# Effect of Pressure on Infrared-Spectra of Ice VII

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The effect of pressure on the infrared spectra of $H_2O$ and $D_2O$ ice VII has been studied at room temperature and pressures between 2 and 15 GPa with a Fourier transform infrared spectrometer and a diamond anvil high-pressure cell. Two librational modes ($v_R E_u^2$ and $v_R E_u^3$), one bending mode ($v_2 A_{2u}^1$), and various overtone bands are well resolved. The stretching modes, $v_1$ and $v_3$, are poorly resolved due to overlap with diamond window absorption. Although $v_R E_u^3$ shows a very strong shift to higher frequency with pressure, $v_1$ and $v_3$ shift to lower frequencies, and all other lines vary only slightly with pressure. Differences between the spectra of $H_2O$ and $D_2O$ are discussed.

## INTRODUCTION

Liquid water and the ices are of interest for understanding the structures of several large icy bodies in the solar system [Schubert et al., 1981; Stevenson, 1982], as well as fundamental aspects of hydrogen-bonded systems [Whalley, 1976]. Among the ices, ice VII and VIII have especially simple structures that have been studied by X rays [Kamb and Davis, 1964; Weir et al., 1965; Holzapfel and Drickamer, 1968; Kamb, 1969; Olinger and Halleck, 1975; Walrafen et al., 1982] and Raman spectroscopy, both at high pressures [Holzapfel et al., 1975; Hirsch and Holzapfel, 1982; Walrafen et al., 1982; K. R. Hirsch, personal communication, 1982] and, for ice VIII, quenched at low temperatures near atmospheric pressure [Marckmann and Whalley, 1964; Wong and Whalley, 1976]. These methods also can be useful for identifying ices in laboratory studies of phase equilibria relevant to the icy objects. However, for many purposes, other analytical techniques such as infrared spectroscopy are more appropriate. As far as we know, infrared spectra have been reported only for the liquid [Haas and Hornig, 1960]; ice I [Haas and Hornig, 1960; Bertie et al., 1969]; a few low-pressure phases that were not identified [Lippencott et al., 1960]; and quenched samples of ice II, III, IV, V, VI, and IX [Bertie and Whalley, 1964; Bertie and Bates, 1977; Englehardt and Whalley, 1979]. The spectra of ice VII and VIII are unknown, and little is known about spectra of other ices under pressure. Such circumstances motivated this study of the infrared spectra of ice VII under high pressure.

The high symmetry of ice VIII, space group $I4_1/amd$ ($D_{4h}^{19}$) with proton ordering, makes its Raman and infrared spectra mutually exclusive. The mutual exclusion rule does not hold for ice VII if one considers the average structure, that is, if the O atoms occupy a body-centered cubic lattice, $Im3m$ ($O_h^5$), and the four protons occupy 16 equivalent sites along the body with equal probability [Kamb, 1969]. However, close similarities of the Raman spectra of ice VII and VIII [Whalley, 1977; K. R. Hirsch, personal communication, 1982] show that strong correlations and short-range order persist in ice VII, at least near room temperature ($22° \pm 4°C$), where these spectra were recorded; thus little information about the infrared-active modes can be obtained from the Raman spectra of ice VII. These observations suggest instead that the infrared spectra of ice VII and VIII will also be similar. Thus for this first IR absorption study of ice under very high pres-

sures, we considered only ice VII in order to avoid the additional problems related to cooling of the high-pressure cell in the spectrometer sample compartment [Hirsch and Holzapfel, 1981].

## EXPERIMENTAL

A Bassett-type [Bassett et al., 1967] diamond anvil high-pressure cell, with 0.6-mm culet Type IIa diamonds and Inconel gaskets [Block and Piermarini, 1976] was used for these studies. The sample of distilled $H_2O$ or, in some runs, 99.8% $D_2O$ was injected into the central 300-$\mu$m diameter hole of the gasket by means of a syringe. Also included in the hole were one to three ruby grains so that the pressure could be monitored by the ruby luminescence method [Block and Piermarini, 1976], the factor, 0.365 nm/GPa, was used to convert the shift of the $R_1$ ruby luminescence line to pressure. The initial thickness of the prepressed gasket was typically 30 $\mu$m; however, in some runs, the thickness was reduced to as little as 10 $\mu$m, which crushes the ruby. The diamond cell was adapted to the sample compartment of a commercial Fourier transform-infrared (FTIR) spectrometer (Nicolet MX-1) by a translational stage with which it could be precisely positioned in the plane perpendicular to the optical axis of the instrument. The alignment of the cell was checked carefully for each spectrum by maximizing the intensity of the calibration laser, which also passed through the diamond cell.

