Interoscillator coupling effects on the OH stretching band of liquid water

D. E. Hare and C. M. Sorensen

Department of Physics, Cardwell Hall, Kansas State University, Manhattan, Kansas 66502-2601

We have studied the OH stretch spectrum in water to explore the effects of interoscillator coupling. Both H_2O, which may have significant intra and intermolecular coupling, and dilute HOD in D_2O, which is isotopically decoupled, were studied over a broad range of temperature from -33 °C to 160 °C. By adding a small amount of a calibration dopant, we obtained quantitative spectra. We found interoscillator coupling plays a large role at all temperatures. At high temperature, intramolecular coupling contributes to a downshift in the peak position for H_2O as compared to HOD. Intermolecular coupling, however, still has some influence at high temperature. At low temperature, the large excess intensity below 3200 cm^{-1} in H_2O compared to HOD we find is due to an enhanced Raman cross section due to intermolecularly coupled in-phase OH stretch oscillations. We define a degree of delocalization for coupling as the idealized number of perfectly in-phase oscillators that could cause the enhanced scattering and find $N \simeq 2$ for liquid H_2O at -33 °C. An exact isosbestic crossing is not found and this can be understood given the changing line shape that the intermolecular coupling can induce. All the properties of the spectrum approach those found in amorphous solid water or ice near the supercooled water anomalous temperature, $T_s \simeq -45$ °C.

I. INTRODUCTION

Raman spectroscopy has served as a useful tool for studying the structure of liquid water.[1] The spectra of dilute HOD in D_2O solution is related to the liquid's local structural properties in a relatively simple fashion, due to the localized nature of the isotopically decoupled vibrations.[2-8] The Raman spectrum of pure H_2O liquid is considerably more complicated. This essentially stems from the uncertainty in the extent of the delocalization of the OH vibration due to the competition between effective inter- and intramolecular OH coupling which promotes delocalization, and the structural disorder in the liquid which promotes localization. Delocalization of an OH vibrational mode is the process in which the mode represents the correlated motions of many OH oscillators, i.e., a collective mode. For example, in HOD vapor the single OH vibrational mode is very much localized to the OH group itself. The OD oscillator participates to a negligible extent in this vibration. In H_2O vapor, we have two OH oscillators, thus two OH vibrational modes. The two equivalent OH oscillators are effectively coupled, creating the symmetric stretch, v_1, and the antisymmetric stretch v_3. Neither vibration can be described as the motion of a single oscillator; both oscillators contribute equally. In v_1 the two oscillators vibrate in phase; in v_3, out of phase. The v_1 and v_3 vibrations can be described as being delocalized between the two OH oscillators of the H_2O vapor molecule. To quantify this concept we will define a degree of delocalization of the OH vibration and specify it with the number N, the number of perfectly in-phase oscillators which could yield the same Raman intensity. For example, $N = 1$ for HOD and 2 for H_2O vapor. The main purpose of this paper is to further refine and quantify the present understanding of the role of this delocalization in the Raman spectra of H_2O liquid.

Much of the present understanding of the liquid comes from the understanding of ice Ih and the vapor deposited amorphous ice. The Raman OH stretch of ice Ih is dominated by a strong band at 3080 cm^{-1}. This vibration is characterized by the H_2O molecules executing v_1 vibrations all in-phase with each other but with vibrational amplitude varying from molecule to molecule.[9,10] Green, Lacey, and Sceats proposed that the low frequency feature in the liquid was a collective mode of essentially the same origin as the v_1 in-phase ice Ih vibration.[11] This differed from previous analyses in that for the first time the Raman spectrum of the liquid was viewed as related to ice Ih and not perturbations of v_1, v_3 vaporlike modes. Another intriguing aspect of that work was a causal connection between the temperature dependence of this collective mode's intensity in the liquid and the singular temperature T_s. Several of the thermodynamic and transport properties of supercooled water display anomalous behavior, apparently diverging in a power-lawlike fashion, as T_s is approached.[12]

On the other hand, the efforts of Walrafen and co-workers have indicated the existence of isosbestic behavior in the spectra of the pure liquid H_2O system.[13,14] Isosbestic behavior is indicative of a relatively simple system composed of two distinct classes of scatterers, the simplest possibility being hydrogen bonded and nonbonded OH oscillators scattering as localized vibrations with invariant line shapes. If collective, delocalized modes exist, this simple picture should complicate with the hydrogen bonded mode line shape changing with temperature. Thus it is hard to understand how an isosbestic could result even in a simple two-state model.

In this paper we present more OH stretch Raman data for water. We are most interested in the effects of coupling and hence delocalization of the OH vibration. Thus we have

studied both pure H_2O and HOD in D_2O, the latter system having isotopically decoupled OH. We have used a wide range of temperatures, from the homogeneous nucleation limit near $-30\,°C$ to $+160\,°C$, in order to fully exercise the possible extent of hydrogen bonding. We have also taken great care to obtain quantitative spectra by introducing a dopant (methanol) in small concentrations which do not affect the total integrated intensity from the OH band but which allows us to quantitatively determine both the integrated intensity and relative line shapes.

The results of our measurements have allowed us to determine the extent of validity of isosbestic behavior and determine the temperature dependence of the total integrated VV intensity in the OH stretch regime. Comparison of the isotopically coupled and uncoupled liquids at high temperature to the same vapors will show the importance of intramolecular coupling in the high temperature liquid and the manner in which the liquid begins looking like the vapor at high temperature. Our studies at low temperature begin with arguments against the Fermi resonance and bifurcated hydrogen bond explanations of the low frequency mode near 3200 cm^{-1}. Instead, comparison of both isotopically coupled and decoupled systems at supercooled temperature leads us to embrace the concept proposed before that the dominant feature near 3200 cm^{-1} in pure H_2O is due to collective in-phase ν_1 vibrations similar to those seen in ice Ih. We then define and quantify the degree of delocalization, N, of this collective mode and measure it in H_2O at $-33\,°C$. We show for both liquid systems that the OH stretch spectrum shape, peak frequency and width of the major mode, and integrated intensity all approach either the ice Ih or amorphous solid values as the temperature approaches the singular temperature near $-45\,°C$.

