Vibrational Analysis of a Model for the Hydroxide Ion in Aqueous Solution

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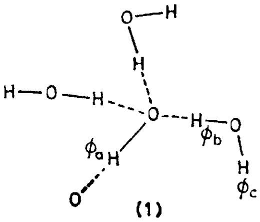
A vibrational analysis of a model for the solvated hydroxide ion in which OH^- is hydrogen-bonded to three H_2O molecules has been carried out. Force constants were assigned to give calculated frequencies consistent with: (a) i.r. and Raman measurements of alkali metal hydroxide solutions and solid hydrates; (b) the magnitude and temperature dependence of the equilibrium constant K_G for the isotope exchange reaction, $2DO^-(D_2O)_3 + 7H_2O(g) \rightleftharpoons 2HO^-(H_2O)_3 + 7D_2O(g)$; and (c) alternative combinations of fractionation factors, ϕ_a for the hydroxide ion and ϕ_b for its three hydrogen bonded water hydrogens, consistent with the experimental value of K_G. Best agreement of calculated with observed hydroxide stretching frequencies (3 600 cm^{-1}) was achieved with ϕ_a 1.15 and ϕ_b 0.57, implying that hydroxide solvent isotope effects are dominated by contributions from the solvation shell; however, the calculated librational frequency was high. A lower librational frequency was obtained with ϕ_a 0.57 and ϕ_b 0.91, but then the stretching frequency was low (*ca.* 3 000 cm^{-1}). The results are discussed in the light of current interpretations of hydroxide spectra in condensed phases.

SOME years ago we reported a vibrational analysis of the hydrated hydronium ion in aqueous solution.[1] Because of difficulties with the interpretation of vibrational spectra of hydronium ion hydrates in condensed phases, difficulties which may yet not be fully resolved,[1-7] calculated frequencies were required to be consistent with the measured equilibrium constant for hydrogen isotope exchange between the aqueous ion and water vapour [reaction (1)].

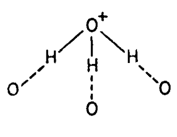
$$2D_3O^+(aq) + 3H_2O(g) \rightleftharpoons 2H_3O^+(aq) + 3D_2O(g) \quad (1)$$

A similar situation arises for the aqueous hydroxide ion. Again the interpretation of i.r. and Raman measurements may not be straightforward,[4,8,9] but a vibrational analysis can be carried out using solution spectra [4,8-11] and spectra of metal hydroxides [12,13] and their hydrates [12,14-17] in the solid state as a guide, and choosing force constants so that calculated frequencies yield the measured value at 25° and the temperature dependence of the equilibrium constant for the water vapour–aqueous hydroxide isotope exchange [18,19] analogous to the corresponding reaction of the hydronium ion (1).

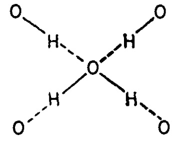
Such an approach has been used by Goldblatt and Jones,[20] who treated the hydroxide ion primarily as a diatomic species. For our analysis we developed an extended model for the hydroxide ion (1) from models previously used for the solvated hydronium ion and liquid water, (2) and (3), in which a central molecule is bound to three or four water fragments. This takes account of the possibility that hydrogens directly hydrogen-bonded to hydroxide, as well as the hydroxide ion itself, contribute to isotope exchange equilibria.[21]



(1)



(2)



(3)

In model (1) the hydroxide and hydrogen-bonding hydrogens are denoted *a* and *b*, and their contributions to hydroxide solvent isotope effects may be expressed in terms of fractionation factors ϕ_a and ϕ_b measuring the equilibrium ratio of D to H atoms at the positions in question relative to that in a mixed H_2O–D_2O solvent. Thus if the exchange equilibrium between aqueous hydroxide and water vapour is written as equation (2), its equilibrium constant is given by equation (3), in

$$2DO^-(D_2O)_3 + 7H_2O(g) \xrightleftharpoons{K_G} 2HO^-(H_2O)_3 + 7D_2O(g) \quad (2)$$

$$K_G = \left(\frac{p_{D_2O}}{p_{H_2O}}\right)^7 \frac{1}{\phi_a{}^2\phi_b{}^6} \quad (3)$$

which p_{H_2O} and p_{D_2O} represent the vapour pressures of H_2O and D_2O. The product of the hydroxide fractionation factors, $\phi_a\phi_b{}^3$ 0.434 at 25°, and the corresponding value of K_G, 1.920, are well established,[19] but as noted in the preceding paper, attempts to separate ϕ_a and ϕ_b lead not only to uncertainty in the individual values but to two distinct solutions implying quite different isotopic behaviour for the hydroxide ion. In one solution $\phi_a \cong 0.5$ and $\phi_b \cong 1.0$ and hydroxide isotope effects are dominated by the hydroxy hydrogen; in the other $\phi_a \cong 1.0$ and $\phi_b \cong 0.7$ and the dominating influence is the hydrogens of the solvation shell.

The existence of the two solutions was initially recognised by Gold and Grist [21] and Walters and Long.[22] Previously it had been supposed that only the hydroxy hydrogen was implicated in the isotope effects, but Gold and Grist argued that the similarity of $\phi_b \cong 0.7$ to the measured fractionation factors for methoxide and ethoxide ions,[23] where effects can arise only from the solvation shell, favours the second alternative.[21] Since the solutions imply different force fields for the hydroxy group and its solvation shell an object of the present calculations was to choose force constants consistent with both possibilities and determine which leads to the more reasonable vibration frequencies.

