JOURNAL
OF THE AMERICAN CHEMICAL SOCIETY

Registered in U. S. Patent Office © *Copyright, 1971, by the American Chemical Society*

VOLUME 93, NUMBER 1 JANUARY 13, 1971

Physical and Inorganic Chemistry

Vibrational Analyses of Liquid Water and the Hydronium Ion in Aqueous Solution[1]

R. A. More O'Ferrall,*[2] G. W. Koeppl,*[3] and A. J. Kresge[4]

Contribution from the Departments of Chemistry, Illinois Institute of Technology, Chicago, Illinois 60616, and Rice University, Houston, Texas 77001.
Received May 12, 1970

Abstract: A vibrational analysis of liquid water, considered as a mixture of molecules with different numbers of hydrogen bonds, is reported. A nine-atom model consisting of H_2O surrounded tetrahedrally by two oxygens and two OH groups is used for the fully bound species. Molecules in lower states of hydrogen bonding are represented by removing one or more of the peripheral groups. Frequencies are calculated for intramolecular bending and stretching modes as well as for intermolecular stretching and bending of hydrogen bonds. Apart from discrepancies in the stretching modes of $\sim$100 cm^{-1}, substantial agreement with experimentally based assignments for different water species, due mainly to Walrafen, is obtained. It is predicted that the HDO bending band should broaden with increasing temperature, and evidence for strong intermolecular coupling of librational modes is presented. Observed frequencies of 60 cm^{-1} and less are ascribed to intermolecular bending modes. Calculations for H_3O^+ using a comparable model are also reported and compared with measured frequencies of $H_9O_4^+Br^-$ crystals and H_3O^+ in solutions of sulfur dioxide and water. The calculated frequencies for aqueous H_3O^+ are subjected to the condition that they reproduce the equilibrium constant for the isotopic exchange process, $2D_3O^+(aq) + 3H_2O(g) \rightleftarrows 2H_3O^+(aq) + 3D_2O(g)$. It is concluded that the reported intramolecular frequencies are too high. This supports an earlier conclusion [Th. Ackermann, *Z. Phys. Chem.* (*Frankfurt am Main*), **27**, 253 (1961)] that in aqueous solution the vibrational spectrum of H_3O^+ is obscured by the high rate of proton transfer between solvent molecules.

In the past few years, interest in the structure of water has prompted a number of careful measurements of its infrared, Raman,[5–17] near-infrared,[17,18] and neutron inelastic scattering[17,19] spectra. There have also been several investigations of the vibrational spectra of hydronium ion salts and their solutions.[5,15,20–28] As

---

(1) Presented in part at the 159th National Meeting of the American Chemical Society, Houston, Texas, Feb 1970, Abstract PHYS 009; based in part upon a Ph.D. thesis submitted by G. W. Koeppl to the Illinois Institute of Technology, June 1969.

(2) Rice University. Present address, University College, Belfield, Dublin, Ireland.

(3) NASA Fellow, 1964–1967. Present address, Queen's College of the City University of New York, New York, N. Y. 11367.

(4) Illinois Institute of Technology.

(5) G. E. Walrafen, *J. Chem. Phys.*, **36**, 1035 (1962).

(6) G. E. Walrafen, *ibid.*, **44**, 1546 (1966); 40, 3249 (1964).

(7) G. E. Walrafen, *ibid.*, **47**, 114 (1967).

(8) G. E. Walrafen, *ibid.*, **48**, 244 (1968).

(9) G. E. Walrafen in "Hydrogen-Bonded Solvent Systems," A. K. Covington and P. Jones, Ed., Taylor and Francis, London, 1968, p 9.

(10) W. A. Senior and R. E. Verrall, *J. Phys. Chem.*, 73, 4242 (1969).

(11) (a) J. Schiffer and D. F. Hornig, *J. Chem. Phys.*, **49**, 4150 (1968); (b) T. T. Wall and D. F. Hornig, *ibid.*, **43**, 2079 (1965).

(12) M. Falk and T. A. Ford, *Can. J. Chem.*, **44**, 1699 (1966).

(13) R. E. Weston, Jr., *Spectrochim. Acta*, **18**, 1257 (1962).

(14) D. A. Draegert, N. W. B. Stone, B. Curnutte, and D. Williams, *J. Opt. Soc. Amer.*, **56**, 64 (1966).

(15) D. A. Draegert and D. Williams, *J. Chem. Phys.*, **48**, 401 (1968).

(16) E. U. Franck and K. Roth, *Discuss. Faraday Soc.*, **43**, 108 (1967).

(17) G. J. Safford, *Cryobiology*, **3**, 32 (1966), and references cited in papers listed above.

(18) O. D. Bonner and G. B. Woolsey, *J. Phys. Chem.*, **72**, 899 (1968); J. D. Worley and I. M. Klotz, *J. Chem. Phys.*, **45**, 2868, (1966); W. A. P. Luck in "Physico Chemical Processes in Mixed Aqueous Solvents," F. Franks, Ed., Heinemann, London, 1967.

(19) G. J. Safford, P. S. Leung, A. W. Naumann, and P. C. Schaffer, *J. Chem. Phys.*, 50, 4444 (1969); O. K. Harling, *ibid.*, **50**, 5279 (1969); J. O. Burgman, J. Sciesinski, and K. Sköld, *Phys. Rev.*, **170**, 808 (1968).

(20) J. T. Mullhaupt and D. F. Hornig, *J. Chem. Phys.*, **24**, 169 (1956); C. C. Ferriso and D. F. Hornig, *ibid.*, **23**, 1464 (1955); *J. Amer. Chem. Soc.*, **75**, 4113 (1953).

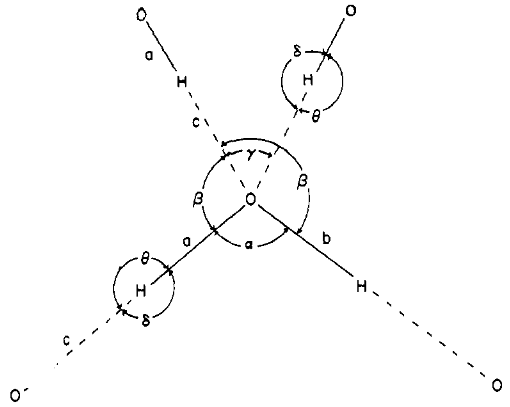
a preliminary to carrying out calculations of solvent deuterium isotope effects upon acid-catalyzed reactions,[29] we have performed vibrational analyses for models of water and the hydronium ion in which the molecule and ion are situated in tetrahedral hydrogen-bonded lattices. The vibration frequencies calculated are reported here.

