy below -13.13 kJ mol^{-1}; repulsive energies above 393.83 kJ mol^{-1} are disregarded. The absolute and square average deviations between quantum values and those given by the different functions are shown in table 1; in table 2, the position of the minima is compared with that calculated quantum mechanically.

V_4 is to be adopted as it correctly reproduces the position of the minimum, and the corresponding energy is the closest to the calculated value. The economy in computer time that results from prefering a simpler potential like V_3 does not compensate for the loss of accuracy (in a test performed for the $n = 20$ cluster at 298 K, a decrease of 2% in the computing time resulted in a marked loss of quality in the radial distribution function). The statistical parameters in table 1 point towards this same choice as the best fit. The full set of parameters of V_4 are shown in table 3.

The good quality of V_4 is also apparent in fig. 4, where calculated interaction energies are plotted against those predicted by V_4. The agreement is good overall and it is particularly close in the region of the lower energies according to the weighting system used. Moreover, the quality of the fitting can also be verified in fig. 2 and 3, where the
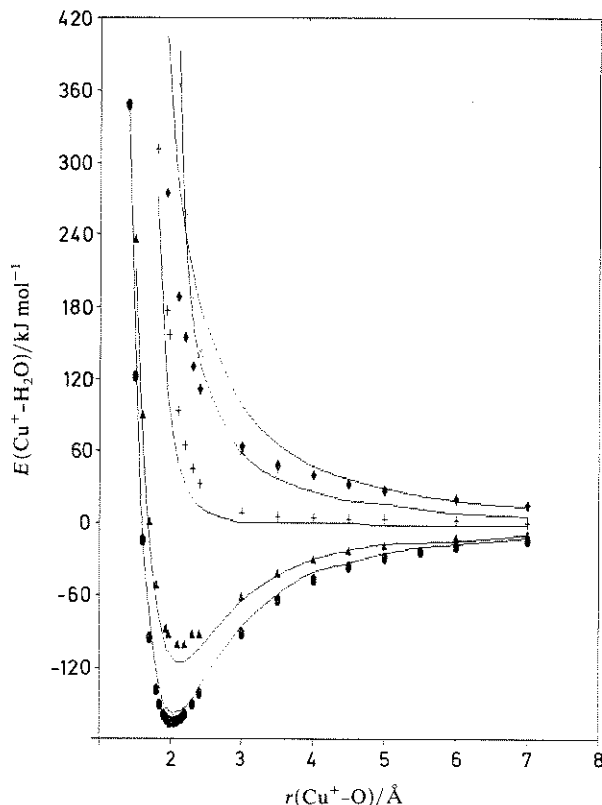
Fig. 2. Potential-energy curves for Cu^+-H_2O in the planar configurations. The points were calculated by the pseudo-potential method described in the text. The solid lines correspond to the fitted potential V_4. $\alpha/°$: $\diamond$, 180; $\times$, 135; +, 90; $\triangle$, 45; $\bigcirc$, 0.

points calculated by the pseudo-potential method are very close to the solid lines corresponding to the fitted potential V_4. V_4 may thus be expected to be adequate for Monte Carlo simulations of the systems $[Cu(H_2O)_n]^+$.

3. Application to $[Cu(H_2O)_n]^+$ Clusters

3.1. Method

The statistical simulation of the $[Cu(H_2O)_n]^+$ clusters at several temperatures has been performed by the Monte Carlo method[15] using the Metropolis algorithm.[16] The minimum-energy configuration (0 K) has been obtained by geometry optimization of the $n = 6, 8, 10, 15$ and 20 clusters with a modified version of Monte Carlo procedure. The temperature effect has been analysed by statistical simulation of the same clusters at 50, 298 and 500 K.

