ADVANCES IN INORGANIC CHEMISTRY, VOL. 34

THE COORDINATION OF METAL AQUAIONS

G. W. NEILSON and J. E. ENDERBY

H. H. Wills Physics Laboratory, University of Bristol,
Bristol BS8 1TL, England

I. Introduction

> The logical place to begin a discussion of the formation and stability of complex ions in aqueous solutions is with the aqueous ions themselves.... If we regard the (metal) ion as being an aqueous complex $(M(H_2O)_n)^{p+}$, which is then further and more loosely solvated, we wish to know the coordination number n and also the manner in which the n molecules are arranged around the metal ion.

These two sentences, taken from Cotton and Wilkinson's *Advanced Inorganic Chemistry* (*17*), form the starting point to this article. Articles in which information on aqua metal ions has appeared include refs. (*9*) and (*33*).

The first question that must be addressed concerns the stability of the aqueous complex (hereafter referred to as the aquaion). The stability, though usually thought of in a temporal sense, is related, albeit indirectly, to the real space structure at the level of the partial radial distribution functions $g_{\alpha\beta}(r)$. This measures the probability of finding a β-type particle at a distance r from an α-type particle placed at the origin. To understand $g_{\alpha\beta}(r)$ quantitatively, consider an α-type particle at the origin and ask what is the average number of β-type particles that occupy a spherical shell of radius r and thickness dr at an instant of time. That number is given by

$$dn_{\alpha\beta} = 4\pi\rho_\beta g_{\alpha\beta}(r)r^2\,dr \qquad (1)$$

Here $\rho_\beta = N_\beta/V$, and N_β is the number of species contained in the sample of volume V.

In Fig. 1 we sketch a hypothetical $g_{\mathrm{MO}}(r)$ for an aqueous solution consisting of a salt M_qX_p (M = cation of valence p; X = anion of valence q) dissolved in H_2O. The chance of finding the ion M^{p+} and the oxygen atom separated by a distance less than r_c is negligible. Thus, r_c mea-

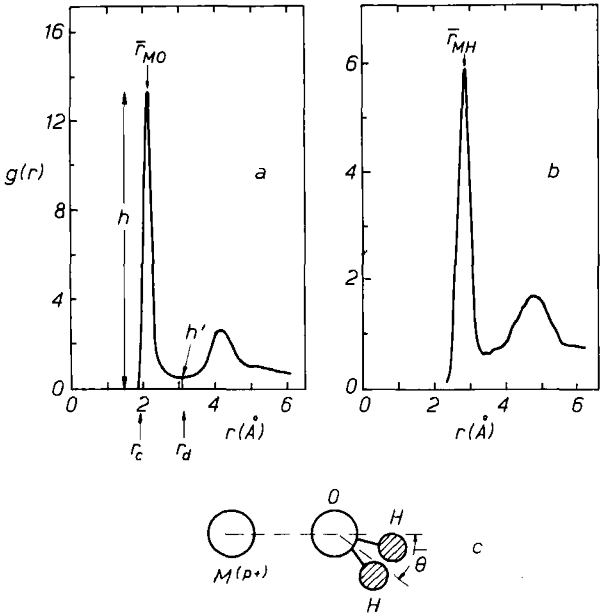

FIG. 1. (a) and (b) Hypothetical radial distribution functions $g_{MO}(r)$ and $g_{MH}(r)$ for aquaions in solution. (c) The geometry of an aquaion.

sures the closest approach of M and O in the system. On the other hand, the value of $\bar{r}_{MO}$ enables us to define the most probable separation, and r_d tells us the spatial extent of the short-range MO interactions. The values of $g_{MO}(r)$ with r equal to $\bar{r}_{MO}$ and r_d are denoted h and h', respectively. It follows from the definition of $g_{\alpha\beta}(r)$ in Eq. (1) that the value of the integral is the running coordination number.

$$4\pi\rho_0 \int_{r_c}^{r_s} g_{MO}(r) r^2 \, dr$$

That is, the average number of oxygen atoms within a spherical shell of radius r_s for a metal ion chosen to be at the origin. If r_s is chosen as r_d, this value of the running coordination number is usually referred to as the coordination number, which we write in a generalization of the Cotton–Wilkinson notation as $\bar{n}_{MO}$. Thus far, the temporal stability of the aquaion has not been mentioned; even for labile aquaions such as K^+ or Cl^-, $\bar{n}_{MO}$ can always be defined in the preceding sense. Whether the concept of an aquaion is useful in the Cotton–Wilkinson description is a different matter.

If the mean lifetime t_b of a water molecule attached to the ion is long enough, the translation diffusion coefficient D_W of the water molecule acquires a value equal to that of the ion itself (D_M). Furthermore, the ion and its intact hydration shell diffuses in this limit over a characteristic length scale l given by $\sqrt{6D_M t_b}$. If l is taken as the separation of two hydrated ions (5 Å), the shortest length for which the concept of a stable aquaion is valid, it follows that $t_b \geqslant 5 \times 10^{-10}$ sec.

A glance at the often quoted values of t_b contained in the table by Cotton and Wilkinson (*17*) shows that all cations satisfy the requirement $t_b \geqslant 5 \times 10^{-10}$ sec. In fact, the values quoted for t_b are overestimates, particularly for the more labile aquaions; the values shown in Fig. 2 are more reliable. These data show that for many ions of chemical interest, the associated aquaion is a labile species, and this accounts for the large differences in "coordination numbers" quoted in the literature if nondiffraction techniques are used.

From a single diffraction experiment, it is possible to deduce a weighted average of the ten partial radial distribution functions [i.e., $g_{OO}(r)$, $g_{OH}(r)$, $g_{HH}(r)$, $g_{MO}(r)$, $g_{MH}(r)$, $g_{XO}(r)$, $g_{XH}(r)$, $g_{MM}(r)$, $g_{MX}(r)$, and $g_{XX}(r)$] that characterize the generic system. This weighted average is usually referred to as the total radial distribution function $G(r)$. The determination of a single partial radial distribution [e.g., $g_{MH}(r)$], a highly desirable aim, can in principle be established by the method of

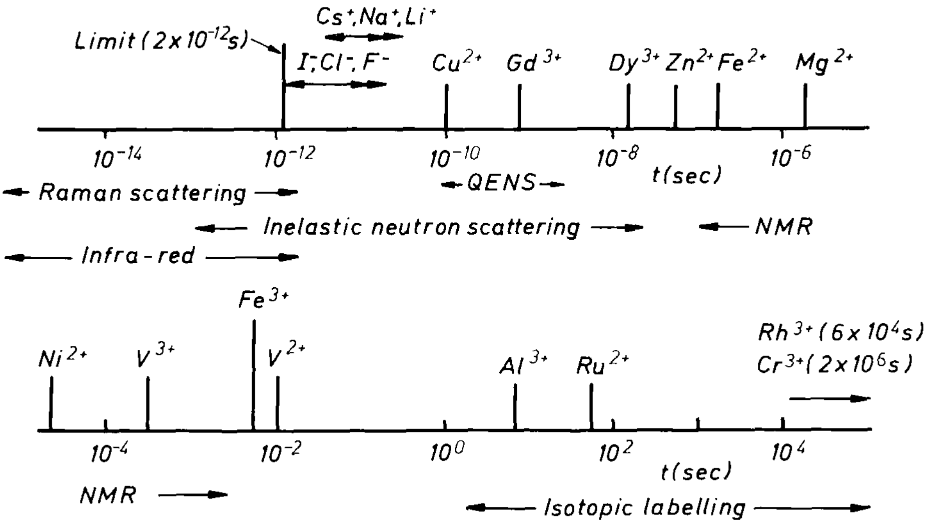

FIG. 2. Residence times (t_b) of water molecules in the neighborhood of an aquaion and ranges of experimental techniques (*23*, *36*).

differences if carried out to second order. A simpler experiment is to work at first order, which yields (for cation differences) a weighted combination of $g_{MO}(r)$, $g_{MH}(r)$, $g_{MM}(r)$, and $g_{MX}(r)$. The difference is achieved by changing the scattering amplitude appropriate to the radiation used, in this example, the cation. Detailed accounts of how diffraction data can be transformed into real space results, have been described in the literature [see, e.g., Enderby and Neilson (*21*)] and need not detain us here.

II. Comparison of Experimental Methods

Several techniques have been used to derive information about the structure and stability of an aquaion. The most powerful from the structural viewpoint are X-ray and neutron diffraction. At the level of total diffraction patterns, sophisticated modeling techniques are usually required to interpret experimental data; in general, for stable ions, these methods have been successful.

