

Evidence for the importance of intermolecular coupling in the OD band's vibrational structure in deeply supercooled liquid D₂O

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We present the Raman spectrum of pure liquid D₂O at -27.0°C , 17°C lower than any previously reported Raman spectrum of liquid D₂O. The liquid's OD stretch band at -27.0°C displays a prominent feature which is clearly analogous to the ν_1 in-phase mode in D₂O ice Ih providing strong evidence that the structure of cold liquid D₂O's OD band is principally due to strong intermolecular coupling. Deeply supercooled liquid D₂O displays this ν_1 in-phase feature more clearly than deeply supercooled liquid H₂O due to the smaller disparity in the D/O mass ratio compared to that of H/O which enhances this coupling.

1. Introduction

The precise nature of the vibrational mode structure of the OH and OD stretching bands of liquids H₂O and D₂O, respectively, is still a matter of contention. Both of these bands display significant, highly polarized Raman intensity at their low-frequency limits [1,2]. This low-frequency feature is absent from the Raman spectra of the corresponding dilute OH and OD stretching bands [3,4] (e.g. dilute HOD in D₂O is the dilute OH system). The origin of this extra feature has at various times been attributed to strong intramolecular coupling [1], strong Fermi resonance with the bending overtone [5,6], strong intermolecular coupling [4,5,7] and the formation of strong linear hydrogen bonds vis à vis a bifurcated bond [8,9]. As late as 1987 and 1988 the strong linear hydrogen bond picture [9] and strong Fermi resonance picture [6], respectively, were being actively advocated, and to this day there is still dissent on the subject.

The proposition that intermolecular coupling was mainly responsible for the low-frequency polarized feature in the stretching bands of the isotopically pure liquid waters had its origin in the simpler problem of the structure of the corresponding bands of ice Ih. The proton disorder of ice Ih makes this substance

technically a non-crystalline solid, and thus not tractable by the standard lattice dynamics method. Wong and Whalley first proposed the correct assignment of the most prominent Raman feature in the ice Ih stretching band, the intense, relatively narrow, highly polarized feature at the low-frequency end of the band. [10] Their assignment was later confirmed and detailed by Whalley in a classic paper which assigned the stretching bands of ice Ih by careful analogy with the structure of ice VIII, which is proton ordered, and thus known from lattice dynamics [11]. This feature is the ν_1 in-phase vibration. Locally, each molecule executes the symmetric stretch. Globally, the vibration is delocalized, and neighboring molecules all execute this symmetric vibration in-phase with one another, hence the designation. Later theoretical calculations not only confirmed the nature of this mode, but also showed the paramount importance of intermolecular coupling to its structure [12,13].

The proposition that intermolecular coupling might also be an important factor in the isotopically pure liquid's vibrational structure goes back at least to the work of Wall and Hornig (1965) [14]. By 1983 there was substantial evidence that the polarized low-frequency edge of the liquid's stretching band was connected to intermolecular coupling effects [3]. How-

ever, it was Green, Lacey and Sceats who in 1986 suggested that the polarized low-frequency intensity in the liquid and the ν_1 in-phase mode in ice Ih were essentially the same thing [7].

In the Raman spectra of both H_2O and D_2O ice Ih, the ν_1 in-phase mode shows up as the most prominent feature in the OH and OD stretching band, respectively [11]. In the coldest liquid H_2O spectrum available (-33°C), the polarized low-frequency intensity shows up as a slightly protruding hump on the rest of the band [2]. The resulting resemblance is suggestive but not obvious. On the other hand, the features in both liquid D_2O and D_2O ice Ih are considerably sharper than those of the corresponding H_2O spectra at the same temperature [1,15]. This suggests that D_2O is in some sense more "waterlike" than H_2O , and for some purposes is the more profitable of the two systems to study. However, past measurements on pure D_2O have been limited to relatively high temperatures, due, perhaps, to the relatively high cost of D_2O and the elaborate and wasteful procedures necessary to prepare samples which will deeply supercool. To our knowledge, the lowest temperature previously attained for the Raman spectra of pure liquid D_2O in the OD stretch region was -10°C [1].