The initial configuration has been obtained from a cubic distribution of water molecules by replacing one of them by the Cu^+ cation. At 0 K, the geometry optimization is complete when a stable configuration is obtained, corresponding to a energy minimum. At a non-zero temperature, statistical equilibration is achieved after the calculation of $4000n$ configurations and the statistical calculations have been performed over an additional $4000n$ configurations. This is the number of calculations used by Clementi and coworkers[6(a)] and we confirmed that their total energy is stable.
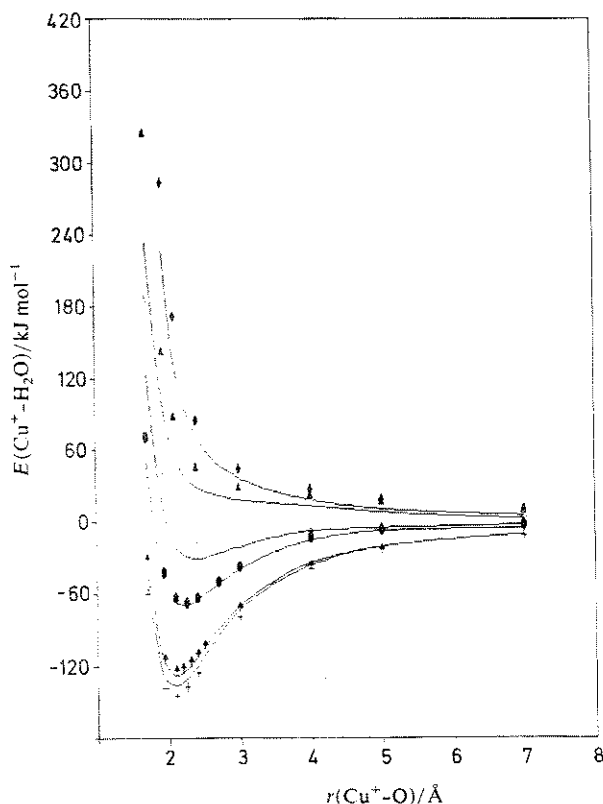
Fig. 3. Potential-energy cvurves for Cu^+-H_2O in the non-planar configurations. The points were calculated by the pseudo-potential method described in the text. The solid lines corresponds to the fitted potential V_4. ◆, $\beta = 45°$, $\gamma = 45°$; ▲, $\beta = 45°$, $\gamma = 0°$; ×, $\beta = 0°$, $\gamma = 45°$; ↑, $\beta = 45°$, $\gamma = 45°$; +, $\beta = 45°$, $\gamma = 0°$.

Table 1. Average of absolute deviations and standard deviations for the fitting of the Cu^+-H_2O energy calculated points to functions V_1, V_2, V_3 and V_4

type of function	absolute deviations[a]	standard deviations[a]
V_1	21.24	32.56
V_2	17.67	27.57
V_3	13.18	20.64
V_4	11.11	19.64

[a] In kJ mol^{-1}.

The energy of each configuration has been caluiated in the pair-potential approximation with the MCY[5] water-water interaction potential already mentioned; for the Cu^+-H_2O interaction, the potential function described in section 2 has been used.

In order to examine the microscopic structural characteristics of the first solvation shell we have used a procedure suggested by Tapia and Lluch.[17] In this procedure, the final configurations generated in the simulation are divided into groups which have an equal number of water molecules inside a sphere of radius 4 Å centred on the Cu^+

Table 2. Energy minima of the fitted functionals V_1, V_2, V_3 and V_4

type of function	energy/ kJ mol^{-1}	Cu$^+$-O distance/ Å
V_1	-146.24	1.96
V_2	-149.73	2.00
V_3	-154.27	2.10
V_4	-169.95	2.05