The use of difference methods offers a means whereby a detailed picture of ionic hydration can be obtained (*22*). For neutron diffraction, the first-order isotopic difference method (see Section III,A) provides information on ionic hydration in terms of a linear combination of weighted ion–water and ion–ion pair distribution functions. Since the ion–water terms dominate this combination, the first-order difference method offers a direct way of establishing the structure of the aquaion. In cases for which counterion effects are known to occur, as, for example, in aqueous solutions of Cu^{2+} or Zn^{2+}, it is necessary to proceed to a second difference to obtain, for example, g_{MX} and thereby possess a detailed knowledge of both the aquaion–water and the aquaion–counterion structure.

For X-rays, the first-order isomorphic difference offers a means of enhancing the resolution of g_{MO}. The method depends on finding suitable isomorphs and is limited by the chemistry of the ionic species.

The generation of a first-order difference by the use of anomalous scattering methods (either X-ray or neutron) offers the advantage that only a single sample is required. However, little use has been made of this possibility so far. On the other hand, extended X-ray absorption fine structure (EXAFS) spectroscopy has been used to investigate, in a limited way, $g_{MO}(r)$ and the existence of inner-sphere complexing (*69*).

Spectroscopic techniques have also been used to study aquaions, NMR and quasielastic neutron scattering (QENS) being particularly useful. Infrared (IR) visible and ultraviolet (UV) spectroscopies have been employed to infer coordination properties of ions, especially the formation of complex species.

Attempts to deduce hydration numbers from classical thermodynamics and transport data have, in general, had limited success.

Finally, the role of computer simulation has served to deepen our understanding of ionic hydration in systems that can be characterized by pairwise additive potentials (*29*). Since pressure and temperature are parameters characteristic of simulations, ionic hydration changes at nonambient conditions in regions far from those presently accessible to experiment can be studied.

It should be emphasized that comparison of results obtained from the various experimental techniques of diffraction, spectroscopy, and thermodynamics is not straightforward. Whereas diffraction, especially difference diffraction, offers a direct probe of ionic structure, spectroscopic and thermodynamic probes are indirect and require assumptions that may lead to conflicting results. This is the main reason that large discrepancies appear in the literature for hydration numbers, particularly for the more labile ions. For example, the quoted value of $\bar{n}_{\mathrm{NaO}}$ for Na^+ varies from 2–13, depending on the technique used and the assumptions made (*9*).

III. Diffraction Methods

We now discuss the structural information accessible from neutron and X-ray techniques.

A. NEUTRON DIFFRACTION AND ISOTOPIC DIFFERENCES

Although the formalism for X-ray and neutron diffraction is essentially the same, it is appropriate to treat them separately because of the nature of the basic interaction. For the case of neutron diffraction, neutrons are scattered isotropically by all the nuclei of the system. The degree to which this takes place is determined by the coherent neutron scattering length b, which varies from isotope to isotope (Table I). Because the scattering is isotropic, the results of a given experiment can readily be presented in terms of a total radial distribution function.

By use of a single isotopic substitution of ion (I = M or X), a first-order difference function $G_{\mathrm{I}}(r)$ can be obtained by direct differencing of all $G(r)$ that contain all ten pair-distribution functions of the solution. $G_{\mathrm{I}}(r)$ is then a linear combination of only the four radial distribution functions specific to I and can be written as in Eq. (2) (*74*).

TABLE I

NEUTRON SCATTERING PARAMETERS FOR AQUA CATIONS SUSCEPTIBLE TO STUDY BY THE DIFFERENCE METHOD OF NEUTRON DIFFRACTION

Cation	Isotope[a]	$\bar{b}$(× 10^{-12} cm)	$\Delta\bar{b}$(× 10^{-12} cm)	Neutron data?/ref.	Comments
Li^+	^{6}Li	0.187	0.409	Y/*35, 59*	^{6}Li high absorption cross section
	^{7}Li	−0.222			
Mg^{2+}	^{N}Mg	0.538	0.176	N	
	^{25}Mg	0.362			
K^+	^{39}K	0.379	0.121	Y/*56*	
	^{41}K	0.258			
Ca^{2+}	^{N}Ca	0.49	0.31	Y/*32*	
	^{44}Ca	0.18			
Ti^{3+}	^{N}Ti	−0.382	0.855	N	
	^{46}Ti	0.473			
Cr^{3+}	^{N}Cr	0.364	0.784	Y	Feasibility demonstrated
	^{53}Cr	−0.42			
Fe^{2+} or Fe^{3+}	^{N}Fe	0.954	0.534	Y/*30*	
	^{54}Fe	0.42			
Ni^{2+}	^{58}Ni	1.44	2.33	Y/*54*	
	^{62}Ni	−0.87			
Cu^{2+}	^{63}Cu	0.672	0.437	Y/*67*	
Zn^{2+}	^{N}Zn	0.568	0.186	Y/*65*	
	^{67}Zn	0.754			
Ga^{3+}	^{69}Ga	0.788	0.148	N	
	^{71}Ga	0.640			
Sr^{2+}	^{N}Sr	0.702	0.146	N	Experiment arranged for 1989
	^{86}Sr	0.568			
Ag^+	^{107}Ag	0.755	0.338	Y/*68*	
	^{109}Ag	0.417			
Te^{6+}	^{122}Te	0.38	0.375	N	Experiments have been carried out
	^{124}Te	0.755			
Ba^{2+}	^{N}Ba	0.507	0.867	N	
	^{130}Ba	−0.36			
Nd^{3+}	^{144}Nd	0.24	0.53	Y/*51*	
	^{146}Nd	0.87			
Sm^{3+}	^{152}Sm	−0.50	1.3	Y	C. Cossy (unpublished)
	^{154}Sm	0.80			
Dy^{3+}	^{N}Dy	1.69	1.83	Y/*4, 16*	
	^{162}Dy	−0.14			
Er^{3+}	^{N}Er	0.803	0.427	N	
	^{166}Er	1.23			
Yb^{3+}	^{N}Yb	1.24	0.56	Y/*16*	
	^{170}Yb	0.68			
Tl^+,Tl^{3+}	^{203}Tl	0.65	0.30	N	
	^{205}Tl	0.95			

[a] Superscript N denotes the natural element.

$$G_I(r) = Ag_{IO}(r) + Bg_{ID}(r) + Cg_{IJ}(r) + Dg_{II}(r) + E \qquad (2)$$

Here, A is $2c_Oc_Ib_O\,\Delta b_I$, B is $2c_Dc_Ib_D\,\Delta b_I$, C is $2c_Ic_Jb_J\,\Delta b_I$, D is $c_I^2\,(b_I^2 - b_I'^2)$, E is $-(A + B + C + D)$, $\Delta b_I = b_I - b_I'$, and c_α is the atomic fraction of species α whose coherent neutron scattering length is b_α. (Note that neutron-diffraction experiments are usually carried out on heavy-water solutions because ordinary water has a large incoherent cross section.) Further isotopic substitutions of either M, X, or (as has recently been proved possible) H for D (*64*) enables the determination of g_{MM}, g_{XX}, g_{MX}, and g_{MH}. The latter function is particularly useful when discussing details of the ion–hydrogen structure, particularly beyond the first hydration shell.

For most systems Eq. (2) can be approximated by a sum over the first two terms, though care must be taken when inner-sphere penetration occurs because in that case the C term cannot be neglected.

Successful application of the first-order difference method depends on availability of isotopes that have significantly different coherent scattering lengths. Table I lists the b's for nuclei of the ions that can be studied by the method.

B. X-RAY DIFFRACTION AND ISOMORPHIC SUBSTITUTION

The formalism for X-ray diffraction is the same as that for neutron diffraction. However, because X-rays are scattered anisotropically by the electrons of the system, the form of the total radial distribution $G_X(r)$ is a sum over the individual radial distribution functions convoluted by the X-ray form factor. It is therefore difficult to obtain detailed information regarding ion–water structure from a total $G_X(r)$, and recourse is usually made to models based on solid-state structures. Indeed, this procedure is at the heart of the comprehensive work of the Italian groups of Magini and Licheri (*47*).

A way of improving the resolution of X-ray diffraction results was proposed by Bol and co-workers (*6*), who applied a technique of isomorphic substitution to a variety of divalent cations. The method enabled them to determine neighbor cation–oxygen coordination to much greater accuracy than is possible from the inherently poorly resolved total X-ray diffraction result. However, the justification for isomorphism of ionic species was not discussed in detail. In 1986 a new isomorphic procedure was introduced (*71, 72*), which included a systematic method to check the degree of isomorphism between ionic species. The choice of isomorphs is made on the basis of (i) identical solid-state coordinating properties (i.e., radii for a given coordination), (ii) similarity of chemical properties, and (iii) susceptibility of one of the isomorphic pairs to be checked by the neutron method. Once an isomorphic pair has been selected and isomorphism demonstrated, either by reference to the neutron-diffraction results or to a self-consistency check of three X-ray diffraction patterns of equimolar solutions of MX_n in H_2O, M^1X_n in H_2O, and a fifty-fifty mixture of both, a complete study can be made of ion–oxygen and ion–ion correlations as a function of ion concentration, counterion type, pressure, and temperature. The technique is not as straightforward as the neutron method because of the convolution problem. However, it does not require the use of expensive isotopes and can be based in a home laboratory. Furthermore, X-ray beams are usually more intense than neutron beams, and statistical errors are consequently less.

