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The structure of the first coordination shell of the yttrium ion in concentrated aqueous solutions of YBr_3 and YCl_3

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Abstract. Yttrium hydrates with eight-coordinated water molecules seem to be the predominant species in concentrated aqueous solutions of yttrium bromide and chloride. For molarities from ~ 2.1 down to 0.6M in H_2O EXAFS experiments yield an average $\text{Y}^{3+}-\text{O}$ distance of $2.33 \pm 0.02 \text{ \AA}$ for the YBr_3 and $2.34 \pm 0.02 \text{ \AA}$ for the YCl_3 . Investigations by means of Raman spectroscopy with substitution of the solvent by D_2O for a 2.1M solution of YCl_3 lead to an isotopic shift of 1.052 ± 0.007 for the polarized band assigned to the stretching vibrational mode of the complex $((m_{\text{H}_2\text{O}}/m_{\text{D}_2\text{O}})^{1/2} = 1.054)$, which corroborates the idea of the presence of a (relatively) stable hydrate of the yttrium ion.

1. Introduction

In this paper attention is centred on EXAFS and Raman experiments with concentrated aqueous solutions of salts of yttrium. In a series of earlier studies [1–8] on concentrated aqueous solutions of copper, zinc, strontium and cadmium halides EXAFS was used to investigate the structure of the corresponding cation complexes. Applications of this technique to solutions of halide salts of indium recently permitted the confirmation of molecular models [7, 8] suggested [9] to interpret earlier x-ray diffraction data. Similar investigations of the yttrium ion are here presented to obtain an accurate value for the cation–water molecule distance, and to estimate the hydration number of its first coordination shell, in some concentrated aqueous solutions of its halide salts.

Raman spectra of concentrated solutions of yttrium chloride in ordinary water and deuterium oxide were obtained in order to detect bands that may be plausibly assigned to yttrium hydrates. The presence of identical Raman bands in the spectra of concentrated aqueous solutions of yttrium bromide indicates the existence of similar cation hydrates in these ionic liquids. Analogous methodology has been used in earlier and recent studies of the structure of aqueous solutions of aluminium, magnesium, zinc, beryllium and indium salts [10–12].

The results here reported will be combined with results of x-ray experiments to investigate the existence of medium-range positional correlations between ions in these concentrated solutions, in accordance with earlier studies of this subject [9, 13–17].

2. Experiment

Yttrium chloride was obtained from Alfa-Ventrom (99.9%), yttrium bromide from Johnson Matthey-Alfa (99.99%). For the EXAFS experiments three different concentrations of yttrium chloride aqueous solutions were prepared from their hydrated salts. The solutions were contained in a cell of variable thickness having Mylar windows. As the crystallographic structure of the hydrated crystals was not known, no reference compound was used.

X-ray absorption measurements were performed in transmission mode at Laboratoire pour l'Utilisation du Rayonnement Electromagnétique (Orsay, France) using radiation from the DCI storage ring operated at 1.85 GeV with maximum current of 300 mA. All data were taken at room temperature. The spectra were obtained on a spectrometer using a Si(331) channel-cut crystal as the monochromator. I_0 and I were measured using two ion chambers.

For Raman experiments water was slowly distilled in a Pyrex apparatus in presence of KMnO_4 to oxidize the organic impurities. Deuterium oxide was obtained from Merck-Schuchardt ($\text{D}_2\text{O} > 99.75\%$). The presence of water in the heavy water solutions was monitored by following the intensity of the 1200 cm^{-1} Raman band of D_2O in the spectra. All the solutions were filtered through nitrocellulose membranes prepared in our laboratory. The walls of the Raman cells are not seen by the spectrometer, a Spex 1403 with a Spectra-Physics 2016 Ar^+ laser and a R-920 Hamamatsu photon counter. The exciting line was at 514.5 nm and a spectral slit width of 5 cm^{-1} was used. The compositions of the samples were determined by chemical analysis.