CALCULATIONS AND RESULTS

Bond lengths, bond angles, atomic masses, and force constants were assigned to the hydroxide model (1), and vibration frequencies were calculated using Wilson's FG matrix method.[24] Zero point energy differences and isotopic partition function ratios for hydrogen and deuterium modifications were evaluated from isotopic masses and vibration frequencies making use of the product rule.[25] These when combined with the corresponding values for gaseous H_2O gave the equilibrium constant K_G for reaction (2), which was calculated over the temperature range 0—50°. Force constants were assigned to give agreement with experimental values of K_G obtainable from the fractionation factor product $\phi_a\phi_b^3$ (0.434 at 25°) [19] and the ratio of vapour pressures of isotopic waters $p_{H_2O} : p_{D_2O}$ [equation (3)],[26] and also to give dissected values of ϕ_a and ϕ_b for the hydroxy and hydrogen bonded hydrogens of the model. The procedure was similar to that followed previously for the hydronium ion.[1]

TABLE 1

Calculated and observed hydrogen and deuterium frequencies (cm^{-1}) for the hydrated hydroxide ion

Vibration [a] (degeneracy)		Calculated				Observed		
		Case (i) ϕ_a 1.15, ϕ_b 0.72		Case (ii) ϕ_a 0.57, ϕ_b 0.91		LiOH, H_2O [b] (solid)		NaOH or KOH [c] (solution)
		H	D	H	D	H	D	H
$O-H_s$		3 670	2 670	3 115	2 270	3 574	2 632	3 600
$O-H_{llb}$	(2)	1 025	750	505	380	680, 635	490	
H_2O_s	(3)	2 790	2 015	2 965	2 140	2 965	~2 185	2 800
	(3)	3 440	2 510	3 445	2 520	3 200—2 800		3 400
H_2O_b	(3)	1 560	1 140	1 600	1 165	1 586	1 167	
		750	545	840	605			
H_2O_{llb}	(2)	585	425	855	615	1 000—860	740—600	1 100—500 [d]
		450	330	535	390			
	(2)	440	340	575	435			

[a] Degeneracies refer to calculated frequencies. Frequencies differing by < 10 cm^{-1} are included as 'degenerate'. [b] From L. H. Jones, *J. Chem. Phys.*, 1954, **22**, 217; I. Gennick and K. Harmon, *Inorg. Chem.*, 1975, **14**, 2214; E. Drouard, *Compt., rend.*, 1958, **247**, 68; J. O. Clifford, J. A. S. Smith, and F. A. Temme, *J.C.S. Faraday II*, 1975, 1352. [c] From P. Rhine, D. Williams, G. M. Hale, and M. R. Querry, *J. Phys. Chem.*, 1974, **78**, 1405; W. R. Busing and D. F. Hornig, *ibid.*, 1961, **65**, 284. [d] Includes hydroxide liberation.

The model includes sufficient atoms to meet Wolfsberg and Stern's 'cut-off' requirement for calculation of isotope effects for hydrogens at positions *a* and *b*.[27] It incorporates stretching force constants of bonds to positions of isotopic substitution and bending force constants at atoms one bond removed. It is formally deficient in omitting hydrogen bonding to the oxygens of the solvating waters and the corresponding hydrogen-bond bending force constants which affect isotopic substitution of the water hydrogens *b*, but the influence of these weak force constants is small and could be allowed for by slightly increasing the H–O–H bending force constant. The model also includes an oxygen atom formally associated with the hydroxy hydrogen, but here very weak force constants indeed were assigned, consistent with the non-bonded length of this O–H distance in solid LiOH,H_2O.[28]

Anharmonic corrections were not included in the calculations, and for this reason force constants for gaseous H_2O were fitted to observed rather than zero-order frequencies.[29] With the usual notation, the H_2O force constants in mdyn Å^{-1} were f_1 7.66, f_2 0.643 8, and f_{12} -0.091, giving ω_1 3 755, ω_2 3 656, and ω_3 1 594 cm^{-1}.[29] The bond length and bond angle were 0.957 5 Å and 104° 47′.

For the hydroxide model (1) bond angles were tetrahedral and bond lengths for covalent and hydrogen bonded O–H distances were 1.0 and 1.76 Å, respectively. Calculations were carried out for two sets of force constants, each yielding $\phi_a\phi_b^3$ 0.434 at 25° but with different individual values of ϕ_a and ϕ_b and different stretching and librational frequencies for the hydroxy group, ω_S and ω_L:

	ϕ_a	ϕ_b	ω_S/cm^{-1}	ω_L/cm^{-1}
(i)	1.15	0.72	3 669	1 026
(ii)	0.57	0.91	3 115	505

In case (i) the force constants in mdyn Å^{-1} were f_{r_1} 7.5, f_{r_2} 0.5, f_{r_3} 0.02, f_{r_4} 3.94, f_{r_5} 6.55, f_α 0.30, f_β 0.02, f_γ 0.005, f_δ 0.095 (in plane and out of plane), f_ϵ 0.6, and $f_{r_4r_5}$ -0.24, where the subscripts follow the co-ordinate notation in model (1) (in which all three H_2O units are equivalent). For (ii) the force constants were the same as in (i) save for f_{r_1} 5.4, f_{r_4} 4.52, f_α 0.11, and f_δ 0.15. The force constant f_{r_1} principally controls the hydroxide stretching frequency, while f_α and f_δ determine the (degenerate) frequency of hindered rotation (since f_γ is weak). In choosing force constants for the hydrogen-bonded waters, values previously used in the model (3) for liquid water [1] were taken as a guide.

