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The Raman Spectrum of Ice XII and Its Relation to that of a New "High-Pressure Phase of H₂O Ice"

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By comparison of Raman spectra we propose that the new "high-pressure phase of H₂O ice" reported by Chou et al. (*Science* **1998**, *281*, 809) is in fact ice XII. Pure ice XII was prepared in a reproducible manner on heating high-density amorphous ice (HDA) at a pressure of 0.81 GPa up to ≈180 K at a rate of 25 K min^{-1}, quenching thereafter to 77 K, and recovering the sample under liquid N₂ at 1 bar. Recovered ice XII was characterized by X-ray diffraction and it was free of HDA, of low-density amorphous ice, and of ice IV. H₂O ice XII containing 11 mol % HOD and D₂O ice XII with 9.0 mol % HDO were studied by Raman spectroscopy between 80 and 150 K. The decoupled O−D (O−H) stretching band in H₂O (D₂O) ice XII consists of a nearly symmetric band, slightly skewed at low frequency, which is centered at 80 K at 2473 (≈3340) cm^{-1}, with full-width at half-height (fwhh) of 44 (≈80) cm^{-1}. At low frequency a broad band at ≈470 (≈360) cm^{-1} and a sharp band at 195 (190) cm^{-1} are assigned to the librational and translational mode in H₂O (D₂O) ice XII. The main feature of the decoupled O−D stretching band is attributed to the hydrogen bonds with O−D−O distance of 2.803 Å and multiplicity 6 obtained from neutron diffraction. The second O−D−O distance of 2.766 Å with multiplicity 2 is expected to give a decoupled O−D component peak separated only ≈28 cm^{-1} from the main peak. These two component bands would appear as distinct peaks only when their fwhh is small, that is when ice XII is proton ordered. However, the composite band shape is consistent with large fwhh and proton disorder in ice XII. We did not observe indication for formation of an amorphous phase as intermediate on the ice XII→cubic ice phase transition, which is consistent with our previous X-ray diffraction study. However, our results are in conflict with a recent report of the Raman spectrum of ice XII and of "formation of amorphous ice on careful annealing of ice XII" by Tulk and Klug (*Phys. Rev. B* **2001**, *63*, 212201−1).

Introduction

The polymorphic forms of ice illustrate the structural variety possible for the hydrogen-bonded polymers of four-coordinated water, and studies of the water/ice phase diagram and of the crystalline phases of ice, in which the water molecules form tetrahedral networks by hydrogen bonding, are important not only for further understanding of the hydrogen bond itself, but also for its relevance in the interaction of water molecules with biological structures.[1] The recent discovery of a new phase of ice, crystallizing in the much investigated medium-pressure range,[2] came as a surprise. This new high-pressure phase of ice, called ice XII, was first prepared and characterized by Lobban et al.,[3] by slow crystallization from the liquid phase at 260 K at a pressure of 0.55 GPa, which is within the stability

region of ice V.[2] Ice XII "contains only seven- and eight-membered rings and is the first example of a 4-connected net of this type".[4] In the same year Chou et al.[5] reported a new "High-Pressure Phase of H_2O Ice" in the ice VI domain, at 0.7 to 1.2 GPa and 3 to 26 °C. They speculated on the relation of their new phase to ice XII reported by Lobban et al.[3] but, because of the lack of data, could not confirm it or rule it out (note 24 in ref 5). Subsequently to form ice XII from the liquid phase,[3] Koza et al.[6] reported formation of ice XII in a completely different region of water's phase diagram, namely as an incidental product in the preparation of high-density amorphous ice (HDA)[7−10] at 77 K on compression of hexagonal ice (ice Ih) up to 1.8 GPa. Kohl et al.[11] then showed that by this route ice XII forms on compression of ice Ih at 77 K only via HDA, and not directly from ice Ih, and that its formation requires a sudden pronounced pressure drop at pressures $\approx \geq 1.1$ GPa. They further proposed that "shock-waves generated by the pressure drops cause transient local heating up to the temperature range of the ice V domain, and that this induces nucleation and crystal growth of ice XII". It follows that the apparent observation of a "second regime of metastability" of ice XII postulated by Koza et al.[12] between 77 to $\approx$150 K and 1.0 to 1.8 GPa in order to account for its unexpected formation at low temperatures (see Figure 1 in ref 12) seems to be an effect of pressure drops and shock-wave heating during compression of ice Ih. Ice XII is metastable with respect to ice V,[13] like metastable ice IV which is also found within the stability region of ice V,[2,14−16] and its density is similar to that of ice IV.[3] Ice XII can be prepared in a reproducible manner, without contamination by HDA and low-density amorphous water (LDA), by isobaric heating of HDA kept at pressures between $\approx$0.7−1.5 GPa.[17] HDA transforms in this pressure range on heating from 77 K directly into ice XII, and between $\approx$158−212 K it has an extended region of (meta)stability before its phase transition to other high-pressure phases (see Figure 1 in ref 17). Recently Tulk and Klug[18] reported in a Raman spectroscpcic study "formation of amorphous ice on careful annealing of ice XII".