II. EXPERIMENTAL METHOD

Samples were made containing H_2O, D_2O, and CH_3OH in various concentrations. Standard 5 mm pyrex tube was thoroughly washed with ordinary laboratory glassware soap solution, thoroughly rinsed, and then boiled for 1 h in distilled water. The clean tubing was pulled into "fat" (0.5 to 1 mm i.d.) capillaries. These were filled with the appropriate solution and rapidly flame sealed at both ends with a small oxymethane flame. The resulting pyrolysis of the sample's CH_3OH content was always negligible. If the samples were to be used in the deeply supercooled regime ($-30°$), they were heat treated for four hours at $+160\,°C$. This produced the desire supercooling ability in 20% of the samples thus treated. This ability is attributed to the enhanced potency of high temperature water as a solvent, in particular for heterogeneous nuclei which would nucleate ice Ih in the supercooled liquid. Because the H_2O became a better solvent, it could also become polluted with solute. In fact, the water would visibly etch the inside of the pyrex capillaries when left at $+160\,°C$ for an entire day. This same problem was encountered by Ratcliffe and Irish in their high temperature Raman studies of water.[6] Thus the sample should be heat treated for the minimal time necessary to achieve the desired result. Some samples exposed to the 4 h treatment were analyzed for sodium and silicon content and

contained less than 0.01 mol % of either constituent.

The small quantities of CH_3OH added to the samples served as a standard of Raman intensity used to calibrate our spectra and thus make them quantitative.[8] This is done via the CH stretching band at 2837 cm^{-1} which is insensitive to changes in liquid structure and temperature. Constancy of band width and constancy of integrated intensity relative to the broader CH feature at 2950 cm^{-1} (with which it might conceivably have been in Fermi Resonance and thus able to exchange intensity) attest to the constancy of this band's total intensity, and thus its reliability as an intensity standard. We were also concerned that methanol could induce changes in the structural properties of water and hence changes in the OH stretch spectrum. To study this possibility several different mole% of methanol were used. It was found that in the limit of a few mole % or less no changes in the total integrated intensity (Fig. 1) could be detected. Line shape studies were always performed on *undoped* water and then their total intensity calibrated with that found in the doped systems at the same temperature. In this way we obtained quantitative line shape comparisons between different temperatures.

The Raman excitation setup has been previously described.[15] Excitation was accomplished with an Ar^+ laser generating 100 mW at $\lambda = 4880\,Å$. The scattering cell maintained the sample temperature between $+160$ and $+100\,°C$ with $\pm1\,°C$ accuracy and between $+80$ and $-34\,°C$ with $\pm0.5\,°C$ accuracy. The scattered light was collected at right angles to both the incident laser beam's path and polarization, passed through a polarizer and wedge scrambler set to detect VV polarization, dispersed by a *SPEX* 1404 double grating spectrometer, and detected by a Hamamatsu R943-02 photomultiplier tube. The resulting signal was shaped and then stored on a computer.
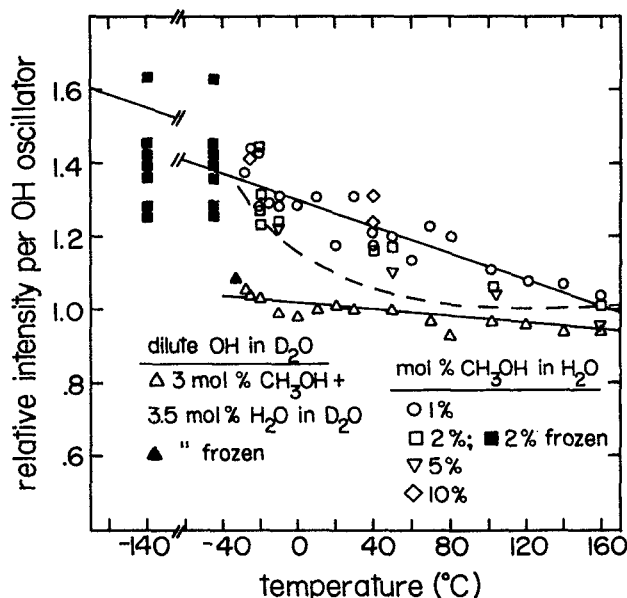

FIG. 1. Stokes Raman VV integrated OH band intensity per OH oscillator as a function of temperature. The large-dashed line is the hypothetical intensity behavior that would be necessary to maintain an isosbestic crossing at 3403 cm^{-1} in the spectra from $+160$ to $-33\,°C$. The ■ data were actually taken at $-25\,°C$.

The spectra are all Stoke's Raman of the VV polarization. They have a resolution of 15 cm^{-1}. They have been corrected for all instrumental response factors, but not for any inherent frequency bias [i.e., $\nu(\nu_0 - \nu)^{-4}$].[16] Thus, they represent OH Stoke's Raman VV intensity per OH oscillator as seen by an ideal instrument.

III. ANALYSIS AND DISCUSSION

A. Total integrated Raman intensity, quantitative Raman spectra and isosbestics

Figure 1 represents integrated OH stretch intensity per OH oscillator (hereafter simply "integrated intensity"), for water between -28.5 and $+160$ °C under conditions in which both inter and intramolecular coupling may be very important (principal constituent is H_2O) as well as unimportant (dilute HOD in D_2O). For the vibrationally isolated system of dilute HOD in D_2O (hereafter simply the "dilute" system), OH intensity climbs a modest 10% in going from $+160$ to -30 °C. On the other hand, OH intensity climbs by 33% for the systems containing principally H_2O (the "concentrated" systems). At $+160$ °C concentrated OH intensity is only 7% greater than in the dilute system. It is probable that they will asymptotically approach a common constant value at higher temperature.

Ratcliffe and Irish[6] also observed an increase of the total OH stretch intensity with decreasing temperature. For H_2O their measured linear increase had slope only slightly less than ours. On the other hand, for HOD they again measured a large increase with decreasing temperature, significantly greater than what we show in Fig. 1. This discrepancy may be due to the fact that the Ratcliffe and Irish data were at best semiquantitative, in that while care was taken to correct for density changes no correction for the local field effect via the changing index of refraction was made.

The results of Fig. 1 for concentrated systems may be used to generate quantitative VV Raman spectra for pure H_2O. A set of nonquantitative spectra were each rescaled by the appropriate constant factor which forces their integrated intensities to conform to the concentrated curve in Fig. 1. The resultant quantitative spectra are displayed in Fig. 2. Over the full 193 °C range of temperature, there is no isosbestic. However, in the range 0 to $+80$ °C we reproduce the results of Walrafen et al. within experimental uncertainty.[14]

If the spectra of Fig. 2 are forced to have the 3400 cm^{-1} isosbestic crossing found by the aforementioned authors, this will generate the large-dashed line curve of integrated intensity vs temperature in Fig. 1. The curvature of this line is quite apparent. This curvature does not agree with the actual data. As in our previous publication of dilute HOD in H_2O,[8] we conclude that an isosbesticlike crossing exists over a small range of temperature, but this crossing gradually moves to higher frequency as the temperature is increased.