With three weak H–O–H–O–H torsional modes omitted, the calculations gave 28 vibration frequencies, including one redundancy, and Table 1 lists the principal values, rounded to 5 cm^{-1}, for fully protiated and fully deuteriated modifications of the model. The principal co-ordinates implicated in the vibrations are indicated, and were assigned from inspection of isotopic shifts and eigenvectors. For each set of force constants calculations were carried out for ten partially or completely deuteriated species. The right hand columns of Table 1 show experimental hydrogen and deuterium frequencies reported for solid lithium hydroxide hydrate and for aqueous solutions of NaOH or KOH. Calculated and observed temperature dependences of the equilibrium constant K_G are compared in Table 2 and Figure 1. To avoid superfluous contributions from p_{H_2O}/p_{D_2O} the tabulated and plotted values are K_G $(p_{H_2O}/p_{D_2O})^3$.* In Figure 1 the points are experimental and the correlation line is calculated using the force constants of

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* This confines the isotopic exchange to the hydroxide hydrogen and the innermost three hydrogens of its solvation shell.

Table 2

Experimental and calculated temperature dependences of K_G [a]

			$K_G\ (p_{H_2O}/p_{D_2O})^3$		
T/°C	$\phi_a\phi_b^3$ [b]	p_{H_2O}/p_{D_2O} [c]	Expt.	Calc. (ϕ_a 1.15)	Calc. (ϕ_a 0.57)
5	0.411	1.210	2.77	2.80	2.79
10	0.415	1.195	2.84	2.84	2.84
15	0.422	1.181	2.88	2.89	2.89
20	0.428	1.168	2.94	2.93	2.93
25	0.434	1.156	2.97	2.97 [d]	2.97 [d]
30	0.439	1.145	3.02	3.01	3.01
35	0.445	1.135	3.04	3.04	3.04
40	0.450	1.126	3.07	3.07	3.07
45	0.445	1.117	3.10	3.10	3.10
50	0.460	1.109	3.12	3.13	3.13

[a] Reaction (2) in text. [b] Evaluated from experimental measurements as described in the preceding paper. [c] From ref. 26. [d] Calculations were ' normalised ' to the experimental value at 25° assuming that discrepancies represented differences in zero-point energy. Corrections applied were $<0.3\%$.

case (i) above with ϕ_a 1.15 and ϕ_b 0.72; the correlation for case (ii) with ϕ_a 0.57 and ϕ_b 0.91 differs insignificantly. Figure 1 also shows temperature dependences calculated for a two atom hydroxide model in which the isotopic shift in librational frequencies corresponds with the reduced mass of OH and OD. The calculations were based on reaction

$$2HO^- + D_2O(g) \xrightleftharpoons{K_1} 2DO^- + H_2O(g) \qquad (4)$$

(4), with the equilibrium constant K_1 now depending upon the single fractionation factor ϕ_a as $K_1 = (p_{H_2O}/p_{D_2O})/\phi_a^2$, and related to K_G by $K_G = K_1(p_{H_2O}/p_{D_2O})$.[4] The lines labelled ZPE and Free Rotation in Figure 1 represent calculations in which the contributions of OH^- and OD^- to the equilibrium, respectively, derive from zero point energy only or include two free rotations.

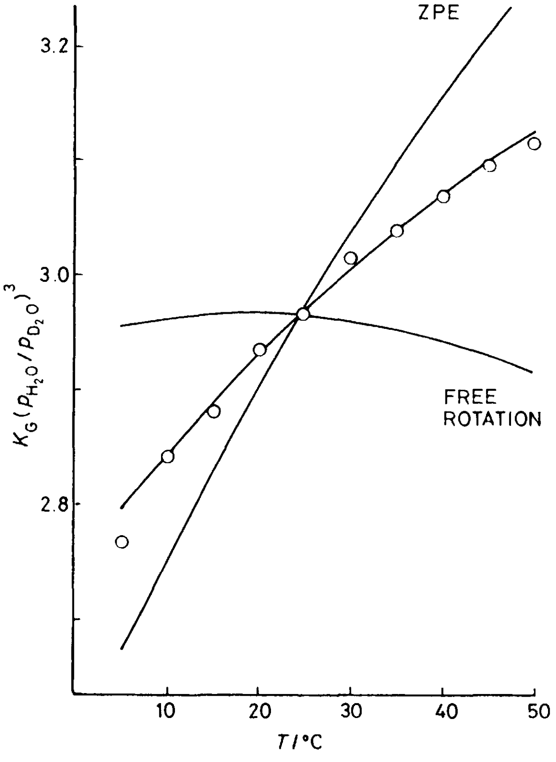

Figure 1 Calculated and observed temperature dependences of the equilibrium constant for H–D exchange between aqueous hydroxide ion and water vapour. The circles are experimental measurements. The calculations assume the hydroxide contribution to the exchange equilibrium arises from zero-point energy only (ZPE) or includes two free rotations (Free Rotation)

Since ϕ_a for a two atom model depends upon only one stretching and one (degenerate) hindered rotational frequency its value may be represented by contours on a diagram having these frequencies as co-ordinates. Such a diagram is shown in Figure 2 and is approximately applicable also when ϕ_a is calculated from model (1), save in so far as hindered rotational motions of hydroxy and solvating hydrogens may now be coupled.

