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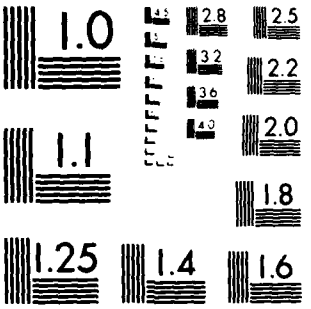

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Temperature dependence of the Raman OH-stretching overtone from liquid water

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The first Raman overtone of the OH-stretching vibration from highly purified liquid water has been examined quantitatively in the temperature range of 20–95 °C, and at frequencies from about 5500–8000 cm^{-1}. The overtone Raman spectra show contour shapes, depolarization ratio dispersion, and an isosbestic frequency (6960 ± 25 cm^{-1}, uncorrected; 6900 ± 25 cm^{-1}, density and refractive index corrected) which, apart from the effects of anharmonicity, tend to mimic the fundamental, including its major four-component substructure. The two components at about 7030 and 6850 cm^{-1} were interpreted, respectively, in terms of nonhydrogen-bonded OH, and triply hydrogen-bonded OH groups, which are common to the three-bonded H_2O species, whereas two components at about 6665 and 6160 cm^{-1} were interpreted as intermolecular coupling components of the fully hydrogen-bonded, i.e., four-bonded H_2O species. A $\Delta H°$ value of −2.5 Kcal/mol hydrogen bond was obtained from the temperature dependence of ratios of the combined component intensities of these two pairs, in agreement with results from previous Raman fundamental measurements. The feature near 6160 cm^{-1} was found to be better resolved in the spectrum than its fundamental analog, indicating that anharmonicity is advantageous in elucidating contour substructure.

I. INTRODUCTION

The overtones of the OH-stretching vibration from liquid water have been studied for many years by infrared techniques, and some of the most thorough infrared overtone work on aqueous systems has been reported by Luck and coworkers.[1] The infrared spectra of liquid H_2O, D_2O, and HDO are characterized by a large number of intense overtone and combination bands.[1,2] Unfortunately, the Raman OH-overtone spectrum is extremely weak, and thus all of the Raman work was restricted, until recently,[3,4] to the fundamental region of the spectrum (i.e., below −4000 cm^{-1}).

The OH-stretching vibration has been found to be very sensitive to the details of the hydrogen bonding in water.[5–8] This sensitivity is useful because it gives rise to spectral features related to various perturbations of the OH vibration. Unfortunately a unique interpretation of the observed broad spectral features has been difficult to achieve. The available data for the most part are supportive of a mixture model involving hydrogen-bonded species, plus OH groups that are essentially free, but some workers have not entirely abandoned continuum models.[9] However, because the free OH groups and the hydrogen-bonded species, particularly the latter, are distributed in frequency, it is evident that the mixture and continuum descriptions are, in some regards at least, a matter of semantics.

Two further mechanisms, namely, Fermi resonance and intermolecular coupling have led to contour breadth and have caused problems in interpretation. Fermi resonance may occur because the symmetric stretching vibration of the H_2O molecule has the same A_1 symmetry species as the overtone of the bending vibration. Intermolecular coupling arises from the coupling that nearby oscillators experience when they are strongly perturbed by hydrogen bonds. The Fermi resonance effects have never been unequivocally isolated in the spectrum, although clear evidence for intermolecular coupling has recently been developed from dilution experiments.[10]

The Raman OH-stretching overtone spectrum has recently been reported for liquid water by Belsley and Sceats.[3] Their results, however, were complicated by the presence of an intense sloping background due to fluorescence from an impurity. We now present new results based on Raman data which represent a considerable improvement over those previously reported.[3] This improvement resulted from the use of very rigorously purified water, which lowered the fluorescence level, and also from relatively higher[3] Raman signal levels, resulting from high (4.5 W, 488 nm) laser power levels.

Our improved Raman OH-stretching overtone results show new features (e.g., a broad, strongly polarized component is now seen toward the low-frequency side of the OH peak). This new feature is thought to be the analog of the shoulder observed in the fundamental spectrum near −3250 cm^{-1}. Our spectra also show an isosbestic frequency in the temperature range 20–95° C which agrees with reported infrared overtone isosbestic values,[1] and which is consistent with isosbestic frequencies obtained from the fundamental Raman region of liquid water.[11,3] We also have measured depolarization ratios over the entire frequency range of the OH-stretching overtone contour.