IV. The Structure of Aquaions

The structural properties of aquaions are best characterized by the radial pair-distribution functions $g_{MO}(r)$ and $g_{MH}(r)$, and it is at this level that comparison between theory and experiment should be made. It is, however, convenient not only for tabulating data but also for making contact with other experimental techniques, to extract from $g_{MO}(r)$ and $g_{MH}(r)$ the nearest-neighbor distances $\bar{r}_{MO}$ and $\bar{r}_{MH}$ (or more appropriately, $\bar{r}_{MD}$) and the coordination number $\bar{n}_{MO}$. Moreover, if the coordinated water molecules are regarded as rigid and characterized by a well-defined bond length $\bar{r}_{OH}$ and HOH bond angle, $\bar{r}_{MO}$ and $\bar{r}_{MD}$ can be related by a root mean square angle-of-tilt $\bar{\theta}$. However, this should not be thought of as anything other than a measure of the wagging distortion of the aquaion [see, e.g., refs. (*23*) and (*54*)].

In the following section, diffraction results are presented and discussed for various groups of ions. The basis for discussing these ions is a selection of results from the neutron and X-ray diffraction difference methods (ND and XD), total X-ray and neutron diffraction methods (TX and TD), and EXAFS (EX). A selection of results are contained in Tables II–VII and, where appropriate, will be contrasted with results derived from other methods. A more complete tabulation of TX results is available in table 2 of ref. (*53*) or in ref. (*47*).

A. MONOVALENT CATIONS

The first-order difference method of neutron diffraction (ND) can be carried out on Li^+, K^+, Ag^+, and Tl^+ (Table I). The sodium ion can be investigated at an approximate level by total X-ray diffraction and

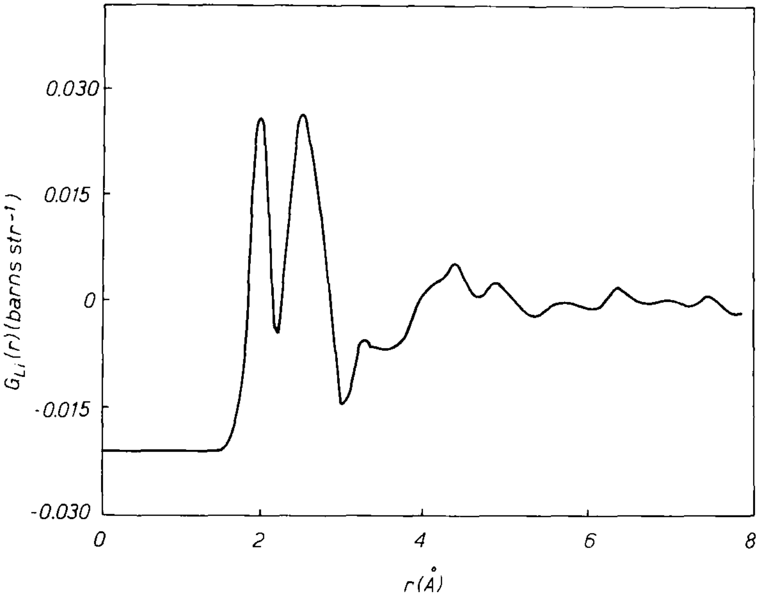

FIG. 3. The total lithium-ion radial distribution functions G_{Li} for 3.57-molal LiCl in heavy water (*59*).

isomorphic substitution and X-ray diffraction using the Na^+/Ag^+ pair (*73*).

ND studies show that Li^+ has a well-defined hydration shell (Fig. 3). The value of $\bar{n}_{LiO}$ changes with concentration, being significantly greater than 4 at low concentration and dropping well below 4 at high concentration (Table II). Computer simulation gives a value of 6 for Li^+ at infinite dilution, in broad agreement with experiment. The sodium ion Na^+ has been studied by both TX and XD using Ag^+ as the appropriate isomorph. A value of 5 ± 1 was found for $\bar{n}_{MO}$ for aqueous solutions of $(Ag/Na)NO_3$. Results for $\bar{n}_{NaO}$, based on analysis of TX data, give values between 4 and 6.

An ND study of K^+ hydration gives a $G_K(r)$ that shows little structure (Fig. 4), a result in marked contrast to that for Li^+. Clearly the larger K^+ ion coordinates water molecules relatively weakly and so forms a labile aquaion. One can show from $G_K(r)$ that $\bar{n}_{KO}$ is 5.5 ± 0.5 in the range $2.3 \leqslant r \leqslant 3.4$. However, such a value cannot be taken as a hydration number in the same sense as for a stable species. Indeed, the value from computer simulation of 10 for $\bar{n}_{KO}$ can be equally useful (*7*).

Preliminary EXAFS and anomalous scattering results for a 4.6-molar aqueous solution of rubidium bromide (*43*) suggest that the Rb^+–water interaction is relatively weak, in good agreement with thermo-

TABLE II

HYDRATION SHELL PROPERTIES FOR MONOVALENT CATIONS[a]

Ion	Counter-ion	Concentration (molality)	Ion–water distances (Å)		Hydration number	Tilt angle[b]	Method[c]/ reference
			$\bar{r}_{MO}$	$\bar{r}_{MD}$	$\bar{n}_{MO}$	$\bar{\theta}$ (deg)	
Li^+	Cl^-	27.77	1.95(2)	2.31(2)	2.3(2)	75(5)	ND/*35*
	Cl^-	9.95	1.95(2)	2.50(2)	3.0(5)	52(5)	ND/*59*
	Cl^-	3.57	1.95(2)	2.55(2)	5.5(3)	40(5)	ND/*59*
	Cl^-	6.9	1.95	—	4 (1)	—	TN,TX[d]/*50*
Na^+	NO_3^-	3.1	2.4(2)	—	5 (1)	—	XD/*71, 73*
	NO_3^-	5 molar	2.44(1)	—	6	—	TX/*11*
K^+	Cl^-	4	2.7(1)	3.1 (2)	—	—	ND/*56*
	OH^-	2.02	2.8	—	4	—	TX/*8*
Cs^+	OH^-	50	3.2	—	3	—	TX,TN/*5*
Ag^+	ClO_4^-	4.1	2.41(2)	2.97(4)	4.1(3)	45(4)	ND/*68*
	NO_3^-	3.1	2.40(2)	2.90(5)	3.7(5)		ND/*71, 73*
Tl^+	HCO_2^-	3.5 Molar	3.2	—	4	—	TX/*61*

[a] Errors are in parentheses.

[b] Based on a model of the D_2O molecule in which r_{OD} = 0.98 Å and DÔD = 104.5°.

[c] ND, neutron isotopic difference diffraction; XD, X-ray isomorphic difference diffraction; TX, total X-ray diffraction; TN, total neutron diffraction; EX, EXAFS (extended X-ray absorption fine structure).

[d] A more comprehensive list of TX results can be found in Magini (*46*) and Neilson and Enderby (*53*).

dynamic investigations (*24*). Similarly, a TX study of Cs^+ indicates that the relatively large cesium ion is also weakly hydrated, and on the basis of a recent quasielastic neutron scattering (QENS) experiment is labile.