Here we report the Raman spectra of pure H_2O ice XII containing 5 wt % D_2O and of D_2O ice XII containing 5 wt % H_2O, which were recorded in vacuo between 80 and 150 K. Thus, the decoupled O−D (O−H) stretching transition of HOD molecules in a dilute solution of H_2O (D_2O) ice XII crystals can be used as a probe for hydrogen bonding with neighboring molecules and for hydrogen-bonded O−H−O (O−D−O) distances.[19−22] We did not observe indication for formation of an amorphous phase as intermediate in the ice XII→cubic ice (ice Ic) phase transition. This is consistent with our previous study of the ice XII→ice Ic phase transition by X-ray diffraction,[13] but it is in conflict with the recent report of "formation of amorphous ice on careful annealing of ice XII".[18] By comparison of Raman spectra we propose that the new "high-pressure phase of H_2O ice" reported by Chou et al.[5] is in fact ice XII.

Experimental Section

The procedure for preparing ice XII on isobaric heating of HDA is described in ref 17). Briefly, 0.300 cm³ of either D_2O water (from Aldrich, No. 15,188-2, 99.9 atom % D) containing 5.0 wt % H_2O, or of deionized H_2O water with 5.0 wt % D_2O, was pipetted into a precooled piston-cylinder apparatus with 8-mm diameter piston. HDA was then made by compression of ice Ih at 77 K up to 1.6 GPa by using a computerized "universal testing machine" (Zwick, Model BZ100/TL3S) for compression at a rate of 7000 N min⁻¹. Its positional reproduc-

ibility is ± 5 μm, and the spatial resolution of the drive is 0.01 μm. Pressure-displacement curves were recorded with the TestXpert v7.1 software of Zwick. Indium linings were used as decribed in ref 11 to avoid pressure drops during compression. The pressure-displacement curves have the same shape as that shown in Figure 1a of ref 11 and those reported, e.g., by Mishima et al.[7,8] The plateau region indicates the phase transition of ice Ih to HDA. HDA was then transformed into pure ice XII on isobaric heating to $\approx$180 K at a pressure of 0.81 GPa and at a rate of 25 K min⁻¹.[17] The sample was quenched to 77 K, the pressure released at 77 K and ice XII recovered under liquid N_2 and 1 bar. Recovered ice XII was characterized by X-ray diffraction as shown in Figure 1a (ref 11).

Raman spectra were recorded on a Labram-1B spectrometer equipped with a microscope (from Dilor company), through an ULWD-50 objective (from Olympus company), by coadding three or four sets of spectra over $\approx$10 min. A He−Ne Laser with 632.8 nm wavelength was used, and the 1800 L/mm grating provides a resolution of $\approx$2 cm⁻¹. The abscissa was calibrated with a silicon standard, and the sharp Raman shifts are accurate to ± 2 cm⁻¹. The intensities of the bands are not shown on the same scale. The Oxford Microstat was used as cryostat. Temperature was regulated with a LakeShore CI330 autotuning temperature controller and was kept constant within ± 0.2 K. Spectra were recorded in vacuo at $\approx$10 mbar.