As is well known, there have been differences in the interpretation of the spectra of liquid water, and in particular of the origin of the temperature-dependent asymmetry observed for the broad bands corresponding to the O–H stretching vibrations. The favored interpretation usually has depended on whether water is viewed as a "continuum" of hydrogen-bonded species, in which the length or angle of the bonds varies from molecule to molecule, or as a "mixture" of discrete species possessing integral numbers of hydrogen bonds. In the former view the spectral asymmetry is normally ascribed to overlap of the stretching region with an overtone of the bending frequency strengthened by Fermi resonance.[11,12,30] In the latter it has been ascribed to the presence of molecules with different numbers of hydrogen bonds, each of which possesses a distinct absorption spectrum.[6–10]

No attempt is made here to enter directly into this discussion. However, adoption of the mixture model has permitted resolution of the observed band contours into symmetric components which can be specifically assigned to molecules in different states of hydrogen bonding.[7–9] The legitimacy of this procedure depends on the assumption that the gross features of the spectrum in the stretching region are determined by the immediate local environment of a water molecule, and it follows that it should be possible to reproduce the frequency assignments by a normal coordinate analysis based on a relatively simple model of the type used in the calculations reported here. A comparison between observed and calculated frequencies should therefore provide a test of the model. In this paper the comparison is confined to the mixture model because the continuum model is less susceptible to vibrational analysis. In the calculations for the hydronium ion simple extensions of the models for water are used.

Calculations and Results

Water. The model chosen for the calculations was a water molecule tetrahedrally bonded to two oxygen atom fragments and two O–H groups (1). It is similar to one previously used for ice.[31] The symmetry of the model is C_{2v} and the bond lengths and angles to which different force constants were assigned, in this and in modified models, are indicated by Latin and Greek letters. The O–H covalent and hydrogen-bond lengths were taken as 1.0 and 1.76 Å, respectively, close to the values for ice. The vibration frequencies were calculated using the Wilson FG matrix method.[32] The model has 9 atoms and yielded 22 frequencies including one redundancy. Eigenvectors were calculated and used to assign the frequencies to specific modes. Calculations were also made for incompletely hydrogen-bonded species using the same model but with one or more of the peripheral O or OH groups removed.



I

Stretching force constants were chosen to reproduce the frequencies observed and assignments made by Walrafen.[9] Walrafen has reported stretching frequencies for hydrogen-bonded and non-hydrogen-bonded molecules of pure H_2O,[7] HDO in H_2O,[8] and HDO in D_2O,[9] obtained by resolution of the observed Raman bands into gaussian components. Partly for the sake of consistency, Walrafen's measurements of the intermolecular frequencies, both hindered translations,[6] ν_T, and librations,[7] ν_L, were also used. Comparison with other values indicates good agreement,[9] and although recent measurements yield a somewhat larger value for the highest librational frequency,[19] the difference does not affect the conclusions presented here. The bending frequency, ν_2, was taken from Weston's Raman measurements.[13] There have been no attempts to resolve this band into components and it has been found that its intensity[7] and frequency[12] vary only slightly with temperature. It was assumed, therefore, that the frequency was unaffected by the extent of hydrogen bonding.

The observed frequencies are listed in Table I. The band at 60 cm^{-1} has been considered to be either a hindered translation or a low-frequency hydrogen-bond bending mode, and is denoted ν_b or ν_T. No intermolecular frequencies have been reported in any detail for HDO. The assignments have been grouped into two phenomenological categories of bound and unbound molecules.[9] The relation of these categories to the actual water species with zero, one, two, three, or four hydrogen bonds, postulated by the mixture model, depends on the isotopic molecule and vibrational mode

---

(21) D. E. Bethell and N. Sheppard, *J. Chim. Phys. Physicochim. Biol.*, **50**, C-72 (1953); R. C. Taylor and G. L. Vidale, *J. Amer. Chem. Soc.*, **78**, 5999 (1956).

(22) R. A. Savoie and P. A. Giguère, *J. Chem. Phys.*, **41**, 2698 (1964).

(23) J. Rudolph and H. Zimmerman, *Z. Phys. Chem. (Frankfurt am Main)*, **43**, 311 (1964).

(24) P. A. Giguère, *Rev. Chim. Miner.*, **3**, 627 (1966).

(25) M. Falk and P. A. Giguère, *Can. J. Chem.*, **35**, 1195(1957).

(26) (a) W. R. Busing and D. F. Hornig, *J. Phys. Chem.*, **65**, 284 (1961); (b) C. G. Swain and R. F. W. Bader, *Tetrahedron*, **10**, 182 (1960); C. G. Swain, R. F. W. Bader, and E. R. Thornton, *ibid.*, **10**, 200 (1960)

(27) T. Ackermann, *Z. Phys. Chem. (Frankfurt am Main)*, **27**, 253 (1961); **41**, 113 (1964).

(28) M. Schneider and P. A. Giguère, *C. R. Acad. Sci., Ser. B*, **267**, 551 (1968).

(29) R. A. More O'Ferrall, G. W. Koeppl, and A. J. Kresge, *J. Amer. Chem. Soc.*, **93**, 9 (1971).

(30) M. Falk and H. R. Wyss, *J. Chem. Phys.*, **51**, 5727 (1969).

(31) Y. Kyogoku, *J. Chem. Soc. Jap., Pure Chem. Sect.*, **81**, 1648 (1960); National Research Council of Canada, technical translation 953.

(32) E. B. Wilson, Jr., J. C. Decius, and P. C. Cross, "Molecular Vibrations," McGraw-Hill, New York, N. Y., 1955.

Table I. Frequency Assignments from Observed Spectra for Liquid Water[a]

	Bound			Unbound		
	H_2O	D_2O[b]	HDO	H_2O	D_2O	HDO
ν_1[c]	3247		2525	3535		2645
ν_3[c]	3435		3444[d]	3622		3628[d]
ν_2[e]	1645	1210	1450	1645	1210	1450
ν_L	722	~550				
	550	~375				
	450					
ν_T	166	167				
ν_T or ν_b	60	60				

[a] Frequencies in cm^{-1} are taken from Walrafen's Raman measurements[6–9] except as indicated. All frequencies were reported at 25° except ν_1 and ν_3 which are averages over a range of temperature (~10–95°). [b] Intermolecular frequencies for D_2O have been analyzed in less detail than for H_2O. [c] Assignments to ν_1 and ν_3 followed the relative frequency magnitudes in the gas phase. For HDO, O–H and O–D frequencies are shown. [d] Based on peak and shoulder reported for solutions of 2.8 *M* H_2O in D_2O.[9] [e] Reference 13.

considered as well as the interpretation put on the assignment. This point will be considered below.

