ular detection applications, it is unfortunate that sharp Rydberg structure was not observed. In future experiments we intend to extend the search for Rydberg states to lower energy, using a third fixed-wavelength ionizing beam. However, recent calculations by Birge[23] for polyacenes suggest that, in general, resonance-enhanced transitions, involving valence–Rydberg dipole matrix elements, are exceedingly weak for extended molecular systems.

Acknowledgment. This work was supported by the Office of the Environment, Department of Energy, under Contract 79EV10239.000.

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Vibrational Spectral Studies of Solutions at Elevated Temperatures and Pressures. 5. Raman Studies of Liquid Water up to 300 °C

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The Raman spectra of the stretching-mode regions of liquid H_2O, D_2O, and HDO in a 10% solution with H_2O or D_2O, and the bending-mode regions of H_2O and D_2O, have been obtained in the temperature range 4–300 °C. The results have been interpreted in detail in terms of a continuum-type model, the distribution of oscillator pairs, and considerations of a high-frequency band edge, *but* it is *not* proposed that a mixture model is untenable. Increasing temperature reduces the complexity of the stretching-mode spectra of H_2O and D_2O; the main distribution of intensity narrows and shifts to higher frequency, overlap with the overtone of the bending mode is reduced, and intermolecular coupling decreases. All the changes appear to reflect a steady decrease in the strength of the intermolecular hydrogen-bonding interactions. For D_2O at high temperatures a resolution of the symmetric and asymmetric stretching modes (ν_1 and ν_3) is observed for the first time in the Raman spectrum. The bending mode ν_2 does not shift with increasing temperature, but the combination band of the bending mode with a librational mode ($\nu_2 + \nu_L$) shows a dramatic reduction in frequency.

Introduction

We recently described a new apparatus[1] designed to allow observation of Raman spectra of electrolyte solutions at elevated temperatures and pressures where, among other different properties, the drastically reduced dielectric constant of water might be expected to enhance ion association. The spectroscopy of liquid water itself at high temperatures is an important starting point in the study of such systems, yet apart from the excellent work of Lindner and Franck[2,3] there is no other report of Raman spectra above 100 °C. Hence, although we originally intended obtaining spectra of water at several temperatures merely for purposes of comparison with solution spectra, we felt that the quality of the new spectra and the lack of information warranted a more extended study.

The available literature on water is extensive, and for this reason only those works with immediate relevance will be referred to. The standard and ongoing collection of work on water is the series edited by Franks,[4] but the recent review by Scherer on the vibrational spectroscopy of water,[5] which includes an extensive bibliography, is the most relevant in the current context. Studies of the temperature variation of the IR and Raman spectra of water have generally been confined to the region below 100 °C (ref 6 and 7 to mention recent examples), with the following exceptions: (1) In the early work of Saumagne and Josien[8,9] IR spectra of H_2O were obtained up to 374 °C; (2) Falk and Ford[10] have studied HDO up to 130 °C in the IR; (3) Franck and Roth[11] have studied the IR of the O–D stretching mode of HDO up to 400 °C and 400 MPa; (4) Bondarenko and Gorbatyi[12] studied the IR of the O–H stretching mode of HDO up to 550 °C and ≈50 MPa; (5) Luck and Ditter[13] have studied the IR O–H stretching overtone region of HDO up to the critical point under saturation conditions; and (6) Franck and Linder,[2,3] as mentioned above, have studied the Raman spectra of the stretching regions of O–H in H_2O and O–D in HDO up to 400 °C and 400 MPa.

Controversy has raged over the type of molecular model to be adopted for liquid water. The two extremes may be classed broadly as (1) mixture, involving two or more kinds of water, or intact and broken hydrogen bonds, in equilibrium, and (2) continuum, involving a continuous distribution of intermolecular interactions; some viewpoints fall between these two. In the area of spectroscopy, for instance, Luck[13-15] and in particular Walrafen,[16] who did

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a large number of Raman studies on water, and Murphy and Bernstein[17] have argued the case for a mixture model, whereas Schiffer and Hornig,[18] Falk et al.,[10,19-21] and Carnutte et al.[22,23] have argued for a continuum. Scherer's model[5,7] is intermediate, arguing distributions for different types of water molecules. Efimov and Naberukhin[24] have met with reasonable success in simulating the infrared and Raman spectra of H_2O and D_2O, based on the spectra of HDO and assuming a continuum model. As yet there clearly is no consensus, since no evidence has been sufficient to prove entirely any particular model, and frequently spectroscopic evidence which has been interpreted by some as favoring one model or excluding another has been shown by others to have a conflicting interpretation. However, as Scherer has taken pains to point out,[5] there is a great deal of information which can be extracted from the spectra. We would also draw attention to some results from an entirely different technique; in a recent report Vernon et al.[25] have shown vibrational predissociation spectra (crossed laser and molecular beams) of hydrogen-bonded clusters of three to six water molecules. These spectra show a sharp band at 3715 cm^{-1}, which is attributed to "free" OH oscillators, and which decreases rapidly in intensity as the cluster size increases (as might be expected). What is perhaps of most interest, however, is that even for such small clusters there is also a very broad distribution of intensity in the range 3100–3600 cm^{-1}, which could arise from a broad range of hydrogen-bonding interactions.