3. EXAFS experiments: data analysis and results

Extended x-ray absorption fine structure (EXAFS) spectroscopy refers to oscillations of the x-ray absorption coefficient on the high-energy side of an atomic absorption edge. The normalized EXAFS function is given by

$$\chi(E) = [\mu(E) - \mu_0(E)] / \mu_0(E)$$

where μ is the measured absorption and μ_0 is the smooth post-edge background term.

In order to relate $\chi(E)$ to structural parameters, it is necessary to convert the energy E into the photoelectron wavevector k defined by $k = [2m(E - E_0)/\hbar^2]^{1/2}$, where E is the energy of the incident beam and E_0 the energy of the beam at the absorption edge for the yttrium at 17038 eV (E_0 was calibrated with an yttrium metallic foil).

In single-scattering theories and in the plane-wave approximation the formula which describes the EXAFS oscillations for a Gaussian distribution of neighbours around a central atom [18, 19] may be written

$$\chi(k) = - \sum_j \frac{N_j}{k R_j^2} |f_j(\pi)| \exp(-2\sigma_j^2 k^2) \exp(-2R_j/\lambda) \sin[2kR_j + 2\delta_j' \Psi_j].$$

Here N_j is the number of scattering atoms at a distance R_j , each with a backscattering factor $|f_j(\pi)|$ which is energy dependent. λ is the elastic mean free path of the

photoelectron. σ_j is the relative mean-square displacement between the scattering atom and the central one, δ'_i is the phase shift due to the passage of the photoelectron through the potential of the emitting atom and Ψ_j is the phase of the backscattering factor.

The $\chi(k)$ EXAFS modulations of the absorption coefficient were normalized following a standard procedure [4]: the EXAFS spectra were obtained from the experimental absorption spectra after subtraction of the absorption background obtained by fitting the region below the edge with a Victoreen expression, which was extrapolated beyond the edge. Then μ_0 was simulated using a three-region cubic spline through the EXAFS oscillations beyond the edge. EXAFS simulations and Fourier transforms were carried out using the program EXCURVE88 [20] which is based upon the spherical wave theory developed by Lee and Pendry [19]. The EXAFS spectra were weighed by k^3 to compensate for the diminishing amplitude at high k values. Phase shifts were calculated internally by the program EXCURVE88.

For each halide all the spectra have been analysed over the same energy range of about 44–780 eV (corresponding to a wavevector range of about 3.3–14 \AA^{-1}) for the bromide solutions and of about 47–762 eV (corresponding to a wavevector range of about 3.4–13.8 \AA^{-1}) for the chloride.

The spectra were Fourier filtered to remove features at distances below 1.3 \AA , but not to leave long-distance features of the quasi-radial distribution function (i.e. no noise removal was attempted).

The experimental spectra of EXAFS $k^3\chi(k)$, the EXAFS simulation on the yttrium edge and its Fourier transform are shown in figure 1 for 2.1M, 1.0M and 0.5M yttrium bromide and in figure 2 for 2.3M, 1.2M and 0.6M yttrium chloride aqueous solutions. The spectra were found to be almost identical at all concentrations of each halide solution.

Table 1. Numerical values of the parameters used to simulate the Y K-edge EXAFS spectra of yttrium bromide and yttrium chloride aqueous solutions. R denotes the distance of the yttrium from the oxygen of the water molecule. $A = 2\sigma^2$ is a Debye–Waller factor. N is the number of backscattering atoms. The errors associated with the numerical values given in the table are: for the bond length ± 0.02 \AA , for the number N of backscattering atoms ± 0.3 and 0.001 \AA^2 for the Debye–Waller factor.

	Concentration	R (\AA)	N	A (\AA^2)	FI
YBr ₃	2.1M	2.33	7.5	0.014	1.29
	1.0M	2.33	8.5	0.015	1.62
	0.5M	2.34	7.5	0.012	2.06
YCl ₃	2.3M	2.34	7.5	0.015	2.10
	1.2M	2.34	7.6	0.013	1.61
	0.6M	2.34	7.9	0.013	1.08