An ND study of Ag^+ shows a coordination (Fig. 5) intermediate between that of Li^+ and K^+ with a value of $\bar{n}_{AgO} \sim 4$ (Table II). Based on the assumption that the coordination of monovalent ions scales with bare-ion size, a recent XD experiment has been used to demonstrate that Ag^+(aq) and Na^+(aq) are the same to a first approximation (*71, 73*). Consequently, difference methods have confirmed the trend that $Li^+ > Na^+ > K^+$ in terms of the stability of their hydration shells. The lability of the aquaions in the alkali series is further confirmed in QENS experiments (*31b*), in which results show that the translational dynamics of the protons of the water molecules are not appreciably perturbed for alkali metal cations other than Li^+. Results of computer simulation studies of models in which alkali ion–water potential is based on *ab initio* calculations give good overall agreement with the

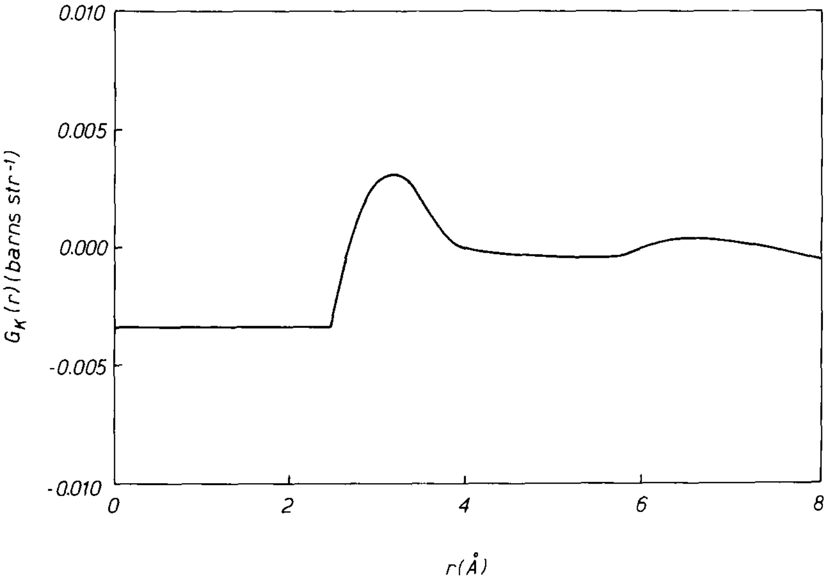

FIG. 4. The total potassium-ion radial distribution function G_K for 4-molal KCl in heavy water (*56*).

ND results (*7*). The single experimental result for Tl^+ is consistent with weak hydration.

The complex cation ND_4^+ has been studied by X-ray diffraction (*49*) and by the neutron isotopic difference method (*31a*), and results show that the coordination is weak, as might be expected for the low charge density. An MD computer simulation study using modified *L-J* potentials for the ion–water interactions gave good agreement with the ND results (*75*).

B. TRANSITION METAL IONS

Aqueous electrolyte solutions of transition metal ions exhibit a rich variety of behaviors. All are suitable for study by ND with the exception of the monoisotopic cation Mn^{2+} and Co^{2+}, which have been successfully investigated by TX (Table III).

It is clear from Table III that all transition metal ions other than Cu^{2+} have a well-defined six-fold coordination, and on the basis of these results and those from NMR, QENS, optical spectroscopy, and kinetic studies with isotopically enriched species, it can be concluded that they form stable hydration complexes.

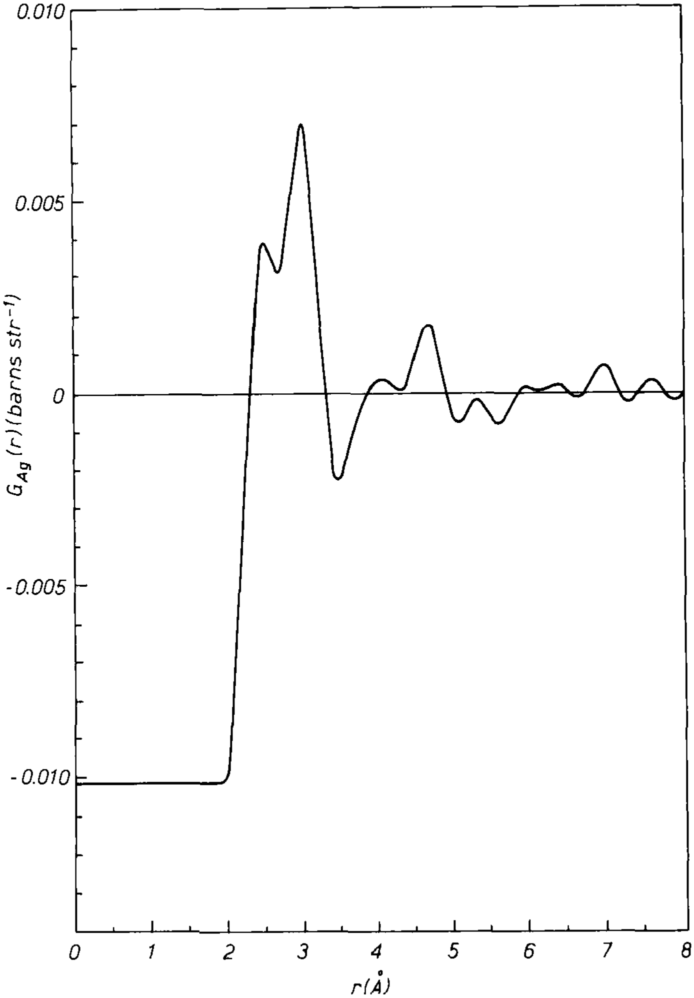

FIG. 5. The total Ag^+ radial distribution function $G_{Ag}(r)$ for 4-molal $AgClO_4$ in heavy water (*68*).

The most extensive study has centered on Ni^{2+}(aq), and results indicate that its coordination to water molecules in terms of $G_{Ni}(r)$ (Fig. 6) is independent of concentration (*52*, *65*), counterion, temperature, and pressure. Furthermore, in a study of solvent exchange, it has been demonstrated that isotopic substitution can be applied to the deuterons of the water molecules. Consequently, $g_{NiH}(r)$ has been uniquely deter-

TABLE III

HYDRATION SHELL PROPERTIES OF TRANSITION METAL IONS[a]

Ion	Counter-ion	Concentration (molality)	Ion–water distances (Å)		Hydration number	Tilt angle[b]	Method[b]/ reference
			$\bar{r}_{MO}$	$\bar{r}_{MD}$	$\bar{n}_{MO}$	$\bar{\theta}$ (deg)	
Cr^{3+}	ClO_4^-	1 molar	1.97(1)	—	6	—	EX/*70*
Cr^{2+}	ClO_4^-	1 molar[d]	1.99(1)	—	4[c]	—	EX/*70*
			2.30(1)	—	+2		
Mn^{2+}	Cl^-	4.2	2.09(2)	2.69(3)	5(1)	43(10)	ND/*55*
	NO_3^-	4.4	2.19		6	—	TX/*13*
Fe^{2+}	ClO_4^-	1 molar	2.12	—	6[e]	—	TX/*60*
	ClO_4	1 molar	2.09(5)	—	6	—	EX/*69*
Fe^{3+}	ClO_4	2[d]	1.96( )	—	6[e]	—	ND/*30*
	ClO_4^-	1 molar[d]	1.99(1)	—	6	—	EX/*69*
Co^{2+}	Cl^-	2.97 molar	2.10	—	6[e]	—	TX/*45*
	Br^-	2.8 molar	2.05	—	6[e]	—	TX/*34*
Ni^{2+}	ClO_4^-	3.8	2.07(2)	2.67(2)	5.8(2)	42(8)	ND/*58*
	Cl^-	4.35	2.07(2)	2.67(2)	5.8(2)	42(8)	ND/*54*
	Cl^-	1.46	2.07(2)	2.67	5.8(2)	42(8)	ND/*52*
	Cl^-	0.5	2.07(2)	2.67	6.0(2)	42(8)	ND/*65*
	Cl^-	2.95 molar	2.07(2)	—	6	—	TX/*45*
	Br^-	3.88 molar	2.08(3)	—	6[e]	—	XD/*71, 72*
					4[c]		
Cu^{2+}	ClO_4^-	2.0	1.96(3)	2.58	+2	—	ND/*67*
	ClO_4^-	1.0	1.96(1)	—	4[c]	—	EX/*70*
			2.60(1)	—	+2	—	
	NO_3^-	1.0	1.96(3)	—	+2	—	ND/*57*
	Cl^-	4.32	1.96(3)	—	3.4	—	ND/*67*
	Cl^-	2.95 molar	1.95; 2.25	—	2.8; 1.2Cl	—	TX/*45*

[a] Errors are in parentheses.

[b] See footnotes in Table II for details.

[c] Jahn–Teller effect (see reference for details).

[d] Acidic solution.