Theoretical calculations simulating water at various temperatures (reviewed recently[26]) are also of great importance, particularly the molecular dynamics calculations of Stillinger et al.,[27,28] Wood et al.,[26] Impey et al.,[29] and Jorgensen.[30,31] These calculations have not provided evidence to support "two-state" or "iceberg" type models, and the water pair interaction distribution is found to be continuous over the energy range considered.[28]

The calculations also show that, as the temperature increases, the distribution of pair interaction energies shifts toward weaker interactions. There is still, however, an element of ambiguity in the way these results may be interpreted; in particular, the use of the terms "broken hydrogen bond" and "intact hydrogen bond" is dependent on an arbitrary fixing of an energy division. This can produce quite different pictures of the "structure" depending on where this broken–intact boundary is taken. When it comes down to fundamentals, this is also the basic distinction between some mixture models and continuum models, in that the latter do not introduce a boundary in the first place. One might even suggest that the two approaches are saying essentially similar things, except for this one distinction. Recently a "correlated site polychromatic percolation" model has been developed by Stanley and Teixera[32] and a random network model by Rice and Sceats,[33] though these are both essentially continuum approaches.

A number of properties of water, other than its spectra, have also been studied at high temperature.[3,4] Of particular interest here is the X-ray work of Narten et al.[34] The radial distribution functions show that the nearest-neighbor (O–O) distance increases from 2.82 Å, at 4 °C and atmospheric pressure, to 2.94 Å, at 200 °C and the vapor pressure of the sample. The radial distribution functions also show that peaks due to second and higher neighbors at 4.5 and 8 Å, clearly visible at 4 °C, slowly disappear as the temperature increases. This indicates a decrease in the distance of short-range order from ≈8 to ≈7 Å between 4 and 200 °C.

Experimental Section

Raman spectra were obtained by using a digitally driven Jarrell-Ash 25-100 spectrometer (1-m double Czerny-Turner monochromator), with an RCA 3134 photomultiplier and an SSR Model 1105/1120 photon counting system. The 4880- and 5145-Å lines of a Spectra Physics argon ion laser, Model 165-03, were used for excitation. Instrument control and data collection were performed by means of a 32K byte PET Commodore computer, which has recently been interfaced to the spectrometer.

The samples used were H_2O distilled in glass stills and 99.7% D_2O courtesy of A.E.C.L. All samples were filtered through 0.6-μm Millipore filters before injection into the capillary sample tubes. To obtain spectra at 4 and 25 °C samples were contained in sealed, thin-walled capillary tubes which were held in a thermostated copper block. The thick-walled, Pyrex glass capillary cells, the high-pressure system, and the furnace, used to obtain spectra at high temperatures, have been described earlier.[1] For temperatures up to 250 °C a hydrostatic pressure of 6–8 MPa (and sometimes higher) was applied and for 300 °C 10–11.5 MPa was applied. These pressures are sufficient to maintain the liquid state.[35] It is not possible with this equipment to maintain a constant density as the tem-

