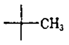
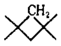
Table IV. Distance d_α along the Various Solute–Solute Curves Measured from the Gas-Phase Points[a]

Solvent	TMS				C_6H_{12}
Acetone	12.3	12.8	12.1	11.7	11.8
CH_2Cl_2	24.5	24.9	24.0	23.3	24.6
CH_3CN	28.2	29.3	28.6	27.7	28.8
$CDCl_3$	29.1	29.9	29.0	28.1	29.5
CCl_4	31.8	32.6	31.4	30.0	31.8
DMSO	33.9	33.9	33.0	31.9	33.4
CH_3I	34.7				
CH_2Br_2	37.4				
CS_2	42.7	43.0	41.5	40.0	42.4
$CHBr_3$	44.1				38.0
CH_2I_2	57.0				50.0
C_5H_{10}	19.7				
C_6H_{12}	21.9				

[a] Values in Hz determined by distance formula between two points on a straight line.

a ratio of van der Waals factors concerning the solvents. Measured values for various d_α's in units of Hz are presented in Table IV. We can again compare the collision model with the solvent ratios thus obtained. The results are

$$\frac{\sigma_w(C_5H_{10})}{\sigma_w(CCl_4)} = 0.62 \text{ exptl, } 0.71 \text{ predicted}$$

$$\frac{\sigma_w(C_6H_{12})}{\sigma_w(CCl_4)} = 0.69 \text{ exptl, } 0.69 \text{ predicted}$$

Again the agreement is surprisingly good considering the crudeness of the Lennard-Jones potential and the fact that these molecules are not really spherical.

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The Effect of Solutes and Temperature on the Structure of Deuterium Oxide

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Abstract: The spectrum of liquid D_2O has been observed over the range 1200–2000 mμ by a differential method in which D_2O at 25° is compared either with a salt solution at the same temperature or D_2O at an elevated temperature. Four combination bands have been observed, which may be identified with the same ones occurring in the vapor phase, and are apparently due to nonbonded D_2O. The band at 1893 mμ was used for quantitative studies, and solvation numbers have been calculated for several electrolytes. It appears that the ions are solvated to a greater extent than in H_2O but that the relative order of solvation is similar. The strength of the deuterium bond, as measured from the temperature dependence of the band intensity, is about 11% less than that of the hydrogen bond. Osmotic and activity coefficients are reported for solutions of tetramethylammonium chloride in D_2O, and a comparison of these data and those for alkali halides appearing in the literature seems to confirm the greater solvation of salts in D_2O.

The structure of water and of deuterium oxide is of considerable current interest. No bibliography of the literature on this subject will be attempted, but it may be noted that numerous experimental techniques have been used to measure the properties of the pure liquids and also a limited number of data are available for solutions of electrolytes and nonelectrolytes in the two solvents. A recent article by Holtzer and Emerson[1] points out some of the difficulties encountered in attempting to establish the relative degree of structure in the two liquids from a consideration of their physical properties. More extensive data for solutions in D_2O as a solvent appear to be needed for a comparison with those for H_2O solutions which are available in the literature.

Near-infrared spectra of water have been used in a recent paper[2] to determine the effect of solutes and temperature on its structure, and a logical extension of this work to the employment of these same techniques to D_2O and its solutions would appear to be profitable.

Experimental Section

Spectral Data. All spectra were recorded using a Cary Model 14M spectrophotometer. Corresponding bands of D_2O, both in the liquid and vapor state, are less intense than those of H_2O and it was necessary to use a special 0–0.2-mμ slide-wire in order to obtain a tenfold increase in sensitivity. Spectra were recorded for both pure D_2O and a saturated solution of LiCl in D_2O over the range 1200–1650 mμ using a 0.5-cm cell. Differential spectra (D_2O *vs.* various solutions) were recorded using the same techniques as previously reported[2] and employing matched 10-cm cells. Matched cells of 2-mm path length were employed for the differential spectra in the 1650–2000-mμ range. It was found that the bands due to "monomeric" D_2O which resulted from the differential measurements were quite similar to those found in H_2O but slightly broader.