[e] Anion penetration.

mined (Fig. 7), and information has been obtained about the relative $Ni^{2+}(aq)$ fractionation of H_2O and D_2O in equimolar mixtures. The derivation of $g_{NiH}(r)$ has also been used to demonstrate that angular correlations between Ni^{2+} and water molecules extend into the second hydration shell (*64*), a result confirmed in computer simulation studies of $Mg^{2+}(aq)$, which can be regarded as isomorphic to $Ni^{2+}(aq)$ (Fig. 7). Little is known about the composition of the second hydration shell, though it is often speculated that for an octahedral ion there are eight

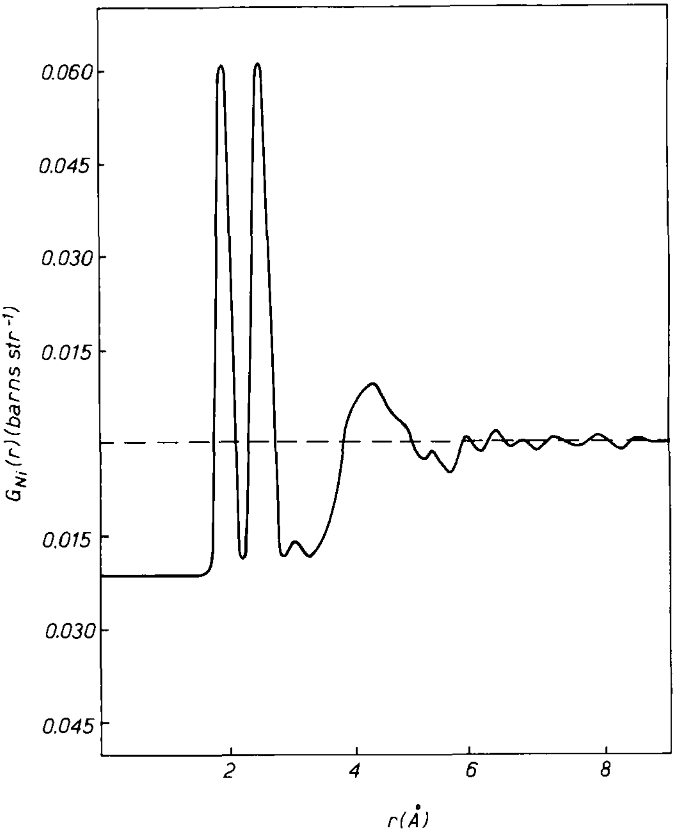

FIG. 6. The total Ni^{2+} radial distribution function $G_{Ni}(r)$ for 1.46-molal $NiCl_2$ in heavy water (*52*).

favorable positions for electrostatic interaction, one over the center of each face.

It is also of interest to note that counterion effects are significant when Br^- replaces Cl^- as the anion in aqueous solutions of the Ni^{2+}/Mg^{2+} pair, and evidence exists for Br^- penetration into the first coordination shell, a result consistent with analysis of total X-ray diffraction patterns. This observation is one of the few cases in which the heavier halogen ion interacts more strongly with a counterion than the lighter one.

The ND method has been applied to Cu^{2+}, and results show that the aquaion structure depends on counterion (see Table III). The $G_{Cu}(r)$ for a 2.00-molal $Cu(ClO_4)_2$ and a 1.0-molal $Cu(NO_3)_2$ solution show that

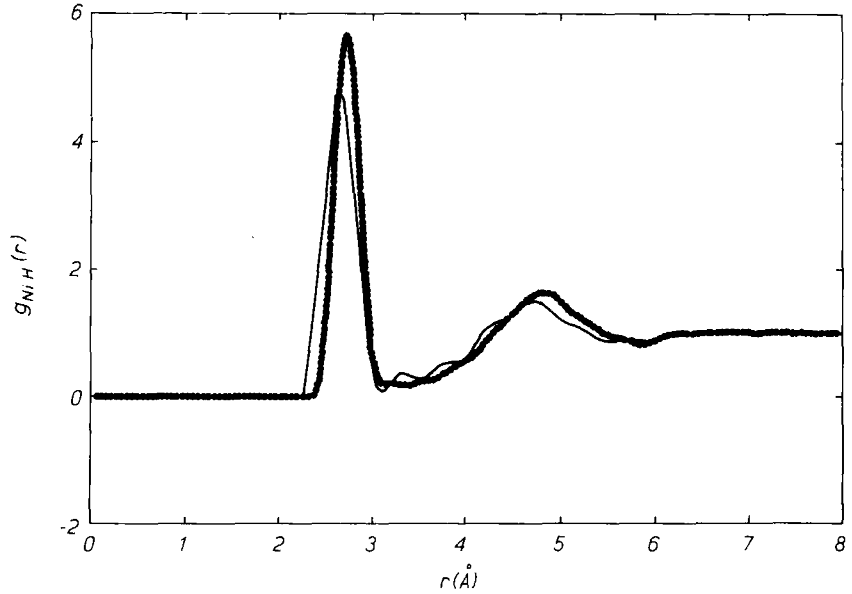

FIG. 7. Radial distribution function $g_{\text{NiH}}(r)$ (solid line) for 2-molal $NiCl_2$ in water (*64*), compared with $g_{\text{MgH}}(r)$ (dotted line) obtained from MD computer simulation (*19*).

Cu^{2+} has four nearest-neighbor oxygens at $r_{\text{CuO}} = 1.96 \pm 0.03$ Å and are consistent with the presence of two more-distant oxygens $r \geqslant 2.21$ Å (Fig. 8). This confirms previous X-ray studies and demonstrates a Jahn–Teller distortion of the complex $[Cu(H_2O)_6]^{2+}$ to give a (4 + 2) coordination group. The results for the 4.32-molal $CuCl_2$ solutions show that the hydration number of Cu^{2+} is less than in the perchlorate solution and suggest the occurrence of inner-sphere complexing of the chloride ion by Cu^{2+}.

Quasielastic neutron scattering results for a 3-molal $Cu(ClO_4)_2$ solution at room temperature give no evidence in support of water molecules having inequivalent dynamic sites about Cu^{2+} for times longer than 10^{-10} sec (*66*). The short binding-time in the case of Cu^{2+} is, on the other hand, usually attributed to a model wherein water exchanges rapidly by virtue of its being loosely bound to the more-distant axial sites of a Jahn–Teller distorted octahedral complex (*9*). If this argument is to hold, there must be an inversion of the complex axes, that is, a dynamic Jahn–Teller effect.

Of particular interest is the aquaion structure for the two cations of iron-Fe^{2+} and Fe^{3+}. A program of research is currently under way to determine the $G_{\text{Fe}}(r)$ for these ions and how it changes as a function of

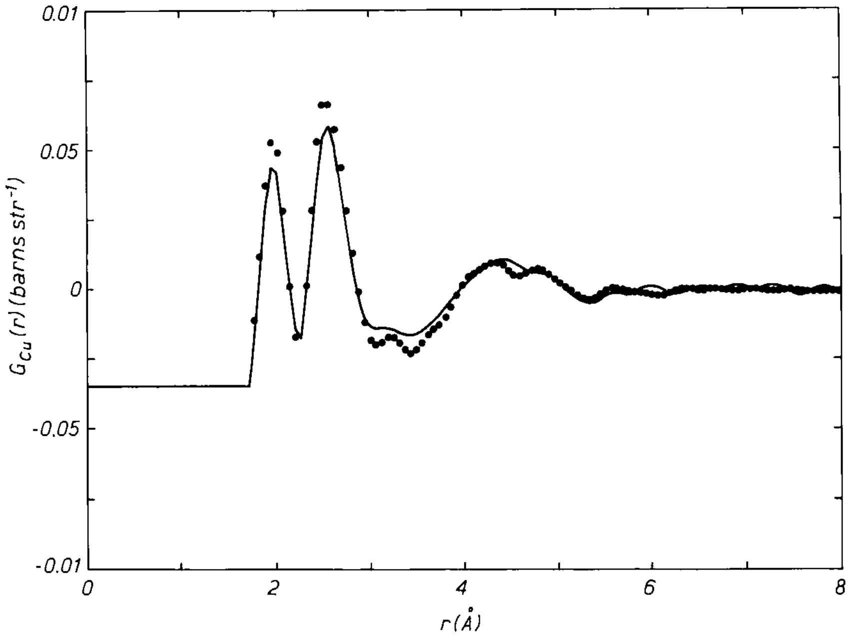

FIG. 8. The total Cu^{2+} radial distribution function $G_{Cu}(r)$ for a 1-molal solution of $Cu(NO_3)_2$ in heavy water (solid line) and 2-molal $Cu(ClO_4)_2$ in heavy water (dotted line). The scaling factor for the concentration difference between the solutions ensures that the contribution of $g_{CuO}(r)$ is the same in both (*57*).

pH, counterion, concentration, pressure, and temperature. A recent study of heavy-water solutions of 2-M $Fe(ClO_4)_3$ in highly acidic (pH $\leq$ 0) clearly demonstrated the 6-fold coordination of Fe^{3+} (*30*). The aquaion structure is complicated by the fact that a large degree of hydrolysis appears at this high ion concentration. Similar effects are observed in 2-M $Fe(NO_3)_3$ heavy-water nitric acid solutions, but with the added effect of dimerization (*30*). Clearly at such high concentrations, little is known of the Fe^{3+}–water structure, and only the ND methods are capable of resolving the structure of Fe–H correlations.