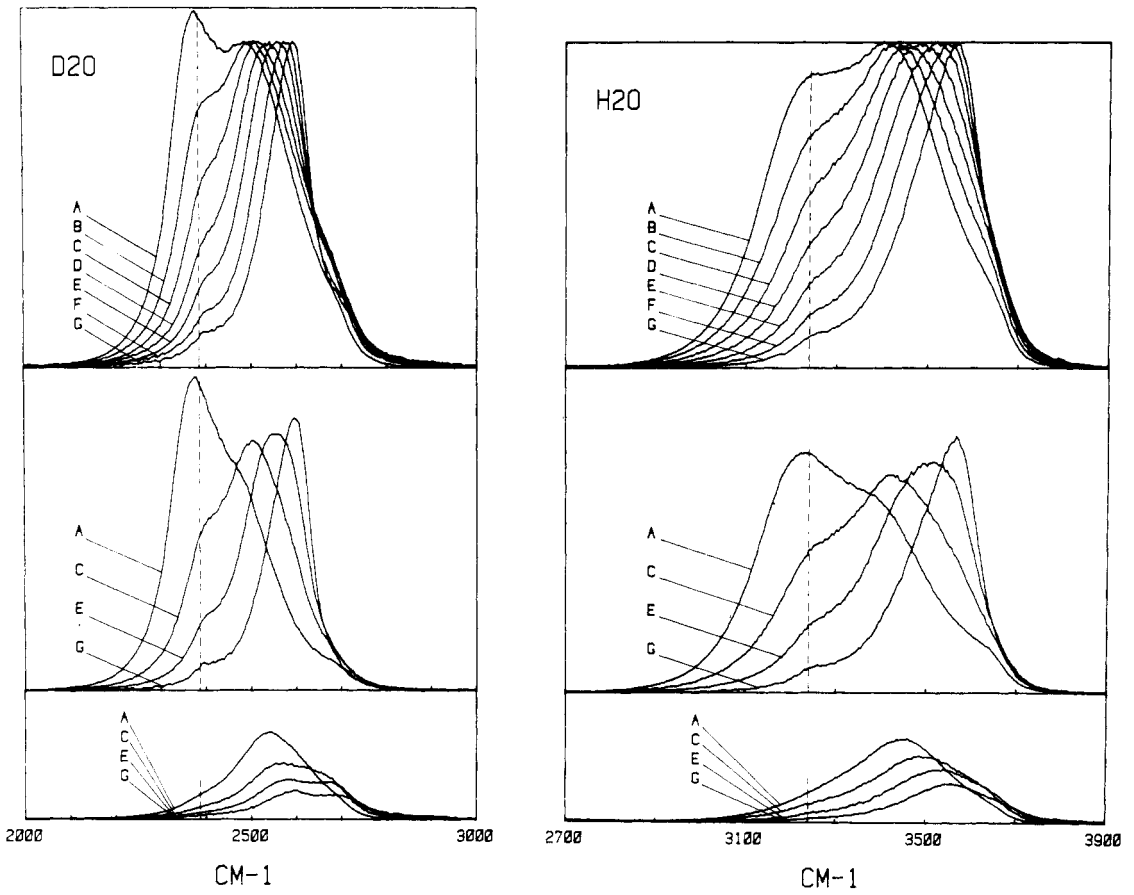

Figure 3. Superimposed spectra as a function of temperature of the stretching-mode regions of H_2O and D_2O: (top) total Raman spectrum ($I_{\parallel} + I_{\perp}$); (middle) isotropic; (bottom) anisotropic. All the spectra are plotted on scales so as to effect the rough normalization on peak displayed in the top figures; this is merely a convenient form of presentation. The dashed lines indicate the calculated position of $2\nu_2$; (A) 4, (B) 50, (C) 100, (D) 150, (E) 200, (F) 250, and (G) 300 °C.

the bands are narrower and the features more pronounced because of this. The spectra of H_2O are again essentially in agreement with those of Lindner.[2] The most striking changes seen as the temperature increases are (1) a rapidly decreasing intensity in the low-frequency region and (2) a steady increase in the frequency, and a decrease in the width of the central region as intensity builds (relative to the rest of the spectrum) toward the high-frequency end. This latter behavior is superficially similar to the HDO spectra.

We believe our results strengthen the arguments that the presence of $2\nu_2$ (bending-mode overtone) and its Fermi resonance with the stretching modes are responsible for the low-frequency feature at ≈3230–3260 cm^{-1} in H_2O and ≈2375–2400 cm^{-1} in D_2O in the range 4–300 °C (see dashed line, Figure 3). It very definitely does not have a counterpart in the HDO spectra, at any temperature, and hence cannot be regarded as representative of a particular "state" of water as recently suggested.[46] The frequency of ν_2 itself does not change significantly with temperature (described later) and from this value and a correction for anharmonicity[5] the expected position of $2\nu_2$ can be calculated at 3240 (H_2O) and 2386 (D_2O) cm^{-1}, in excellent agreement with the observed feature. It is also worth noting that the frequency of the feature changes very little over the range 4–300 °C as indicated in Figure 3. In supercooled water at −10 °C, it is apparently pushed further down to ≈3200 (H_2O) and ≈2360 (D_2O) cm^{-1}, but at −24 °C it appears to be at ≈3220 cm^{-1}.[46] One can also see from the high-temperature spectra that the width of the feature is also compatible with $2\nu_2$ since the width of ν_2 is ≈103 (H_2O) and ≈66 (D_2O) cm^{-1} and the width of $2\nu_2$ may be expected to be roughly twice these values. The polarization data are also very informative: The feature only appears in the isotropic spectra, and at low temperatures it lies in a region of very low depolarization ratios (0.1) (Figure 4). The most striking result, however, is the appearance of a very pronounced dip (at 3240 cm^{-1} in H_2O, 2390 cm^{-1} in D_2O) in the high-temperature depolarization ratios, which is consistent with the feature being more strongly polarized than the tail of the main spectral band. This also is consistent with $2\nu_2$, because it is a totally symmetric mode.