Table II. Calculated Vibration Frequencies for Fully Hydrogen-Bonded Water in a Tetrahedral Lattice[a]

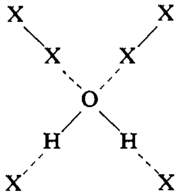
	H_2O	D_2O	HDO in H_2O	HDO in D_2O
ν_1[b]	3355	2425	2505	2505
ν_3[b]	3550	2605	3460	3460
ν_2	1645	1200	1450	1450
ν_L	715	530	710	695
	710	500	460	515
	645	470	460	510
ν_d	530	380	610	400
	530	380	600	390
	530	380	530	380
	(580)	(420)	(580)	(420)
ν_T	168	161	165	163
	168	161	165	163
	167	161	164	162
	105	104	105	103
ν_b	54–35	53–35	54–35	53–35

[a] Frequencies in cm^{-1}. The vibration frequencies for the peripheral O–H and O–D groups in models **1**, **3**, **4**, and **5** were 3445 and 2505 cm^{-1}, respectively, and are not listed in the tables. [b] The interaction constant f_{ab} was chosen to give $\nu_3 > \nu_1$ as in the gas phase.

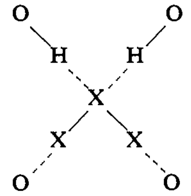
The frequencies calculated from the completely hydrogen-bonded molecule **1** are listed in Table II. The stretching force constants were chosen to reproduce the O–H and O–D frequencies measured for HOD, since these should be considerably more accurate than frequencies derived from the more complex bands for pure H_2O. The actual force constants used were as follows: stretching force constants (mdyn/Å) $f_a = f_b = 6.55$, $f_c = 0.12$, $f_{ab} = -0.25$; bending force constants [(mdyn Å)/rad^2] $f_\alpha = 0.65$, $f_\beta = 0.067$, $f_\gamma = 0.03$, $f_\theta = f_\delta = 0.067$.

The subscripts for the force constants follow the coordinate notation in **1**. The covalent O–H stretching interaction force constant is denoted f_{ab}. The magnitude of the libration frequencies was determined principally by the force constants f_θ, f_δ, and f_β. It was considered that f_γ, the bending force constant between two hydrogen bonds, should be smaller than f_β. The in-plane and out-of-plane force constants for bending of the bonds about hydrogen, f_θ and f_δ, were taken as equal.

A detailed discussion of the results is given below. However, it may be noted here that model **1** yields eight hydrogen bending frequencies. One of these is ν_2, three are librations of the central H_2O unit ν_L, and four are in-plane and out-of-plane deformations of the peripheral O–H groups, denoted ν_d in Table II. Comparison of the magnitudes of these frequencies with those calculated from models in which the peripheral atoms or the atoms in the H_2O group were assigned the large atomic mass $X = 200$, **2** and **3**, respectively, demonstrated that there was strong vibrational coupling between the librations and hydrogen-bond deformations. The uncoupled frequencies calculated from **2** and **3** are compared below with the corresponding coupled values taken from Table II, which are shown in parentheses. Assignment of frequencies as primarily libration or deformation modes was made by inspection of the eigenvectors for coupled and uncoupled modes. The deformation frequency listed in parentheses in Table II is the one frequency in this group which is not appreciably coupled for model **1**.



2



3

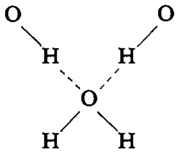
X = atomic mass 200

ν_L 700, 670, 590 cm^{-1}
(715, 710, 645)

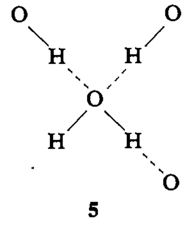
ν_d 550, 578, 581, 582 cm^{-1}
(530, 530, 530, 580)

In addition to ν_L and ν_d there are five bending vibrations which do not involve motion of hydrogen. These are of lower frequency and are denoted ν_b in Table II.

Calculations were also carried out for models **4** and **5** in which one or both of the oxygens hydrogen bonded to the hydrogens of the H_2O are removed.



4



5

Most of the force constants in models **4** and **5** were the same as in **1**. However, in **4** the value of $f_a = f_b = 7.35$ mdyn/Å was assigned to reproduce the frequencies assigned by Walrafen to "unbound" O–H and O–D groups of HDO in H_2O and D_2O. In **5** the hydrogen-bonded and free O–H groups were assigned the stretching force constants used in **1** and **4**, respectively, $f_a = 7.35$ and $f_b = 6.55$ mdyn/Å. In both **4** and **5** bending force constants were chosen to reproduce the same H_2O and D_2O bending frequencies as for **1**. These were $f_\alpha = 0.73$ and 0.69 (mdyn Å)/rad^2, respectively. Calculated frequencies for models **4** and **5** are shown in Tables III and IV.

Table III. Calculated Vibration Frequencies for Water with Unbound Hydroxyl Groups[a]

	H_2O	D_2O	HDO in H_2O[b]
ν_1	3585	2590	2640
ν_3	3670	2695	3630
ν_2	1645	1205	1445
ν_L	410	307	390
	355	254	285
	230	173	200
ν_d	620	440	610
	600	435	600
	580	425	580
	580	420	570
ν_T	158	148	153
	137	132	134
ν_b	41	41	41

[a] All frequencies have units of cm^{-1}. [b] Intramolecular frequencies for HDO in H_2O and HDO in D_2O are insignificantly different.

Table IV. Calculated Vibration Frequencies for a Water Molecule with One Hydroxyl Group Hydrogen Bonded[a]

			HDO in H_2O	
	H_2O	D_2O	(OH bound)	(OD bound)
ν_1	3405	2470	2490	3430
ν_3	3675	2690	3660	2650
ν_2	1650	1200	1470	1425
ν_L	710	515	710	465
	420	300	350	375
	380	280	295	355
ν_d	610	445	600	610
	600	435	580	600
	580	420	580	580
	530	380	530	580
ν_T	162	155	157	161
	161	154	157	159
	126	122	125	125
ν_b	59-39	58-38	58-38	59-38

[a] Frequencies have units of cm^{-1}.

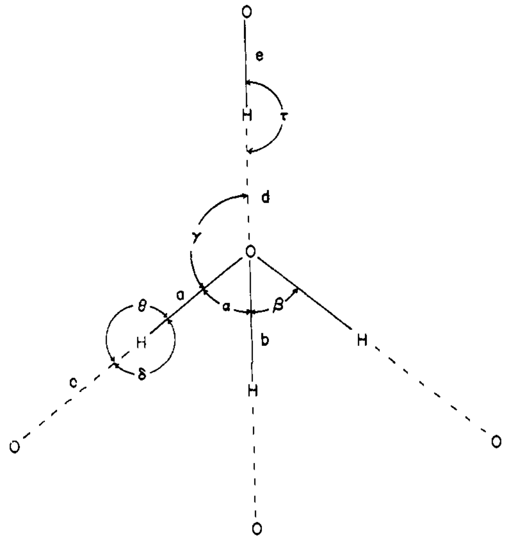
Table V. Calculated and Observed Frequencies for the Hydronium Ion in Aqueous Solution[a]