Table 3. Parameters of V_4 determined in the adjustment

type of parameter	value
c_1	0.945 32
c_2	23.559 80
c_3	$-11\ 151.948\ 66$
c_4	1314.786 01
c_5	359.177 11
c_6	0.282 96
c_7	$-1.105\ 23$
c_8	$-203.393\ 98$
c_9	6.868 21
c_{10}	566.358 72
c_{11}	$-14.574\ 99$
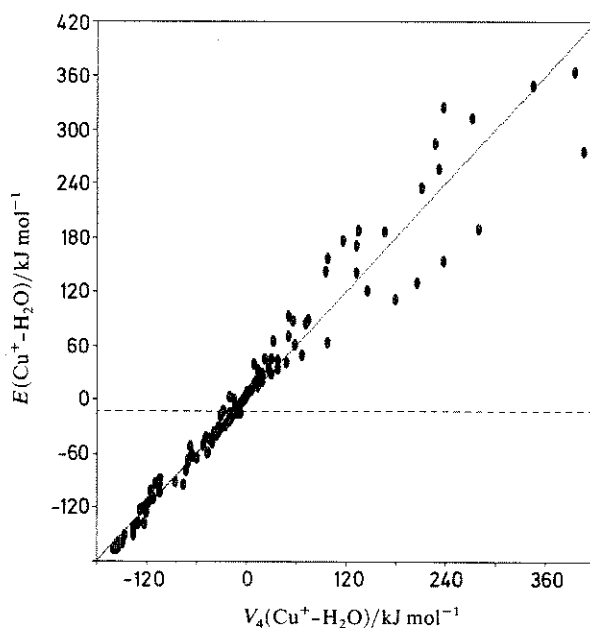
Fig. 4. Comparison between calculated interaction energies and those resulting from the fitting to potential V_4. The weights (w_k) used in the fitting are 1 and 3 for points above and below the dashed lines, respectively.
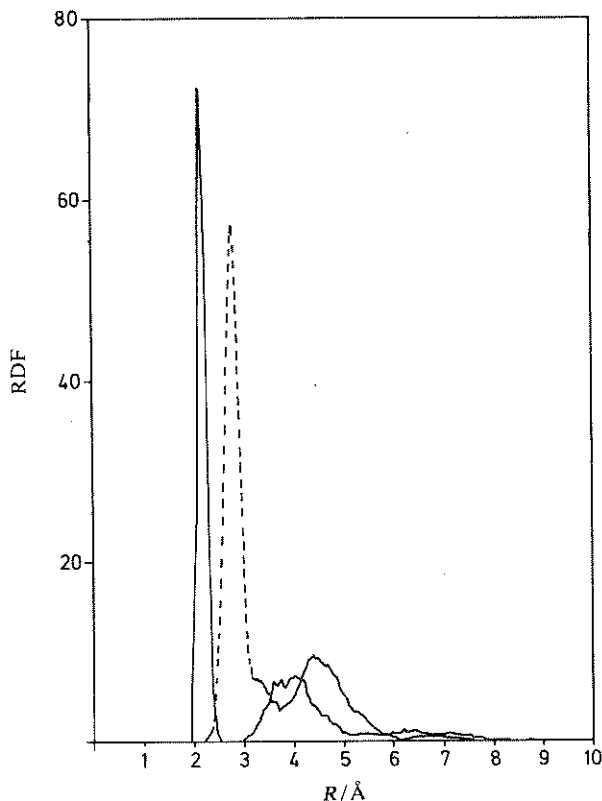
Fig. 5. Radial ion–oxygen (——) and ion–hydrogen (– – –) distribution functions for the [Cu(H$_2$O)$_{20}$]$^+$ cluster at 298 K.

ion. These groups are arranged into several classes in a way that each class is related to an important structure of the solvent. Two configurations are included in a class if all oxygen–oxygen distances of their equivalent water molecules are less than 1.2 Å and the average of these distances is <1.0 Å. The different structures of the configurations belonging to one class are considered as fluctuations around the mean positions of the water molecules of the important solvent structure of the class.

3.2. Results

To study the results of the simulations, we have computed the radial ion–oxygen and ion–hydrogen distribution functions (RDF) for all the [Cu(H$_2$O)$_n$]$^+$ clusters at 50, 298 and 500 K, as well as the corresponding running coordination number of Cu$^+$ metal. This coordination number, $N(R)$, has been defined as the average number of oxygen atoms within a spherical shell of radius R centred at the Cu$^+$ ion.

It should be noted that, there was no significant difference between the results obtained at the three temperatures, for the above mentioned quantities. Thus, as an example, the RDF functions and the running coordination number $N(R)$ for the [Cu(H$_2$O)$_{20}$]$^+$ cluster at 298 K are reported in fig. 5 and 6, respectively.