The following interpretation seems plausible: The feature arises from $2\nu_2$, which is a totally symmetric mode and hence can interact via Fermi resonance with the totally symmetric stretching modes (ν_1 in all cases and ν_3 in C_s cases). At high temperatures the bulk of the ν_1 distribution is at a significantly higher frequency than $2\nu_2$, the sum of all resonance interactions is not very great, and so the intensity at $2\nu_2$ is weakly enhanced. As the temperature decreases, the stretching-mode distribution moves down in frequency and broadens, there is increasing overlap with $2\nu_2$, and an increase in the sum of resonance interactions and hence intensity builds at $2\nu_2$. At room temperature and below the peaks of the $2\nu_2$ and ν_1 distributions are very close. The whole question of the behavior of two distributions of frequencies in Fermi resonance with each other, and particularly the resulting bandshape, is rather complicated and not well understood. Scherer has attempted to model this problem and tried to relate the result to the case of water.[5]

There can be little doubt that intramolecular coupling must play a conspicuous role in the spectrum of H_2O and

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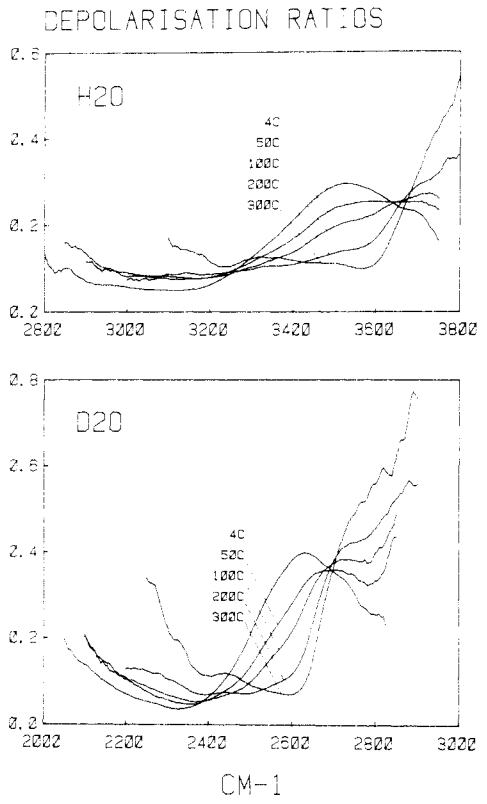

Figure 4. Depolarization ratios in the stretching-mode regions of H_2O and D_2O as a function of temperature. The spectra were smoothed before ratioing to improve the clarity at the extremes of the plots.

D_2O. Since the angular geometry of the two oscillators is fixed under all conditions, the magnitude of intramolecular coupling depends mainly on the degree to which the two oscillators differ by virtue of intermolecular hydrogen bonding. If identical, the coupling is quite strong (see gas-phase splittings mentioned earlier in feature 7 and the calculations of Burneau and Corset[47]), but the greater the difference between the two, the smaller the coupling (for instance in asymmetric complexes[5] and the results of calculations[47]).

For intermolecular coupling the magnitude again depends on the similarity of the interacting oscillators, but it also depends on their spatial relationship (distance and orientation) and the strength of the interaction producing the coupling, both of which can obviously vary in the liquid state. These two factors work together, since the greater the interaction the more likelihood of specific orientations between the two oscillators. Intermolecular coupling manifests itself as a splitting of a mode ν into in-phase ν^+ and out-of-phase ν^- components. (It is, in fact, analogous to correlation splittings in crystals.) It has been clearly seen in the spectra of alcohols[48,49] where intramolecular coupling does not complicate the issue; for neat alcohol the isotropic Raman spectrum shows the ν^+_{OH} component and the anisotropic spectrum shows some intensity due to ν^+_{OH} but largely ν^-_{OH} at higher frequency. ν^+_{OH} and ν^-_{OH} lie on either side of the single mode ν_{OH} observed in a dilute solution. (Further discussion and examples of intermolecular coupling may be found in ref 50–54.) Increasing the temperature is expected to cause changes in the magnitude of intermolecular coupling: at low temperatures there exists come degree of ordering of the molecules with respect to each other (as compared to the strict order in the crystal phase) and hence intermolecular coupling of the vibrational modes is strong. The effect of increasing temperature, however, is to transfer more energy into the molecular translations and librations, which weakens the interactions on average, causing a decrease in ordering and hence a decrease in the intermolecular coupling. This kind of effect has been demonstrated for methanol and ethanol;[49] for instance, ethanol at low temperatures shows a splitting of ν_{OH} of $\approx$100 cm^{-1} but at 400 K the splitting has completely disappeared. Luck et al.[55] have presented evidence which strongly suggests that an infrared band seen for HDO in D_2O in the 6100-cm^{-1} region is due to the combination $\nu_{OH} + \nu_{OD}$ where the two oscillators are on neighboring molecules. Furthermore, it is suggested that the two oscillators are hydrogen bonded to each other. The main point of interest here is that, as temperature increases, this band decreases in intensity, suggesting that the strengths of intermolecular interactions are decreasing. Kint and Scherer[56] have presented Raman difference spectra of the uncoupled OH and OD oscillators of HDO in H_2O, which they interpreted as indicative of intermolecular coupling in water in the temperature range −10 to 70 °C.