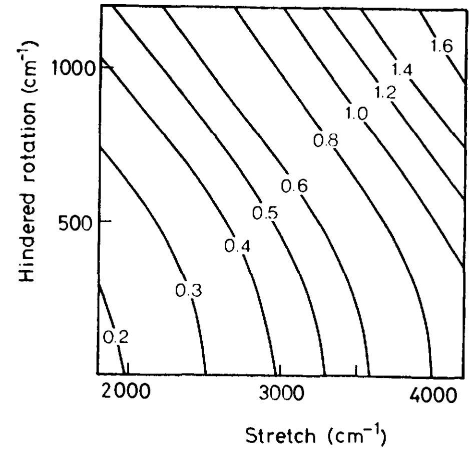

Figure 2 Contour diagram showing the dependence of ϕ_a, the fractionation factor of the hydroxide ion, upon stretching and hindered rotational frequencies of the ion

Deviations from the Rule of the Mean.—Relating the calculations to the fractionation factors ϕ_a and ϕ_b presented the difficulty that in their empirical definition fractionation factors are not constant, and, strictly, may be represented by a simple ratio of isotopic concentrations or partition functions only in the approximation that isotopic substitution at one position of a molecule is independent of that at any other. Breakdown of this assumption, which occurs when more than one exchangeable hydrogen is bound to a common atom and is commonly referred to as Departure from the Rule of the Mean,[30,31] usually introduces errors of $<5\%$ and in most applications is of minor significance. However, the effect is apparent in calculations, and experimentally is manifested in the small but definite dependence of fractionation factors upon isotopic composition in H_2O–D_2O mixtures.[30-32]

For the calculations and for other applications therefore it is helpful to define a ' practical ' constant fractionation factor in terms of partition functions of isotopically homogeneous molecules as illustrated for the symmetrical hydride XH_n in equation (5), in which the square brackets

$$\phi = \frac{[X_nD]^{1/n}[H_2O]^{1/2}}{[X_nH]^{1/n}[D_2O]^{1/2}} = \frac{Q_{XD_n}{}^{1/n}Q_{H_2O}{}^{1/2}}{Q_{XH_n}{}^{1/n}Q_{D_2O}{}^{1/2}} \qquad (5)$$

denote concentrations in isotopically mixed solutions and the Qs are partititon functions exclusive of symmetry numbers. Fractionation factors so defined are appropriate for expressing rate and equilibrium constant ratios in pure isotopic solvents and equilibrium constants for isotopic exchange processes written in terms of fully isotopically substituted species such as (2).[33,34] They approximate the corresponding conventional fractionation factors ϕ' [written for XH_n as equation (6)] and become equal to them when Departures from the Rule of the Mean may be neglected.

$$\phi' = \frac{\sum_{i=0}^{n} i[XD_iH_{n-i}]\{2[H_2O] + [HDO]\}}{\sum_{i=0}^{n} (n - i)[XD_iH_{n-i}]\{2[D_2O] + [HDO]\}} \quad (6)$$

The product of practical fractionation factors ϕ_a, ϕ_b, and ϕ_c for the three types of hydrogens in the hydroxide model (1) may be expressed as a simple partition function ratio as equation (7). To separate individual values however it is

$$(\phi_a\phi_b^3\phi_c^3)^2 = \frac{Q^2{}_{DO^-(D_2O)_3}Q_{H^7{}_2O}}{Q^2{}_{HO^-(H_2O)_3}Q_{D^7{}_2O}} \quad (7)$$

necessary to recognise further that the practical fractionation factors are related to the limiting conventional values, ϕ^0 and ϕ_∞, for H_2O–D_2O mixtures in which the D : H isotopic concentration ratios approach 0 and ∞, respectively, *i.e.* isotopically pure H_2O and D_2O.[34] In these limits the fractionation factors may again be represented by simple concentration or partition function ratios, as shown for the hydroxy hydrogen *a* and hydrogen-bonded hydrogens *b* of (1) in equations (8) and (9).

$$\phi_a{}^0 = \frac{2[OD^-(H_2O)_3][H_2O]}{[OH^-(H_2O)_3][HDO]} \; \phi_a{}^\infty = \frac{[OD^-(D_2O)_3][HDO]}{2[OH^-(D_2O)_3][D_2O]} \quad (8)$$

$$\phi_b{}^0 = \frac{2[OH^-(HDO)(H_2O)_2][H_2O]}{3[OH^-(H_2O)_3][HDO]}$$

$$\phi_b{}^\infty = \frac{3[OD^-(D_2O)_3][HDO]}{2[OD^-(HDO)(D_2O)_2][D_2O]} \quad (9)$$

The relationship between ϕ, ϕ^0, and ϕ^∞ is $\phi = \sqrt{\phi^0\phi^\infty}$, and where interacting isotopic positions are equivalent this identity holds within the validity of Bernstein's rules.[1,35,36] Although strictly speaking the rules apply only to equivalent hydrogens, it is shown in an appendix that ϕ values defined in terms of ϕ^0 and ϕ^∞ for non-equivalent interacting position also correctly express isotope effects and partition functions ratios in pure isotopic solvents.