X-ray diffractograms were recorded on a diffractometer in $\theta-\theta$ geometry (Siemens, model D 5000, Cu-Kα), equipped with a low-temperature camera from Paar. The sample plate was in horizontal position during the whole measurement. Installation of a "Goebel mirror" allowed to record small amounts of sample without distortion of the Bragg peaks.

Results and Discussion

Our major effort was to prepare ice XII without impurities such as HDA, or ice IV. This turned out to be important because when a Raman spectrum of an inhomogeneous sample is recorded through a microscope, the laser beam is highly focused and high spatial resolution in the μm range is obtained.[23] Thus, the Raman spectrum depends on where the sample had been excited, and such Raman spectra cannot easily be related to an average obtained by, e.g., diffraction. Because of that we show first in Figure 1 X-ray diffractograms of pure ice XII (a), and of ice XII containing a small amount of ice IV (b). Open circles indicate the Bragg peaks of ice IV,[16] and its relative amount is estimated by integration of peak areas to be $\approx$16%. Bragg peaks marked with asterisks are from a small amount of ice Ih condensed onto the sample during the transfer. The d spacings of ice XII are about the same as those reported by Lobban et al.[3] and by Koza et al.[6] In our experience, even this minor ice IV impurity can generate Raman spectra where the decoupled O−D stretching band transition is either that of pure ice XII, of pure ice IV, or of a mixture of XII and ice IV. Thus, preparation of ice XII without ice IV contamination, as shown in Figure 1a, was crucial for unambiguous assignment of the Raman peaks. The Raman spectrum of ice IV, which was recorded as a byproduct in this study, will be reported separately.

Figure 2 shows three spectral regions of the Raman spectra of H_2O ice XII containing 9.0 mol % HOD (top), and of D_2O ice XII containing 11 mol % HOD (bottom). These solutions were obtained from 5.0 wt % D_2O in H_2O, and from 5.0 wt % H_2O in D_2O.[19,20] The spectra were recorded at 80 K and 10 mbar. Spectra (a) and (d) (left) show the coupled O−H (O−D) stretching transition region with the peak maximum at 3209 (2364) cm⁻¹ and two shoulders at $\approx$3310 and $\approx$3415 ($\approx$2494

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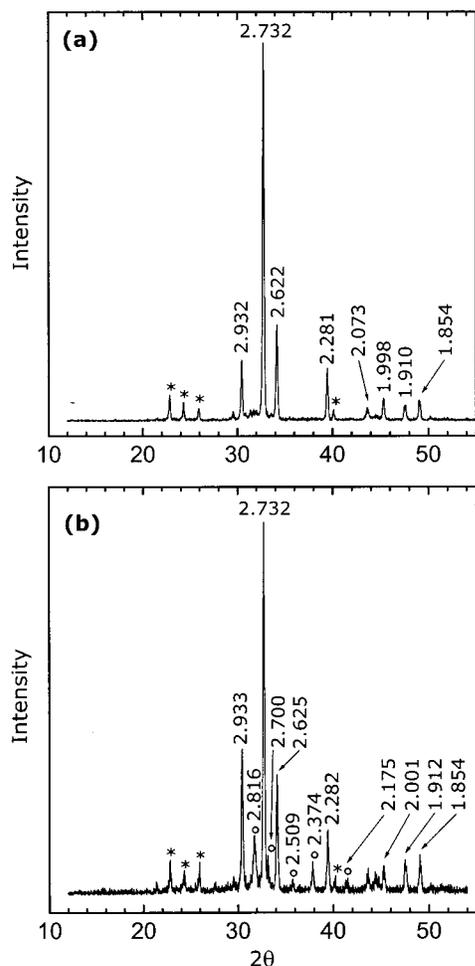*J. Phys. Chem. B, Vol. 106, No. 1, 2002* **3**

Figure 1. (a) X-ray diffractogram (Cu-Kα) of a pure ice XII sample with *d* spacings in Å, and (b) of an ice XII sample containing a small amount of ice IV (marked by open circles). The samples were recovered after decompression under liquid N_2 and diffractograms recorded at 80 K. Bragg peaks of ice Ih from condensation of water vapor during the transfer of the sample are marked with asterisks.