We can now proceed to discuss the stretching-mode spectra of H_2O and D_2O. It seems reasonable to believe, from the HDO spectra, that the changes taking place as the temperature increases reflect a continuous process, so we will chiefly consider the spectra at the two extremes of temperature. Aside from the influence of $2\nu_2$ on the low-frequency end of the spectra, one would expect the spectra of H_2O and D_2O, bearing the effects of coupling, to derive from exactly the same distribution of oscillator potentials as the simpler HDO spectra. (This idea forms the basis of the calculations of spectra by Efimov and Naberukhin.[24]) The intra- and intermolecular couplings arise from a distribution of pairs of oscillator potentials, and consequently there will be a range of different splittings (ranging from large to small) for all the different pair combinations. Regardless of the position of the first oscillator in the distribution of single oscillator potentials, the probability is greatest that it will be paired with an oscillator at the peak of the distribution. This consideration has some important implications:

(1) Most pairs will have both oscillators in the region of the maximum of the distribution of single oscillator potentials, and hence these will give rise to the main body of the spectrum. Since the oscillators will be very similar, one expects to see effects due to coupling.

(2) A smaller number of pairs will have one oscillator in either wing of the distribution while the second is in the region of the maximum of the distribution. Here the situation is not so clear but, assuming the two oscillators are sufficiently different, they will be relatively uncoupled and behave much like HDO.

(3) Very few pairs will have both oscillators in the wings of the distribution of single oscillator potentials, and

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consequently these will make very little contribution to the total spectrum.

The spectra at temperatures below 100 °C have already been discussed in detail by Scherer.[5,7] There is one feature which can be considered immediately. The isotropic spectra of both H_2O and D_2O at 4 and 50 °C show a small but pronounced shoulder at the high-frequency end, and it is rather curious that the band edge of this feature is very nearly the same as that in the HDO spectra (≈3665 (H_2O) and ≈2700 (D_2O) cm^{-1}). The most reasonable explanation is that this is due to the small number of high-frequency oscillators which are paired with oscillators of much lower frequency and are relatively decoupled (case 2 above). The same factors then apply which led to the formation of a band edge in HDO. The fact that the new edge is slightly higher in frequency than in HDO is consistent with the fact that the decoupling would not be expected to be as great as for HDO, since the frequency separation is not as great. (This is basically the same interpretation as that given by Scherer in terms of the weakly hydrogen-bonded oscillator in an asymmetric molecule[5,7].) When one considers the main part of the spectrum, which we expect to correspond with case 1, it is perhaps best to look at the spectra at 50 °C (or even 100 °C) where the $2\nu_2$ feature is no longer dominant. The first observation is that the peak is at lower frequency than the corresponding isotropic spectrum of HDO. This can only be due to coupling. The second observation is that the peak of the anisotropic spectrum is at a higher frequency than the peak of the isotropic (or anisotropic) spectrum of HDO. As we have discussed earlier, this may be indicative of intermolecular coupling. (Note, however, that Efimov and Naberukhin[24] were able to calculate similar spectra without taking into account any intermolecular coupling. In that case the high-frequency peak in the anisotropic spectrum arose because ν_3 was more intense than the ν_1 component.) We might also note here that another obvious effect of the coupling is to broaden the bands, compared to HDO.

A shoulder on the high-frequency side of the intensity distribution is noticeable in the lower-temperature anisotropic spectra (particularly for D_2O). The most plausible explanation is that this is a ν_3^- component of the main distribution of oscillators, pushed up in frequency by intermolecular coupling. It is, of course, rather difficult to unravel completely the combined effects of intra- and intermolecular coupling on the spectrum.

As the temperature increases, there are several general observations: (a) The weak high-frequency shoulder in the isotropic spectrum does not increase in intensity, and, in fact, at 100 °C and above it is not evident. (b) The main band slowly narrows and moves up in frequency, and in the isotropic spectra, clearly seen above 100 °C, intensity builds at the band edge (not to be confused with the high-frequency shoulder (a)); the frequency of this band edge is below that observed for HDO. (c) At 300 °C the isotropic spectra resemble those of HDO except that they are still broader and at lower frequency.

An important piece of evidence then emerges when we look at the anisotropic spectrum of D_2O at 300 °C; there are two maxima, one at the same frequency as the isotropic peak and a second at significantly higher frequency with no counterpart in the isotropic spectrum. The peak of the HDO isotropic spectrum corresponds with the minimum between these two anisotropic maxima. Clearly the components can be attributed to coupling and are sufficiently narrowed that they begin to resolve. One would expect the same behavior for H_2O at 300 °C, and, although the bands are not resolved, there is additional intensity at the high-frequency end in the anisotropic spectrum which is not present in the isotropic spectrum.