Table 1 gives the values of the parameters used in the simulation and their fitting index for the three concentrations of each solution (the fit is done with one shell). The fitting index FI is defined as

$$FI = \frac{1}{100NPT} \sum_1^{NPT} (Res_i k^{WT})^2$$

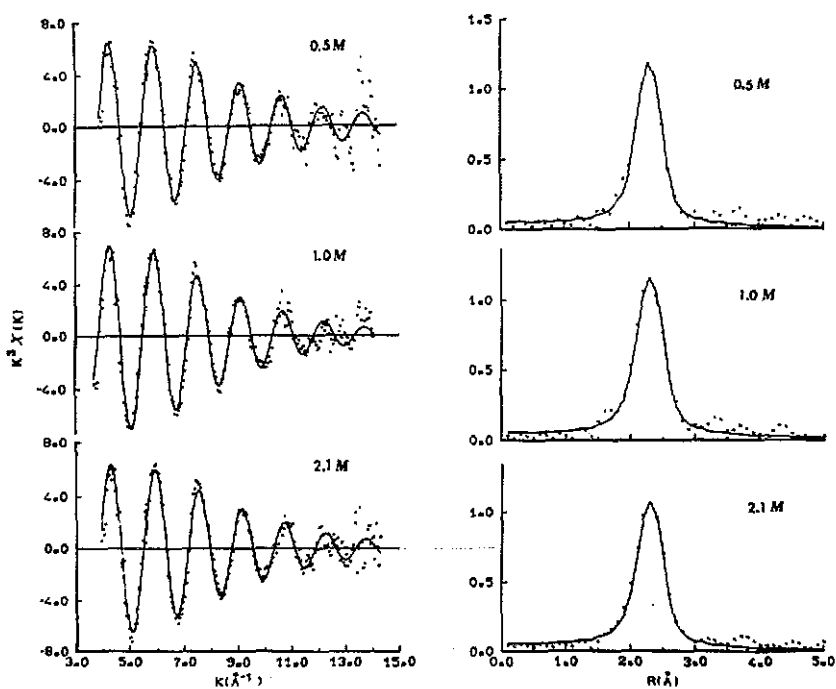


Figure 1. EXAFS and Fourier transform simulations (.....: experiments, —: theory) for the Y K-edge of yttrium bromide aqueous solutions (2.1M, 1.0M and 0.6M).

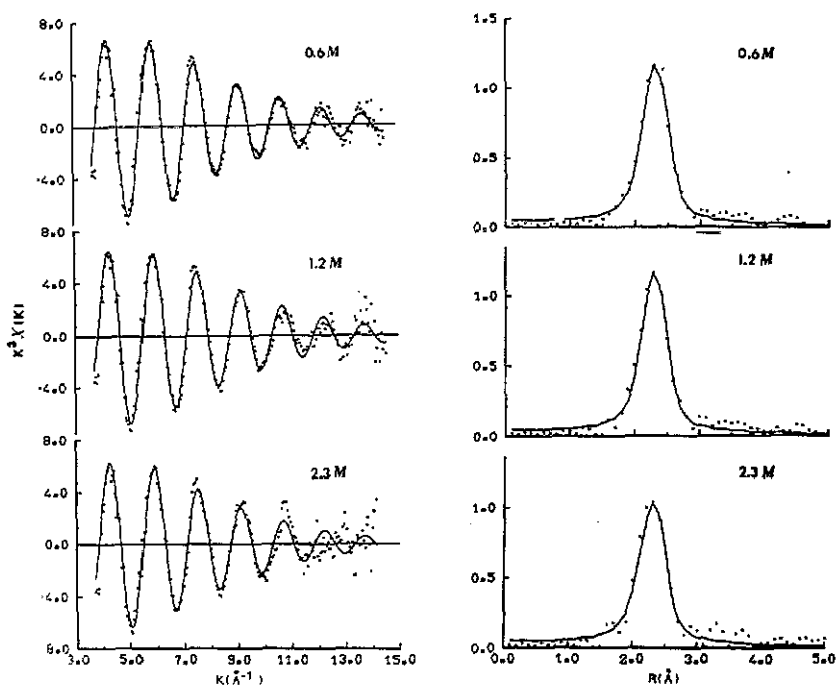


Figure 2. EXAFS and Fourier transform simulations (.....: experiment, —: theory) for the Y K-edge of yttrium chloride aqueous solutions (2.3M, 1.2M and 0.6M).

where $Res_i = \chi_i$ (calculated) $-\chi_i$ (experimental) and NPT is the number of data points. WT is an integral weighting (in our work equal to 3) to offset the decay of χ as the energy increases.