and ≈2527) cm^{-1}. Spectra (b) and (e) (middle) show the decoupled O–D (O–H) stretching transition with peak maximum at 2473 (≈3340) cm^{-1}. The low-frequency region (c and f, right) contains peaks at ≈470 and 195 cm^{-1} for H_2O ice XII, and at ≈360 and 190 cm^{-1} for D_2O ice XII. The sharp band at 195 (190) cm^{-1} in H_2O (D_2O) ice XII seems to be asymmetric and possibly contains a shoulder at high frequency. Other weak features are a shoulder at ≈553 cm^{-1} in H_2O ice XII (c), and a weak broad feature centered at ≈570 cm^{-1} in D_2O ice XII (f). Two sharp lines marked by asterisks at 180.4 and 136.1 cm^{-1} are plasma lines.

The ratio of the peak frequencies of the coupled O–H/O–D and decoupled O–H/O–D stretching bands is close to the square root of 2 (1.351 and 1.357), as expected for motions determined primarily by the hydrogen nuclei.[19–21] Likewise, the H_2O/D_2O peak frequency ratio of the broad band at ≈470 cm^{-1} for H_2O and at ≈360 cm^{-1} for D_2O is close to $2^{1/2}$ (1.31), which allows its assignment to a librational mode. The H_2O/D_2O peak frequency ratio of the sharp peak centered at 195 cm^{-1} for H_2O and at 190 cm^{-1} for D_2O is 1.03. This is close to the square root of the ratio of molecular masses, $(20/18)^{1/2}$ (= 1.05). It shows that this mode involves the motion of whole water molecules and that it must be assigned to the translational mode.[21] The intense sharp coupled O–H (O–D) stretching band centered at 3209 (2364) cm^{-1} (a and d) is polarized (not shown).

Therefore, it is the in-phase O–H (O–D) bond stretching mode that is essentially caused by the symmetric vibration of an H_2O (D_2O) molecule coupled nearly in phase with neighboring H_2O (D_2O) molecules.[2,24]

Figure 3 shows how the decoupled O–D stretching transition of HOD in H_2O ice XII (right) and the coupled H_2O stretching transition (left) develop on heating from 80 K up to 150 K. The spectra were recorded at 80 K after heating the sample at a rate of ≈ 2 K min^{-1} and keeping it at each temperature for 2 min for thermal equilibration. In the decoupled O–D stretching transition region (right), only one broad band is observable between 80 and 130 K: its peak frequency increases on heating from 2473 cm^{-1} at 80 K (marked by dotted line) to 2477 cm^{-1} at 130 K, but its full width at half-height (fwhh) remains constant at ≈44 cm^{-1}. The sharp peak maximum of the coupled O–H stretching band shifts on heating from 3209 cm^{-1} at 80 K (marked by dotted line) to 3220 cm^{-1} at 130 K. On further heating to 140 K, a second peak develops on the low-frequency side that is attributed to ice Ic. This is clearly seen in the coupled O–H stretching transition region and is marked by the second dotted line. Phase transition of ice XII to ice Ic is complete at 150 K. The peak frequency of the decoupled O–D stretching transition of ice Ic centered at 2425 cm^{-1} agrees with that reported in the literature.[20,25] Its fwhh of ≈30 cm^{-1} is the value obtained by Bertie and Whalley,[20] but larger than that reported by Devlin et al.[25] Thus, for this HOD concentration O–D O–D interactions contribute somewhat to the fwhh of the decoupled O–D stretching transition.[19]

Tulk and Klug[18] recently reported the Raman shift of the decoupled O–D stretching band of ice XII recorded at 120 K and 1 bar as 2424 cm^{-1}. In their study ice XII had not been characterized by diffraction, but its formation on pressurization of ice Ih to 1.8 GPa at 77 K had been inferred from the measured Raman shift and from exclusion of other high-pressure ices. This peak frequency is clearly different from our value of 2477 cm^{-1} recorded at 130 K (see Figure 2b and Figure 3). The difference of 53 cm^{-1} is much more than the experimental error and excludes in our opinion that ice XII had been studied in ref 18. We do not know which ice phase had been formed under these conditions. Although the decoupled O–D peak frequency of the phase is close to that of ice Ic,[20,25] it is apparently not ice Ic because the band transforms on heating into a broader band.[18] It can be characterized once its diffraction pattern is known.