A typical FTIR spectrum of the empty high-pressure cell is represented in Figure 1. This spectrum shows the well-known structure of the absorption of type IIa diamonds [Adams and Sharma, 1977] and a transmission of 0.04% in the 500–1500 $cm^{-1}$ region. The steep increases in transmission on both ends of this FTIR spectrum are artifacts of the Fourier transform technique. The low transmission relative to the empty spectrometer is caused primarily by the very small diameter ($< 300 \mu$m) of the hole in the Inconel gasket, which acts as a pinhole for the transmitted beam. Additional losses result from the limited aperture of the diamond cell structure and from reflections at the diamond-air and diamond-sample interfaces.

A reasonable signal-to-noise ratio for background spectra, such as that shown in Figure 1, as well as for the sample spectra, could be obtained by setting the resolution of the spectrometer to the largest bandpass, 16 $cm^{-1}$, and by sampling and integrating for four hours. Longer exposure times with this sample and spectrometer enhanced artifacts in the spectra that are not visible in Figure 1 but probably result from overflow in the memory of the FTIR computer. Perfect
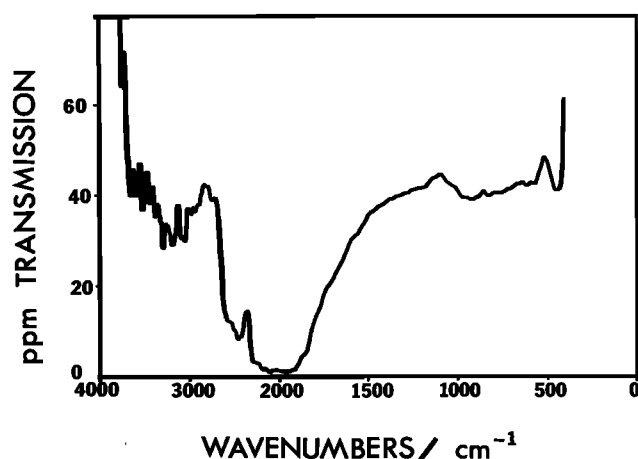
Fig. 1. FTIR spectrum of the empty diamond-anvil high-pressure cell obtained with 16 cm$^{-1}$ bandwidth and 33 cm$^{-1}$ broad smoothing.