Scheme I[a]

	300 °C (band edge)		vapor (peak)[41,42]	
ν_{OD}(HDO)	2685	−57	2727	−56
$\nu_1(D_2O)$	+62	2628	+61	2671
$\nu_3(D_2O)$	2747		2788	
total splitting:	119		117	
ν_{OH}(HDO)	3664	−57	3707	−50
$\nu_1(H_2O)$		3607	+49	3657
$\nu_3(H_2O)$	(3677) not resolved		3756	
total splitting:	?		99	

[a] Frequencies in cm^{-1}.

In terms of oscillator potentials, the maximum in the distribution at 300 °C has shifted considerably toward the weak-interaction end and consequently most of the oscillators are very similar. Hence, most pairs will have two very similar oscillators (as in case 1 again), and a splitting to either side of the HDO band-edge frequency is expected. If the components can be resolved, then they should each also have a high-frequency band edge. If we measure the positions of the band edges in D_2O at 300 °C as before (the lower one from the isotropic spectrum and the higher one from the anisotropic spectrum), the values obtained and that for HDO at 300 °C give a surprisingly good parallel with the behavior of the vapor-phase frequencies (see Scheme I).

For H_2O the comparison for the lower-frequency component is again good but it is not clear that we can see the true band edge of the high-frequency component in the anisotropic spectrum because of the overlap with the low-frequency component. We have already anticipated the disappearance of any intermolecular coupling, as the temperature is increased, earlier in the discussion; as further evidence of this the low-frequency maximum in the anisotropic spectrum of D_2O at 300 °C is more intense than the high-frequency component. This is opposite to the effect expected if intermolecular coupling alone were responsible for the splitting. The two modes may therefore be assigned as ν_1 and ν_3 as indicated.

The resolution into ν_1 and ν_3 components in D_2O at 300 °C is the first evidence for such in the Raman spectra. However, the high-temperature IR spectra of H_2O obtained by Saumagne and Josien[8,9] showed two maxima, which they also suggested was a splitting into ν_1 and ν_3. They give the approximate peak positions as 3520, 3625 cm^{-1} at 300 °C and 3545, 3650 cm^{-1} at 374 °C. The splitting of 105 cm^{-1} is fairly consistent with that in the vapor phase (see above). The reason for the resolution of bands in the IR but not the Raman spectrum may again be connected with the hydrogen-bond strength vs. intensity properties in the IR, which also give rise to a lower peak frequency. (The peak frequency of ν_1, from the isotropic Raman spectrum, occurs at 3565 cm^{-1} in H_2O at 300 °C, 45 cm^{-1} higher than in the IR.)

The information contained in the depolarization ratios strengthens the arguments above. These results (Figure 4) are in agreement with the earlier work of Cunningham and Lyons[57] but extend the temperature range considerably. In the low-temperature spectra at low frequencies the depolarization ratio is very low, because the modes are

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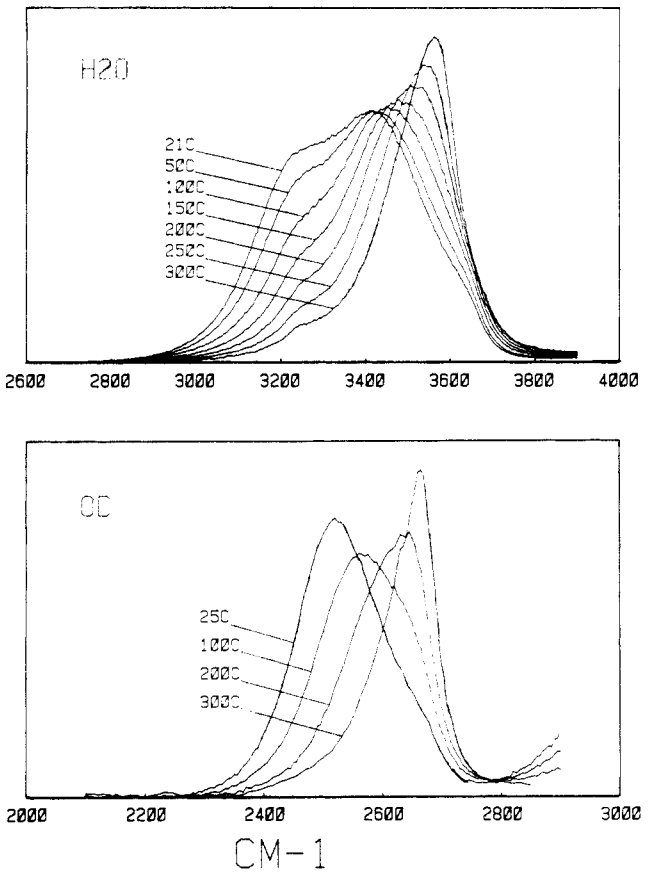

Figure 5. Density-corrected total spectra of the stretching-mode regions of H_2O and of OD in 10% HDO in H_2O.