We emphasize that we did not obtain any indication for phase transition of ice XII to an amorphous phase (LDA) before its conversion to ice Ic. This is consistent with our previous study of the ice XII→ice Ic transition by X-ray diffraction,[13] but it is in conflict with the recent report of "formation of amorphous ice by careful annealing of ice XII",[18] where formation of amorphous ice was inferred from broadening of the decoupled O–D stretching band when keeping the sample at 120 K.

Neutron diffraction studies show that D_2O Ice XII contains two types of O–D–O hydrogen bonds, with distances of 2.803 and 2.766 Å and multiplicities of 6 and 2 (Table 2 in ref 3), and that the hydrogen atoms are considered to be positionally disordered. The decoupled O–D (O–H) stretching transition of HDO in a dilute solution in H_2O (D_2O) ice XII crystals may be used as probes to test for various molecular environments in an H_2O (D_2O) crystal.[19–21] The peak frequencies of decoupled O–D (O–H) stretching vibrations are determined largely by variations in the static perturbations they experience, and, in ice, hydrogen bonds to neighboring molecules account for most of this perturbation.[21] The dominant parameter in determining
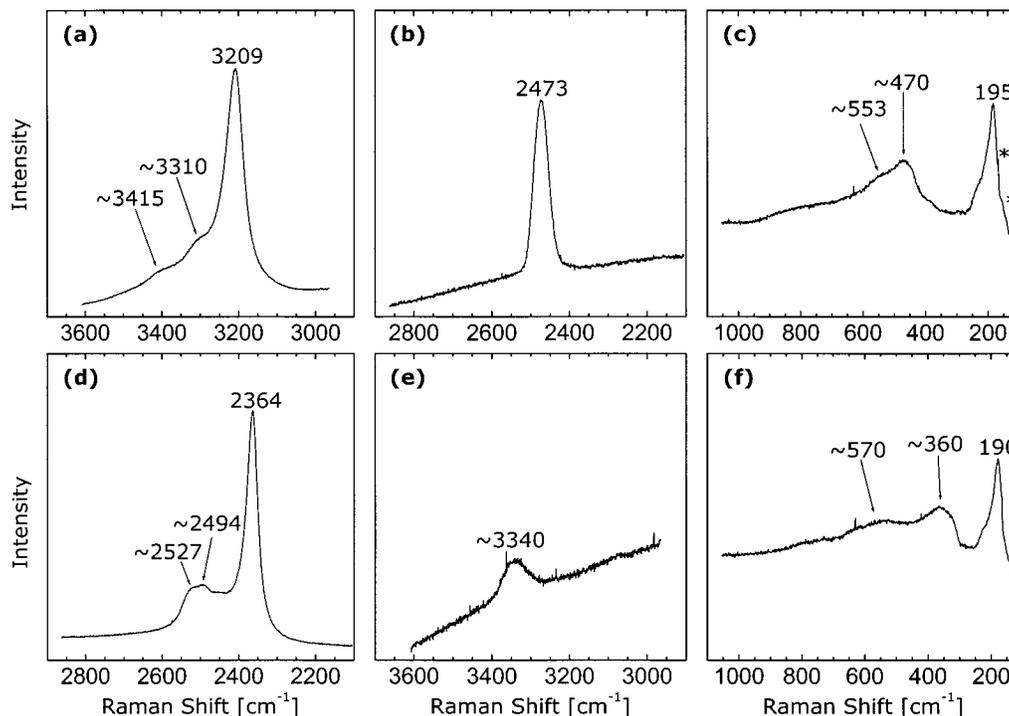
Figure 2. Raman spectra of ice XII recorded at 80 K. On top are shown three spectral regions of H_2O ice XII containing 9.0 mol % HOD, and below the corresponding spectral regions of D_2O ice XII containing 11 mol % HOD. Left: the coupled O−H (O−D) stretching transition region with the peak maximum at 3209 (2364) cm^{-1}; middle: the decoupled O−D (O−H) stretching transition with peak maximum at 2473 ($\approx$3340) cm^{-1}; right: the low-frequency region with peaks at $\approx$470 and 195 cm^{-1} for H_2O ice XII, and at $\approx$360 and 190 cm^{-1} for D_2O ice XII. Two sharp lines at 180.4 and 136.1 cm^{-1} (marked by asterisks) are plasma lines. The ordinate scale differs for each spectral region.
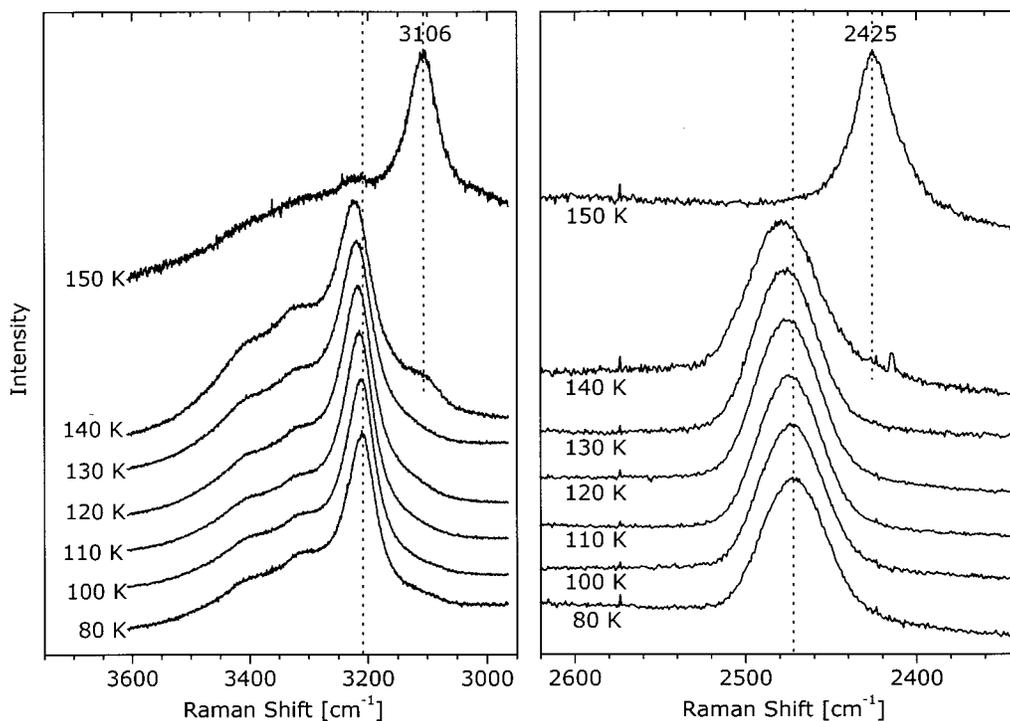