In this letter we will show conclusively that strong intermolecular coupling and the concomitant delocalization of the stretching vibration is responsible for much of the structure of this band in cold isotopically pure liquid water. We will compare the Raman spectra of D_2O liquid and D_2O ice Ih both at -27°C . This temperature is 17°C colder than any previously existent Raman data on liquid D_2O [1]. Our reasoning parallels the classic method of Whalley who assigned the mode structure of the OH band in ice Ih by careful analogy with that of the proton ordered ice VIII, which is well understood [11]. We also argue that the relative strengths of the low-frequency feature in D_2O and H_2O can be explained in terms of intermolecular coupling which is more effective in D_2O .

2. Experimental

The sample preparation method and Raman setup

have been described in detail elsewhere [2,16]. A brief overview is given here.

The samples were prepared by the heat treatment method. Five millimeter pyrex tubing was cleaned with a typical laboratory solution, then rinsed and boiled in distilled water. These tubes were then pulled into capillaries of roughly 1 mm inside diameter, then filled with liquid D_2O and sealed. The critical step is to then heat treat these samples at $+120^\circ\text{C}$ for 8 h followed by 2 h at $+160^\circ\text{C}$. We have found that high temperature water is a potent solvent for the heterogeneous nuclei (i.e. dust particles) which prevent deep supercooling when present in the sample. This process will prepare samples which will nucleate at their homogeneous nucleation temperature (the thermodynamically limited lower bound for supercooling) of -27 to -28°C , for D_2O , with a probability of $\approx 30\%$.

The best sample from a batch of 37 was mounted in the low temperature Raman cell. Excitation was accomplished with an Ar^+ laser operating at 4880 \AA with 100 mW of power. The VV or parallel polarization of the Stokes Raman OH stretch band was collected in the typical 90° scattering geometry. Spectral resolution was 15 cm^{-1} and temperature accuracy was better than $\pm 0.5^\circ\text{C}$.

3. Results

The spectra of pure liquid D_2O at $+25^\circ\text{C}$ and -27.0°C are overlaid with that of D_2O ice Ih at -27.5°C in Fig. 1. Equal integrated OD band intensities are assumed, reflecting the approximately temperature independent behavior of the integrated OD band intensity [4]. The most striking aspect of this spectrum is the clear emergence of an intense, highly polarized mode at the low-frequency end of the -27.0°C liquid's band. Although not very conspicuous at $+25^\circ\text{C}$, as can also be seen from fig. 1, this mode grows rapidly in prominence with decreasing temperature. The similarity between the liquid spectrum at -27.0°C and that of ice Ih at -27.5°C is more clearly enhanced by plotting both to have the same peak intensity, as in fig. 2. This latter figure emphasizes clearly the emergence of the ν_1 in-phase mode as a distinctive feature within the broad OD band of the deeply supercooled liquid. This promi-

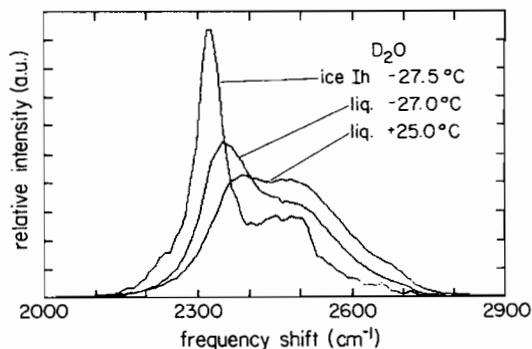


Fig. 1. The VV polarized Stokes Raman spectra of pure D₂O ice Ih (-27.5°C), and the liquid (-27.0 and $+25^{\circ}\text{C}$). All three spectra have been normalized to have the same integrated OD band intensity, approximately simulating their relative intensity behavior.