The details of the present results follow, but the significant feature of the improved Raman data is that they seem to demand the conventional picture of an overtone region which essentially shows the free OH and broad hydrogen-bonded species contributions, plus coupling effects, all as modified by various degrees of anharmonicity across the overtone contour. This picture contrasts strongly with the

recently proposed explanation which stemmed from data of lower reliability and smaller frequency range.[3]

II. EXPERIMENTAL PROCEDURES

Overtone Raman spectra were obtained from highly purified water kindly provided by M. Bernett of the Naval Research Laboratory, Washington, D.C. The water was filtered and deionized prior to triple distillation in a fused silica still. The sloping background reported earlier in the Raman spectrum,[3] still persisted to some extent when this water was used, but it was greatly reduced. For ordinary distilled water, the intense fluorescence background level becomes even more pronounced as the temperature rises, and it may increase by 2 or 3 times its original intensity at 95 °C. Rigorous purification, however, lowers this effect as well. It is also important to clean the water storage container and the Raman cell with chromic acid solution prior to use.

Raman spectra were obtained with a *J-Y* double-monochromator and a cooled Hamamatsu R928 photomultiplier tube. A Spectra-Physics model 171 argon ion laser was used for excitation. It delivered approximately 4.5 W of vertically polarized 488 nm light *at the sample*. For polarization measurements, a sheet polarizer was inserted in front of the collection optics. A polarization scrambler was also employed in front of the entrance slit. A photon counting system was employed with a Nicolet model 1170 multichannel analyzer. Slit widths corresponding to 16 cm^{-1} were used for all spectra.

Decompositions of spectra using Gaussian components was accomplished using a duPont 310 analog computer.

III. EXPERIMENTAL RESULTS

Raman OH-stretching overtone (first overtone) spectra representative of the *S/N* ratio and fluorescence background level generally obtained in this work are shown in Fig. 1 for pure liquid water at 20 °C. The spectra are very weak, despite the fact that they were obtained with a slit width corresponding to 16 cm^{-1} and a power level of 4.5 W at the sample. The number of counts per second recorded at the intensity maximum (without using the polarization analyzer) was about 1000 counts/s, of which approximately 750 counts/s resulted from Raman processes, with approximately 250 counts/s resulting primarily from fluorescence due to impurities. The intensity of the OH-stretching overtone was observed to be about 10^{-6} times that of the corresponding fundamental, see also Ref. 12. This weakness, of course, is partly instrumental, because the overtone contour ranges from 670–770 nm (with 488 nm excitation) where the photomultiplier response, grating efficiency, and geometrical optical spectrometer conditions (e.g., curved slit image scanned by a straight slit) are all unfavorable. Nevertheless, the present signal-to-background ratio of approximately 3 represents a significant improvement over the estimated ratio of 0.8 obtained by Belsley and Scaats.[3] Furthermore, our background-corrected (Raman) signal is about four times larger than theirs. We recognize, nevertheless, that the weakness of our spectra still limits the amount of quantitative information that can be extracted, compared to the fundamental. Hence, only those features that were found to be common in numerous repetitions of the spectra are considered reliable. *Any mention of features relative to a specific spectrum will imply this general reproducibility.*

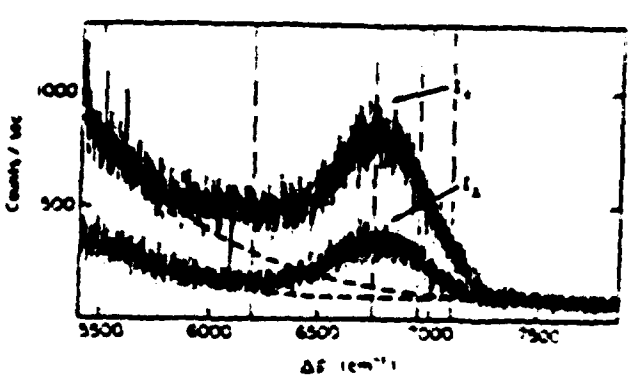

FIG. 1. Raman OH-stretching overtone spectra from liquid water at 20 °C (Raw data). $I_\parallel$ refers to the polarized spectrum, and $I_\perp$ to the depolarized spectrum. Dashed vertical lines refer to peaks, shoulders, or inflections.