In fig. 5, one can observe the occurrence of two sharp and distinct peaks: one at *ca.* 2.15 Å for the ion–oxygen RDF and the other at *ca.* 2.80 Å for the ion–hydrogen RDF.
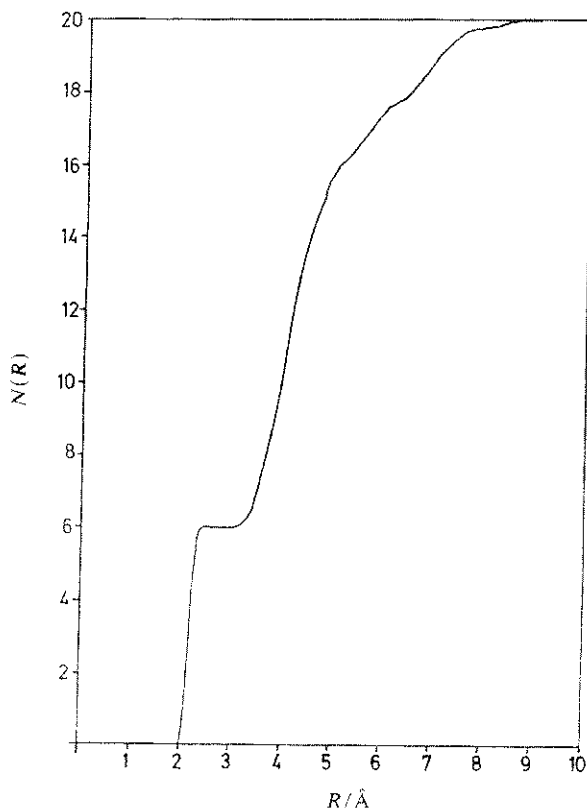
Fig. 6. Running coordination number for the $[Cu(H_2O)_{20}]^+$ cluster at 298 K.

Clearly, they show the positions of the oxygen and hydrogen atoms on the Cu^+ first hydration shell. One can also observe that these two peaks do not overlap, indicating that the first hydration shell has a rigid structure with the oxygens well oriented toward the central ion. It is worth noting that the width of these first peaks increases and their height decreases as the temperature is increased from 50 to 500 K, although they retain the same positions. This reflects a thermal distortion of the first solvation shell.

Another feature that stands out from fig. 5 is the appearance of two small peaks, one for each RDF, at $R > 3$ Å, which can be associated with the second solvation shell. The broadness of these peaks probably indicates that the structure of this second shell is less rigid than that of the first shell. However, to define a second solvation layer unambiguously more than 20 molecules would be required. It must be emphasized that the RDF functions of the $[Cu(H_2O)_6]^+$ cluster do not show those peaks at any temperature. For all the other clusters and at any of the three temperatures, they all appear on the corresponding RDF but are well visible only for the cluster with 20 water molecules.

The above results can be understood by assuming that the first hydration shell is formed by six water molecules. A similar conclusion can easily be obtained through examination of the $N(R)$ curve in fig. 6. In fact, from the value of $N(R)$ at the first plateau, we can find a coordination number of six for the solvated Cu^+ ion. Microscopic structural analysis performed on the different clusters, at the three temperatures and using the procedure described in the last section, shows an octahedral arrangement for the six water molecules of the first layer. This octahedral structure becomes more
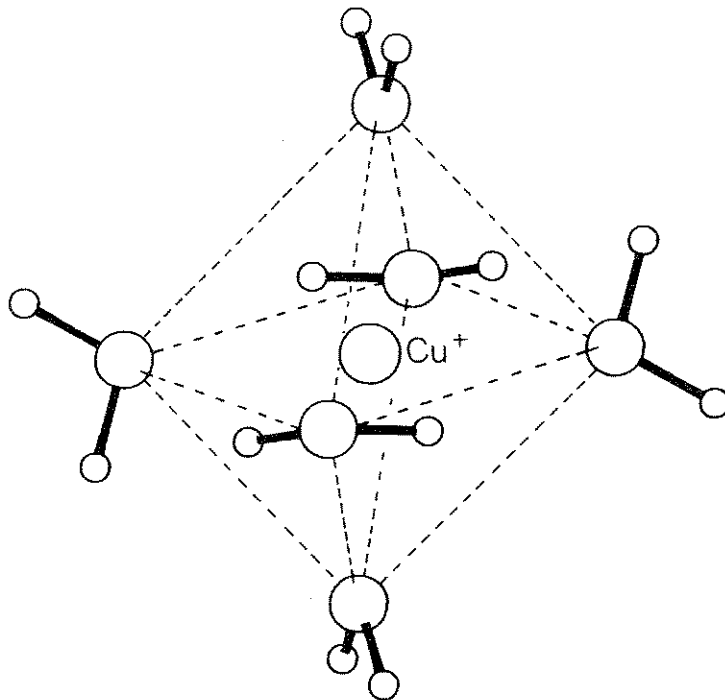
Fig. 7. Minimum-energy structure obtained at 0 K for the $[Cu(H_2O)_6]^+$ cluster.

irregular when the temperature is increased. As an example, we show in fig. 7 the minimum-energy structure obtained at 0 K for the $[Cu(H_2O)_6]^+$ cluster, which is obviously symmetric since there is no thermal motion.