C. DIVALENT CATIONS

The divalent ions of the alkaline earths, calcium, strontium, barium, and magnesium can be studied by ND (see Table I), and the latter can also be studied by XD using Ni^{2+} as a suitable isomorph. It is not possible to apply the isotopic difference method to Be^{2+}, which is mono-

TABLE IV

HYDRATION SHELL PROPERTIES OF DIVALENT CATIONS[a]

Ion	Counter-ion	Concentration (molality)	Ion–water distances (Å)		Hydration number	Tilt angle[b]	Method[b]/
			r_{MO}	r_{MD}	$\bar{n}_{MO}$	θ (deg)	references
Be^{2+}	Cl^-	5.3	1.67	—	4	—	TX/*77*
Mg^{2+}	NO_3^-	1 molar	2.06(2)	—	6	—	XD/*6*
	Cl^-	4.3	2.07(2)	—	6	—	XD/*71, 72*
Ca^{2+}	Cl^-	4.49	2.41(3)	3.04(3)	6.4(3)	34°(9°)	ND/*18*
	Cl^-	2.8	2.39(2)	3.02(3)	7.2(2)	34°(9°)	ND/*32*
	Cl^-	1.0	2.46(3)	3.07(3)	10.0(6)	38°(9°)	ND/*32*
Sr^{2+}	Cl^-	1.53	2.64	—	8	—	TX/*12*
Zn^{2+}	NO_3^-	1 molar	2.09(1)	—	6.2(2)	—	XD/*6*
	Cl^-	4	2.19(5)	2.7(1)	4[c]	48°(7°)	ND/*65*
	Cl^-	2	2.15(5)	2.7(1)	4[c]	54°(7°)	ND/*65*
	Cl^-	2	2.03	—	5.8[c]	—	EX/*20*
Cd^{2+}	NO_3^-	1 molar	2.29(1)	—	5.8(2)	—	XD/*6*
Sn^{2+}	ClO_4^-	3 molar	2.34(2)	—	3.4	—	EX/*76*
	ClO_4^-	3 molar	2.3	—	2.3	—	TX/*40*
Hg^{2+}	ClO_4^-	2 molar	2.4	—	6	—	TX/*39*
Pb^{2+}	ClO_4^-	1.86 molar	2.6	—	Complexation	—	TX/*38*

[a] Errors are in parentheses.
[b] See footnote to Table II for details.
[c] Anion penetration.

isotopic. TX and NMR studies (*9, 77*) of Be^{2+} give a value of 4 for $\bar{n}_{BeO}$ (Table IV), a result in marked disagreement with computer simulation (*77*). ND results for calcium show a variable coordination for the aquaion that depends on ionic concentration. The value of $\bar{n}_{CaO}$ varies from 6.3 to 10 and agrees with recent computer simulation studies (*7*). A value of 10 is unexpectedly high and presumably reflects the size of Ca^{2+}. In contrast, it appears that Mg^{2+} hydration is independent of concentration and is similar to that of Ni^{2+}, though preliminary results by Powell *et al.* (*64*) indicate that there is a difference in M–H correlation of these two cations beyond the first hydration shell.

The study of Zn^{2+}, which normally favors octahedral or tetrahedral coordination, is also feasible by the ND methods. Preliminary (*65*) results show that in aqueous $ZnCl_2$ solutions, a clear coordination exists, but one that has a high degree of inner-sphere penetration. This result is consistent with an extensive ND study of Cl^- hydration in $ZnCl_2$ heavy-water (*63*) solutions, which indicates that based on a model by Irish *et al.* (*37*), $\bar{n}_{ZnCl}$ ranges from 0 at 0.25 molal to 0.84 at 4 molal. Plans are underway to investigate Zn^{2+} hydration in the presence of triflate ions, in which no inner-sphere penetration is expected.

D. THE LANTHANIDE IONS

A section on the lanthamides is appropriate here. There is as yet no systematic study of the actinides using ND and XD difference techniques. An extensive review of the lanthanide ions (L^{3+}) and their solvation has been given by Lincoln (*42*), who pointed out that

> there is still considerable debate about the value of n in the precursor of these complexes, $Ln(OH_2)_n{}^{3+}$. For this species there are protagonists for $n = 10$ and 9 for $Ln^{3+} = La^{3+}$-Nd^{3+}, for $n = 9$ for $Ln^{3+} = La^{3+}$-Lu^{3+}, for $n = 8$ for $Ln^{3+} = Tb^{3+}$-Lu^{3+}, for $n = 9$ for $Ln^{3+} = Tb^{3+}$-Lu^{3+}, and for coexistence of $n = 10$ and 9 and $n = 9$ and 8 for Ln^{3+} between Nd^{3+} and Tb^{3+}.

TABLE V

HYDRATION SHELL PROPERTIES FOR RARE EARTH IONS[a]

Ion	Counter-ion	Concentration (molality)	Ion–water distances (Å)		Hydration number	Tilt angle[b]	Method[b]/ references
			$\bar{r}_{MO}$	$\bar{r}_{MD}$	$\bar{n}_{MO}$	$\bar{\theta}$ (deg)	
La^{3+}	Cl^-	3.81	2.54	—	9	—	TX/*28*
Pr^{3+}	Cl^-	3.80	2.54	—	9	—	TX/*28*
Nd^{3+}	Cl^-	2.85	2.48(2)	3.13(2)	8.5(2)	24°(4°)	ND/*51*
	ClO_4^-	2 molar	2.51( )	—	9.5	—	EX/*78*
Sm^{3+}	ClO_4^-	2 molar	2.45	—	9.3	—	EX/*78*
Eu^{3+}	ClO_4^-	2 molar	2.43	—	8.6	—	EX/*78*
Gd^{3+}	ClO_4^-	2 molar	2.,41	—	7.6	—	EX/*78*
Tb^{3+}	ClO_4^-	2 molar	2.39	—	7.5	—	EX/*78*
	ClO_4^-	1.09 molar	2.40	—	8	—	TX/*41*
Dy^{3+}	ClO_4^-	1.0[c]	2.39(1)	3.03(1)	7.9(2)	28°(4°)	ND/*16*
	ClO_4^-	0.3[c]	2.39(1)	3.03(1)	8.0(2)	28°(4°)	ND/*16*
	ClO_4^-	2 molar	2.37	—	8.1	—	EX/*78*
	Cl^-	2.38[c]	2.37	3.04	7.4	17°(3°)	ND/*4*
	Cl^-	1.0	2.39(1)	3.03(1)	8.0(2)	28°(4°)	ND/*16*
Er^{3+}	ClO_4^-	2.96 molar	2.36	—	8	—	TX/*41*
	ClO_4^-	2 molar	2.34	—	7.8	—	EX/*78*
Tm^{3+}	ClO_4^-	2 molar	2.33	—	7.3	—	EX/*78*
Yb^{3+}	ClO_4^-	1.0	2.32(1)	2.98(1)	7.8(2)	25°(4°)	ND/*16*
Lu^{3+}	ClO_4^-	2 molar	2.31	—	7.7	—	EX/*78*
	Cl^-	3.61 molar	2.34	—	8	—	TX/*27*

[a] Errors are in parentheses.

[b] See footnote to Table II for details.

[c] Acidic solution.

NMR methods have, according to Lincoln, failed to resolve the various controversies. Furthermore, early structural studies were based either on the TX method, with its inherently low resolution, or on the ND method using chloride as the counter ion, and doubt remains as to whether a true hydration had been determined. Accordingly, Merbach and co-workers (*16*) have begun an investigation using ND, at 1 molal and below, and with noncoordinating counterions. Their results so far (Table V and Fig. 9) are consistent with $n = 8$ for $Ln^{3+} = Dy^{3+} - Lu^{3+}$. Results for Dy^{3+} based on EXAFS studies (*78*) are in good agreement with the ND investigation.