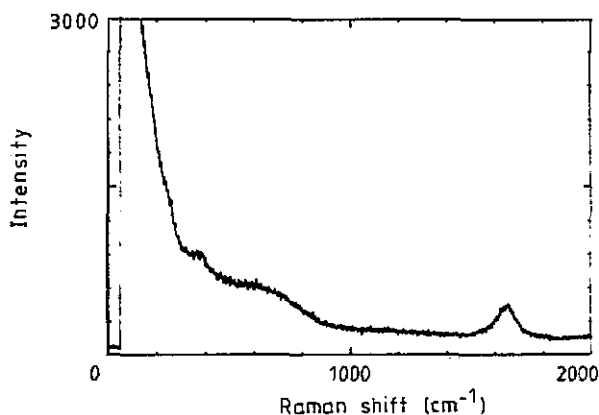


Figure 3. Raman spectrum of a 2.3M aqueous solution of YCl_3 in H_2O . ($21 H_2O/Y^{3+}$). The band assigned to the H_2O-Y^{3+} stretching mode is well visible, although less intense than the 1650 cm^{-1} band corresponding to the H_2O bending mode.

We may conclude that yttrium complexes are found in aqueous solutions of both the chloride and bromide. In the structure of these complexes we do not find coordinated halide ions, but only water molecules (with cubic coordination) with the oxygen atoms at $\approx 2.33\text{ \AA}$ from the yttrium cation. This structure is found for both salts over the concentrations range from at least $\approx 2M$ to $0.5M$.

Johansson and Wakita [21] obtained by x-ray diffraction investigations in aqueous perchlorate and selenate solutions, yttrium complexes with 8 ± 0.3 water molecules at a distance $Y^{3+}-OH_2$ of 2.33 \AA . The existence of $Y(H_2O)_8^{3+}$ complexes in concentrated aqueous solutions of yttrium selenate and perchlorate, with the $Y^{3+}-OH_2$ distance the same as in the halide solutions, is in agreement with the conclusion from previous Raman investigations [10]: the structure of the first coordination shell of small cations with a relatively high electric charge may be considered as relatively independent of the rest of the liquid.

In 1990 Matsubara *et al* [22] studied YCl_3 aqueous solutions at the Y K-absorption by anomalous x-ray scattering and suggested that Y^{3+} ions have 8.1 ± 0.3 and 8.2 ± 0.5 water molecules with the average $Y^{3+}-OH_2$ distances being $2.46 \pm 0.02\text{ \AA}$ and $2.51 \pm 0.02\text{ \AA}$ for $0.5M$ and $1.0M$ YCl_3 aqueous solutions.

4. Raman investigations: models, results and comments

In the perspective of the gas-phase approximation, we assume that the totally symmetric vibration of the hydrate is Raman active and polarized. According to the results of EXAFS experiments a coordination of eight water molecules around the yttrium cation seems plausible. The high value of the quadrupolar moment of the free water molecule corresponding to an axis perpendicular to its HOH plane would suggest that the more stable orientation of the H_2O (or D_2O) molecules coordinated by the