The polarized spectrum of Fig. 1 $I_\parallel$ shows an intensity maximum near ~6750 cm^{-1}, with an inflection near ~7100 cm^{-1} suggestive of a high-frequency shoulder, and a very broad tail centered near ~6200 cm^{-1} indicative of a low-frequency component. The depolarized spectrum $I_\perp$, shown below in Fig. 1, peaks near ~6750 cm^{-1} and shows a low-frequency tail like the $I_\parallel$ spectrum, but it also gives evidence of a high-frequency inflection or shoulder near ~6950 cm^{-1}. Thus, reproducible physical evidence exists that would indicate that the OH-overtone contour is composed of at least four broad components at ~6200, ~6750, ~6950, and ~7100 cm^{-1} at 20 °C. Various aspects of the spectra relating to four components near these frequencies are developed subsequently in this work.

Nonlinear baselines under the $I_\parallel$ and $I_\perp$ spectra are shown by dashed lines in Fig. 1. These baseline estimates were obtained by examinations of a wide frequency range. Their curvature is gradual compared to any Raman features ascertained from their use. We regard intensities above these baselines to represent the true Raman intensity, within our present ability to obtain it. The intensity profiles were smoothed and baseline subtraction was accomplished. Correction for effects of temperature on refractive index and density was then made.[11] No attempt to obtain isotropic spectra [i.e., $I_\parallel - (4I_\perp/3)$] was made here, because of uncertainties in the $I_\parallel$ and $I_\perp$ spectra.

Depolarization ratios $\rho = I_\perp/I_\parallel$ are plotted vs Raman frequency shift in cm^{-1} $\Delta\bar{\nu}$ in Fig. 2 (20° C). Baseline uncertainties are less important here because they tend to cancel, provided that they are consistent in shape for $I_\parallel$ and $I_\perp$. However, the decreasing *S/N* ratio in the wings of the contour leads to correspondingly large errors (shown by bars). Despite such errors, the Fig. 2 data represent the first OH-overtone depolarization measurement made below 6400 cm^{-1} for liquid water.

The maximum depolarization ratio occurs near 6740 ± 50 cm^{-1}. Also the existence of a highly polarized component near 6200 cm^{-1} is obvious, compare also with Fig. 1. A highly polarized low-frequency component near

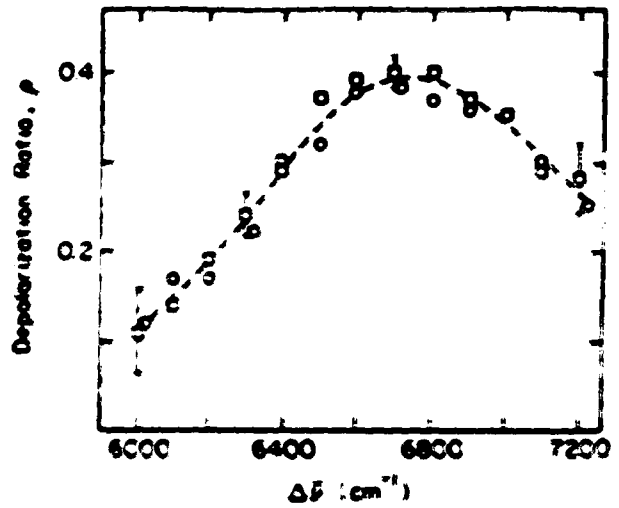

FIG. 2. Depolarization ratio ρ as a function of Raman frequency at 20 °C. Duplicate determinations, ○ and □.

3250 cm^{-1} also occurs as a shoulder on the OH-stretching fundamental. This feature is probably the analog of the 6200 cm^{-1} shoulder.

In contrast to the data of Fig. 2, Bélzky and Sceats concluded from measurements between 6400 and 7400 cm^{-1} that the depolarization ratio was nearly constant and equal to ~0.4. *These conclusions and interpretations arising from it must now be regarded as unreliable in view of the present data.*

In Fig. 3 four overtone Raman spectra are shown which correspond to temperatures between 20 and 95 °C. The integrated Raman intensities of this figure are quantitatively comparable to ~2%.

The Fig. 3 results comprise one of two series of runs accomplished at four temperatures between 20 and 95 °C. A third series of runs was also carried out at six temperatures. Within an intensity accuracy of ~2%, no differences were observed between corresponding spectra from these three series.