	$H_3O^+(aq)$			$D_3O^+(aq)$		
	Obsd[b]	Calcd[c]		Obsd[b]	Calcd[c]	
	Ir or Raman	$L = 9.0$	$L = 11.0$	Ir	$L = 9.0$	$L = 11.0$
ν_1(a)	2900, 2600	2785	2760		1980	1960
ν_3(e)	2900, 3025	2470	2440	2170	1815	1795
ν_2(a)	1205, 1190	1140	1130	960	855	845
ν_4(e)	1750, 1720	1615	1585	1400	1170	1150
ν_L(a)	605–625, 643	580	580	465	410	410
(e)	675, 620–624[d]	610	610	410–450[d]	435	435
ν_T(a)		180	180		175	175
(e)		250	250		240	240

[a] Frequencies have units of cm^{-1}. Assignments of observed values to symmetry classes have frequently not been made. The classifications here pertain mainly to the calculated values. [b] Results of various authors; those not taken from Table IV of ref 33 are indicated by footnotes. [c] Frequencies are calculated under the constraint that when combined with the calculated frequencies for H_2O in the gas phase they yield the value $L(p_{D_2O}/p_{H_2O})^3$ for the equilibrium constant for the exchange process $2D_3O^+(aq) + 3H_2O(g) \rightleftarrows 2H_3O^+(aq) + 3D_2O(g)$. The value of L is specified for each set of frequencies. [d] Reference 15.

The Hydronium Ion. Measurements of the infrared and Raman spectra of the hydronium ion under a variety of conditions have been summarized by Heinzinger and Weston[33] and by Giguère.[24] The measurements of greatest interest here are Giguère's study of hydronium halides and their corresponding deuterated salts in solutions of sulfur dioxide;[28] Rudolph and Zimmerman's infrared studies[23] of the crystalline salt $H_9O_4^+Br^-$ and, of course, direct infrared and Raman measurements of strongly acidic aqueous solutions.[5,15,25,27,33]

The available experimental results are listed in Tables V and VI and, as may be seen from Table V, and even more clearly from the published spectra, the directly measured frequencies for H_3O^+ in aqueous solution are ill defined. Indeed, as shown by Ackermann, and discussed below, whether the observed bands pertain to H_3O^+ at all can be seriously questioned.[27] In choosing a set of "best" frequencies for calculation, therefore, it is helpful to consider results for related systems. The results shown in Table VI for H_3O^+ in SO_2 provide probably the clearest and most easily interpreted measurements of the H_3O^+ stretching frequencies, while the salt $H_9O_4^+Br^-$ apparently offers an attractive model for the hydronium ion in solution.



6

Calculations of frequencies for the hydronium ion in aqueous solution were based on model 6, which is similar to the model used for water 1, except that the symmetry is C_{3v}, and there is a rearrangement of the hydrogen bonds. The bonds and angles to which different force constants were assigned are indicated by Greek

---

(33) K. Heinzinger and R. E. Weston, Jr., *J. Phys. Chem.*, **68**, 744 (1964).

Table VI. Calculated and Observed Frequencies[a] for Solutions of H_3O^+ Salts in SO_2 and Crystalline $H_9O_4^+Br^-$

	H_3O^+/SO_2			D_3O^+/SO_2		$H_9O_4^+Br^-$		
	Obsd[b]			Obsd[b]		Obsd[c]		$D_9O_4^+Br^-$
	Ir	Raman	Calcd	Ir	Calcd	Ir	Calcd	Calcd
ν_1(a)	3405	3415	3410	2580	2425[d,e]	2060	2640[f]	1880
ν_3(e)	3470	3447	3455	2677	2550	2630	2060	1520
ν_2(a)			785		593	1313	1320	985
ν_4(e)	1670	1700	1690		1230	1845	1840	1320
ν_L(a)						902	870	615
(e)						738	920	660
ν_T(a)						569	405	400
(e)						556	570	550
ν_b						78	97–27	97–27

[a] Frequencies have units of cm^{-1}. The assignments of the authors are followed. [b] Reference 28. [c] Reference 23. [d] For H_3O^+ in SO_2 calculated frequencies were fitted to those observed for H_3O^+ only. The calculated frequencies for D_3O^+ are low. [e] Giguère and Schneider (ref 28) report observation of H_2DO^+ and/or HD_2O^+ in SO_2. Calculated frequencies for these ions are: H_2DO^+, 2510, 3455, 3425, 1670, 1420 and 725 cm^{-1}; HD_2O^+, 3440, 2550, 2465, 1530, 1255, and 660 cm^{-1}. [f] For calculation of $H_9O_4^+Br^-$ frequencies a positive stretching interaction force constant between covalent O–H bonds was used. This gave $\nu_1 > \nu_3$.

Table VII. Force Constants for Hydronium Ion Models

f[a]		a, b	c	d	e	ab[b]	ac[b]	α, β	γ	θ, δ	τ	$\alpha\beta$[b]
H_3O^+/SO_2		6.61				0.11		0.58				0.0
$H_9O_4^+Br^-$		3.15	1.6	0.05		0.58	0.9	0.62	0.05	0.18		0.085
H_3O^+(aq)	$L = 11.0$	3.38	0.3	0.02	7.0	0.4	0.0	0.57	0.02	0.08	0.02	0.13
	$L = 9.0$	3.46	0.3	0.02	7.0	0.4	0.0	0.59	0.02	0.08	0.02	0.13

[a] Notation for coordinates to which force constant refer follows that of model **6**. Units are mdyn/Å for stretching force constants and (mdyn Å)/rad² for bending force constants. [b] Interaction force constants between specified coordinates.

and Latin letters, as before. The H–O–H angle, α ($=\beta$), was taken as 115° and the O–H covalent bond length, a ($=$b), as 1.0 Å. These are close to the measured values for various hydronium ion salts.[24] The O–H hydrogen-bond distance was taken as 1.76 Å, the same as that in model **1**.

Calculated frequencies for the three systems considered are also shown in Tables V and VI and the force constants used are listed in Table VII. In the calculations for H_3O^+ in sulfur dioxide, only the four-atom unit H_3O^+ was considered. Also, since only one bending frequency has been reported, the bending interaction force constant $f_{\alpha\beta}$ was taken to be zero. As may be seen, this leads to a relatively low frequency for the bending mode ν_2. For $H_9O_4^+Br^-$, the model was modified by replacing the hydrogen-bonding O–H group by a bromide ion. No crystal structure appears to have been reported for an $H_9O_4^+$ salt, and this structure was inferred[23] from the infrared spectrum.

For H_3O^+ in SO_2 and for $H_9O_4^+Br^-$, force constants were assigned to best reproduce the measured and assigned frequencies. For H_3O^+ in aqueous solution, however, the overriding condition was imposed that the calculated frequencies for H_3O^+ should be consistent with the experimental value of the equilibrium constant, K, for the isotopic exchange process

$$3H_2O(g) + 2D_3O^+ \underset{}{\overset{K}{\rightleftharpoons}} 3D_2O(g) + 2H_3O^+ \qquad (1)$$

K is given by $L(p_{D_2O}/p_{H_2O})^3$, where L is the equilibrium constant for the corresponding exchange with liquid water[33–36] and p_{D_2O}/p_{H_2O} is the ratio of vapor pressures for D_2O and H_2O. In Table V "best" sets of calculated frequencies consistent with L = 9.0 and 11.0 are recorded.