E. OTHER TRIVALENT CATIONS

All cations listed in Table VI have been studied by TX, the results showing 6-fold coordination. In^{3+}, Tl^{3+}, and Ga^{3+} can in principle be studied by ND, but so far no results are available. Evidence has been obtained to $Tl(H_2O)_6{}^{3+}$ (*25*), and Ga^{3+} has been found by NMR to have $\bar{n}_{GaO} = 6$ (*9*). TX, Raman, and IR results for In^{3+} show that this ion

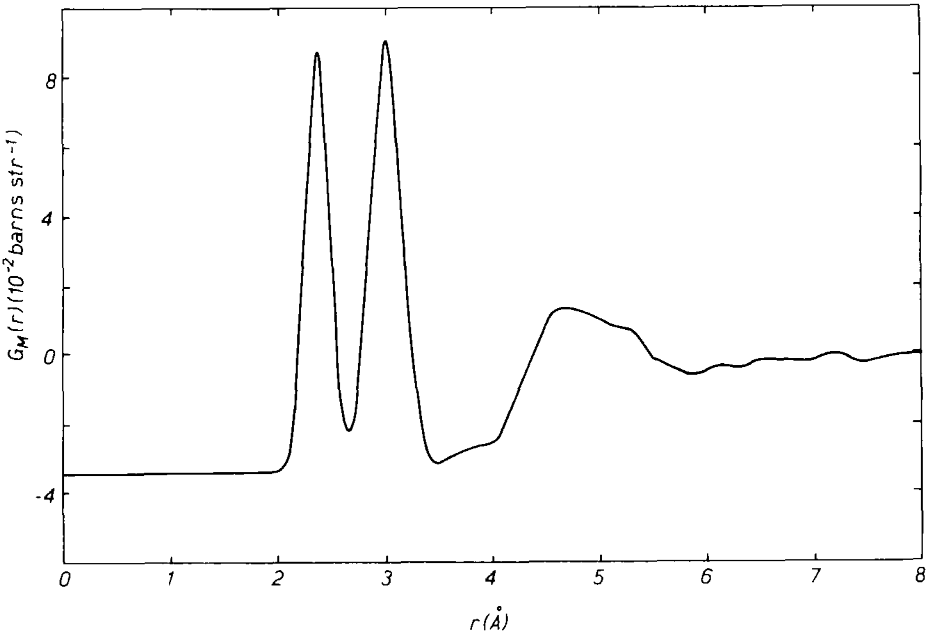

FIG. 9. The total Dy^{3+} radial distribution function $G_{Dy}(r)$ for a 1-m $Dy(ClO_4)_3$ and 0.1-m $DClO_4$ in heavy water (*16*).

TABLE VI

HYDRATION SHELL PROPERTIES OF TRIVALENT IONS

Ion	counterion	Concentration (molarity)	Ion–water distances $\bar{r}_{MO}$ (Å)	Hydration number $\bar{n}_{MO}$	Method[a]/reference
Al^{3+}	Cl^-	1	1.90	6	TX/*10*
In^{3+}	ClO_4^-	—	2.15	6[c]	TX/*46*
	NO_3^-	3.96	2.1	6	TX/*48*
Rh^{3+}	ClO_4^-	0.2[b]	2.02	6[c]	TX/*14*
	NO_3^-	0.9	2.06	6	TX/*15*
Tl^{3+}	ClO_4^-	1.0	2.24	6	TX/*25*
	Br^-	2.6	2.5	6[c]	TX/*25*

[a] See footnote to Table II for details.
[b] Acidic solution.
[c] Counterion penetration.

forms a variety of complexes in aqueous electrolyte solution (*26*). Other information on III-state ions is to be found in the review by Hunt and Friedman (*33*).

F. TETRA- AND HEXAVALENT AQUA CATIONS

With the exception of Te(VI), it would appear that all tetra- and hexavalent cations form oxo/hydroxo hydrolyzed complexes in aqueous solution (Table VII). This is particularly apparent when Cl^- or Br^- are

TABLE VII

HYDRATION SHELL PROPERTIES OF TETRA- AND HEXAVALENT CATIONS

Ion	Electrolyte	Concentration (molarity)	Ion–oxygen distance $\bar{r}_{MO}$ (Å)	Coordination	Method[a]/reference
Th^{4+}	$Th(NO_3)_4$	~1	2.55	Hydrolysis	TX/*44*
Zr^{4+}	$Zr(ClO_4)_4$	2.8	2.2	Polymeric complex formation	TX/*1*
U^{4+}	$U(ClO_4)_4$	2	2.5	8-fold	TX/*62*
UO_2^{2+}	$UO_2(ClO_4)_2$	1	2.42	Pentagonal bipyramial	TX/*2*
Te(VI)	$Te(OH)_6$	1.5	1.94	Octahedral	TX/*3*

[a] See footnote to Table II for details.

present (which coordinate strongly). It is of interest to use the isotopic or possibly the isomorphic methods of neutron diffraction to investigate the local coordination of these metal ions and the extent of complex function. For example, the species $Te(OH)_6$ in solution has been identified by TX methods. However, Te is a good candidate for ND studies (Table I), which would provide a definitive study of the hydrolysis of Te(VI).

G. SECOND SHELL EFFECTS

The reader will have noted that discussion of second-shell coordination has been omitted so far. Except for the case of a 2-M $NiCl_2$ solution in which ND was successfully applied to second order so that g_{NiH} was determined uniquely, little is known beyond the first hydration sphere.

Analysis of data from TX studies indicates that second shells must exist for strong cations such as Ni^{2+} and Fe^{2+}. However, the results are not sufficiently detailed to allow a quantitative discussion.

The QENS data of Hewish *et al.* (*31b*) and of Salmon *et al.* (*66*) show that the influence of ions on the dynamics of the water molecules extends into the second shell and beyond.

V. Conclusions and Future Studies

These results provide an overview of the structure of aquaions and show that a broad classification into labile and stable species can be made. Those of the former category can be represented by a relatively weak and variable hydration shell and include the alkali ions (other than Li^+), Ag^+, Ca^{2+}, and ND_4^+. On the other hand, cations of the transition metals, the rare earths, and small, highly charged ions such as Be^{2+}, Mg^{2+}, and Al^{3+}, which have well-defined hydration shells, form stable aquaions. Cations such as Cu^{2+} and Li^+ are intermediate, having exchange times in the range 10^{-11}–10^{-10} sec.

Results based on other techniques are certainly consistent with the preceding categorization. For example, QENS and NMR offer a means of dividing ions into labile and stable on the basis of the dynamic properties of water molecules.

As well as providing a satisfactory means of characterizing aquaion structure, isotopic difference neutron diffraction measurements provide results that can be used to test computer simulations and theoretical calculations of models of solutions.

For the future, several developments can be anticipated:

1. further exploitation of ND, particularly for those ions not yet investigated (see Table I);
2. extension of XD to include the possibility of tuning isomorphism by the use of physical or chemical variables;
3. use of H_2O/D_2O mixtures to investigate fractionation of water molecules around highly charged ions, as well as angular correlations in the second shell;
4. feasibility studies of introducing long-lived radioactive isotopes such as ^{129}I for use in ND; and
5. extension of EXAFS and the introduction of anomalous X-ray and neutron scattering methods.

ACKNOWLEDGMENTS

We would like to express our deep thanks to colleagues at Bristol and at ILL for their many useful suggestions during the course of this work. We are especially grateful to A. C. Barnes, M-C Bellissent-Funel (Laboratoire Leon Brillouin, C.E.N.-Saclay), C. Cossy (University of Lausanne), G. J. Herdman, M. A. Howe, A. E. Merbach (University of Lausanne), D. H. Powell, and N. T. Skipper, for many stimulating discussions and access to published and unpublished data. We also thank Dr. P. Chieux and Mr. A. Hawes of the ILL staff for technical and scientific support with the neutron diffraction experiments. The continuing financial support of S.E.R.C. is gratefully acknowledged.

REFERENCES

1. Aberg, M., *Acta. Chem. Scand., Ser. B* **B31,** 171 (1977).

2. Aberg, M., Ferri, D., Glasser, J., and Grenthe, I., *Inorg. Chem.* **22,** 3986 (1983).

3. Andersson, E., Lindquist, O., and Yamaguchi, T., *Acta Chem. Scand., Ser. A* **A35,** 591 (1981).

4. Annis, B. K., Hahn, R. L., and Narten, A. H., *J. Chem. Phys.* **82,** 2086 (1985).

5. Bertagnolli, H., Ehrig, R., Weidner, J. U., and Zimmerman, H. W., *Ber. Bunsenges. Phys. Chem.* **90,** 502 (1986).

6. Bol, W., Gerrits, G. J. A., and Van Eck, C. L. van P., *J. Appl. Crystallogr.* **3,** 486 (1970).

7. Bounds, D. G., *Mol. Phys.* **54,** 1335 (1985).

8. Brady, G. W., *J. Chem. Phys.* **28,** 464 (1958).

9. Burgess, J., "Metal Ions in Solution." Horwood, Chichester, England, 1978; "Ions in Solution." Horwood, Chichester, England, 1988.