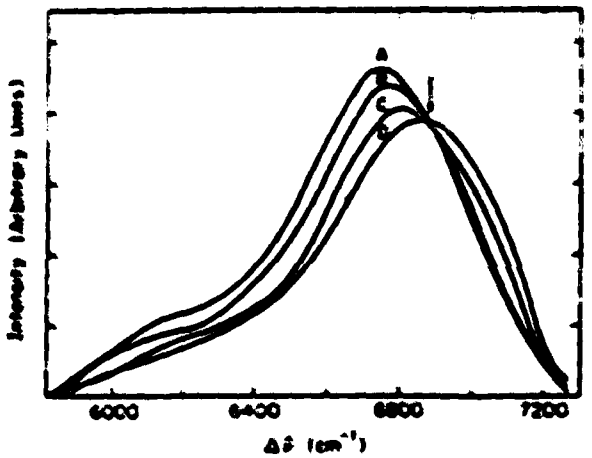

FIG. 3. Four overtone Raman spectra at different temperatures showing an isosbestic frequency indicated by the arrow. The letters correspond to the following temperatures: (A) 20 °C, (B) 45 °C, (C) 70 °C, (D) 95 °C.

Tests for long-term intensity drift were also made. One of the series involving four temperatures (Fig. 3) was begun at 95 °C. Successive runs were conducted at decreasing temperatures to 20 °C. Then the measurements were repeated *in reverse temperature sequence*, from 20 to 95 °C. Spectra corresponding to the same temperature were found to be comparable to within 3% at the intensity maximum, and to 2% or better in the integrated intensity, despite the fact that the time interval between the 95 °C pair was about 10 h.

Baselines for the Fig. 3 spectra were determined as described previously. Smooth curves were drawn through the spectra by averaging the noise excursions. The smooth curves were then digitized using a HP-67 computer. The digital data were corrected for variations in density and refractive index, and replotted using a HP-7470 plotter (Fig. 3).

In addition to evidence cited previously for four contour components, the corrected spectra of Fig. 3 provide evidence for a fifth physical observable, namely, a region of crossing, or an isosbestic frequency, near 6900 ± 25 cm^{-1}. However, an isosbestic frequency was also found for the uncorrected spectra near 6960 ± 25 cm^{-1}. In regard to this, Luck[9] has reported an infrared isosbestic frequency for pure H_2O which occurs (without correction) at 6945 cm^{-1}. The uncorrected infrared and Raman values of 6945 cm^{-1} and 6960 ± 25 cm^{-1}, respectively, thus compare favorably. Also the fact that the infrared and Raman overtone spectra show common isosbestic frequencies indicates that both spectra measure the equilibrium[10] between different hydrogen-bonded species (e.g., four-bonded to three-bonded) as previously concluded from studies of the infrared and Raman fundamentals.

Gaussian decompositions of the Raman OH-stretching fundamental from pure water have been reported previously using four major components.[7,8,15] Similar four-Gaussian decompositions were accomplished in this work for the overtone spectra at temperatures from 20 to 95 °C. To achieve these decompositions, however, it was important to apply specific criteria which resulted from past experience with the OH fundamental. *These six criteria are detailed here in Ref. 16.*

A typical four-Gaussian decomposition of the OH-overtone spectrum corresponding to 65 °C is shown in Fig. 4. This decomposition and other similar decompositions of spectra obtained from 20 to 95 °C, were found to meet the criteria listed in Ref. 16. However, as a further test of the component frequencies, it is useful to examine Table I.

In Table I Raman frequency values corresponding to Gaussian component centers are compared for fundamental and overtone OH regions of pure H_2O. A measure of the % anharmonicity is included, namely, $100\,(2B-A)/2B$, where $2B$ is the first *harmonic* frequency, i.e., twice the fundamental frequency B and A is the frequency of the first overtone.

In regard to Table I and also to Fig. 4 it should be noted that *the Gaussian components are designated from (1) to (4) in order of increasing frequency*. This ordering scheme applies to the OH overtone components as well as to the OH fundamental components, and it is employed extensively below.