parallel alignment of the diamonds also produces Fabry-Perrot interferences in the spectra, which can be avoided by adjustments on the diamond cell or by appropriate smoothing. It should be noted that the present simple adaptation of a diamond cell to this Nicolet MX1 FTIR spectrometer yields spectra with signal-to-noise ratios that are quite similar to those obtained with a double-beam scanning IR spectrometer (Perkin-Elmer 580, 3.7 cm$^{-1}$ resolution, 80-minute scan for the 200–4000 cm$^{-1}$ range) by use of special collimating optics and specially adapted diamonds cells with larger (0.4-mm diameter) holes in the gaskets [Adams and Sharma, 1979]. Similar observations were reported in an earlier IR absorption study of $CO_2$ under pressure [Hanson and Jones, 1981] performed with a diamond cell and a Nicolet 7199 FTIR spectrometer.
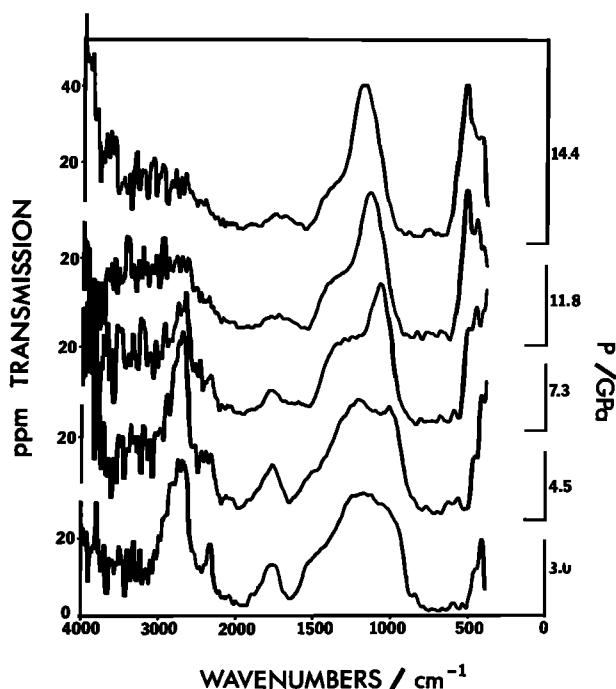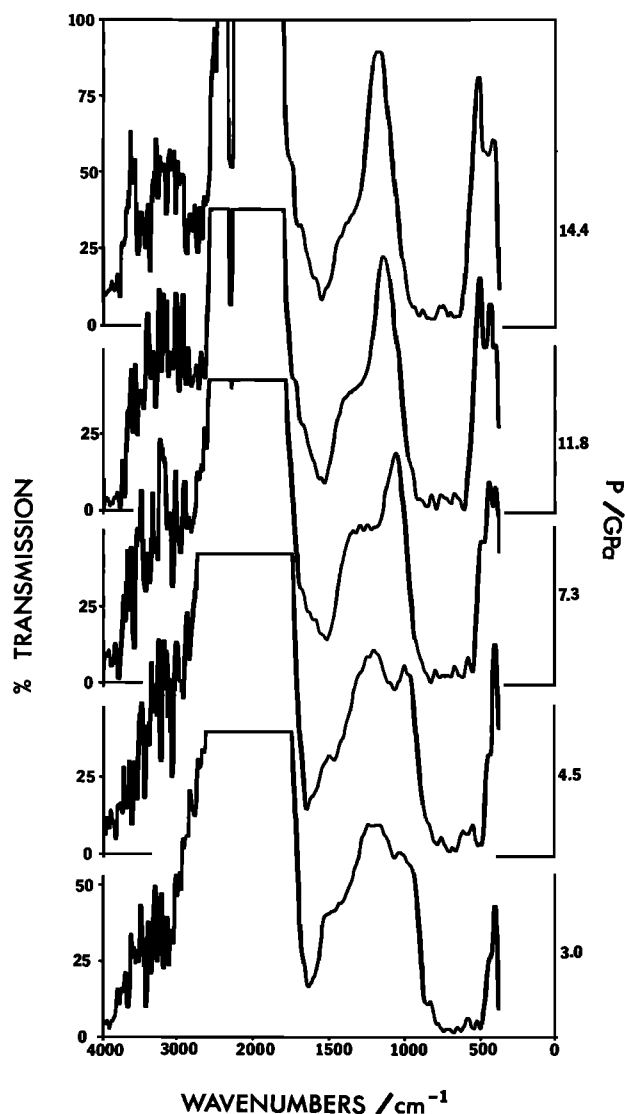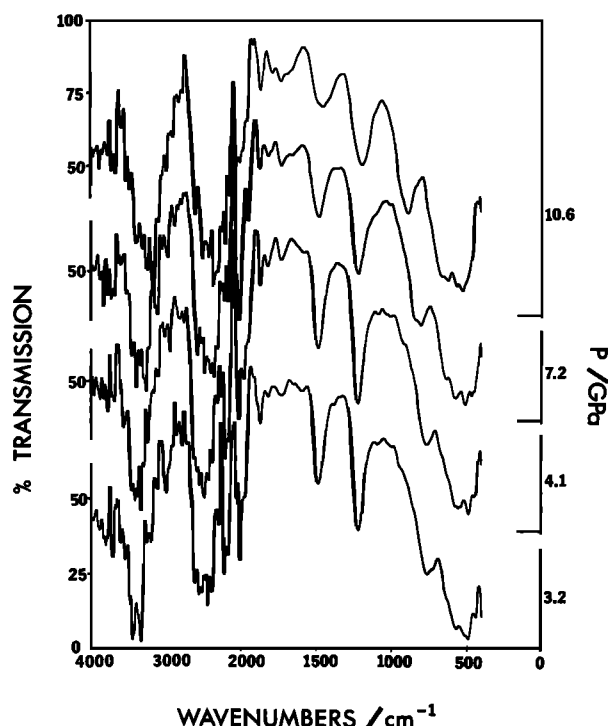


Fig. 3. IR transmission of $H_2O$ ice VII at several pressures.

## RESULTS

A typical set of spectra for $H_2O$ ice VII (250-$\mu$m diameter, 10-$\mu$m thick sample) at room temperature and pressures between 3.0 and 14.4 GPa is shown in Figure 2. Various systematic line shifts are evident in this presentation of the data. For quantitative evaluation, normalized transmittance spectra were computed from these raw high-pressure spectra and the spectrum of the empty cell at atmospheric pressure. Several of these normalized transmittance spectra are shown in Figure 3, where additional computer smoothing corresponding to a band width of 30 cm$^{-1}$ has been used to enhance the prominent features of the spectra.

Several spectra features are well resolved in the range from 400 to 1800 cm$^{-1}$. Between 1800 and 2600 cm$^{-1}$, the strong diamond absorptions make the spectra very noisy, and the data from this region cannot be reasonably evaluated. The transmission of the diamonds increases again between 2600 and 4000 cm$^{-1}$, although the reduced primary intensity of the spectrometer at the upper end of this range introduces some noise into the spectra. Nevertheless, the changes observed in this region of the spectra are qualitatively consistent with what one expects from the Raman measurements [Holzapfel et