The implication for our hydroxide model is that if ϕ_c is unity then the fractionation factor contribution to the exchange (2) will be given by equation (10). Since the

$$\phi_a\phi_b{}^3 = \sqrt{\phi_a{}^0\phi_a{}^\infty(\phi_b{}^0\phi_b{}^\infty)^3} \quad (10)$$

hydroxide partition function ratios in equations (8) and (9) for $\phi_a{}^0$, $\phi_a{}^\infty$, $\phi_b{}^0$, and $\phi_b{}^\infty$ are calculable from the model, $\phi_a\phi_b{}^3$ may be calculated. Although in the model ϕ_c is not in fact unity the assumption that it is has the desired effect of confining isotope effects to the inner four hydrogens of the model while nonetheless including interactions between isotopic substitution of the hydrogen-bonded OHs and of the water-like second hydrogen of the solvating molecule.

Of course in equations (8) and (9) the concentrations of isotopic waters refer to the liquid state. In practice, for calculation of the equilibrium constant K_G, equation (10) was used but with $\phi_a{}^0$, $\phi_a{}^\infty$, $\phi_b{}^0$, and $\phi_b{}^\infty$ calculated from (8) and (9) with concentrations (or partition functions) for the gas phase replacing those for liquid water.

Corrections to Solvent Isotope Effects.—The calculated partition function ratios allow correction of hydroxide solvent isotope effects for departures from the Rule of the Mean.[19] The authors have shown previously that interdependence of isotopic substitution may be expressed in terms of parameters δ reflecting interaction between isotopically substituted positions and defined by the equilibrium constant for exchange of a single hydrogen between fully protiated and fully deuteriated molecular species.[34] The definition may be written from inspection of adjacent H–D interactions introduced by the exchange. For model (1), substitution of D at *a* leads to three interactions between *a* and *b* atoms and δ_{ab} is defined by equation (11). Substitution of D at *b* leads to one *a*–*b* and one *b*–*c* interaction

$$1 - 3\delta_{ab} = \frac{Q_{OD(H_2O)_3}Q_{OH(D_2O)_3}}{Q_{OH(H_2O)_3}Q_{OD(D_2O)_3}} \quad (11)$$

and at *c* to one *b*–*c* interaction, and δ_{bc} is defined by equations (12) or (13).

$$1 - \delta_{ab} - \delta_{bc} = \frac{Q_{OH(DOH)(H_2O)_2}Q_{OD(HOD)(D_2O)_2}}{Q_{OH(H_2O)_3}Q_{OD(D_2O)_3}} \quad (12)$$

$$1 - \delta_{bc} = \frac{Q_{OH(HOD)(H_2O)_2}Q_{OD(DOH)(D_2O)_2}}{Q_{OH(H_2O)_3}Q_{OD(D_2O)_3}} \quad (13)$$

A relationship exists between δ and the parameter p used by Albery and Davies[33] to correct isotope measurements in H_2O—D_2O mixtures for departures from the Rule of the Mean. For model (1) this relationship and a definition of p * in terms of ϕ^∞/ϕ^0, is expressed in equations (14)—(16), where δ_{HDO} represents the interaction between the

$$1 + 3p_{ab} = \phi_a{}^\infty/\phi_a{}^0 \cong 1 + 3\delta_{ab} - \delta_{HDO} \quad (14)$$

$$1 + p_{ab} + p_{bc} = \phi_b{}^\infty/\phi_b{}^0 \cong 1 + \delta_{ab} + \delta_{bc} - \delta_{HDO} \quad (15)$$

$$1 + p_{bc} = \phi_c{}^\infty/\phi_c{}^0 \cong 1 + \delta_{bc} - \delta_{HDO} \quad (16)$$

hydrogens of water and it is assumed that the δs are small enough that $(1 + \delta_1)/(1 + \delta_2)$ may be written as $(1 + \delta_1 - \delta_2)$.

Values of δ_{ab} and δ_{bc} have been calculated for cases (i) and (ii) with ϕ_a = 1.15 and 0.57, respectively:

	$\phi_a = 1.15$	$\phi_a = 0.57$
δ_{ab}	0.002 78	0.000 48
δ_{bc}	0.021 8	0.019 8

The magnitudes of the δ values reflect the force constants for bending co-ordinates linking interacting atoms,[34] and not surprisingly δ_{bc} is close to δ_{HDO} 0.021 4 for water, implying a cancellation of corrections between waters in the hydroxide solvation shell and bulk solvent. Although calculations of δ_{HDO} underestimate the experimental value (0.05) it seems reasonable that relative magnitudes should be correct. The larger value of δ_{ab} for ϕ_a 1.15 than ϕ_a 0.57 reflects a larger hydrogen bond bending force constant for the hydroxide ion in that case, as discussed below.