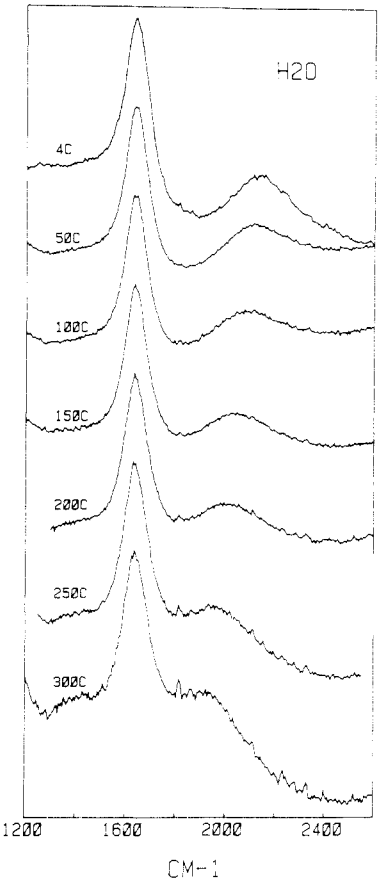

Figure 6. Raman spectra of the bending mode ν_2 and combination mode ($\nu_2 + \nu_L$) of H_2O as a function of temperature (slit width, 15 cm^{-1}; step interval, 5 cm^{-1}).

largely totally symmetric, i.e., ν_1, $2\nu_2$, and ν_1^+ if, as has been suggested, intermolecular coupling is strong at low temperature. At intermediate frequencies the ratio is higher due to increasing ν_3 and ν_1^- components. At high frequency the ratio decreases due to the uncoupled oscillators which give rise to the weak high-frequency shoulder; these are totally symmetric and hence similar to HDO which has low depolarization ratios. As the temperature increases, we see that the falling-off trend of the ratio at the high-frequency end gradually reverses. This shows that the strongly polarized decoupled oscillators have disappeared at high temperature and the ratio rises steadily due to the increasing ν_3 components of the coupled oscillators. A curious feature of the depolarization ratio plots is the relatively constant point at the high-frequency end, at 3660 ± 20 cm^{-1} for H_2O and 2690 ± 20 cm^{-1} for D_2O. Although one must be careful not to read too much significance into this, its position is at about the same frequency as the isolated OH or OD oscillator band edge seen in HDO, which perhaps suggests that the feature is associated with the redistribution of modes into ν_1 and ν_3 types in this region.

Relative Intensities in the Stretching-Mode Regions. Relative intensity spectra of H_2O are shown in Figure 5. The counts were divided by the density of H_2O at the particular temperature[35] and at 10.5 MPa (this pressure was maintained throughout the experiment), so that to a first approximation this gives the intensity scattered from a fixed number of water molecules per unit volume. For the spectra of HDO in H_2O the counts were also divided by the density of pure water. Any further interpretation of these results must then rely on the tentative assumption that other factors affecting intensity are of minor consequence. The total corrected intensity under the bands decreases as a linear function of temperature, although the changes of intensity at a particular frequency are generally quite nonlinear. The least-squares linear fits of total band intensity vs. temperature gave correlation coefficients better than 0.999. (Linear base-line corrections, between 2700–3900 cm^{-1} for H_2O and 2200–2800 cm^{-1} for HDO in H_2O, were subtracted from the spectra beforehand.) The results of the fits are best expressed by the equation

$$I_T/I_{298} = M(T - 298) + 1$$

where the intensities are normalized to the intensity at 298 K (25 °C) and $M = (-1.264 \pm 0.023) \times 10^{-3}$ K^{-1} for H_2O and $(-1.117 \pm 0.023) \times 10^{-3}$ K^{-1} for HDO in H_2O. The total intensity falls by 30–35% from room temperature to 300 °C. Although the significance of the observed linearity is puzzling, the decrease in itself indicates that the absolute Raman scattering of an OH oscillator decreases as the intermolecular interactions decrease (and the frequency increases). This parallels the reported higher specific infrared intensity associated with strongly hydrogen-bonded OH oscillators.

Spectra of the Bending Mode ν_2 and the Combination Mode ($\nu_2 + \nu_L$). Initially, interest in the ν_2 bending mode was centered largely on its frequency, to help in the investigation of $2\nu_2$ in the stretching-mode region. This band is very much weaker than the bands in the stretching region and for this reason much longer counting times, increased slit width, with no polarization analysis were needed to acquire spectra within a reasonable time period. The most noticeable feature of the band (Figure 6), as mentioned earlier, is that its frequency does not change within experimental error, between 4 and 300 °C (1637.5 ± 2.5 (H_2O) and 1202 ± 2.5 (D_2O) cm^{-1}), nor is there any appreciable change in bandwidth, although it is difficult to measure this accurately (103 ± 5 (H_2O) and 66 ± 10