As seen from Table I, three overtone components at 7030, 6850, and 6665 cm^{-1} have anharmonicities of ~3%,

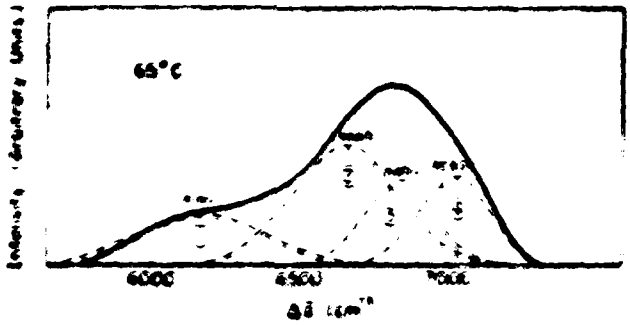

FIG. 4. Overtone spectrum at 65 °C showing the decomposition into four Gaussian components (1–4) defined in the text.

which distinguishes them from the component at 6160 cm^{-1} whose anharmonicity is higher ~ 5%. This division of components according to anharmonicity provides support for the subsequent assignment of the 6160 cm^{-1} component.

Integrated Gaussian component intensities are plotted vs temperature in °C in Fig. 5. The intensities of components (1) and (2) I_1 and I_2 decrease with temperature rise, whereas the opposite dependence is observed for the component (4) intensity I_4. The intensity of component (3) I_3 is roughly constant from 20 to 95 °C. This near constancy is discussed subsequently.

In Fig. 6 $\ln(I_b/I_a)$, where $I_b = I_1 = I_2$ and $I_a = I_3 = I_4$, is plotted vs $1/T$. The straight line shown represents the linear least-squares fit of the data, and its slope corresponds to a ΔH° value of -2.5 kcal/mol, in excellent agreement with other reported values which correspond to a mole of hydrogen bonds.[4,6] Other plots were also constructed using individual component intensities,[7] but the method used for Fig. 6 may be the most reliable because the sums $I_1 + I_2$ and $I_3 + I_4$ are subject to smaller errors than the individual component intensities.

IV. DISCUSSION

A. General Assignment

In this work four reproducible contour features were observed visually from the combined polarized and depolarized Raman OH-overtone spectra near ~6300, ~6750, ~6950, and ~7100 cm^{-1}, see Fig. 1 and its discussion.

TABLE I. Comparison of overtone and fundamental Gaussian component frequencies, % anharmonicities shown in last column to the right. Frequencies corresponding to maximum depolarization ratio ρ_{max} and maximum frequency ν_{max} are compared below. Components are designated by numbers as presented, from column to the left.

	A	B	(B/2.0 − A)/A
(4)	7080	3625 (7250)	3%
(3)	6850	3530 (7060)	3%
(2)	6660	3425 (6850)	3%
(1)	6160	3250 (6500)	5%
	ρ_{max} @ 6750 ν_{max} = 6900	ρ_{max} @ 3530 ν_{max} = 3480	

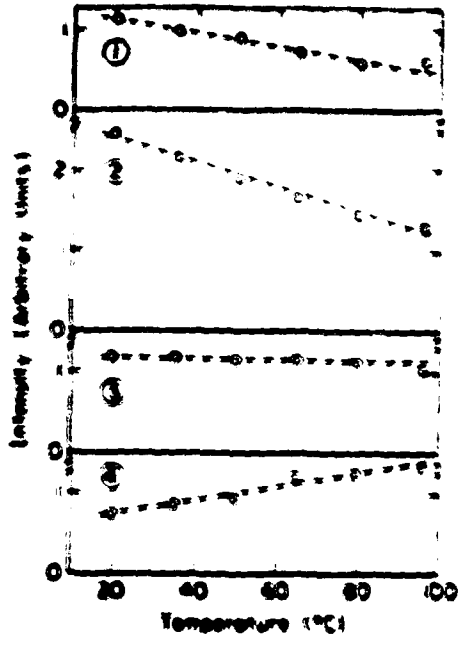

FIG. 5. Integrated Gaussian component intensities as a function of temperature. For component frequencies, see Fig. 4 or Table I.

However, when the overtone contours were decomposed using four Gaussian components, the corresponding component centers actually occurred near 6160, 6660, 6850, and 7080 cm^{-1}, and these values are regarded as more accurate than the visually observed features. From Table I it is probable that these four Gaussian components are the analogs of the four Gaussian components from the fundamental at 3250, 3425, 3530, and 3625 cm^{-1}, respectively.[4] Thus, in agreement with a previous fundamental assignment,[4] component (1) at 6160 cm^{-1} is assigned to intermolecular coupling, component (2) at 6660 cm^{-1} to fully hydrogen-bonded four-bonded H_2O molecules, component (3) at 6850 cm^{-1} to three-bonded near hydrogen bond disrupted H_2O mole-