An exact isosbestic has long stood as an indication of two-state behavior for liquid water. Isosbestics result if there are two temperature dependent populations whose total is temperature independent and if the Raman line shapes for each population is temperature invariant. From our earlier work and the results we will describe below, we feel the hy-
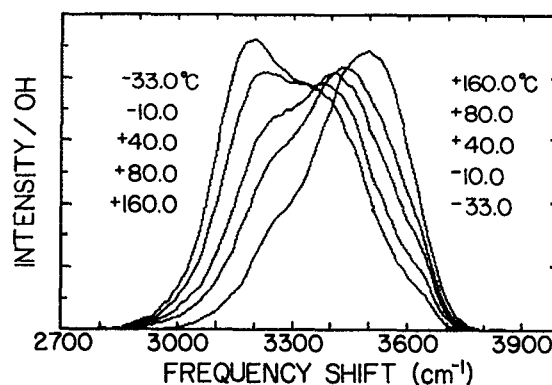

FIG. 2. Quantitative Stokes Raman VV spectra of the OH band. Accurate intensity comparisons between different isotherms may be made.

drogen bonded Raman cross section, and hence line shape, is far too complex to be temperature independent, especially over a broad temperature range. Thus, the lack of an observed isosbestic is not surprising, if only for this reason.

B. The effects of hydrogen bonding and coupling on the density of states

One of the basic tasks of this paper is to explain the general features of the quantitative spectra of Fig. 2. Fundamental to this understanding is a knowledge of the density of states. The Raman intensities I_R of Fig. 2 do not in general reflect the density of vibrational states ρ but are related through the Raman cross section σ by $I_R = \sigma\rho$. [Note that although $\Delta\nu$ is perhaps more appropriate notation for Stokes Raman frequency shift, we use ν to simplify the notation. Also, we will suppress the independent variables of a quantity when no confusion arises from doing so: Thus, $I_R(\nu,T)$ is often simply referred to as I_R.] If we could scatter from isolated noninteracting OH oscillators, we would find ρ to be a narrow spike at the free OH stretch frequency (about 3700 cm^{-1}). This situation is well modeled by the OH stretch of HOD vapor. On the other hand, the OH band is very broad in liquid H_2O and this is due to a broadening of the density of states for two reasons: First, hydrogen bond disorder amongst the OH oscillators can give considerable breadth to the OH stretch. The width in this case is indicative of the extent to which hydrogen bond strength directly affects the OH bond strength and thus the OH oscillator's "spring constant." Second, strong coupling between OH oscillators will induce vibrational delocalization of the OH band and thus split the vibrational frequency degeneracy by an amount proportional to the strength of this interaction. This interaction can be both intermolecular and intramolecular in nature.

The system of dilute OH oscillators in D_2O is an example of broadening due to hydrogen bond disorder without the influence of delocalization. In this system the OH oscillators act as isolated and independent Raman scatterers. The Raman cross section σ is only weakly dependent on frequency, and the shape of the Raman spectrum is very similar to the vibrational density of states. Thus, the shape of the density of

OH vibrational states curve in the dilute system is well represented by the Raman OH stretch spectrum of the dilute system.

It is important to realize that the density of OH vibrational states for the dilute OH system is not equal to that of pure liquid H$_2$O. The former is the result of variation in OH oscillator environment only, whereas the latter is both due to variation of oscillator environment and effective intercoupling (delocalization) of the oscillator vibrations. This is why the pure H$_2$O spectrum is always broader than the dilute spectrum. Because the dilute system is only sensitive to local oscillator environment and I_R is simply related to ρ, this system is best for studying local properties such as the possible continuum or two-state behavior of hydrogen bonds and estimates of hydrogen bond strengths and probability of bonding. Of course this information is also contained in the pure H$_2$O spectrum, but it is convoluted with the variation in σ caused by the different Raman activities of the delocalized vibrations.

C. The effects of coupling on the Raman cross section

Given this understanding of the density of states, we next consider the effects of coupling on the Raman cross section. Of particular interest for our work is the mode responsible for the large increase in intensity with declining temperature near 3200 cm^{-1} in the concentrated system. In ice Ih this has been ascribed to the v_1 in-phase motion of the OH oscillators and strong arguments have been made that this is the source of the mode near 3200 cm^{-1} in liquid H$_2$O. Thus we will consider a set of N in-phase OH oscillators and determine the Raman cross section of this mode relative to N uncoupled and random oscillators. The number N defines the extent of coupling and we will call it the delocalization of the coupled mode.

Consider a single OH oscillator Raman scattering photons at a rate designated by the intensity I_1 while itself absorbing energy $\hbar\omega$ where ω is the frequency of the OH vibration. This energy is related to the vibrational amplitude of the oscillator χ_1 by

$$\hbar\omega = k\chi_1^2/2. \tag{1}$$

The polarizability change α_1 is directly proportional to χ_1 so we have Raman intensity

$$I_1 \propto |\chi_1|^2. \tag{2}$$

Now consider N OH oscillators vibrating in the totally in-phase mode. The N oscillators Raman scatter one photon with intensity I_c, picking up energy $\hbar\omega$. However, this $\hbar\omega$ is shared equally among the N oscillators. Each oscillator receives $\hbar\omega/N$. Then for the amplitude of the nth oscillator

$$\hbar\omega/N = k\chi_n^2/2. \tag{3}$$

Thus

$$\chi_n = \chi_1/\sqrt{N}. \tag{4}$$

The vibrational amplitude per OH oscillator has decreased by a factor of $\sqrt{N}$ over that for a single oscillator. However, the polarizability for the N oscillator system in the totally in-phase mode will be

$$\alpha_c \propto \sum_{n=1}^N \chi_n = \sum_{n=1}^N \chi_1/\sqrt{N} = \sqrt{N}\chi_1. \tag{5}$$

Then, the Raman intensity is

$$I_c \propto \left| \sum_{n=1}^N \chi_n \right|^2 = N|\chi_1|^2. \tag{6}$$

Thus,

$$I_c = NI_1. \tag{7}$$

This hypothetical totally in-phase vibration is very effective at Raman scattering. What about the other $N-1$ modes? The Raman intensity of each of these other $N-1$ modes is zero. This is because normal modes of different frequency must be orthogonal.[17] Thus, if the interoscillator coupling splits the OH stretch into a band, those normal vibrational coordinates which do not have the collective frequency must all be orthogonal to the collective mode's normal coordinate. The totally in-phase normal coordinate can be represented by the normalized vector $(1/\sqrt{N})$ $(1,1,1,...,1)$. The Raman intensity for this vector is just the square of the sum of the components, i.e.,

$$I = \left[\frac{1}{\sqrt{N}}(1 + 1 + 1 + \cdots + 1) \right]^2 = N.$$

For any vibrational coordinate $\bar{a}$ to be orthogonal to the totally in-phase coordinate $\bar{a} \cdot (1,1,1,...,1) = 0$. Thus, $\Sigma_{n=1}^N a_n = 0$ and therefore the Raman intensity of coordinate $\bar{a}$ is also zero.