DISCUSSION

Calculated protium and deuterium vibration frequencies for the hydrated hydroxide model (1) consistent with measurements of the isotope exchange equilibrium constant K_G at 25° and alternative values of the hydroxide and solvating hydrogen fractionation factors ϕ_a and ϕ_b are shown in Table 1. Also shown are experimental frequencies, for aqueous hydroxide solutions[10,11] and measurements of i.r.,[12,15] Raman,[16] and neutron inelastic scattering[17] spectra of the hydrogen bonded solid $LiOH,H_2O$.

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* This definition of p is equivalent to Albery and Davies' within the limits of Bernstein's rules.

It is convenient to consider first calculated frequencies consistent with the combination of fractionation factors ϕ_a 1.15 and ϕ_b 0.57. These values represent the solution of $\phi_a\phi_b^3$ 0.434 favoured by Gold and Grist,[21] with ϕ_a for the hydroxy-group close to unity and the dominant influence upon hydroxide isotope effects arising from the hydroxide solvation shell. Strictly, the experimental results imply a larger value of ϕ_a and smaller value of ϕ_b; however, separation of ϕ_a and ϕ_b is subject to considerable uncertainty and these values give a better fit to the spectroscopic measurements.

Before considering results from model (1) directly however it is useful to examine the qualitative implications of the experimental frequencies, and try to calculate the hydroxide fractionation factor ϕ_a using a simple two-atom model.

From the right hand columns of Table 1 it can be seen that the stretching frequency assigned to the hydroxide ion of solid LiOH,H_2O is 3 574 cm^{-1}, close to the value of 3 600 cm^{-1} reported from Raman measurements of potassium and sodium hydroxide in concentrated aqueous solutions.[11,37,38] Since these frequencies differ little from the highest OH stretching frequency assigned to liquid water [39] (*ca.* 3 450 cm^{-1}), a value of $\phi_a > 1.0$ must imply an unusually high librational frequency for the hydroxide ion, to balance the isotopically sensitive zero point energy of bending and librational modes of hydrogen-bonded water.

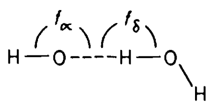
The two atom model for the hydroxide ion allows calculation of one stretching frequency and one (degenerate) hindered rotation. As shown in Figure 2, the dependence of ϕ_a upon these frequencies can be represented by a contour diagram, and it can be seen that the combination of ϕ_a 1.15 with a stretching frequency of 3 600 cm^{-1} requires hindered rotations of >1 000 cm^{-1}. For free rotation of hydroxide, with the same stretching frequency, ϕ_a would be only 0.5.

In a previous analysis of a two-atom model Goldblatt and Jones suggested that evidence for the existence of hindered rotations of high frequency was provided by the temperature dependence of isotopic equilibria involving hydroxide.[20] The electrochemical measurements on which the product of fractionation factors $\phi_a\phi_b^3$ 0.434 at 25° is based were carried out over the temperature range 0—50°.[18] When combined with values of p_{D_2O}/p_{H_2O} these yield the temperature dependence of the equilibrium constant K_G, and values of K_G are shown plotted as $K_G(p_{D_2O}/p_{H_2O})^3$ against temperature in Figure 1. This temperature dependence is readily calculated for alternative hydroxide models and is sensitive to the magnitude of low frequency vibrations; for free rotations the contribution to the isotope effect is temperature independent, while for vibrations of high frequency it approaches the exponential dependence characteristic of zero-point energy.

In Figure 1 calculated temperature dependences assuming that the hydroxide contribution to the isotope effect arises from zero point energy only or includes two free rotations are shown as the full lines labelled ZPE and Free Rotation respectively. A good fit to the experimental points was obtained with a librational frequency of 950 cm^{-1}, which compares with a value of 820 cm^{-1} found by Goldblatt and Jones using slightly modified data for K_G.[20]

In principle these librational frequencies may be used in Figure 2 with ϕ_a 1.15 to derive a hydroxy-stretching frequency of *ca.* 3 900 cm^{-1}, somewhat larger than the experimental value. In practice, however, the two-atom model is too simplified to interpret the temperature dependence, because the experimental measurements do not separate contributions of the hydroxy-group itself from those of its solvation shell.

With model (1) the temperature dependence of K_G is determined by librational frequencies of both hydroxide and solvating water molecules, and a more flexible fit to the experimental data is possible. The frequencies of the librations are controlled chiefly by the force constants f_α and f_δ, shown in (1) and in the abbreviated formula (4). The fractionation factor ϕ_a depends only upon f_α, and f_α may be chosen to make ϕ_a consistent with the observed OH stretching frequency. The temperature dependence is then adjusted by varying f_δ.



(4)

	f_α/mdyn Å^{-1}	f_δ/mdyn Å^{-1}
H_2O	0.115	0.115
ϕ_a 1.15	0.30	0.10
ϕ_a 0.57	0.11	0.15

H and D vibration frequencies calculated from model (1) with ϕ_a 1.15 are shown in the first two columns of Table 1. The OH stretching frequency of 3 670 cm^{-1} is close to the observed value, and the temperature dependence of K_G is well reproduced, as shown by Table 2 and the line through the experimental points in Figure 1. The hydrogen-bonded O–H stretching force constant of the solvating waters was chosen to give ϕ_b 0.72 and the calculated stretching frequency of 2 790 cm^{-1} is consistent with the broad band between 2 800 and 3 200 cm^{-1} observed in i.r. spectra of LiOH, H_2O [12,15] and around 2 800 cm^{-1} in the i.r. [5] and reflectance spectra of aqueous NaOH and KOH.