Isopiestic Data. The osmotic and activity coefficients of tetramethylammonium chloride were determined by isopiestic comparison of its solutions with those of lithium chloride which served as a standard. Values of these coefficients of lithium chloride are tabulated by Kerwin.[3]

Results and Discussion

A. Vibrational Bands. The positions of the fundamental vibrational bands of D_2O vapor and their over-

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[1] A. Holtzer and M. F. Emerson, *J. Phys. Chem.*, **73**, 261 (1969).

[2] O. D. Bonner and G. B. Woolsey, *ibid.*, **72**, 899 (1968).

[3] R. E. Kerwin, Ph.D. Dissertation, University of Pittsburgh, 1964.

tones and combination bands have been reported.[4] The same observations about the broadening and shifting of bands to longer wavelengths in H_2O in the condensed phase are also applicable to D_2O. Waggener and coworkers[5] have noted the effect of temperature on the position and intensity of liquid D_2O bands over the temperature range from 5 to 250°. The bands become increasing sharper and shift toward the blue, asymptotically approaching a constant wavelength, as the temperature is raised. The fraction of nonbonded D_2O should increase at higher temperature and the position of the band at 250° should correspond with that of monomeric D_2O in the liquid phase. It may be noted that there is almost perfect agreement for the 201- and 111-mμ bands between the wavelengths reported in ref 4 and those obtained here by the differential technique.

It may be noted at this point that Luck[6] has made similar observations of the effect of temperature on H_2O spectra and has shown rather conclusively that near-infrared spectra may be used to determine the fraction of "free" or nonbonded OH groups. This observation is made independently of the controversial question as to whether the nonbonded OH groups are associated with "monomeric interstitial water" or are merely groups hanging free from matrix water or clusters. It also avoids the question as to whether the portion of the spectrum due to hydrogen-bonded water can be interpreted in terms of the *number* of hydrogen bonds per molecule.

Four combination bands have been observed for "nonbonded" D_2O. A comparison of the band positions with those of D_2O vapor is given in Table I.

Table I. Combination Bands of Monomeric D_2O

Band position, mμ Vapor	 Liquid	Band assignment
1266	1283	$2\nu_1 + \nu_3$
1531	1542	$\nu_1 + \nu_2 + \nu_3$
1861	1893	$\nu_1 + \nu_3$
1890	1965	$2\nu_1$

The shift is about that which would be expected[7] from the closer proximity of the nearest neighbors in the liquid state. It is interesting that the combination bands involving the ν_2 mode are shifted to a lesser extent than those involving the ν_1 and ν_3 stretching modes. An identical trend was also apparent in the water spectra which were reported previously.[2] This is not unexpected since the frequency shifts of the fundamental vibrational and bending modes are in opposite directions upon condensation of the vapor.

Spectra of pure D_2O and of a saturated solution of LiCl in D_2O were recorded over the range 1250–1350 mμ. The band maxima occurred at 1319 and 1327 mμ, respectively. The relationship of the positions of bands for the pure liquid, the monomer, and the saturated LiCl solution are similar for H_2O and D_2O.

B. Solvation of Simple Electrolytes. The effectiveness of various electrolytes in changing the fraction of nonbonded OH groups in H_2O has been observed by a technique described previously[2] and in the experimental section of this paper, and "spectroscopic solvation numbers" have been reported[2] for electrolytes in dilute aqueous solutions. The same experimental procedures may now be applied to D_2O solutions. The first consideration was the choice of a combination band for the measurements. It is probably desirable to use a band involving only combinations of stretching frequencies, since the ν_2 fundamental band shifts in a different manner from the ν_1 and ν_3 bands.[8] Preliminary work was performed using the 1283-mμ band, but the intensities obtained for dilute solutions were rather low for accurate work. The relative intensity of the 1893- and 1283-mμ bands for concentrated solutions of different electrolytes were in good agreement and the data in Table II were obtained using the 1893-mμ band.