10. Camaniti, R., Licheri, G., Piccaluga, G., Pinna, G., and Radnai, T., *J. Chem. Phys.* **71,** 2473 (1979).

11. Camaniti, R., Licheri, G., Paschina, G., Piccaluga, G., and Pinna, G., *J. Chem. Phys.* **72,** 4522 (1980).

12. Camaniti, R., Musimu, A., Paschina, G., and Pinna, G., *J. Appl. Crystallogr.* **15,** 482 (1982).

13. Camaniti, R., Cucca, P., and Pintori, T., *Chem. Phys.* **88,** 155 (1984).

14. Camaniti, R., Atzei, D., Cucca, P., Squintu, F., and Bongiovanni, G., *Z. Naturforsch., A* **40A,** 1319 (1985).

15. Camaniti, R., Atzei, D., Cucca, P., Anedda, A., and Bongiovanni, G., *J. Phys. Chem.* **90,** 238 (1986).

16. Cossy, C., Barnes, A. C., Enderby, J. E., and Merbach, A. E., *J. Chem. Phys.* (submitted).

17. Cotton, F. A., and Wilkinson, G., "Inorganic Chemistry," 5th Ed., Chap. 29. Wiley, New York, 1988.

18. Cummings, S., Enderby, J. E., and Howe, R. A., *J. Phys. C* **13,** 1 (1980).

19. Dietz, W., Reide, W. O., and Heinzinger, K., *Z. Naturforsch., A* **37A,** 1038 (1982).

20. Dreier, P., and Rabe, P., *J. Phys. Colloq.* **47,** 809 (1986).

21. Enderby, J. E., and Neilson, G. W., *Rept. Prog. Phys.* **44,** 593 (1981).

22. Enderby, J. E., Cummings, S., Herdman, J. G., Neilson, G. W., Salmon, P. S., and Skipper, N., *J. Phys. Chem.* **91,** 5851 (1987).

23. Friedman, H. L., *Chem. Scr.* **25,** 42 (1985).

24. Friedman, H. L., *in* "Water, a Comprehensive Treatise" (F. Franks, ed.), Vol. 3, p. 117. Plenum, New York, 1973.

25. Glaser, J., and Johannson, G., *Acta Chem. Scand., Ser. A* **A36,** 125 (1982).

26. Goggin, P. L., and Carr, C., *in* "Water and Aqueous Solutions" (G. W. Neilson and J. E. Enderby, eds.), p. 149. Hilger, Bristol, England, 1986.

27. Habenschuss, A., and Spedding, F. H., *J. Chem. Phys.* **70,** 2797 (1979).

28. Habenschuss, A., and Spedding, F. H., *J. Chem. Phys.* **70,** 3758 (1979).

29. Heinzinger, K., and Palinkas, G., *in* "Interactions of Water in Ionic and Non Ionic Hydrates" (H. Kleeberg, ed.), Chap. 1, p. 1. Springer-Verlag, Berlin, 1987.

30. Herdman, G. J., personal communication.

31a. Hewish, N. A., and Neilson, G. W., *Chem. Phys. Lett.* **84,** 425 (1981).

31b. Hewish, N. A., Enderby, J. E., and Howells, W. S., *J. Phys. C.* **16,** 1777 (1983).

32. Hewish, N. A., Neilson, G. W., and Enderby, J. E., *Nature (London)* **297,** 138 (1982).

33. Hunt, J. P., and Friedman, H. L., *Prog. Inorg. Chem.* **30,** 359 (1983).

34. Ichikashi, M., Wakita, H., and Masuda, I., *J. Solution Chem.* **13,** 505 (1984).

35. Ichikawa, K., Kaneda, Y., Matsumoto, T., and Misawa, M., *J. Phys. C* **17,** 1725 (1984).

36. Impey, R. W., Madden, P. A., and McDonald, I. R., *J. Phys. Chem.* **87,** 5071 (1983).

37. Irish, D. E., McCarroll, B., and Young, T. F., *J. Chem. Phys.* **39,** 3436 (1963).

38. Johannson, G., and Olin, A., *Acta Chem. Scand.* **22,** 3197 (1968).

39. Johannson, G., *Acta Chem. Scand.* **25,** 2787 (1971).

40. Johannson, G., and Ohtaki, H., *Acta Chem. Scand.* **27,** 643 (1973).

41. Johannson, G., Ninitso, L., and Wakita, H., *Acta Chem. Scand. (Short Commun.)* p. 359 (1985).

42. Lincoln, S. F., *Inorg. Bioinorg. Mech.* **4,** 217 (1986).

43. Ludwig, K. F., Warburton, W. K., and Fontaine, A., *J. Chem. Phys.* **87,** 620 (1987).

44. Magini, M., Cabrini, A., Scibona, G., Johannson, G., and Sandstrom, M., *Acta Chem. Scand., Ser. A* **A30,** 437 (1976).

45. Magini, M., *J. Chem. Phys.* **74,** 2523 (1981).

46. Magini, M., *in* "Ions and Molecules in Solution" (N. Tanaka, H. Ohtaki, and R. Tamanushi, eds.), p. 97. Elsevier, Amsterdam, 1982.

47. Magini, M., Licheri, L., Paschina, G., Piccaluga, G., and Pinna, G., "X-Ray Diffraction of Ions in Aqueous Solution: Hydration and Complex Formation." CRC Press, Boca Raton, Florida, 1988.
48. Marques, M. A., and Cabaco, M. I., *Chem. Phys. Lett.* **123,** 73 (1986).
49. Narten, A. H., *J. Phys. Chem.* **74,** 765 (1970).
50. Narten, A. H., Vaslow, F., and Levy, H. A., *J. Chem. Phys.* **58,** 5017 (1973).
51. Narten, A. H., and Hahn, R. L., *J. Phys. Chem.* **87,** 3193 (1983).
52. Neilson, G. W., and Enderby, J. E., *J. Phys. C* **11,** L625 (1978).
53. Neilson, G. W., and Enderby, J. E., *J. Chem. Soc. Annu. Rep. C* p. 185 (1979).
54. Neilson, G. W., and Enderby, J. E., *Proc R. Soc. London, Ser. A* **390,** 353 (1983).
55. Neilson, G. W., Newsome, J., and Sandstrom, M., *J.C.S. Faraday II* **17,** 1245 (1981).
56. Neilson, G. W., and Skipper, N. T., *Chem. Phys. Lett.* **114,** 35 (1985).
57. Neilson, G. W., and Salmon, P. S., *J. Phys. C Condens. Matter* (accepted).
58. Newsome, J. R., Neilson, G. W., Enderby, J. E., and Sandstrom, M., *Chem. Phys. Lett.* **82,** 399 (1981).
59. Newsome, J. R., Neilson, G. W., and Enderby, J. E., *J. Phys. C* **13,** L923 (1980).
60. Ohtaki, H., Yamaguchi, T., and Maeda, M., *Bull. Chem. Soc. Jpn.* **49,** 701 (1976).
61. Ozutsumi, K., Ohtaki, H., and Kusumegi, A., *Bull. Chem. Soc. Jpn.* **57,** 2612 (1984).
62. Pocev, S., and Johannson, G., *Acta Chem. Scand.* **27,** 2146 (1973).
63. Powell, D. H., Barnes, A. C., Enderby, J. E., Neilson, G. W., and Salmon, P. S., *Faraday Discuss. R. Soc. Chem. No.* 85, 137 (1988).
64. Powell, D. H., Neilson, G. W., and Enderby, J. E., *J. Phys. C: Condens. Matter* (submitted).
65. Powell, D. H., personal communication.
66. Salmon, P. S., Howells, W. S., and Mills, R., *J. Phys. C: Solid State Phys.* **20,** 5727 (1987).
67. Salmon, P. S., Neilson, G. W., and Enderby, J. E., *J. Phys. C: Solid State Phys.* **21,** 1335 (1988).
68. Sandstrom, M., Neilson, G. W., Johannson, G., and Yamaguchi, T., *J. Phys. C: Solid State Phys.* **18,** L1115 (1985).
69. Sham, T. K., Hastings, J. B., and Perlman, M. L., *J. Am. Chem. Soc.* **102,** 5904 (1980).
70. Sham, T. K., Hastings, J. B., and Perlman, M. L., *Chem. Phys. Lett.* **83,** 391 (1981).
71. Skipper, N. T., Ph.D. Thesis, Univ. of Bristol, 1987.
72. Skipper, N. T., Neilson, G. W., and Cummings, S., *J. Phys. C: Condens. Matter* (to be published).
73. Skipper, N. T., and Neilson, G. W., *J. Phys. C: Condens. Matter* (submitted).
74. Soper, A. K., Neilson, G. W., Enderby, J. E., and Howe, R. A., *J. Phys. C* **10,** 1793 (1977).
75. Szasz, G., and Heinzinger, K., *Z. Naturforsch., A* **34A,** 840 (1979).
76. Yamaguchi, T., Lindquist, O., Claeson, T., and Boyce, J. B., *Chem. Phys. Lett.* **93,** 528 (1982).
77. Yamaguchi, T., Ohtaki, H., Spohr, E., Palinkas, G., Heinzinger, K., and Probst, M. M., *Z. Naturforsch., A* **41A,** 1175 (1986).
78. Yamaguchi, T., Masaharu, N., Wakita, H., and Ohtaki, H., *J. Chem. Phys.* **89,** 5153 (1988).