Calculations for different degrees of isotopic substitution of model (1) reveal some coupling between librational frequencies of the hydroxide ion and its solvation shell, but the degenerate frequency at 1 025 cm^{-1} stands out as predominantly a hydroxide mode. The frequency is larger than the 650 cm^{-1} ascribed to hydroxide torsional modes in the i.r. and neutron inelastic scattering spectra of LiOH,H_2O,[16,17] and the higher value in solution may reflect an increase in the number and strength of hydrogen bonds.

Thus our hydroxide model reasonably accommodates the fractionation factors favoured by Gold and Grist.

One may now ask whether it is sufficiently flexible also to fit the solution of $\phi_a\phi_b^3$ with a small fractionation factor, ϕ_a 0.57, for the hydroxide hydrogen, and a value close to that for solvent water, ϕ_b 0.91, for the solvating hydrogens.

To maintain the same stretching force constant for hydroxide the smaller value of ϕ_a requires a much smaller hydrogen bond bending force constant f_α. With model (1) there is no difficulty in accommodating a low value of f_α and low frequency librations with the temperature dependence of K_G (Table 2), but the maximum stretchng frequency that can be achieved in the limit that $f_\alpha \rightarrow 0$ for ϕ_a 0.57 is only 3 400 cm^{-1}, significantly lower than the 3 600 cm^{-1} reported experimentally. Indeed a very small value of f_α seems unreasonable, and in Table 1 a lower stretching frequency of 3 100 cm^{-1} is listed, corresponding to f_α 0.11 and a librational frequency of 505 cm^{-1}. The large value of ϕ_b 0.91 for solvating hydrogens leads to an increase in stretching frequencies of hydrogen bonded waters to nearly 3 000 cm^{-1}, but this is within mid-range of the broad band assigned to this mode for LiOH–H_2O and only a little higher than the band centre for aqueous solutions.

It thus seems clear that Gold and Grist's solution for the fractionation factors,[21] with its implication that hydroxide isotope effects are dominated by contributions from the solvation shell rather than the hydroxide hydrogen itself, offers the more satisfactory interpretation of the spectroscopic measurements. However, this conclusion should perhaps be regarded with caution, in so far as the structure and spectra of hydroxide ion in condensed phases remain actively under investigation.[4,5,9,10,37,38,40]

Thus it is noteworthy that the frequency at 3 600 cm^{-1} assigned to the OH^- stretch appears strongly only in Raman spectra.[11,38] It is true that its appearance in i.r. and reflectance spectra may be masked by an accompanying decrease in absorption from solvent water molecules, but the possibility that the hydroxide stretching mode is associated not with the solvent stretching band but with the broad band centred at 2 800 cm^{-1} which increases in intensity with increasing hydroxide concentration, and is reasonably assigned principally to the low frequency OH stretching vibration of water molecules directly hydrogen bonded to hydroxide cannot be entirely dismissed. The peak at 3 600 cm^{-1} [11,37,38] might then represent an ion pair or other species less fully hydrated than the $OH^-(H_2O)_3$ presumably present in dilute solution and of principal relevance to isotope measurements.* It is also not certain that the sharp hydroxide peak at 3 574 cm^{-1} in the spectrum of solid LiOH,H_2O is an appropriate guide to the solvated hydroxide ion in solution; for other hydroxide hydrates, *e.g.* tetraalkylammonium salts, a hydroxide peak distinct from the water absorptions is not seen.[14]

At a more general level speculations regarding the origin of the broad and intense background absorptions appearing in H_3O^+ and OH^- solution spectra have prompted suggestions that the spectra may be modified by the influence of double-well hydrogen bonding potentials, leading to doubling of vibrational levels and perturbation of potential energy surfaces, even in the region of zero point vibrational levels.[4,7] The influence of these factors remains controversial,[41,42] and the integrity of measured H_3O^+ solution spectra has been defended.[5,6] However in calculations of H_3O^+ spectra carried out on the same basis as the present,[1] constraining the frequencies to fit H_3O^+ isotopic fractionation measurements led to calculated values considerably lower than those observed. Whatever the reason for this it suggests that the significance of the discrepancy between observed and calculated frequencies for ϕ_a 0.57 and ϕ_b 0.91 should not be exaggerated.

But the most interesting implication of Gold and Grist's fractionation factors is the high librational frequencies for the hydroxide ion. Model (1) is too restricted to properly represent the water librations, but for ϕ_a 1.15 the dominance of the hydroxide frequency of 1 025 cm^{-1} is quite clear and is reflected in the greater value of the force constant f_α than f_δ in (4). Greater magnitudes for hydroxide than water librational frequencies in solution contrasts with the assignment for solid LiOH,H_2O of a moderate frequency of 615 cm^{-1} to the OH torsional motion and higher frequencies to water librations,[17] as well as with the intuitive expectation that for an unsymmetrical hydrogen bond the dominant hydrogen bond bending force constant should be that for deformation about the central hydrogen atom. Unfortunately experimental measurements in solution offer little guidance. Reflectance spectra show an isosbestic point consistent with some increase in librational frequencies with increasing KOH or NaOH concentrations, but the variation in absorption is small and there is a net decrease in intensity in the region.[10] There is no way of apportioning frequencies between the hydroxy-group and its solvating waters.