Table II. Table of Spectroscopic Solvation Numbers

Electrolyte	Solvation number	Electrolyte	Solvation number
LiCl	7.2	$LaCl_3$	21.7
NaCl	3.0	NH_4Cl	10.4
KCl	5.5	NH_4I	9.3
CsCl	8.0	KI	3.6
$(CH_3)_4NCl$	24.9		

These solvation numbers were calculated in the same manner as those reported[2] for H_2O solutions. The fraction of the radiation absorbed at 1283 mμ by the shoulder of the band due to polarized D_2O was again determined using concentrated solutions of LiCl and $LaCl_3$. A comparison of these solvation numbers with those obtained in water yields two immediate observations: (a) the solvation numbers are in the same order as those for H_2O; *i.e.*, NaCl is less solvated than LiCl or KCl, and (b) all solvation numbers are larger than those for the corresponding salts in H_2O. The consequences of these observations will be discussed in the last section of this paper.

C. The Effect of Temperature on the Structure of D_2O and the Strength of the D–O···D Bond. Intensities of the 1283-mμ band have been measured in the range 25 to 60° with D_2O at 25° being used as the reference in each instance. The absorbance is found to increase linearly with temperature. The absorbance at 1283 mμ due to nonbonded D_2O at 25° was found to be 1.66 from a comparison of pure D_2O with concentrated solutions. It was observed that this absorbance would be twice as great at 87 or 88°. This doubling of the absorbance at 62 or 63° in D_2O compares with the figure of 55° for H_2O[2] and enables the calculation of a value of $\Delta H = 2.34$ kcal for the O–D···O bond. This value is 11% less than that of the O–H···O bond and is in good qualitative agreement with the data of Grimison[9] in which the N–D···N bond was found to be 8% weaker than the N–H···N bond.

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(4) W. S. Benedict, N. Gailar, and E. K. Plyler, *J. Chem. Phys.*, 21, 1301 (1953).

(5) W. C. Waggener, A. J. Weinberger, and R. W. Stoughton, Annual Progress Report ORNL-3832, UC-1 Chemistry, Oak Ridge, Tenn., May 1965, pp 76–81.

(6) W. Luck, *Fortschr. Chem. Forsch.*, 4, 653 (1964).

(7) G. Herzberg, "Molecular Spectra and Molecular Structure. II. Infrared and Raman Spectra of Polyatomic Molecules," Van Nostrand, Princeton, N. J., 1959, p 534.

(8) It is realized that there is the possibility of these bands having minor contributions from other combinations such as $2\nu_2 + \nu_3$ at 1893 mμ and $\nu_1 + 4\nu_2$ at 1283 mμ. The change in band shape and intensity with temperature is, however, the criterion which has been recognized in all work in this area as relating these bands to the structure (degree of hydrogen bonding) of the liquid.

(9) A. Grimison, *J. Phys. Chem.*, 67, 962 (1963).

It should be noted that in the calculations of parts **B** and C that the numbers reported are dependent upon the value of 1.66 which was calculated for the absorbance due to monomeric D_2O at 1283. If this number were larger, the solvation numbers in D_2O would decrease (approaching those in H_2O), but the value of 2.34 kcal for the D–O···D bond would also be less. A smaller value than 1.66 would yield better agreement between the strengths of the hydrogen and deuterium bonds but would yield an even greater increase in the solvation numbers of the salts in D_2O over those in H_2O.

It is interesting to compare these results with those reported by Luck.[6] His treatment of the bands was similar except that he measured the intensities directly as a function of temperature with no correction for the underlying hydrogen-bonded band. He observed the intensity of the nonbonded band of H_2O to double between the temperatures of 0 and 80° and that of D_2O to increase by a factor of 1.9 between 4 and 84°. This would lead to lower energies for both the hydrogen and deuterium bonds but would qualitatively confirm our data that the hydrogen bond strength is about 5% greater than that of the deuterium bond.