While at first glance this result may seem surprising, it stems from fundamental causes. We considered our system of N oscillators to be coupled in such a way as to give rise to the hypothetical, totally in-phase mode without ever explicitly considering the coupling. Because the coupling between the oscillators was not explicitly considered, both the incoherent vibrational coordinate system and the orthonormal coordinate system containing the totally in phase mode are equivalent ways of describing the system (and arbitrary, there are an infinite number of orthonormal coordinate systems that will describe this N oscillator system). An observable quantity such as total Raman intensity of the system cannot depend on a particular choice of vibrational coordinate system, as long as it is a valid one. Hence, for N degenerate OH oscillators, the total Raman intensity is NI_1 regardless of the coordinate system used to analyze the problem. If the degeneracy is only weakly split by the coupling (i.e., bandwidth small compared to median band frequency as in the OH stretch of H$_2$O) then integrated intensity should still be approximately NI_1.

Let us apply the above result to two very good examples of $N = 1$ and $N = 2$, namely the OH stretches of HOD and H$_2$O vapor, respectively. Two HOD molecules will have two OH vibrational degrees of freedom, scattering like two isolated, independent OH oscillators each giving unit intensity to the OH stretch mode for a total contribution of 2 to OH stretch intensity. If we instead couple these two OH vibrational degrees of freedom in a single H$_2$O molecule, our original two degenerate vibrational degrees of freedom are split by the (intramolecular) coupling into a symmetric and an antisymmetric vibration (Fig. 3). The symmetric vibra-
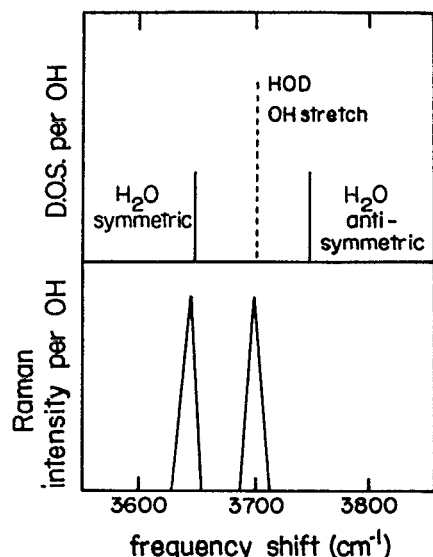
FIG. 3. A schematic illustration of what happens to the vibrational density of states and Raman intensity when two degenerate OH oscillators are effectively coupled as in H_2O vapor.

FIG. 4. A quantitative comparison, per OH oscillator, of the dilute liquid HOD in D_2O and pure liquid H_2O Raman spectra near $+160\,^\circ C$. The intensities of the vapor spectra are not quantitative here.

tion is a single degree of freedom (for one H_2O molecule) and corresponds to the hypothetical totally in-phase mode of our previous argument with $N = 2$. Thus, it should have 2 units of intensity per molecule. The antisymmetric stretch which is orthogonal to the symmetric stretch has no intensity. Note that the total intensity per OH oscillator is conserved and the end result may be described as a shifting of all of the intensity from the independent OH oscillator band into the totally in-phase mode when the coupling between oscillators is turned on (Fig. 3). This picture is experimentally verified by intensity measurements on the vapor bands from 50% D/50% H water mixtures.[18]

D. Comparison of the high temperature liquid to the vapor

Figure 4 is an I_R per OH oscillator comparison between the dilute and concentrated OH systems at high temperature T. At $+160\,^\circ C$ integrated intensity is nearly the same for both systems and given the behavior with T shown in Fig. 1 will probably asymptotically approach the same value as the temperature continues to rise. Although the extent and importance of hydrogen bonding and thus intermolecular coupling are continually diminishing with increasing temperature, the two liquid spectra of Fig. 4 do not appear to be asymptotically approaching each other. Indeed they display considerable differences at temperatures as high as $+300\,^\circ C$.[6] This is mostly due to the important role played by intramolecular coupling in the concentrated OH system at high temperature. In the vapor the Q branches ($\Delta J = 0$) of the OH stretch of HOD (3703 cm^{-1}) and the symmetric stretch of H_2O (3652 cm^{-1}) differ by 51 cm^{-1}. These two Q branches can be conveniently thought of as the high temperature upper bounds in frequency for the dilute system and liquid H_2O, respectively, since the vapor systems are virtually hydrogen bond free and the general qualitative
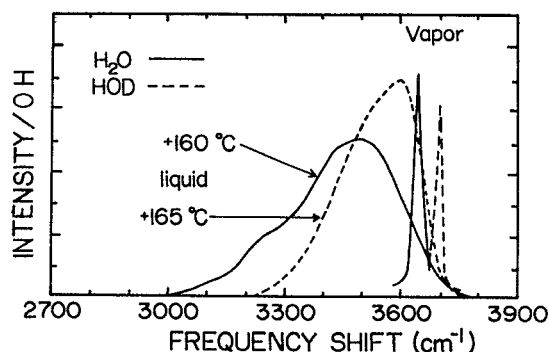
trend is a decrease in OH frequency with increasing hydrogen bond strength. Implicit in the above argument is the assumption that vibrational delocalization through intermolecular coupling is negligible at 160 °C because the effective intermolecular coupling of two H_2O molecules, for example, could conceivably split the originally degenerate symmetric stretch of the free molecules into two new modes, one of which will have ν greater than 3652 cm^{-1}. This lack of intermolecular coupling is consistent with the concept that hydrogen bonding is largely vitiated by the high temperature. Thus, in the pure H_2O system the possibility exists for creating modes that actually have a higher frequency than the Q branch of the vapor. It is of value to note, however, that some Raman intensity is seen in the concentrated OH liquid at frequencies higher than the vapor mode, especially when compared to the dilute system, indicating some small splitting does occur. This type of broadening is not possible in the dilute system, and indeed the HOD vapor Q branch forms a sharp and distinct upper bound to the dilute liquid spectrum.

Intermolecular coupling depends directly on the strength of the hydrogen bond for its effectiveness. Intramolecular coupling is only indirectly dependent on hydrogen bond properties. Thus, at high temperature we expect the effects of intramolecular coupling to increasingly dominate the observed differences in the dilute and concentrated spectra. At 160 °C the dilute and concentrated peak frequencies in the liquid are different by 100 cm^{-1}. This difference should asymptotically approach 51 cm^{-1} (the Q branch separation) at yet higher temperature as intramolecular coupling completely dominates the vibrational behavior of the system.

The data of Ratcliffe et al. show that the slight bump in our $+160\,^\circ C\ H_2O$ spectrum at 3250 cm^{-1} continues to persist even in H_2O liquid at $+300\,^\circ C$ and 10 MPa pressure.[6] It represents a minuscule number of intermolecularly delocalized vibrational states that continue to persist even at such high temperatures. This is consistent with the slight splitting to frequencies above the vapor discussed above.