While allowing reservations the conclusion that a hydroxide structure with high stretching and librational force constants, consistent with the fractionation factor combination ϕ_a 1.15 and ϕ_b 0.72 rather than ϕ_a 0.57 and ϕ_b 0.91, better accommodates the condensed-phase spectral data seems nonetheless clear. It should be recalled that the alternative sets of fractionation factors considered were selected at the limits of their experimental uncertainty most easily reconciled with the spectral data,[19] and experimentally more probable values further polarise the alternatives without easing a choice between them. However, as already emphasised [19] the experimental uncertainties are large, and the calculated frequencies may be taken as favouring values not too far removed from those used.

In conclusion it may be noted that the results again illustrate the usefulness of combining isotopic with spectral measurements in vibrational analyses of the difficultly accessible lyonium and lyate species of hydroxylic solvents. And yet the poor agreement

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* We acknowledge discussion with M. Moskovits on this point.

between observed frequencies and calculated values, based on isotopic fractionation measurements and vibrational analyses of extended molecular models, for both OH^- and H_3O^+,[1] remains a puzzle, especially as in the corresponding comparison for liquid water agreement is satisfactory.[1]

APPENDIX

For the generalised molecule $A_1H_{n_1}A_2H_{n_2} \ldots A_iH_{n_i}$ containing exchangeable hydrogens attached to each of i heavy atoms (A), denoted below as X(H) for short, we wish to demonstrate that the product of the geometric means of fractionation factors $\phi_i{}^0$ and $\phi_i{}^\infty$ taken over all hydrogens is given by equation (17) where X(H) and X(D) represent

$$\prod_i \{\phi_i{}^0\phi_i{}^\infty\}^{n_i/2} = \frac{Q_{X(D)}Q_{H_2O}^{\Sigma n_i/2}}{Q_{X(H)}Q_{D_2O}^{\Sigma n_i/2}} = \frac{[X(D)][D_2O]^{\Sigma n_i/2}}{[X(H)][H_2O]^{\Sigma n_i/2}} \qquad (17)$$

fully protiated and fully deuteriated molecules respectively, i is the number of heavy atoms, and n_i the number of (equivalent) hydrogens at position i. Beginning with the simpler case of a molecule AH_nBH_m with two sets of exchangeable hydrogens we have equations (18), and if the logarithms of the partition functions are approximately

$$\begin{aligned} \phi_A{}^0 &= \frac{Q_{ADH_{n-1}BH_m}Q_{H_2O}}{Q_{AH_nBH_m}Q_{HDO}} & \phi_A{}^\infty &= \frac{Q_{AD_nBD_m}Q_{HDO}}{Q_{AHD_{n-1}BD_m}Q_{D_2O}} \\ \phi_B{}^0 &= \frac{Q_{AH_nBDH_{m-1}}Q_{H_2O}}{Q_{AH_nBH_m}Q_{HDO}} & \phi_B{}^\infty &= \frac{Q_{AD_nBD_m}Q_{HDO}}{Q_{AD_nBHD_{m-1}}Q_{D_2O}} \end{aligned} \qquad (18)$$

additive functions of isotopic substitution, with discrepancies conforming to Bernstein's rules generalised to take account of interactions between hydrogens at non-equivalent positions,[6,31,32] we may write equations (19).

$$\begin{aligned} \frac{Q^n{}_{ADH_{n-1}BH_m}}{Q_{AD_nBH_m}Q^{n-1}_{AH_nBH_m}} &= \frac{Q^n{}_{AHD_{n-1}BH_m}}{Q^{n-1}_{AD_nBH_m}Q_{AH_nBH_m}} \\ \frac{Q^m{}_{AH_nBDH_{m-1}}}{Q_{AH_nBD_m}Q^{m-1}_{AH_nBH_m}} &= \frac{Q^m{}_{AD_nBHD_{n-1}}}{Q^{m-1}_{AH_nBD_m}Q_{AH_nBH_m}} \end{aligned} \qquad (19)$$

These relationships may be used to eliminate partition functions for molecules involving partial deuteriation at atoms A or B in the expressions for the fractionation factors (18). Taking the product $(\phi_A{}^0\phi_A{}^\infty)^n(\phi_B{}^0\phi_B{}^\infty)^m$ then leads to cancellation of partition functions involving deuterium at one position and protium at the other, *i.e.* $Q_{AH_nBD_m}$ and $Q_{AD_nBH_m}$, and we obtain equation (20). It is straightforward

$$\{\phi_A{}^0\phi_A{}^\infty\}^{n/2}\{\phi_B{}^0\phi_B{}^\infty\}^{m/2} = \frac{Q_{AD_nBD_m}Q_{D_2O}^{(n+m)/2}}{Q_{AH_nBH_m}Q_{H_2O}^{(n+m)/2}} \qquad (20)$$

to extend the results to more than two exchangeable positions. Each new position introduces a new pair of fractionation factors ϕ° and ϕ^∞ and a new relationship (19) between partition functions for mixed and homogeneous isotopic substitution at one position. For the case of the i exchangeable positions of equation (17) there are i such equations.

One may conclude that solvent isotope effects in pure H_2O and D_2O may quite generally be represented in terms of the limiting fractionation factors ϕ° and ϕ^∞ for individual exchangeable positions.

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