Y^{3+} cation is not radial, in agreement with suggestions for the Ni^{2+} cation [23]. The physical significance of the 'mean angle tilt' has been questioned in a recent article [24]. However a detailed investigation of the more stable configuration of this hydrate is not at present feasible because accurate values of the multipolar moments of *coordinated* water molecules are not known†. The permanent dipole moment of the water molecule is assumed to be directed along the bisector of the valence angle HOH (or DOD) and the (dipolar) polarizability tensor is considered to be symmetric; its three principal axes are coincident with the three axes of the water molecule. It is then presumed that the eight water molecules, located at the vertices of a cube, are radially coordinated. A value for the frequency of the totally symmetric vibration of the O_h hydrate can be estimated from a potential function as indicated in the appendix. The water molecules are treated as isolated particles inside the cation complex. No coupling between intramolecular and intermolecular dynamics is considered in the model. To calculate the values of the frequencies corresponding to the oscillational modes of these molecular aggregates only electrostatic interactions and additive repulsive overlap forces are considered. The electrostatic properties are described by dipolar moments, the quadrupole being ignored. (The intervention of quadrupolar moments of the order of the observed ones for the free water molecule would not change by more than 2% the estimated values of the frequency). The repulsive forces are considered to be centred on the nucleus of the oxygen in the coordinated water molecule. To calculate these overlap forces, data on the compressibility of the crystalline oxides were considered in the Born formula c_1/r^n as indicated by Pauling [26]. (In the appendix the way the c_1 values are calculated is indicated). The electrostatic properties and the Born exponents were fixed *a priori* as close as possible to the values given in the literature for the free water molecule and yttrium, and are given in table 2.

Table 2. Comparison of the calculated frequencies of the totally symmetric vibration, ν , of the yttrium hydrates with the value observed of the Raman bands attributed to this vibrational mode. r_{catw} is the distance from the cation to the centre of the dipole moment of the water molecule, assumed as located on the nucleus of the oxygen, μ^p the permanent dipole moment of the coordinated water molecule, $\alpha \parallel$ the principal polarizability corresponding to the symmetry axis of the water molecule, n the Born exponent, ν the wavenumber of the totally symmetric vibrational mode and ν_{exp} the averaged value of the frequency of the observed Raman band.

r_{catw} (Å)	μ^p (10^{18} esu)	$\alpha \parallel$ (10^{-24} esu)	n	ν (cm^{-1})	ν_{exp} (cm^{-1})
2.335	1.7	1.5	10	360	381.5 ± 2
2.335	1.84	1.5	10	368	
2.335	1.7	1.5	11	383	
2.335	1.84	1.5	11	391	

In considering the model used to calculate the frequency of the vibrational modes we do not intend to suggest that all the water molecules are coordinated in an 8-hydrate at a well defined distance. The overlap of the different, but almost coincident, bands produced by the vibrational motion of cation hydrates may give a resultant

† A redistribution of the electric charge is plausible in the water molecule when it is coordinated by cations, as suggested in Hermansson *et al* [25].