Discussion

Water. Stretching Modes. As already noted, the most accurate measurements of stretching frequencies have been made for dilute solutions of HDO in H_2O or D_2O. For the HDO molecule there is no intramolecular coupling of stretching modes, and if the reasonable assumption is made that the principal factor determining the frequency is whether or not the hydrogen atom is hydrogen bonded, the frequency bands may be resolved into two components corresponding to bound and unbound O–H groups[8,9] (Table I). In the calculations, therefore, stretching force constants for bound and free O–H groups were assigned to reproduce the corresponding frequencies (Tables II and III). Good agreement was obtained for both O–H and O–D frequencies, even though measurements of the OH frequencies have been reported only in a preliminary form.[9] The discrepancies are of the order that might be expected from neglect of anharmonicity.

The same force constants were used to calculate ν_1 and ν_3 for bound and unbound molecules in pure H_2O. In this case the experimental situation is more complex because the frequency bands must consist of at least four components A resolution has been achieved by Walrafen,[7] but agreement between the derived frequencies and those calculated on the assumption that both (Table II) or neither (Table III) of the O–H groups is hydrogen bonded is less satisfactory than for HDO. Discrepancies are now as high as 115 cm^{-1}.

It is noticeable that measured values of ν_3 for H_2O in Table I are close to the corresponding uncoupled frequencies of HDO. In fact, application of the product or sum rules to the stretching modes leads to the expectation that the O–H and O–D frequencies for HDO should be close to the geometric means of ν_1 and

---

(34) K. Heinzinger, *Z. Naturforsch. A*, 20, 269 (1965)

(35) P. Salomaa and V. Aalto, *Acta Chem. Scand.*, 20, 2035 (1966).

(36) A. J. Kresge and A. L. Allred, *J. Amer. Chem. Soc.*, **85**, 1541 (1963); V. Gold, *Proc. Chem. Soc.*, **141**, (1963); V. Gold and B. M. Lowe, *J. Chem. Soc. A*, 936 (1967); P. Salomaa, A. Vesala, and S. Vesala, *Acta Chem. Scand.*, **23**, 2107 (1969).

ν_3 for H_2O and D_2O, respectively.[37] For models **1** and **4**, this is true of the calculated frequencies, even when hydrogen bond–covalent stretch, or stretch–bend interaction force constants are included. It is also true of the observed frequencies in the gas phase.

For the low-intensity frequencies assigned to unbound water, abnormal behavior may arise from the presence of molecules in which one hydrogen atom is hydrogen bonded and the other not, since partial hydrogen bonding (as in model **5**) can itself cause substantial "decoupling" of the stretching modes, as may be seen in Table IV. However, it is unlikely that the same can be true of the high-intensity components assigned to bound water molecules since, at low temperatures, fully hydrogen-bonded molecules (model **1**) probably comprise the major absorbing species.[40]

It is possible that the discrepancy represents the uncertainty involved in decomposing the H_2O stretching band into four gaussian components. However, a casual inspection of published spectra[11] for the OH stretching region of H_2O and HDO indicates that the band maxima occur at practically the same frequency (and, indeed, Hornig and Schiffer have concluded that a pronounced intramolecular decoupling of stretching modes is characteristic of water in the liquid state[11a]). Moreover, a close identity of OD stretching frequencies has been observed in HDO and D_2O cubic ice (though not of OH frequencies in HDO and H_2O ice).[39] Thus, the possibility that the simple models used here are not adequate for interpreting the stretching region of liquid-water spectra cannot be ruled out.

The success of the "two-state" treatment of hydrogen stretching modes for HDO[8–10] is consistent with the view that hydrogen bonding of the oxygen lone pair has a much smaller effect on the stretching force constant of the covalent O–H bond than does bonding of the hydrogen. In Tables III and IV calculations are reported for molecules in which it is assumed that both lone pairs of the oxygen are hydrogen bonded. The only available indication of a possible effect of bonding at oxygen appears to be Franck and Roth's demonstration that at elevated temperatures and pressures the isosbestic point observed for HDO spectra at lower temperatures is no longer found.[16] This could be ascribed to increasing concentrations of water molecules with no hydrogen bonds as the temperature is raised.[42]

Bending Frequencies. The intramolecular bending mode for water has been studied in less detail than the stretching modes, although it has been shown that there is little change in frequency[12] and integrated Raman intensity[7] with increasing temperature. In the calculations, force constants were assigned to yield the same frequencies for molecules in which the O–H groups were hydrogen bonded or free. This entailed assigning different bending force constants, f_α (*cf.* model **1**) to molecules with different numbers of hydrogen bonds, because the hydrogen-bond bending force constants also contribute to the intramolecular bending frequency. For molecules with zero, one, and two bound OH groups the bending force constants were $f_\alpha = 0.73, 0.69$, and 0.65 (mdyn Å)/rad^2.

As seen in Tables I, II, III, and IV, there was generally little difficulty in reproducing the observed isotopic frequencies. However, a consequence of the contribution of hydrogen-bond bending force constants is that for singly bound HDO molecules, the magnitude of the bending frequency depends on whether the hydrogen or deuterium is bound. As seen in Table IV, the calculated frequencies of 1425 and 1470 cm^{-1} bracket the "normal" value of 1445–1450 cm^{-1} for symmetrically bound molecules. It would seem that the difference is large enough that it should show up as a broadening of the frequency band for HDO bending under conditions for which the concentration of asymmetrically bound molecules is high, possibly at elevated temperatures. So far, no such effect has been reported.

Librational Modes. As already noted, the use of model **1** leads to the calculation of several hydrogen-bond bending frequencies, three of which correspond to librations of the H_2O unit, ν_L, and four to deformations of the hydrogen-bonding O–H fragments, ν_d. The calculated values of ν_L and ν_d have been grouped separately in Table II, and assignments were made from inspection of the eigenvectors. However, the separation is largely artificial because there is strong coupling between the modes. The existence of this coupling is indeed the principal conclusion suggested by these calculations, and it is well illustrated by comparison of the frequencies calculated from model **1** with those obtained from models **2** and **3** in which decoupling is effected by assigning large atomic masses respectively to the peripheral and central atoms of the model.

The existence of coupling makes it impossible to obtain realistic frequencies from a model as restricted as **1**. In reality, the deformation modes ν_d of the peripheral OH groups would correspond to librational modes of adjacent molecules. However, the spread in the calculated frequencies from 500 to 700 cm^{-1} does suggest that coupling offers a reasonable interpretation of the breadth of the librational band. Moreover, the grouping of frequencies at 700 and 530 cm^{-1} is not inconsistent with the resolution of the experimental band into two or three components with peaks close to these values.