Figure 3. The temperature dependence of the peak frequency of the decoupled O−D stretching transition of H_2O ice XII containing 9.0 mol % HOD, and the transition to cubic ice. The spectra are shown on the same ordinate scale, but are shifted vertically for clarity.

the peak frequency of an uncoupled O−D (O−H) stretching band is the O−H−O (O−D−O) bond length, and several correlations have been reported (reviewed in ref 26).[22] The bandwidth also contains information about environments of the HDO molecules. For example, the fwhh of an uncoupled O−D stretching transition in proton-ordered H_2O ice II is only $\approx$5 cm^{-1}, but it is $\approx$30 cm^{-1} in disordered ice I.[20,21] This had been

attributed by Bertie and Whalley[20] to disorder in the positions of the oxygen atoms in ice I and confirmed subsequently in neutron diffraction studies by Kuhs and Lehmann (reviewed in ref 26).

The decoupled O−D stretching transition region shown in Figures 2 and 3 consists of one band only, which seems slightly asymmetric, skewed toward low frequency. Band narrowing via
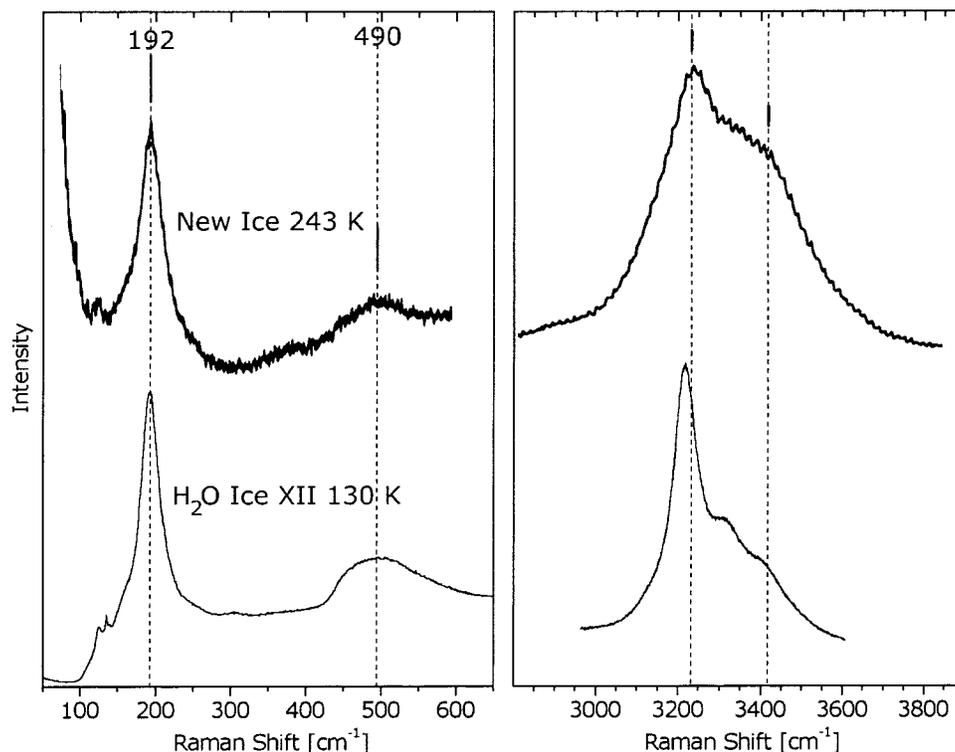
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Figure 4. Comparison of the (top) Raman spectrum of a new "high-pressure phase of H_2O ice" reported by Chou et al.[5] in their Figure 4 and recorded at 243 K and 0.7−1.2 GPa; (bottom) with the Raman spectrum of H_2O ice XII recorded at 130 K in vacuo. In the O−H stretching band region (top), two positions are marked and given in ref 5 as 3215 and 3410 cm^{-1}. However, according to the reported abscissa these two positions seem to be at slightly higher frequency.

second derivative curves or deconvolution did not indicate a second feature attributable to a second O−D−O hydrogen bond distance. However, the fwhh of this band of ≈ 44 cm^{-1} is fairly large and could be a superposition of two bands from the two types of O−D−O hydrogen bonds with multiplicity 6 and 2. Several correlations have been proposed for estimation of the O−D−O (O−H−O) distance from the peak frequency of the decoupled O−D (O−H) stretching mode (reviewed in ref 26). A correlation based on extensive ice VII data was proposed by Tulk et al.[22] and is used here (eq 1),

$$\nu_{OD} = 2782.1 - 1560.1 \exp(-R/1.474) -$$
$$269251.6 \exp{-(R/0.9938)}^2 \quad (1)$$

where ν_{OD} is the decoupled O−D peak frequency and R the mean O−D−O distance. This relation gives 2.831 Å for the ν_{OD} value of 2473 cm^{-1}. Although this is larger than the 2.803 Å distance with multiplicity 6 obtained from neutron diffraction,[26] we assign the main feature of the peak to this type of hydrogen bond, the difference apparently reflecting the error in this simplified correlation and similar ones listed in ref 26. This then raises the question whether the second type of hydrogen bond, with 2.766 Å distance and multiplicity 2,[26] is observable in the decoupled O−D stretching band region. Calculation of ν_{OD} via eq 1 from the 2.803 and 2.766 Å distances gives 2455 and 2427 cm^{-1} as peak positions. Even when these values are not correct, as pointed out above, their difference of 28 cm^{-1} could be a fairly good estimate. For spectra of low signal-to-noise ratio, reliable resolution of overlapping bands into the component bands requires that separation of peak maxima is larger than the average fwhh.[27−30] It follows that the decoupled O−D band can only be separated into its two component bands when their fwhh is less than ≈ 28 cm^{-1}. This is unlikely for a proton-disordered ice phase, as a fwhh of