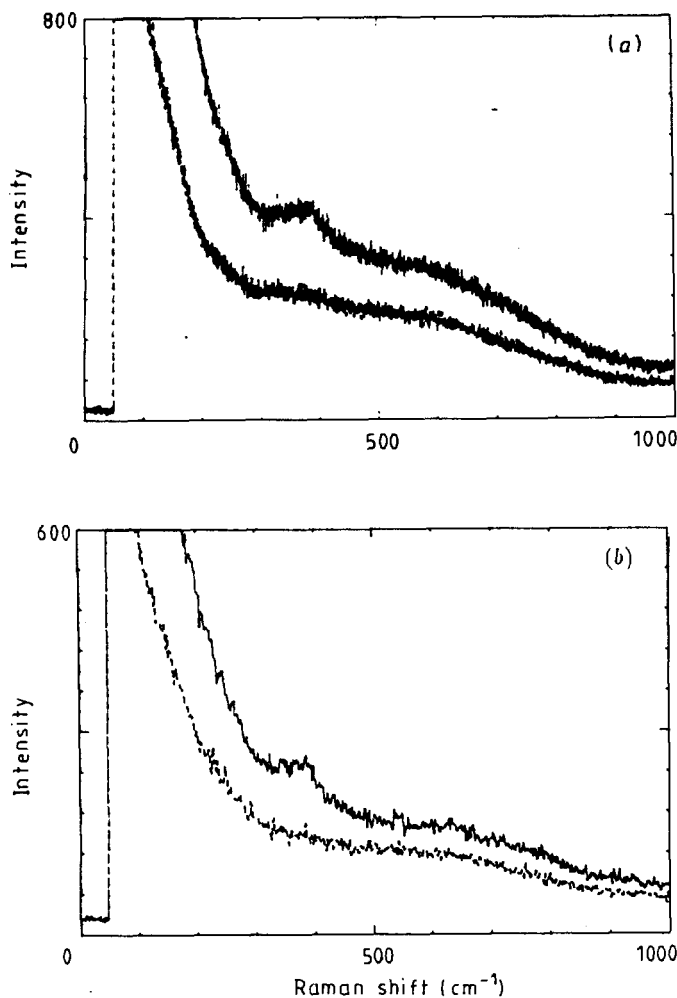


Figure 4. Polarized and depolarized components of the Raman spectra of concentrated solutions of yttrium halides in ordinary water. (a) 2.1M solution of YBr_3 in H_2O ($\approx 25 H_2O/Y^{3+}$), (b) 2.3M solution of YCl_3 in H_2O ($21 H_2O/Y^{3+}$). The upper spectra correspond to the vv running, the lower to the hv running. The total polarization of the 382 cm^{-1} bands assigned to the 'breathing' mode of the $Y(H_2O)_8^{3+}$ is evident. Their profiles and intensities are similar for the two solutions.

spectrum which can be used to simulate the Raman experimental data (figures 4–6). The experimental results are summarized in table 3. The observed polarization of the Raman band that is attributed to the hydrate leads to the assumption of a totally symmetrical vibrational mode, schematically described as the dilation–contraction of the first hydration shell. The value of the observed isotopic shift ($ish = 1.052 \pm 0.007$) is coincident, within the experimental error, with the square root of the ratio of the values of the mass of the coordinated water molecules ($(m_{H_2O}/m_{D_2O})^{1/2} = 1.054$). In the aluminium hydrates, $ish = \nu^{H_2O}/\nu^{D_2O} \approx 1.04$ for the corresponding polarized bands [11], and is smaller than the ratio m_{H_2O}/m_{D_2O} . The interpretation suggested [11] for this was that the polarized Raman bands are assigned to normal modes that result from the coupling of the pulsation H_2O-Al^{3+} (or D_2O-Al^{3+}) with