E. Delocalization of the intermolecular coupling in the low temperature spectra

Figure 5 displays the shapes of the dilute and concentrated OH spectra in the deeply supercooled regime. They
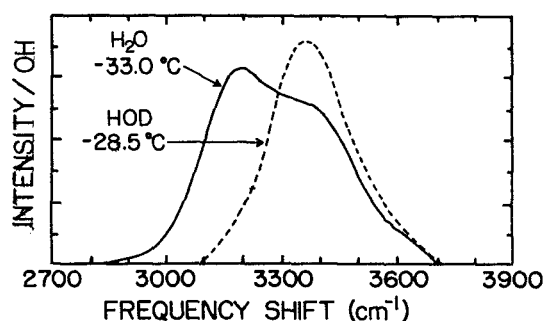
FIG. 5. A quantitative comparison, per OH oscillator, of the dilute liquid HOD in D_2O and pure liquid H_2O Raman spectra near -30 °C.

are quite similar above 3400 cm^{-1}, below this they are quite different. More specifically, there is a large amount of intensity in the concentrated OH system below 3250 cm^{-1}, and very little in the same region of the dilute system. We have two systems consisting predominantly of liquid water at -30 °C. Their hydrogen bond properties are roughly the same.

Three possible explanations have been proposed to explain this extra, low frequency intensity found in the concentrated system. These are the bifurcated hydrogen bond model of Giguère,[19] Fermi resonance with the bending overtone $2v_2$,[6] and broadening due to intermolecular coupling.[7]

Giguère,[19] attempting to explain the temperature behavior of the pure liquid H_2O Raman spectra, proposed a new model for the liquid involving three classes of hydrogen bonds: strong linear hydrogen bonds which are responsible for the excess low frequency intensity in the concentrated system; weak broken bonds, responsible for the high frequency intensity around 3615 cm^{-1}; and intermediate strength bifurcated hydrogen bonds with intensity around 3430 cm^{-1}. To consistently explain the dilute HOD spectrum it was necessary for Giguère to postulate that the isotopically dilute oscillators were much more likely to form bifurcated hydrogen bonds than the linear type. However, this model leads to several surprising predictions for H_2O/D_2O mixtures. The strong similarity in the Raman spectra of supercooled liquid and frozen 5% D_2O in H_2O leads to the conclusion that if OD oscillators in the liquid mixture are engaged in intensive bifurcate hydrogen bonding, then so are those in the frozen mixture. Thus, the presence of the isotopic impurity should seriously disrupt the formation of Ice Ih from a 5% D_2O in H_2O mixture, for example. It is easily verified that the 5% mixture freezes into large crystals, presumably of Ice Ih, just as readily as does pure liquid H_2O. Compare this to 2 mol % CH_3OH in H_2O which manifests a definite tendency to polycrystallize on freezing. Thus, we conclude that there are few if any bifurcated hydrogen bonds in frozen H_2O/D_2O mixtures. Thus, to keep Giguère's postulate we must conclude that the OD stretch Raman spectra of frozen and supercooled liquid 5% D_2O in H_2O are unrelated, which is inconsistent with the strong similarity between supercooled liquid H_2O (or D_2O) and the respective ice or amorphous solid.[11,15] Another example is the necessary conclusion that perhaps the majority of the hydrogen

bonds in a 50/50 mixture of liquid D_2O and H_2O are bifurcated from examination of the OD and OH Raman spectra of such a mixture. Giguère mentions that the bifurcated hydrogen bond is about 2.5 kcal per mol higher in energy than the linear hydrogen bond. A simple calculation shows that if 10% of the total number of OH and OD groups switched from linear to bifurcated hydrogen bonds then equal volumes of H_2O to D_2O at room temperature would cool to 0 °C when mixed. This effect would be easily detected if it existed. From casual observation of the Raman spectrum of a 50/50 H_2O in D_2O mixture at room T, one can easily conclude that well over 10% of the linear hydrogen bonds in the unmixed H_2O and D_2O samples must have been converted to bifurcated bonds upon mixing.[7] Thus, the spectroscopic evidence suggests that this cooling upon mixing will strongly manifest itself if Giguère's explanation of water's Raman spectra is correct. We have not been able to detect this predicted cooling tendency, and if it exists, it is much smaller than that exacted by Giguère's explanation of the dilute OH and OD liquid spectra.

Ratcliffe and Irish[6] proposed that the Fermi resonance between the OH stretch and $2v_2$ (bending mode overtone) predicted to be at 3240 cm^{-1} was "responsible" for the low frequency, low temperature feature in liquid H_2O. Just how "responsible" Fermi resonance is was never quantified by Ratcliffe and Irish, and later in their paper they discuss the importance of coupling for this low frequency feature as well. Thus, we interpret their position to be that both Fermi resonance and coupling contribute to this low frequency feature. We wish, however, to contend that Fermi resonance has only at most a small effect on the low frequency feature. In support of the Fermi resonance picture Ratcliffe and Irish use the temperature independence of the observed peak in the bending band v_2 and the temperature independence of the low frequency feature near $2v_2$. We find, to the contrary, that the peak and width of this low frequency feature are temperature dependent (see Fig. 9, below) a fact which weighs against the Fermi resonance argument. Also, the band in ice Ih at 3083 cm^{-1} has been attributed to the v_1 inphase vibration.[9] Even if this seemingly firm assignment were to again come into question, this band cannot be an artifact of a Fermi resonance simply because it is by far the most intense band in the OH stretch region as was pointed out by Whalley.[9] If the low frequency polarized intensity in liquid H_2O's OH stretch band is predominately attributed to Fermi resonance with $2v_2$, then there can be no physical connection between this feature and the polarized mode in ice Ih at 3083 cm^{-1}. The similarity of these two features, especially in the supercooled liquid and the manner in which this similarity continues to grow stronger with deeper supercooling, suggests that Fermi resonance cannot be in the main responsible for the polarized low frequency feature of the liquid.

Thus, neither the bifurcated bond model nor Fermi resonance adequately explain the difference between the dilute and concentrated OH spectra at low frequency and low temperature. We begin to explain the observed differences in the dilute and concentrated spectra of Fig. 5 by noting that the extent of hydrogen bonding has increased greatly from the

160 °C case of Fig. 4. This is true for both the dilute and concentrated systems. However, isotopic decoupling prevents delocalization in the dilute system, thus the low temperature dilute intensity curve of Fig. 5 is a fairly accurate representation of the vibrational density of states of the dilute system at low temperature. In the concentrated system (pure H_2O) the enhanced hydrogen bonding allows for additional broadening of the density of states due to intermolecular coupling beyond that due to hydrogen bond disorder, as we discussed above. In addition to this extra broadening the Raman cross section becomes strongly dependent on both temperature and frequency. The temperature dependence arises because as more hydrogen bonding occurs with declining temperature more intermolecular coupling can occur which makes the mode structure dependent on normal modes of groups of oscillators rather than single oscillators. The frequency dependence arises because, as we have seen above, the in-phase normal mode will have a large cross section at its particular frequency and this will occur at the expense of the other modes. This should all occur in the frequency regime where strongly hydrogen bonded OH groups contribute to the spectrum; the regime below ca. 3300 cm^{-1}.