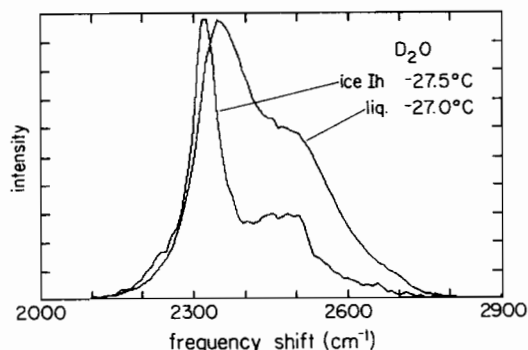


Fig. 2. The ice Ih and -27°C liquid spectra of fig. 1 renormalized to have the same peak heights. This figure emphasizes the strong similarities in the shapes of these two bands, hence in their structure also.

nent mode is very clearly the liquid's analog of the intense ν_1 in-phase mode of ice Ih. The nature of the ice ν_1 in-phase mode is now well understood as was previously mentioned. Intermolecular coupling is known to play a paramount role in the structure of this mode. Thus, very simply, fig. 2 clearly confirms the importance of intermolecular coupling and the presence of vibrational delocalization in the structure of the stretching band of liquid D₂O at low temperatures.

4. Discussion

The evidence for intermolecular coupling as the

predominant factor in the structure of the stretching bands of cold liquid H₂O and D₂O has not been so obvious before now because of the difficulties of preparing D₂O samples that would deeply supercool. Consequently, all of the previous body of work on deeply supercooled water has been with the cheaper and more plentiful, but less "waterlike" H₂O.

Why does deeply supercooled liquid D₂O seem to be more "waterlike" than liquid H₂O? The relationship between D₂O ice Ih and liquid spectra at -27°C is considerably more apparent than between the analogous set of H₂O spectra at its homogeneous nucleation temperature near -33°C [4]. Although one can see evidence of the ν_1 in-phase structure in liquid H₂O at -33°C , it is much less striking and obvious than that which the liquid D₂O displays at -27°C . It is tempting to attribute this to the known ability of OD groups to form slightly stronger hydrogen bonds than OH groups. On the other hand, the homogeneous nucleation temperature for H₂O is 5°C colder than liquid D₂O, and this is in fair correspondence with the difference in the melting (triple) points of the two substances ($+0.01$ and $+3.83^{\circ}\text{C}$ for H₂O and D₂O, respectively) [17], temperatures of maximum density ($+3.984$ and $+11.185^{\circ}\text{C}$ for H₂O and D₂O, respectively) [18], and their respective singular temperatures (-45 and -40°C for H₂O and D₂O, respectively) [19]. This suggests that the slightly stronger OD hydrogen bonding at a given temperature is just compensated for by the deeper supercooling attainable in the H₂O liquid. Thus liquid D₂O at -27°C and liquid H₂O at -33°C have about the same degree of hydrogen bonding and therefore the greater band structure of the former system cannot be attributed to stronger hydrogen bonding.

Consider the following possibility: Notice that each OD group must couple to another OD group through the motion of at least one oxygen nucleus. If the mass of the oxygen nucleus became infinitely large in comparison to that of deuterium then the two deuterium atoms cannot couple together because they cannot move the infinitely massive particle, and thus have no way to influence each other's motion. Clearly the ratio of the masses of the light to the heavy nuclei plays a role in the effectiveness of the coupling. Because the D/O mass ratio is only 8 as opposed to 16 for the H/O mass ratio, the OD oscillators are able

to couple more effectively to each other. In liquid water, the effect of coupling, which creates mode structure, is in competition with the liquid's lack of order, which acts to destroy this mode structure. Thus the greater coupling in D₂O results in more distinctive mode structure in comparison to H₂O. This greater prominence of the low-frequency feature in D₂O compared to H₂O at different temperatures such that the extent of their hydrogen bonding is the same is further evidence that this feature is due primarily to intermolecular coupling.

5. Conclusion

The OD stretching band of deeply supercooled liquid D₂O at -27°C has a structure very similar to that of D₂O ice Ih. Intermolecular coupling of OD groups is the dominant factor affecting the OD band's structure in D₂O ice Ih, and thus we infer that it is the dominant factor in deeply supercooled liquid D₂O as well. In particular, the ν_1 in-phase mode character of the low-frequency end of the liquid's OD band becomes clearly evident at -27°C . The more ice-like appearance of the cold liquid D₂O spectrum in comparison to that of H₂O is due to the smaller disparity in D/O mass compared to H/O mass, which affects the ability of the OD or OH groups to vibrationally couple together.

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