It is interesting to note that the average position of the water molecules and the mean ion–water distance for the most relevant structure of each cluster analysed are very similar to those of the minimum-energy structure in fig. 7.

In order to analyse the energetic features of the first Cu$^+$ solvation layer, the ion–water, water–water and the total interaction energies per water molecule are given in table 4 as functions of cluster size, n, and temperature, T. For completeness, the results computed at 0 K are also given. All energies presented were divided by the number of water molecules to allow a direct comparison.

For a given temperature, the ion–water interaction energy has its highest attractive value for $n = 6$ and tends to be less stabilizing as the cluster size is enlarged. The water–water interaction has its maximum repulsive value for the $[Cu(H_2O)_6]^+$ cluster and then starts to be less destabilizing, attaining attractive values for the larger clusters. In addition, the stabilizing total interaction energy decreases when one goes from $n = 6$ to $n = 20$.

These observed trends are consistent with our assumption of a coordination number of six. The water molecules in the first layer appear to be oriented to obey the dominant ion–water interaction, the water–water interaction energy being repulsive as a side-effect. Outside the first layer, the ionic field is much weaker and the water molecules may adopt orientations which are no longer repulsive.

Concerning the effect of temperature, we note the expected trend in the total interaction energy, *i.e.* the higher the temperature, the less attractive is the total interaction

Table 4. Interaction energies per water molecule as a function of cluster size, n, and temperature, T

T/K	n	$E(Cu^+-H_2O)^a$	$E(H_2O-H_2O)^a$	E^a
0	6	−149.30	20.94	−128.36
	8	−118.39	6.36	−112.03
	10	−95.53	−4.87	−100.40
	15	−71.98	−13.11	−85.09
	20	−56.63	−17.92	−74.55
50	6	−151.00	23.78	−127.22
	8	−118.21	7.45	−110.76
	10	−98.44	−0.69	−99.13
	15	−70.53	−8.28	−78.81
	20	−55.91	−17.83	−73.74
298	6	−143.27	22.00	−121.27
	8	−112.67	10.73	−101.94
	10	−95.25	5.99	−89.26
	15	−67.85	−5.16	−73.01
	20	−54.28	−11.42	−65.70
500	6	−137.62	20.46	−117.16
	8	−110.37	15.61	−94.76
	10	−91.00	9.41	−81.59
	15	−65.47	3.89	−61.58
	20	−51.17	−0.91	−52.08

[a] In kJ mol^{-1}.

energy. In fact, this behaviour can be rationalized if one thinks that the increase of the temperature raises the population of the higher-energy states.

4. Conclusions

We have built an analytical interaction potential for the Cu^+-H_2O system which has been applied, together with the MCY H_2O-H_2O potential, in the study of Cu^+ clusters containing 6, 8, 10, 15 and 20 water molecules. The study of these clusters has been done by energy minimization ($T = 0$ K) and by Monte Carlo simulation at different temperatures ($T = 50, 298$ and 500 K).

This potential appears to be accurate enough, judging from the results obtained here, and allowed us to predict a first hydration shell with six water molecules for the Cu^+ ion. This was to be expected since, for instance, the Na^+ aqueous coordination number is also six[18,19] and its ionic radius differs very little from that of the Cu^+ ion.[4] It should be noted that experimental work by high-pressure mass spectrometry[3] suggests that the $[Cu(H_2O)_4]^+$ cluster is the most stable in the gas phase, apparently in conflict with the results presented in this work. However, this may be explained by the well known difficulty of observing the higher clusters with water by this experimental technique.[20]

It must be emphasized that there are some limitations inherent in the methodology of the present work, namely, the neglect of the multibody effects and the the study of only a very small number of molecules of water in the clusters, especially at $T = 298$ K. Simulations at infinite dilution are required, but the results reported in this paper are sufficient for preliminary estimates of the structure and coordination number of the hydrated Cu^+ ion.

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