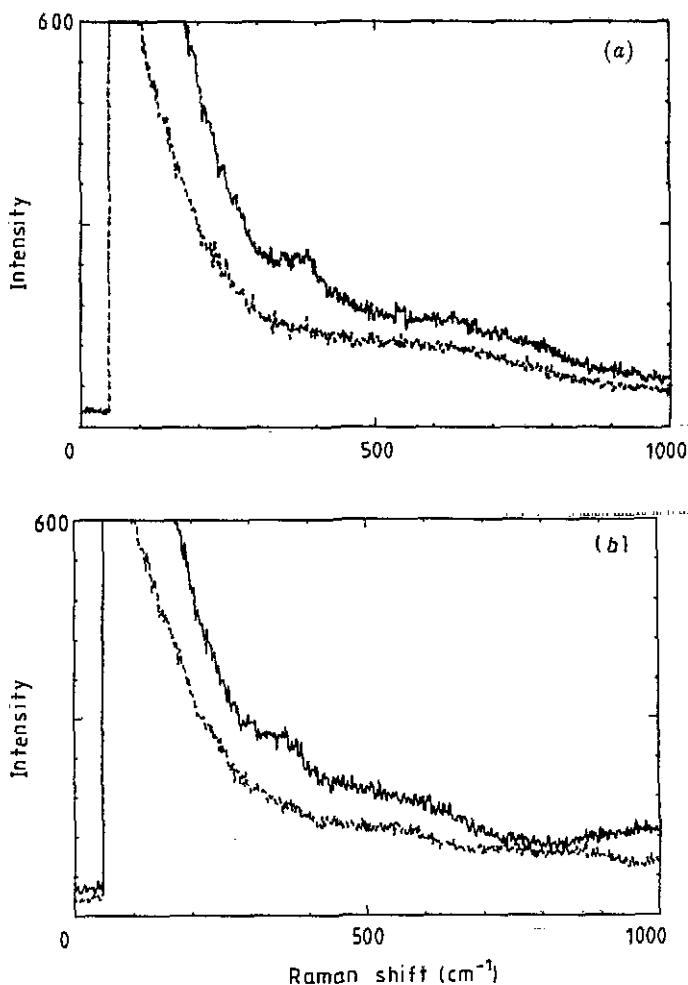


Figure 5. Polarized and depolarized components of the Raman spectra of concentrated solution of yttrium halides in ordinary water and in deuterium oxide. (a) 2.3M solution of YCl_3 in H_2O (21 $\text{H}_2\text{O}/\text{Y}^{3+}$), (b) 2.2M solution of YCl_3 in D_2O (20 $\text{D}_2\text{O}/\text{Y}^{3+}$). The upper spectra correspond to the vV running, the lower to the vH running. The total polarization of the bands assigned to the 'breathing' mode of the hydrates $\text{Y}(\text{H}_2\text{O})_8^{3+}$ and $\text{Y}(\text{D}_2\text{O})_8^{3+}$ is evident. The isotopic shift ($\approx 19 \text{ cm}^{-1}$), clearly noticed, is in consonance with the mass ratio of the coordinated water molecules. The profiles and the intensities are alike for the two solutions. Isotopically shifted bands observed at wavenumbers higher than $\sim 380 \text{ cm}^{-1}$ (the frequency of the hydrate line) are plausibly originated by librational motions of free and/or coordinated water molecules; but no precise assignments seem possible at present.

the rocking motion of the coordinated H_2O (or D_2O). Assuming that the frequency of the rocking motion of the H_2O molecule is higher than the frequency of the pulsation $\text{H}_2\text{O}-\text{Al}^{3+}$ and that for the deuterated hydrate the frequency of the pulsation $\text{D}_2\text{O}-\text{Al}^{3+}$ is higher than the frequency of the rocking, the coupling occurs with a phase inversion between them, when the oscillational motions of the hydrogen and of the deuterated hydrates are compared (figure 6). With yttrium hydrates this phase inversion apparently does not occur. We can interpret this by assuming that the

frequency of the rocking motions are higher than the frequency of the pulsation 'water molecule- Y^{3+} ' for both the hydrogen and deuterium hydrates.

Table 3. Experimental results obtained from the Raman spectra of concentrated aqueous solutions of yttrium chloride and bromide. ISH indicates the isotopic shift of the corresponding Raman band. 'p' stands for polarized.

	Solution	Frequency (cm^{-1})	
YCl ₃	2.26 mol dm ⁻³ (21 H ₂ O/ Y^{3+})	382	p
	2.20 mol dm ⁻³ (22 D ₂ O/ Y^{3+})	363 (ISH = 1.052 ± 0.007)	p
YBr ₃	2.08 mol dm ⁻³ (25.5 H ₂ O/ Y^{3+})	381	p

The agreement between the experimental and the calculated value of the frequency of the totally symmetric vibrational mode of the cation hydrate is reasonable (table 2) taking into account the approximations employed.

No Raman bands that could be assigned to cation-anion interactions were observed in the spectra. From the width of the Raman band the existence of stable hydrates, with well defined vibrational motion, is evident. The duration of the mean life, τ , is at least one order of magnitude larger than the value of the period of the vibrational mode ($\tau \approx 10^{-12}$ s).

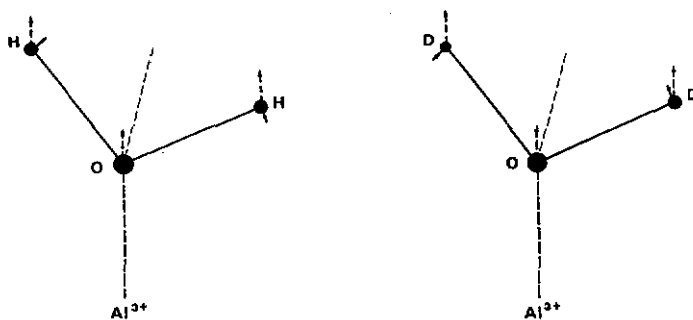


Figure 6. Coupling of the stretching (*) with the rocking oscillation of the (↑) of the coordinated water molecules in the hydrogen and deuterated hydrates.