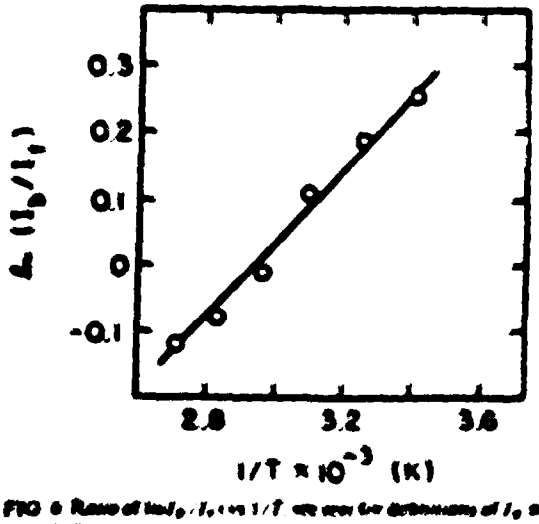

FIG. 6. Ratio of $\ln(I_b/I_a)$ vs $1/T$ are raw for determinations of I_a and I_b. The straight line represents the linear least-squares fit of the data, and corresponds to a ΔH° value of -2.5 kcal/mol.

cules, and component (4) at 7030 cm^{-1} to nonhydrogen-bonded OH oscillators (i.e., to the nonhydrogen-bonded OH of the three-bonded entity). More detailed assignments for components (1) and (2) at 6160 and 6665 cm^{-1} are given subsequently. *Component (3), however, may also contain hydrogen-bonded combinations from two- and one-bonded H_2O molecules (namely, the nonhydrogen bonded OH groups of the two- and one-bonded molecules would contribute to component (4).*

The production of three-bonded H_2O molecules from four-bonded H_2O molecules is shown schematically in Fig. 7, where the four-bonded H_2O molecule on the left is indicated by a closed dashed curve. The three-bonded H_2O molecule on the right is indicated by the open dashed curve, and the nonhydrogen bonded or dangling OH is emphasized by a heavy line. The H_2O molecules shown, for example, on the left, outside of the dashed curve, are fully hydrogen bonded but the hydrogen bonds are omitted for simplicity.

B. Assignments of components (3) and (4)

As shown in Fig. 7 the production of three-bonded H_2O from four-bonded H_2O involves the formation of a species with one nonhydrogen bonded or dangling OH group. The other OH group of this three-bonded species has C_s symmetry and is involved in three hydrogen bonds. The dangling OH group of this C_s species is thought to produce components (4), i.e., the 3625 cm^{-1} fundamental component, and the corresponding 7030 cm^{-1} overtone component. The singly hydrogen-bonded OH group of this species is thought to produce component (3), i.e., the 3530 cm^{-1} component in the fundamental and the corresponding 6850 cm^{-1} component in the overtone. It should be mentioned here, however, that the hydrogen bond involving the proton of the three-bonded OH group is probably much more effective in perturbing the OH stretching frequency than interactions at the lone pair oxygen electrons, because the hydrogen bond may be nearly co-linear with the OH bond. This effect is discussed below in relation to the HDO molecule.

C. Assignments of components (1) and (2)

The central H_2O molecule of the four-bonded entity shown to the left in Fig. 7 would, if free, give rise to a symmetric stretching motion (A_1, species of the C_{2v} point group) and to an antisymmetric stretching motion (B_2, species). The antisymmetric stretching motion, however, seems never to have been unequivocally identified for liquid water. It would be weak in the Raman spectrum, and it may be unresolved from component (3), namely, the fundamental and overtone components at 3530 and 6850 cm^{-1} due to the singly hydrogen-bonded OH group. Also, if a B_2 from four-bonded H_2O is unresolved from component (3) of three-bonded H_2O, it is apparent that the anomalous constancy discussed relative to Fig. 5 is explained.

If the asymmetric stretching motion for liquid water occurs near component (3), an explanation for the remaining two components, (1) and (2), is required. A possible assignment for component (1) involves Fermi resonance, but this assignment is not greatly favored here for reasons described subsequently. An assignment for components (1) and (2) that is considered to be in agreement with observed depolarization ratios,[18] with dilution studies involving HDO,[19] and with effects of electrolyte addition[12] follows.