D. Osmotic and Activity Coefficients of $(CH_3)_4NCl$ in D_2O. It was noted earlier that the solvation numbers of salts in D_2O were larger than in H_2O. Solvation plays a prominent role in the colligative properties of aqueous solutions, especially in the case of salts such as LiCl or $LaCl_3$ which are highly solvated. A correlation may be made between the osmotic and activity coefficient data of Kerwin[3] and these solvation data in that the osmotic coefficient of LiCl in 5.0 aquamolal solutions is approximately 2% higher in D_2O than in H_2O, while the osmotic coefficients of NaCl are only slightly larger in D_2O and those of KCl are almost the same in the two solvents.

Tetramethylammonium chloride is also highly solvated in both solvents. This is, of course, "solvation of the second kind," in which the water structure is tightened around the hydrophobic methyl groups[10] and the effect of solvation on the colligative properties is balanced to some extent by "solvent-enforced ion pairing." The osmotic and activity coefficients reported in Table III may be compared with those reported by Lindenbaum and Boyd in H_2O solutions.[11] The osmotic coefficients of $(CH_3)_4NCl$ in D_2O are slightly but definitely larger than those of the same aquamolality in H_2O. The differences are greater in the more concentrated solutions where solvation would tend to "bind" a larger fraction of the solvent. It is of interest to note that the trend of osmotic coefficients (*i.e.*, LiCl and $(CH_3)_4NCl$ are larger in D_2O, NaCl is only slightly larger in D_2O and KCl is unchanged) parallels the conductivity data of Kay and Evans[12] in that the ratio of the conductance–viscosity product in D_2O to that in H_2O is larger for KCl than for NaCl or $(CH_3)_4NCl$.

Table III. Osmotic and Activity Coefficients of Tetramethylammonium Chloride in D_2O

Aquamolality	ϕ	γ	Aquamolality	ϕ	γ
0.1	0.914	0.746	1.8	0.896	0.517
0.2	0.892	0.683	2.0	0.906	0.518
0.3	0.880	0.644	2.5	0.932	0.521
0.4	0.872	0.617	3.0	0.962	0.532
0.5	0.867	0.597	3.5	0.993	0.544
0.6	0.863	0.580	4.0	1.025	0.564
0.7	0.861	0.566	4.5	1.056	0.585
0.8	0.860	0.556	5.0	1.086	0.609
0.9	0.860	0.546	5.5	1.118	0.636
1.0	0.863	0.540	6.0	1.148	0.662
1.2	0.866	0.528	6.5	1.177	0.691
1.4	0.876	0.521	7.0	1.210	0.721
1.6	0.885	0.518			

E. Conclusions Concerning the Association of D_2O and H_2O. It is possible that the association of H_2O and D_2O may not have a direct correspondence with the relative "structure" of the two liquids, but the two phenomena are certainly closely related. The new evidence produced by this work further indicates that hydrogen bonds are stronger than deuterium bonds in that the value of ΔH is found to be greater for the hydrogen bond than for the deuterium bond. There appears now to be little doubt as to the validity of this result since it is substantiated by at least four other measurements: (1) the hydrogen bond is stronger in imidazole[9] than in its deuterated analog; (2) methanol is observed to be associated to a greater extent in carbon tetrachloride than is the deuterated isomer;[13] (3) the shifts in the N–H and N–D stretching vibrations of HNCS and DNCS upon solidification have a ratio of 1.52 rather than the value of 1.34, which would be due solely to an isotope effect;[14] and (4) infrared measurements of O–H and O–D stretching modes of HDO in H_2O or D_2O indicate[15] a larger fraction of free or nonbonded O–D groups. The solvation of ions is also found to be greater in D_2O than in H_2O. The simplest explanation would appear to be that the ions are better able to change the structure of D_2O than H_2O from the hydrogen- or deuterium-bonded solvent structure to that required for solvation of the ion. Further evidence is the fact that the osmotic and activity coefficients of highly solvated ions are larger in D_2O than in H_2O, while there is little difference in the colligative properties of solutions of lesser solvated salts in H_2O and D_2O.

The lack of a direct correlation between hydrogen bond strength and water structure is apparent from the conclusions which may be drawn from the physical properties of H_2O and D_2O.[16]

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(11) S. Lindenbaum and G. E. Boyd, *ibid.*, **68**, 911 (1964).

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