5. Conclusion

EXAFS investigations suggest the existence of yttrium hydrates with eight water molecules in the first coordination shell. No $Y^{3+}-Cl^-$ or $Y^{3+}-Br^-$ contacts are apparent. In agreement, no Raman bands attributable to $Y-Cl$ or $Y-Br$ interactions were found in the spectra. The isotopic shift, when the H_2O solvent is substituted by D_2O , of the sole polarized Raman band observed is well explained by the assignment to a dilation-contraction of a hydration shell of the yttrium cation. Rough estimates of the electrostatic and elastic properties of the yttrium ion and of the water molecules yield a numerical value of the frequency of this totally symmetric vibrational mode that is in good agreement with that observed in the Raman spectrum. The width

of the band gives a lower limit of about 10^{-12} s to the mean life of the complex. The presence of this type of cation complexes with such a large number of electrons suggests the use of these aggregates as convenient probes to investigate the existence of positional correlations of cations of high valence in concentrated aqueous solutions of their salts, as a sequel to earlier experimental work [9, 13–17].

Acknowledgments

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Appendix. Calculation of the frequency of the stretching normal mode of the hydrate $Y(H_2O)_8^{3+}$ [or $Y(D_2O)_8^{3+}$]

If a polarizable particle, in this case a water molecule, is displaced in an electrostatic field E , obtained as a sum of two terms, the electrostatic field of the cation, E_{cat} , and the electrostatic field of the other coordinated water molecules, then the amount of the electrostatic energy dW_{el} that is supplied may be calculated as follows:

$$dW_{el} = -dE_{cat} \cdot \mu_{tot} - \frac{1}{2} dE_w \cdot \mu_{tot} + (E_{cat} + E_w) \cdot d\mu$$

where dE_{cat} and dE_w are the changes of the values of the fields during the displacement, $d\mu$ the corresponding variation of the dipolar moment μ_{tot} of each coordinated water molecule. Multipoles of higher order are neglected.

$$E_{cat} = ze/r_{catw}^2 \quad E_w = -2D\mu_{tot}^2/r_{catw}^3$$

where ze is the electric charge of the Y^{3+} cation, r_{catw} , the distance from the cation to the oxygen atom of the water molecule and D is a form factor that has the value 1.99 for an 8-fold (spherically symmetric) coordination.

$$\mu_{tot} = \mu_p + \mu_{ind}$$

where μ_p is the permanent dipolar moment of the water molecule ($\mu_p = 1.84$ for the free water molecule), μ_{ind} may be calculated approximately as

$$\mu_{ind} = \alpha \parallel \left(E_{cat} + \frac{2D\mu_p}{r_{catw}} \right) / \left(1 + \frac{2D\alpha \parallel}{r_{catw}^3} \right)$$

where $\alpha ||$ is the polarizability component corresponding to the symmetry axis of the valence angle HOH.

To the variation of the electrostatic energy must be added the variation of the Born (overlap) energy corresponding to the different pairs, cation-water molecule or water-water molecules, existing in the yttrium hydrate. Other terms of the energy were considered to be less relevant. We assume that the role played by these short-range interactions may be estimated by one sole Born (energy) term $W_B = c_1/r_{catw}^n$ (c_1 being an appropriate numerical value in a totally symmetric coordination). The c_1 value is fixed by the condition $d(W_{el} + W_B)/dr = 0$ for $r = r_{catw} = 2.335 \text{ \AA}$, the equilibrium (\bar{R}) distances given by EXAFS experiments. The compressing action of the environment of the hydrate in the solution is neglected.

The value of the frequency, ν , of the spherically symmetric vibrational mode of the hydrate is then given by

$$4\pi^2 m c^2 \nu^2 = d^2(W_{el} + W_B)/dr^2 \quad r = r_{catw}$$

where m is the mass of the water molecule, c the velocity of light.

As the values of electric or elastic properties of the coordinated water molecule are, plausibly, different from those of free water molecules, calculations were performed with two slightly different values (table 3) for each magnitude.

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