These conclusions are pertinent to Walrafen's measurements and interpretation of the temperature dependence of the librational bands.[7,9] Walrafen found that the frequencies and relative intensities of the gaussian components of the librational band undergo little change with an increase in temperature in the range 10–90°, but that the *net* integrated Raman intensity decreases sharply. Measurement of ΔH for the process leading to loss of intensity gave a value close to that expected for the breaking of two hydrogen bonds, and roughly twice the value obtained from the temperature dependence of the intensity of gaussian components for the stretching frequency bands. Walrafen interpreted this behavior by supposing that the librational intensity in the Raman spectrum arises solely from fully hydro-

---

(37) This point has been made with reference to the frequency assignments for ice.[38,39]

(38) C. Haas and D. F. Hornig, *J. Chem. Phys.*, 32, 1763 (1960).

(39) J. E. Bertie and E. Whalley, *ibid.*, **40**, 1637 (1964).

(40) Estimates vary very widely,[41,12] but this view is supported by the low integrated intensity of the gaussian component of the Raman and ir bands assigned to unbound molecules in the temperature range studied.[8]

(41) W. A. P. Luck, *Fortschr. Chem. Forsch.*, 4, 653 (1964).

(42) Although the asymmetrically hydrogen-bonded HDO molecule represented by model **5** gives four O–H and O–D stretching frequencies, depending on whether D or H is bound, the magnitudes of these frequencies should be close to those for the symmetrically bound and unbound molecules (models 1 and 4) and therefore should not disturb the isosbestic relationship (*cf.* Tables II–IV).

gen-bonded water molecules, with a short-range symmetry close to C_{2v}, and that molecules with three, two, one, or zero hydrogen bonds do not absorb appreciably in this region. With this assumption, the change in absorption intensity with temperature corresponds to a change in equilibrium concentration of the tetrahedrally coordinated molecules, and Walrafen suggested that ΔH for this process should indeed correspond to the breaking of two hydrogen bonds.

This interpretation takes no explicit account of intermolecular coupling of the librational modes, but it would not appear to be inconsistent with coupling, particularly if, as seems likely, the strongest coupling occurs between adjacent molecules. According to the calculations, the existence of coupling, and in part the actual spread of frequencies, depends on the assignment of an appreciable force constant for deformation of the angle made by a hydrogen bond and a covalent bond to oxygen; *i.e.*, the angle β in model **1**. When this force constant is zero the calculated values of ν_L are grouped closely together; *e.g.*, 710, 700, and 690 cm^{-1} (*cf.* ref 43).

Other explanations of the wide separation of librational bands, consistent with the mixture model, are possible. As may be seen from Tables III and IV, low librational frequencies could be ascribed to partially hydrogen-bonded molecules. However, if these molecules were contributing substantially to the Raman intensity, a clearer indication might have been expected from the temperature dependence of the librational bands. Furthermore, broad asymmetric bands have been observed in the librational region for ice, in which tetrahedrally coordinated molecules must very largely predominate. Here, too, the breadth of the bands has been ascribed to vibrational coupling.[38,39,44] A further possibility is that the in-plane and out-of-plane bending force constants of uncoupled molecules differ substantially. This might be possible if the hydrogen bonds were appreciably bent in their equilibrium configuration, but such behavior would more readily accord with a continuum water model. It seems clear, therefore, that vibrational coupling offers the most attractive explanation of the observed behavior within the framework of a mixture model.

Low-Frequency Hydrogen-Bond Stretching and Bending Modes. Hindered translational modes and the low-frequency deformations not involving hydrogen are listed in Table II as ν_T and ν_b. The three frequencies close to 167 cm^{-1} correspond to the hindered translations of the H_2O unit in model **1**, while the lower value at 105 cm^{-1} is a breathing mode of the peripheral oxygens which disappears when the oxygens are replaced by heavy atoms, as in model **2** (ν_T = 145, 157, 166 cm^{-1}). There is some coupling of the modes, but it seems quite likely that in an extended lattice the major absorption would be centered at a single frequency, particularly if, as Walrafen suggests,[6,9] the Raman intensity is much greater for fully hydrogen-bonded molecules than others. However, as seen in Tables III and IV, the translational modes for doubly and triply bonded molecules are not likely to be greatly different. Thus, the calculations are quite consistent with the observation of a broad, nearly symmetrical, band at 170 cm^{-1}.

Five heavy-atom bending modes in the range 53–35 cm^{-1} are also calculated from model **1**. These are considerably lower in frequency than the translational modes and there seems little doubt that if the bands observed at 60 cm^{-1} in the Raman,[6,9] and at slightly lower frequencies in the neutron inelastic scattering spectrum,[9,18] are fundamentals, they should be considered as bending modes. They could, in principal, be ascribed to rotations of free or lattice water molecules, but this would seem to be precluded by the sharp decrease in absorption intensity with rising temperature.

The Vapor Pressures of H_2O and D_2O. The calculated liquid frequencies as a whole may be put to a further test by evaluating isotopic partition function ratios Q_{H_2O}/Q_{D_2O}. These, when combined with Q_{H_2O}/Q_{D_2O} for the gas phase, should yield reasonable values for the vapor pressure ratio[45] p_{H_2O}/p_{D_2O}. At 25° models **1** and **5** give p_{H_2O}/p_{D_2O} = 1.273 and 1.192, respectively, which may be compared with the experimental value[46] of 1.152.

In making the calculations, harmonic frequencies for H_2O in the gas phase were fitted to directly observed[47] rather than zero-order values. Insofar as anharmonic corrections are likely to be greater for the liquid than for the gas, the derived values of p_{H_2O}/p_{D_2O} represent lower limits. If the fully hydrogen-bonded water species (model **1**) is considered to be at high concentrations[40] at 25°, the comparison suggests that the zero-point energy for the liquid models is significantly overestimated. However, the discrepancy is quite small and can hardly be greater than 100 cm^{-1} in the hydrogen frequencies, which is well within the combined uncertainties of the librational and stretching modes.

The Hydronium Ion. The addition of strong acids to liquid water leads to a pronounced intensification of infrared absorption throughout the fundamental region.[25,27] Bands assigned to intramolecular vibrations of H_3O^+ appear as broad shoulders on the H_2O stretching and bending bands and as a very broad maximum centered near 1200 cm^{-1}. Vibration frequencies reported by different authors are shown, together with calculated values, in Table V. For comparison, frequencies of H_3O^+ in sulfur dioxide[28] and of crystalline $H_9O_4{}^+Br^-$ [23] are listed in Table VI.

Because the frequencies for aqueous H_3O^+ have to be separated from the background absorption of water they cannot be determined with accuracy. Furthermore, it has been convincingly argued that the observed spectra arise not from H_3O^+ itself but from frequency shifts and intensification of bands of the aqueous solvent.[27] For these reasons it seemed worthwhile subjecting the calculated frequencies to the condition that when combined with frequencies for H_2O in the gas phase they yield a reasonable value for the equilibrium constant K for isotopic fractionation of deuterium and hydrogen between aqueous H_3O^+ and H_2O vapor (eq 1). This

---

(43) R. W. Blue, *J. Chem. Phys.*, 22, 280 (1954).