≈ 30 cm^{-1} had been observed in disordered ice I containing the same amount of D_2O as in this study.[20,21] The decoupled O−D band shown in Figure 2 seems to be slightly asymmetric, skewed at low frequency, which is consistent with a second weak component band at low frequency. Separation into component bands is possible even for highly overlapping bands such as the decoupled O−D stretching transition when spectra of very high signal-to-noise ratio are available. These can be obtained by Fourier transform infrared spectroscopy, and Fleissner et al.[30] show that reliable curve resolution of highly overlapping bands is possible by comparison of fourth-derivative curves.

We finally discuss whether the new high-pressure phase of H_2O ice reported recently by Chou et al.[5] is in fact ice XII. This "previously unknown solid phase of H_2O has been identified by its peculiar growth patterns, distinct pressure−temperature melting relations, and vibrational Raman spectra".[5] Formation of a new high-pressure phase of H_2O ice at 0.7 to 1.2 GPa was inferred mainly by comparison of its Raman spectrum with those of other high-pressure ices (see Figure 4 in ref 5). For lack of data it was difficult so far to speculate on the relation of this new phase of ice to ice XII (note 24 in ref 5). Until now its Raman spectrum could not be compared with that of ice XII, and its diffraction pattern had not yet been reported. This has changed with our report of the Raman spectrum of ice XII.

In Figure 4 we compare the Raman spectrum of the new high-pressure phase of H_2O ice reported by Chou et al.[5] (top, recorded at 243 K and 0.7−1.2 GPa) with that of H_2O ice XII (bottom, without D_2O, recorded at 130 K in vacuo). The correspondence at low frequency (left) between the two Raman spectra is remarkable and, since the low-frequency region is very characteristic for the type of high-pressure ice, is a strong support that the new high-pressure phase is in fact ice XII. In particular,

observation of only one band in the translational region is very characteristic because the other high-pressure ice phases have several bands in this region (see Figure 4 in ref 5).

The comparison of the coupled O−H stretching band region (right) is not as convincing, and pronounced differences exist with respect to overall band shape and resolution of the shoulders. These could be caused by the difference in temperature and/or pressure, and ideally the comparison should be made with the Raman spectrum of a sample of the new high-pressure phase recovered under liquid N_2 and atmospheric pressure. In particular, the fwhh of the coupled symmetric OH stretching band in ice Ih increases markedly with increasing temperature,[31] and the Raman spectrum of ice Ih recorded close to the melting temperature is remarkably similar to the broad and relatively featureless Raman spectrum of vapor-deposited amorphous solid water recorded at 90 K.[32,33] Similar effect of temperature on the OH stretching band region seems possible for ice XII. The pronounced effect of pressure and temperature on the shape of the decoupled O−D stretching transition in proton-disordered ice VI is further demonstrated in Figure 4 of ref 34. The increase of the OH stretching peak frequency with increasing temperature (Figure 4, broken line) is consistent with that reported for ice Ih.[31,35] The peak maximum of the OH stretching band region (Figure 4, top), given in ref 5 as 3215 cm^{-1}, agrees nicely with the peak value of 3217 cm^{-1} observed in our study (Figure 4, bottom). We therefore propose that the new "high-pressure phase of H_2O ice" is in fact ice XII. Its melting curve depicted in Figure 1 of ref 5 thus extends the metastability region of ice XII from the ice V domain[3] to higher pressures into the ice VI domain. We note that molecular dynamics simulations can produce a "quartzlike polymorph of ice" under pressures of 0.3−0.5 GPa and at temperatures of 225−240 K.[36]

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