On the other hand, the concentrated system may still contain some vibrations of a localized nature, the result of the structural disorder in the liquid. The most direct and obvious contributors to the localized vibrations are the OH oscillators engaged in weak highly-distorted and broken hydrogen bonds, which contribute to the high frequency region above 3400 cm^{-1}. These localized vibrations can be found in both the dilute and concentrated systems and their Raman intensity closely follows the density of vibrational states. Thus, the dilute and concentrated systems' spectra are very similar in shape above 3400 cm^{-1} because both represent the density of vibrational states of localized OH vibrations, and this is similar in both systems because it depends mostly on the similar structural characteristics of the two systems.

What then is the source of the large intensity found near 3200 cm^{-1} in the low temperature concentrated system? From the above considerations we conclude that intermolecular coupling broadens the density of states into this regime, and that while the density of states may be small there, the Raman cross section is large due to an in-phase collective mode. This point of view is not new. Green et al. contended that this intensity is of the same origin as the 3083 cm^{-1} band in ice Ih, namely a highly delocalized, in-phase mode with a correspondingly high Raman cross section.[11] Vibrational calculations on a 64 molecule model of Ice Ih by McGraw et al. revealed that this 3083 cm^{-1} band has enormous Raman intensity and stems from an exceedingly small number of vibrational modes (exactly 1 out of 128 but this was partly because $N = 128$ in their model).[10] We essentially agree with this view that the mode near 3200 cm^{-1} in cold liquid H_2O is the in-phase collective mode.

We can estimate the degree of delocalization N in the concentrated liquid system near -30 °C. If σ_0 is the cross section for a localized OH oscillator, then, as we have seen, $N\sigma_0$ is that for N oscillators engaged in the in-phase collective mode. If the collective mode has a density of vibrational

states ρ_c then $I_c = N\sigma_0\rho_c$ for this collective mode. Notice that if the density of states curve is renormalized to have the same area as the dilute integrated intensity this has the effect of absorbing the constant σ_0 into ρ. For such a renormalized density of states curve the collective intensity becomes simply

$$I_c = N\rho_c. \tag{8}$$

If we can estimate $\rho(\nu)$ for the concentrated system, then we can also estimate the degree of delocalization N for the collective mode. We estimate ρ for the concentrated system at -33 °C by (1) insisting $\rho(\nu) \neq 0$ everywhere $I_R(\nu) \neq 0$. (2) At high frequencies the shape of I_R is indicative of the shape of ρ because the higher frequency vibrations tend to be localized. (3) The peak of the concentrated ρ should be at the same position as the peak of the dilute ρ. Although not strictly true in general, it frequently happens that the effect of coupling two oscillators is to split the degenerate oscillator frequency into modes having both higher and lower frequencies than the original mode in the uncoupled system. For example, the OH stretch of HOD is split into the higher and lower frequency symmetric and antisymmetric stretch in H_2O. Furthermore, the average of the symmetric and antisymmetric frequencies is in good agreement with the OH stretch of HOD. $3652 + 3756 = 3704$ compared with 3703 (± 5) cm^{-1} observed for HOD (from Fig. 3). Thus we might expect that the concentrated ρ is approximately a broadened version of the dilute ρ without much of a shift in the peak position. (4) Force concentrated ρ to have the same integrated area as dilute system I_R at the same temperature.

The estimated concentrated ρ of Fig. 6 conforms to the above four guidelines. From this ρ we can estimate N for the collective mode in the supercooled liquid by

$$N = \frac{I_c}{\rho_c}. \tag{9}$$

Both I_c and ρ_c were taken to be the value of $I_R(\nu)$ and $\rho(\nu)$, respectively, at the peak frequency of the collective mode in the respective spectrum. Thus the degree of delocalization of the collective mode in the supercooled liquid at -33 °C is approximately 2. Compare this with N approximately 3 for ice Ih at -24.5 °C (see Fig. 7), 14 for ice Ih at 90 K, and 3 for the amorphous solid at 90 K. Whalley concluded $N > 50$
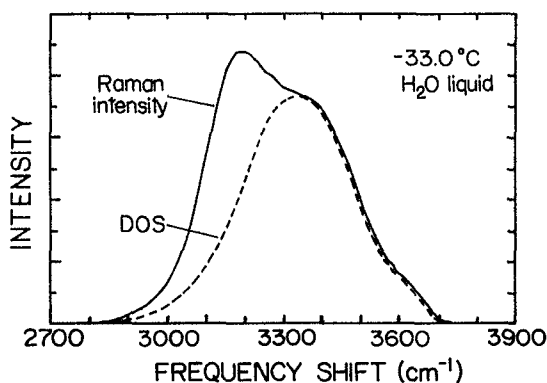

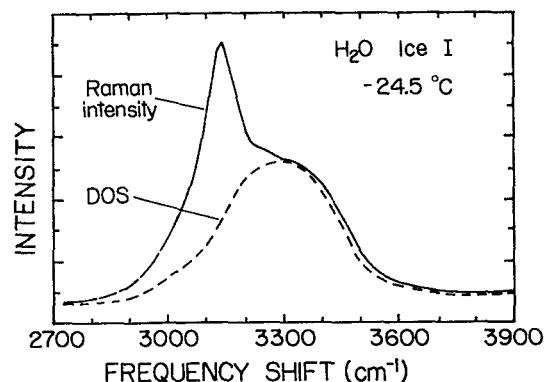FIG. 6. A comparison of the density of vibrational states and the Raman intensity in the supercooled liquid H_2O.

FIG. 7. A comparison of the density of vibrational states and the Raman intensity in H_2O ice Ih at -24.5 °C.

FIG. 8. A quantitative comparison, per OH oscillator, of the Raman spectra of the dilute HOD in D_2O system.

(more than 25 H_2O molecules) for ice Ih, deduced from the width of the ν_1 in-phase band by semi-intuitive arguments but did not state at what temperature this result was deduced.[9,20]

We have made a semiquantitative estimate of N. We must ask "what is the meaning of this number?" We view the degree of delocalization as a measure of the effective number of perfectly coherently coupled OH oscillators that would give rise to the same cross section. $N \simeq 2$ for -33 °C H_2O seems surprisingly small until we recognize this value is a lower bound for the total number of imperfectly coupled oscillators in a given coherence region of the liquid. The values for -24.5 °C ice and the amorphous solid are not much different than the -33 °C liquid, thus lending support to the liquid value. On the other hand, ice Ih at 90 K shows $N \simeq 14$ to imply extensive coherent intermolecular coupling which is ultimately expected as thermal disordering effects decline.