(44) D. F. Hornig, H. F. White and J. P. Reding, *Spectrochim. Acta*, **12**, 338 (1958); J. E. Bertie and E. Whalley, *J. Chem. Phys.*, 40, 1646 (1964); N. Ockman, *Advan. Phys.* 7, 199 (1958).

(45) Corrections due to gas imperfections and differences in molar volumes between H_2O and D_2O can be neglected at the temperature considered: W. A. Van Hook, *J. Phys. Chem.*, 72, 1234 (1968).

(46) L. Merlivat, R. Botter, and G. Nief, *J. Chim. Phys. Physicochim. Biol.*, 60, 56 (1963); W. M. Jones, *J. Chem. Phys.*, **48**, 207 (1968); F. D. Rossini, J. W. Knowlton, and H. L. Johnston, *J. Res. Nat. Bur. Stand.*, **24**, 369 (1940).

(47) W. S. Benedict, N. Gailar, and E. K. Plyler, *J. Chem. Phys.*, **24**, 1139 (1956).

procedure is similar to that just described of using the calculated frequencies of liquid water to derive the ratio of vapor pressures, p_{H_2O}/p_{D_2O}, for H_2O and D_2O.

As noted above, K may be factored into the contributions $(p_{D_2O}/p_{H_2O})^3L$, where L is the equilibrium constant for the isotope exchange process

$$2D_3O^+ + 3H_2O(l) \rightleftarrows 2H_3O^+ + 3D_2O(l)$$

The value of p_{H_2O}/p_{D_2O} is known accurately,[45,46] and uncertainty in K attaches mainly to L. At 25° the best value of L is 9.0,[35] but recent determinations[33–36] have given values ranging from 8.0 to 11.0. Fortunately, the calculated frequencies are quite insensitive to the precise magnitude of L (or K), as may be seen by comparing the values calculated for $L = 9.0$ and $L = 11.0$ shown in Table V. This point has been noted previously[33] in emphasizing the difficulty of attempting the reverse process of using observed frequencies to calculate L.

As can be seen from Table V, the frequencies of intramolecular vibrations calculated in this way are substantially lower than those observed. This is true even though, contrary to normal assignments for pyramidal molecules with C_{3v} symmetry,[48] the degenerate stretching mode ν_3 is assumed to have a lower frequency than the nondegenerate mode ν_1. With the most favorable selection of hydrogen frequencies, the difference between calculated and observed values is 600 cm^{-1} for the six vibrations. For the single set of observed deuterium frequencies, the difference is 1450 cm^{-1}.

Several explanations of these discrepancies which are consistent with assignment of the observed frequencies to the hydronium ion may be considered. (i) Although in the calculation of K a harmonic force field yielding observed rather than zero-order frequencies was used for H_2O vapor, cancellation of anharmonic corrections between H_2O and H_3O^+ is probably incomplete. (ii) Measurements of L were made in dilute acid solutions, and the solvation of H_3O^+ may differ significantly from that at the concentrations for which vibrational spectra have been reported (≥ 5 N). (iii) Overestimation of librational frequencies of H_3O^+ may have led to underestimation of frequencies for intramolecular modes. (iv) In the calculation of K it was assumed that only the unit H_3O^+, and not its solvation shell, need be considered.

Points i and ii seem unlikely to account for more than a small part of the observed differences. With regard to point iii, despite the substantial change in hydrogen-bond strength, the force constants determining the librational frequencies of H_3O^+ were only 20% larger than those of H_2O. If the frequencies of crystalline $H_9O_4{}^+Br^-$ may be taken as a guide (Table VI), the librational frequencies for H_3O^+ are probably underestimated.

The most important discrepancy may come from assuming that isotopic zero-point energy changes in the primary solvation shell of H_3O^+ do not differ from those of molecules in the bulk solvent (point iv). However, for the three firmly bound water molecules in the $H_9O_4{}^+$ species, the effect of strengthened hydrogen bonding is ameliorated by the fact that each molecule forms only one bond to H_3O^+, and that the bonding occurs through its oxygen atom. Moreover, while the bonding almost certainly does lead to some decrease in the O–H stretching force constant for these water molecules, the effect must at least partially be compensated by increases in hydrogen-bond bending force constants and by the weakness or lack of hydrogen bonding of the water molecule adjacent to the H_3O^+ lone pair. That the net effect on the zero-point energy is indeed small is supported by the finding that, within the (admittedly limited) sensitivity of exchange measurements, isotopic fractionation in the hydronium ion is confined to three equivalent hydrogens.[33–36]

The most likely explanation of the difference between observed and calculated frequencies would seem to be offered by Ackermann's suggestion[27] that the observed frequencies are not those of H_3O^+. Ackermann's conclusion was originally based on his observation that the spectra of aqueous solutions of strong acids are nearly identical with those of strong alkali, in both H_2O and D_2O, and that the intense and continuous background absorption found in each case could be interpreted as resulting from proton transfer between water molecules or hydroxide ions at a frequency, $\sim 10^{13}$ sec^{-1}, comparable to the frequencies for intramolecular vibrations of H_3O^+ in the fundamental region (*cf.* ref 49 and 50). Consistent with this, a lifetime of 10^{-13} sec has been measured for H_3O^+ in ice.[51] Although in liquid water long-range proton mobility is limited by structural relaxation of unfavorably oriented solvent molecules, and is slower by a factor[51] of 10–100, provided that a fully hydrogen-bonded ice-like structure extends for more than one molecule beyond the central H_3O^+ unit, it can be expected that the half-life of a proton in association with any one molecule within that local structure will be comparable with that in ice itself.

Of course, if this conclusion is correct, no direct comparison of measured and calculated frequencies is possible. However, the calculations may be compared with the observed frequencies of salts of $H_9O_4{}^+$,[23] which probably provide the closest models for H_3O^+ in aqueous solution, and of H_3O^+ in sulfur dioxide[28] (Table VI). In passing from H_3O^+ in SO_2 to crystalline $H_9O_4{}^+Br^-$, it is probable that the strength of hydrogen bonding to H_3O^+ increases considerably. It is apparent that this change is associated with a very marked decrease in stretching frequencies and, probably, a significant increase in bending frequencies. Since the primary hydration shell of H_3O^+ is likely to be less strongly bound in solution than in the crystal, it is reasonable that in solution the calculated frequencies for intramolecular modes, and especially the stretching frequencies, should be intermediate in value between those for H_3O^+ in SO_2 and $H_9O_4{}^+Br^-$, and considerably closer to the latter, as indeed they are calculated to be. Although less firm conclusions can be drawn about the librational frequencies, it is again reasonable that they should be somewhat lower in solution than in the crystal. Qualitatively, therefore, the calculated frequencies appear to be of the correct magnitude, and the comparison with authentic experimental spectra suggests no fault in the conclusion that the measured solution frequencies are too high to be assigned to H_3O^+.