Component (1) is assigned to a tetrahedral grouping of five hydrogen-bonded H_2O molecules whose symmetric stretches are all in-phase (Fig. 7, left). Component (2) is also assigned to symmetric stretching, but in this case some of the symmetric stretches of the five H_2O molecules are out-of-phase. The H_2O molecules giving rise to component (2) are thus decoupled to some extent, hence component (2) would be expected to persist under conditions of dilution or of structure-breaking electrolyte addition when component (1) is very weak or absent. For example, the breakdown of hydrogen bonds or the strong intermolecular decoupling in the case of HDO would tend to be expected to reduce the intensity of component (1) while only slightly affecting component (2).

Examination of Fig. 7 (left) structure in relation to the assignments of components (1) and (2) indicates that the combined in-phase symmetric stretches of the five H_2O molecules shown would, if the overall symmetry of the five-molecule unit is C_{2v}, i.e., T_2 at the oxygen atoms, correspond to a totally symmetric stretching motion of A_1 symmetry. The depolarization ratio for this mode might be expected to tend toward zero—the observed value is 0.04.[19] On the other hand, the out-of-phase symmetric stretches would lead to B_2 symmetry and the corresponding depolarization ratio might tend toward 0.75, except for the decoupling mentioned. This decoupling causes the H_2O molecules involved to yield a depolarization ratio well below 0.75, as expected for the symmetric stretches of individual H_2O molecules. The experimental depolarization value for the fundamental component (3) is ~0.3.[19]

In relation to intermolecular decoupling, the right structure of Fig. 7 should also be mentioned. If the left proton of the central H_2O molecule (i.e., the hydrogen-bonded proton) were replaced by deuterium, the hydrogen-bonding along the OD bond would in a major effect compared to that involving the lone pair electrons of the central atom would not be coupled with the motion of the dangling or nonhydrogen-bonded proton. Hence this OD stretch would be expected to assume a "normal" hydrogen bonded or four-bonded value near 2525 cm^{-1}. This means that the analogous OH value would be near the four-bonded value of 3450 cm^{-1}, not at 3530 cm^{-1}. Thus, in dilute HDO, not only is the totally in-phase component (1) weak, but component (3) is weak

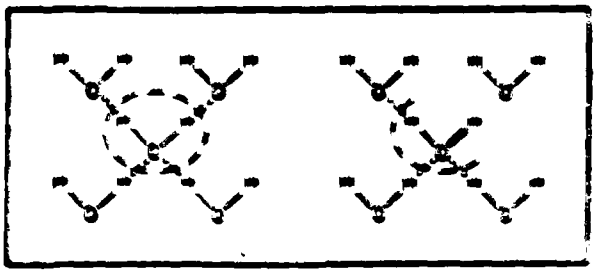

FIG. 7. Schematic diagram representing formation of three-bonded H_2O molecules from four-bonded H_2O molecules.

as well, as observed previously in comparisons involving HDO, D_2O and H_2O.[6,7]

D. Other Assignments

Component (1) has often been assigned to Fermi resonance, i.e., the overtone of [illegible] engages in resonance with [illegible], because both are of [illegible] species. However, in the overtone OH spectrum this assignment would require that [illegible] engage in Fermi resonance with [illegible]. Such resonance seems possible, but highly improbable in view of the intensity of the overtone component (1) relative to the other overtone components. The vibration [illegible] involves four optical phonon modes, and such a four-phonon mode should be extremely weak, compared to the two-phonon modes that make up the OH overtone spectrum.

V. SUMMARY

The complete OH-stretching Raman overtone region from 5500–8000 cm^{-1} has been examined from 20 to [illegible] °C. Contour substructure is indicated, with components centered near (1) 6160 cm^{-1}, (2) 6665 cm^{-1}, (3) 6850 cm^{-1}, and (4) 7050 cm^{-1}. An isosbestic frequency corrected for density and refractive index was observed at 6800 ± 25 cm^{-1}. This isosbestic frequency is indicative of an equilibrium between different hydrogen-bonded species, believed to be mainly four-bonded and three-bonded, in the temperature range studied. Plots of the four components' intensities vs temperature also are indicative of a four-bonded to three-bonded equilibrium, and a logarithmic plot involving [illegible] yields a $\Delta H°$ value of [illegible] of hydrogen bonds in agreement with other reported values. All of the observations of this work are thus indicative of an equilibrium between species, contrary to the previous interpretations of [illegible] and Sceats, but in agreement with Luck and others.

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