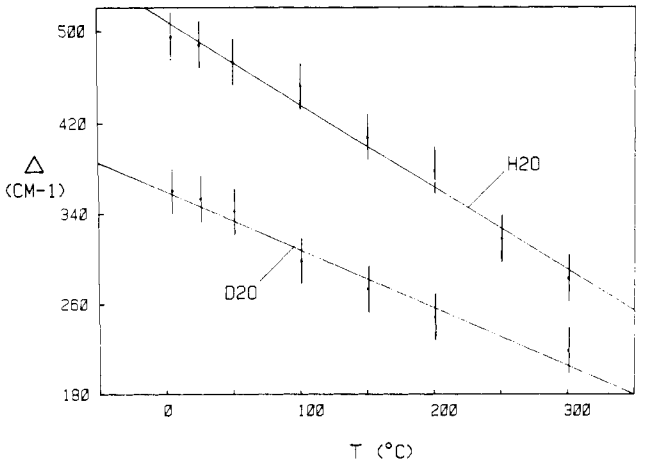

Figure 7. Plots of Δ as a function of temperature for H_2O and D_2O. The linear least-squares fits are shown. $\Delta = (\nu_2 + \nu_L) - \nu_2$.

TABLE I

	$d\Delta/dT$, $cm^{-1}/°C$	intercept at 0 °C, cm^{-1}	R^a
H_2O	−0.729 ± 0.041	509.8 ± 6.9	0.991
D_2O	−0.513 ± 0.040	359.7 ± 6.2	0.985

[a] Correlation coefficient.

(D_2O) cm^{-1}). This behavior reflects the peculiarities of water. Normally, as the temperature increases, one expects bands to broaden, and the obvious factor counteracting this in water would be a decreasing width of the distribution of vibrational potentials, i.e., a greater similarity among the individual molecules. Scherer has pointed out that there is no rigorous correlation between ν_2 frequencies and the hydrogen-bonding interaction strength[5] and the present results tend to strengthen this view.

Attention is drawn to the even weaker and much broader combination band, at higher frequency than ν_2, which was found to decrease rapidly in frequency as the temperature increased (Figure 6): from ≈2132 cm^{-1} at 3 °C to ≈1920 cm^{-1} at 300 °C in H_2O, and from 1562 cm^{-1} at 4 °C to ≈1420 cm^{-1} at 300 °C in D_2O. This band is usually assigned to a combination $(\nu_2 + \nu_L)$, where L is a librational mode, chosen in preference to a translational mode because of the larger frequency and the large decrease in $\Delta = (\nu_2 + \nu_L) - \nu_2$ on deuteration.[6] Polarization studies (present work and ref 5) show that the band is depolarized and, since ν_2 is polarized, the combination band must have the same symmetry as the ν_L fundamental. Unfortunately this is not very informative since the only possibility that this observation excludes is an R_z libration for C_s cases, which would be totally symmetric. Plots of Δ vs. temperature for the combination band are shown in Figure 7. It was found possible to fit the results by linear least squares as shown in Table I. Pinkley et al.[6] have noted that the maximum in the librational region of the infrared spectrum shows a strong temperature dependence (590 cm^{-1} at 1 °C and 555–560 cm^{-1} at 50 °C) and the combination band $(\nu_2 + \nu_L)$ which is also seen in the infrared has been observed to decrease in frequency as the temperature increases.[58] The band is of interest since in effect Δ gives a measure of the changing librational potential with temperature. One word of caution must be mentioned, however, in that this might also reflect, to some extent, the change in density between room temperature and 300 °C. The decreasing frequency, however, is clearly compatible with a decreasing average interaction energy, as expected.

In conclusion we might return to the question of the suitability of the various models. We have interpreted the spectra from a continuum viewpoint; however, we would not discard a mixture model of the type which considers strong and weak hydrogen-bonded oscillators as the two components, on the basis of the spectroscopic results. A great many of the arguments and observations could apply equally well to such a model. The results do not seem to be compatible, however, with a two-state type mixture model, where icelike clusters exist in a sea of relatively "free" non-hydrogen-bonded water. The free water in such a system would have virtually identical oscillators and hence intramolecular splitting should produce the split into ν_1 and ν_3 at the high-frequency end of the spectrum *at all temperatures*. There is no indication that this occurs in the lower-temperature spectra.

Regardless of model, the changes in the spectra as the temperature increases are quite compatible with the view that the hydrogen-bonding interactions become weaker and the ordering which these impose is reduced.

Note Added in Proof. At the 8th International Conference on Raman Spectroscopy, Bordeaux, France, Sept 6–11, 1982, where this paper was presented, Professor Z. Kecki noted that the temperature dependence of the O–H band intensity was consistent with early measurements in the range 2–90 °C from his laboratory (*Roc. Chem.*, **40**, 919 (1966)) and work done in collaboration with H. J. Bernstein.

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