---

(48) K. Nakamoto, "Infrared spectra of Inorganic and Coordination Compounds," Wiley, New York, N. Y., 1963.

(49) J. M. Williams and M. Kreevoy, *J. Amer. Chem. Soc.*, **89**, 5499 (1967).

(50) G. Zundel, *Angew. Chem., Int. Ed. Engl.*, **8**, 499 (1969); E. G. Weidemann and G. Zundel, *Z. Phys.* **198**, 288 (1967).

(51) M. Eigen, *Angew. Chem., Int. Ed. Engl.*, **3**, 1 (1964).

A final point of uncertainty concerns the relative magnitude of the two stretching frequencies ν_1 and ν_3. A number of measurements of crystals of hydronium ion salts have led to the assignment of widely separated frequencies to these two modes.[20] These assignments have not been followed in all such measurements,[22,24] but $H_9O_4^+Br^-$ offers an example of where they have.[23] Giguère's recent demonstration that ν_1 and ν_3 are very closely spaced for solutions of hydronium halides in liquid sulfur dioxide,[28] however, strongly suggests that the same may be true of aqueous solutions. Indeed, this is certainly the normal situation[47] for pyramidal hydrides of the type XH_3. Calculations were carried out, therefore, with the covalent O–H stretching interaction force constant for H_3O^+ taken as zero. Other force constants were unchanged from model **6** (Table VII), and there was no effect on the calculated value of L. For $L = 9.0$, values of $\nu_1(a) = 2530$ and $\nu_3(e) = 2620$ were obtained.

Acknowledgments. The authors are indebted to the Computation Laboratories of Rice University and the Illinois Institute of Technology and to the Common Research Computer Facility of the Texas Medical Center, supported by U. S. Public Health Service Grant No. FR00254, for grants of computation time.

Solvent Isotope Effects upon Proton Transfer from the Hydronium Ion

R. A. More O'Ferrall,*[1] G. W. Koeppl,*[2] and A. J. Kresge[3]

Contribution from the Departments of Chemistry, Illinois Institute of Technology,
Chicago, Illinois 60616, and Rice University, Houston, Texas 77001.
Received May 12, 1970

Abstract: Model calculations of solvent isotope effects for reactions of H_3O^+ in H_2O are described. Models for H_2O and H_3O^+ take account of librational modes, and force constants are chosen to yield the constant $L = 9.0$ for the equilibrium $2D_3O^+ + 3H_2O \rightleftharpoons 2H_3O^+ + 3D_2O$. Primary and secondary isotope effects $(k_H/k_D)_I$ and $(k_H/k_D)_{II}$ for proton transfer from H_3O^+ are calculated. It is found that as the structure of the transition state is varied from reactant-like to product-like the secondary isotope effect increases monotonically, while the primary isotope effect passes through a maximum. The parameter α defined by $(k_H/k_D)_{II} = L^{-\alpha/3}$ provides a measure of the extent of proton transfer in the transition state. Contributions from "transfer" isotope effects are taken into account. Deviations from the rule of the geometric mean (RGM) for isotopic exchange equilibria are considered in detail within the framework of Bernstein's rules, and are ascribed mainly to contributions from bending vibrations. The deviations are underestimated by harmonic calculations, but calculations and experiment combined yield practical estimates for both D and T fractionation in H_2O and H_3O^+. Deviations are canceled between H_2O and H_3O^+ but cause discrepancies of up to 10% in the fractionation of single exchangeable hydrogens. Their effect upon the separation of primary and secondary kinetic isotope effects for proton transfer from H_3O^+ is tested. Maximum discrepancies between experimental methods based on (i) kinetic dependence in H_2O–D_2O mixtures, (ii) isotope distribution in the products, and (iii) tritium transfer in H_2O and D_2O are again 10% and are associated principally with fractionation of the reacting hydrogen. Neglect of deviations from the RGM does not obscure the strong correlations between isotope effects and transition state structure.

It has been recognized for some time that solvent isotope effects[4,5] upon rate-determining proton transfer from the hydronium ion in H_2O and D_2O comprise two contributions; a primary effect $(k_H/k_D)_I$ from the reacting hydrogen of the H_3O^+ unit, and a secondary effect $(k_H/k_D)_{II}$ from the nonreacting hydrogens.[6,7]

$$H_3O^+ + S \longrightarrow [\underset{\text{II}}{H_2O}\text{---}\underset{\text{I}}{H}\text{---}S]^{\ddagger} \longrightarrow H_2O + SH^+$$

Methods have been developed for separating the two effects,[8-11] and it has been suggested that $(k_H/k_D)_{II}$ may be related to the equilibrium isotope effect for the reaction[8,12,13] through a free-energy relation of the form $(k_H/k_D)_{II} = L^{-\alpha/3}$, where L is the equilibrium constant for isotope exchange between H_3O^+ and H_2O

$$2D_3O^+ + 3H_2O \rightleftharpoons 2H_3O^+ + 3D_2O$$

and α is a parameter analogous to the exponent of the Brønsted relation.[5,13-15]

This is of interest because α may be interpreted as an index of the "extent of proton transfer" in the transi-

---

(1) Rice University. Present address, University College, Belfield, Dublin, Ireland.

(2) NASA Fellow, 1964–1967. Present address, Queen's College of the City University of New York, New York, N. Y. 11367.

(3) Illinois Institute of Technology.

(4) P. M. Laughton and R. E. Robertson in "Solute-Solvent Interactions," J. F. Coetzee and C. D. Ritchie, Ed., Marcel Dekker, New York, N. Y., 1969, p 399.

(5) V. Gold, *Advan. Phys. Org. Chem.*, 7, 259 (1969).

(6) C. A. Bunton and V. J. Shiner, *J. Amer. Chem. Soc.*, **83**, 3214 (1961).

(7) C. G. Swain and E. R. Thornton, *ibid.*, **83**, 3884 (1961).

(8) A. J. Kresge, *J. Pure Appl. Chem.*, **8**, 243 (1964).

(9) M. Kreevoy and R. A. Kretchmer, *J. Amer. Chem. Soc.*, **86**, 2435 (1964).

(10) A. J. Kresge and D. P. Onwood, *ibid.*, **86**, 5014 (1964).

(11) V. Gold and M. A. Kessick, *J. Pure Appl. Chem.*, **8**, 421 (1964); *Discuss. Faraday Soc.*, **39**, 84 (1965); *J. Chem. Soc.*, 6718 (1965).

(12) M. Kreevoy, P. Steinwand, and W. Kayser, *J. Amer. Chem. Soc.*, **86**, 5013 (1964).

(13) V. Gold, *Trans. Faraday Soc.*, **56**, 255 (1960).

(14) M. Kreevoy, *Advan. Phys. Org. Chem.*, **6**, 63 (1968).

(15) W. J. Albery, *Progr. React. Kinet.* **4**, 353 (1967).