Intermolecular coupling of the OH oscillators dominates intramolecular coupling in the concentrated OH liquid near -33 °C. This is why these low temperature liquid spectra begin to assume the shapes of their crystalline counterparts. The dominance of intermolecular coupling in ice Ih has been suspected at least since 1960 by Haas and Hornig,[21] but only recently conclusively proven by Devlin who showed that the OH Raman spectra of intact H_2O molecules in D_2O ice Ih is very different from that of pure H_2O ice Ih.[22]

F. Trends as $T \rightarrow T_s$

We leave the subject of the interpretation of the OH band shape and again look at Fig. 1. From a purely empirical standpoint we see that the integrated intensity of the concentrated system rises steadily as T is lowered from $+160$ to -30 °C. Will the integrated intensity of the liquid extrapolate to that of polycrystalline ice Ih at the glass temperature, T_g (-140 °C) or at the singular temperature T_s (-45 °C)? In Fig. 1 we compare the relative intensity for frozen, polycrystalline H_2O, taken at -25 °C, with that of the liquid. Although it is difficult to obtain the ice Ih values with the same accuracy as in the liquid, the statistical evidence from three different capillaries used in seven different nucleation
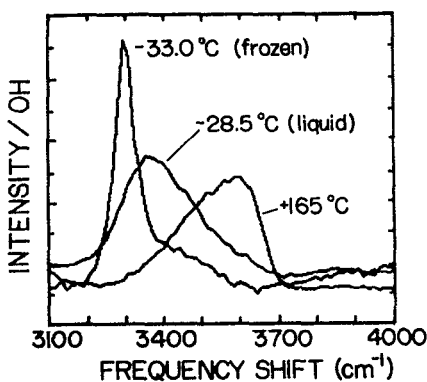
events clearly favors extrapolation of the liquid's intensity to that of ice Ih near T_s. This result agrees well with the known behavior of the function $C(T)$ representing that fraction of total OH intensity belonging to the in-phase collective mode.[11] This function in the liquid achieves its limiting value equal to that of ice Ih and the amorphous solid at T_s. The $C(T)$ measurements have the advantage over our integrated intensity in that the interpretation of what $C(T)$ represents and how it is connected to C_{ice} at T_s is relatively simple. However, the integrated intensity has the advantage of not requiring the necessarily somewhat subjective separation of the collective mode from the rest of the OH band which is required to obtain $C(T)$.

Figure 8 displays quantitative spectra for the dilute OH system at the lowest and highest liquid temperatures and the dilute ice Ih. There is clearly a trend in the peak frequency to decrease with decreasing T. At what T will this trend extrapolate to the ice Ih or amorphous solid value? We can also look for a possible trend in the full width at half maximum.

These trends are displayed in Fig. 9. The peak frequency of the liquid intersects the extrapolated amorphous solid value in the region of T_s, not T_g, and this agrees with the behavior of dilute OD oscillators in H_2O.[8] This gives further support to the idea that the liquid approaches the structure of the amorphous solid at T_s. In contrast, Green et al. state that the function $C(T)$ is the only vibrational spectroscopic property of water which tends to that of ice Ih or H_2O amorphous solid at $T \rightarrow T_s$.[11] In particular, they state that the peak of the in-phase collective intensity does not extrapolate to the amorphous solid value at T_s. We claim that the collective mode extrapolates to the amorphous value nearer to T_s than T_g. However, Green et al. first removed the collective band from the rest of the OH stretch spectrum and then measured the collective peak frequency whereas we simply measured the position of the low frequency maximum of intensity in the OH band without attempting deconvolution. Therefore, it is not surprising that our result deviates from theirs. It is more difficult to say whether the full width at half maximum of the dilute system's spectra will extrapolate to T_g or T_s, but its behavior is not inconsistent with extrapolation to the amorphous solid or ice value at T_s.
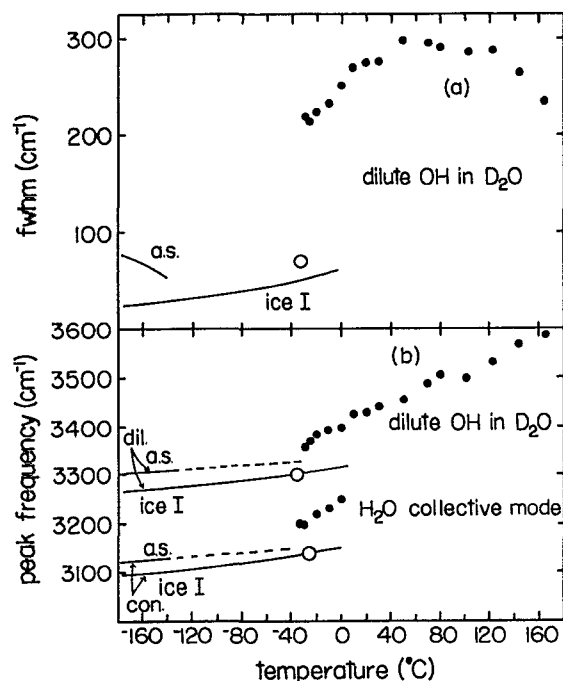
FIG. 9. (a) The full width at half maximum of the OH stretch band in dilute HOD in D$_2$O vs temperature. (b) The peak frequency of the OH stretch band for dilute HOD in D$_2$O vs temperature. The peak frequency of the collective mode in pure H$_2$O vs temperature. The data for the amorphous solid (AS) and ice Ih (except the open circles) were taken from Ref. 11.

G. The nonconstancy of the integrated intensity

The behavior of the integrated intensity of Fig. 1 is perhaps the most enigmatic feature of this paper. In our simplistic analysis of Raman intensity we saw that the mere process of vibrational delocalization by itself will not explain this behavior. Delocalization brings about the in-phase coherent Raman scattering of large groups of OH oscillators, causing large intensity in the collective mode, yet this extra intensity is taken from other modes in the OH band, conserving total OH band intensity. The same conclusion was reached by McGraw et al., stating that "the integrated (Raman) intensity of the OH stretching band in ice Ih is, within the harmonic approximation, independent of the oscillator coupling and equal to the sum of the integrated intensities of the uncoupled oscillators."[10] Thus although $I_R(\nu)$ is strongly dependent on N, the integrated intensity is not.

The liquid water systems at $+160\,°C$ and $-30\,°C$ are distinctly different in which case the change in OH bond polarizability during bond elongation $\partial\alpha/\partial r$ may be different in the high and low temperature liquid systems. Our data, which shows that the integrated intensity increases with decreasing temperature, suggest that $\partial\alpha/\partial r$ also increases with decreasing temperature. It is well known from infrared studies of H$_2$O in an N_2 matrix[23] and high temperature and pressure HOD studies[24] that the dipole moment derivative with respect to OH bond elongation $\partial\mu/\partial r$ increases by a factor of 3 on passing from vapor to liquid densities in water. Thus, it is certainly plausible that $\partial\alpha/\partial r$ is significantly effected by hydrogen bonding, which would ex-

plain why the integrated intensity is temperature dependent. However, this mechanism will not explain why the integrated intensity is different in the dilute and concentrated systems when both are at the same temperature.

How then can we understand the difference in the integrated intensity in the dilute and concentrated system at the same temperature? Perhaps the explanation is to be found in the theoretical work of Crawford, who indicated that the actual sum invariant for Raman scattering under isotopic substitution is not the integrated VV intensity of a single band, but rather the sum over all the fundamentals of the isotropic (VV-4/3 VH) intensity divided by the frequency.[25] We can understand Crawford's intensity sum invariant and its relevance to the OH band as follows: the integrated OH band intensity is invariant under isotopic substitution to the same extent that this band does not interact with the other fundamentals nor with pure rotation. For example, in an HOD molecule the ν_3 and ν_1 vibrations are well separated in frequency space, thus the higher frequency ν_3 vibration principally involves motion of the higher frequency OH group hence it is often called the OH stretch. Nevertheless ν_3 also involves vibration of the OD group with an amplitude much smaller than the OH group. As Herzberg suggested, we can view the HOD vibrations in terms of a complete normal coordinate analysis or alternatively as a free OH oscillator interacting with a free OD oscillator through a small harmonic coupling term in the framework of time-independent perturbation theory.[26] In H$_2$O water, the only fundamental of significant intensity is the OH band. Thus Crawford's sum would only involve the OH stretch. This is not true in the HOD system where Crawford's invariant is the sum of both OH stretch and OD stretch intensity. Crawford's invariant gives us two explanations of the discrepancy in dilute and concentrated integrated intensity at $-30\,°C$. One is that the dilute system's OH stretch looses intensity to its OD stretch band with increasing hydrogen bonding. This would explain nicely why the integrated OD intensity of dilute HOD in H$_2$O is found to increase at a significantly faster rate than the integrated OH intensity of dilute HOD in D$_2$O as temperature is lowered. The other possibility is that a comparison of isotropic integrated intensity would have yielded better agreement. It is possible that both of the above effects contribute considerably to the observed discrepancy.

IV. CONCLUSION

By comparing quantitative OH stretch spectra in both H$_2$O and isotopically decoupled dilute HOD in D$_2$O over a broad temperature range, we studied the effects of interoscillator coupling on the spectrum of liquid water. At high temperature both liquids have spectra which appear to be approaching the vapor spectra with a 100 cm^{-1} difference in peak positions due to intramolecular coupling. Even at $T = 160\,°C$, however, the effects of intermolecular coupling are seen as the liquid H$_2$O spectrum has a small intensity at frequencies greater than in the vapor indicating broadening due to this coupling. At low, supercooled temperatures, the large enhancement in intensity below 3200 cm^{-1} in H$_2$O over that in the decoupled HOD is ascribed to intermolecu-

lar coupling which both broadens the density of states so it can be nonzero at low frequencies and causes a large Raman cross section due to an in-phase OH stretch. It was argued that other explanations for this difference were not viable. We quantified the coupling by introducing the degree of delocalization, N, which measures the effective number of perfectly coherent OH oscillators over which the mode is delocalized. We found $N \simeq 2$ in liquid H_2O at -33 °C. This value is reasonable when compared to values for ice Ih, $N \simeq 3$ at -24.5 °C to $N \simeq 14$ at 90 K, and the amorphous solid, $N \simeq 3$. Exact isosbestics were not found; a result not surprising given the changes in line shapes brought about as the coupling changes with temperature. Finally, we found that the characteristics of the spectrum, such as peak position and total intensity, were all approaching solid like values and the temperature where this approach would be complete was roughly near the singular temperature, $T_s \simeq -45$ °C, where liquid water's properties appear to diverge.

ACKNOWLEDGMENT

[1] D. Eisenberg and W. Kauzmann, *The Structure and Properties of Water,* (Oxford University, London, 1969), p. 228.

[2] T. T. Wall and D. F. Hornig, J. Chem. Phys. **43**, 2079 (1965).

[3] G. E. Walrafen, J. Chem. Phys. **48**, 244 (1968).

[4] J. R. Scherer, M. K. Go, and S. Kint, J. Chem. Phys. **78**, 1204 (1974).

[5] R. Bansil, J. Wiafe-Akenten, and J. L. Taaffe, J. Chem. Phys. **76**, 2221 (1982).

[6] C. I. Ratcliffe and D. E. Irish, J. Phys. Chem. **86**, 4897 (1982).

[7] J. Wiafe-Akenten and R. Bansil, J. Chem. Phys. **78**, 7132 (1983).

[8] D. E. Hare and C. M. Sorensen, J. Chem. Phys. **93**, 6954 (1990).

[9] E. Whalley, Can. J. Chem. **55**, 3429 (1977).

[10] R. McGraw, W. G. Madden, M. S. Bergen, S. A. Rice, and Mark, G. Sceats, J. Chem. Phys. **69**, 3483 (1978).

[11] J. L. Green, A. R. Lacey, and M. G. Sceats, J. Phys. Chem. **90**, 3958 (1986).

[12] R. J. Speedy and C. A. Angell, J. Chem. Phys. **65**, 851 (1976).

[13] G. E. Walrafen, J. Chem. Phys. **47**, 114 (1967).

[14] G. E. Walrafen, M. S. Hokmabadi, and W.-H. Yang, J. Chem. Phys. **85**, 6964 (1986).

[15] D. E. Hare and C. M. Sorensen, J. Chem. Phys. **93**, 25 (1990).

[16] G. W. Chantry, in *The Raman Effect,* edited by A. Anderson (Marcel Dekker, New York, 1971), Vol. 1.

[17] G. Herzberg, *Molecular Spectra of Molecular Structure Vol. II, Infrared and Raman Spectra and Polyatomic Molecules* (Van Nostrand Reinhold, New York, 1945), p. 72.

[18] D. E. Hare and C. M. Sorensen (unpublished).

[19] P. A. Giguère, J. Raman Spectrosc. **15**, 354 (1984).

[20] E. Whalley (private communication).

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

[22] J. P. Devlin, J. Chem. Phys. **90**, 1322 (1989).

[23] M. Van Thiel, E. D. Becker, and G. C. Pimentel, J. Chem. Phys. **27**, 486 (1957).

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

[25] B. Crawford, Jr., J. Chem. Phys. **20**, 977 (1952).

[26] G. Herzberg, *Molecular Spectra of Molecular Structure Vol. II, Infrared and Raman Spectra and Polyatomic Molecules* (Van Nostrand Reinhold, New York, 1945), p. 217.