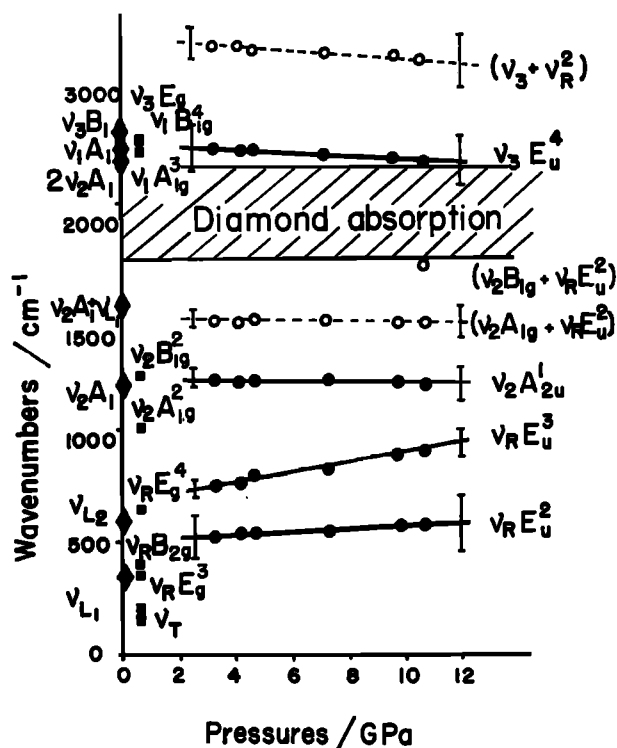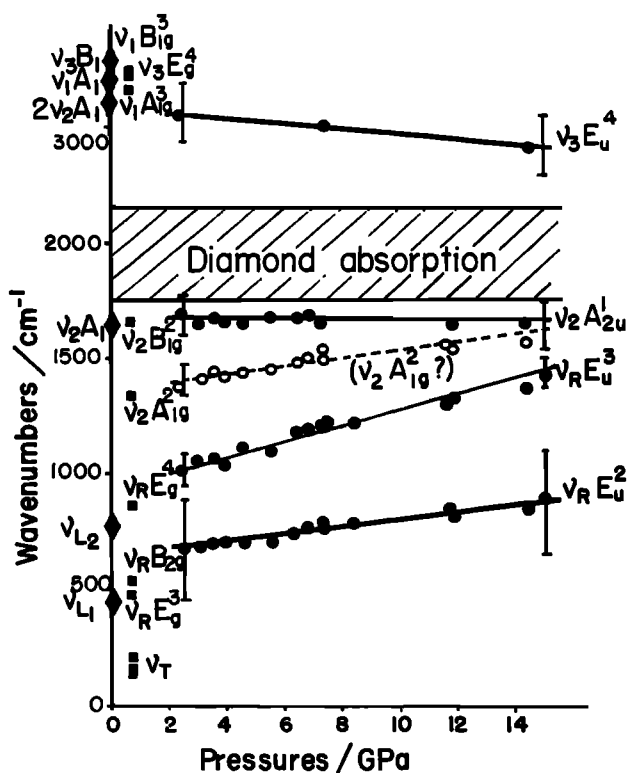Fig. 2. FTIR spectra of the diamond cell with $H_2O$ ice VII at several pressures.

Fig. 4.   IR transmission of D₂O ice VII at several pressures.



Fig. 6.   Comparable plot to Figure 5 for D₂O, except that open circles are data for overtone bands.



Fig. 5.   Effect of pressure on the wavenumbers of the IR absorption bands of $H_2O$ ice VII at room temperature: solid circles, bands that are IR active in ice VIII; open circles, a band that is IR active only in ice VII; I, schematic representation of bandwidths; solid squares, wavenumbers and assignments of Raman active bands of quenched ice VIII [*Wong and Whalley*, 1976]; solid diamonds, wavenumbers and assignments of IR absorption of liquid water at ambient pressure and 25° C [*Walrafen*, 1966].

*al.*, 1975; *Walrafen et al.*, 1982]. Similar results for a sample of $D_2O$ ice VII of almost the same thickness (~13 μm) are shown in Figure 4. A detailed evaluation of the line shifts observed from these and other samples is given in Figure 5 for $H_2O$ ice VII and in Figure 6 for $D_2O$ ice VII. Both Figures 5 and 6 include 0-GPa IR data for liquid water [*Walrafen*, 1966] and, at 0.7 GPa, Raman data for quenched ice VIII with their respective assignments [*Wong and Whalley*, 1976].

The disorder in ice VII does not permit precise assignments for the Raman or IR active modes under any space group. However, the close similarity of the spectra of ices VII and VIII suggests that both systems have similar short-range order and an assignment of the ice VII spectra with respect to the symmetry species of ice VIII may represent a reasonable correlation. These correlative assignments for the IR absorption lines of $H_2O$ and $D_2O$ ice VII are given on the right-hand sides of Figures 5 and 6. These mode assignments, the pressure dependencies of the frequencies of the modes, and the corresponding mode-Grüneisen parameters are presented in Table 1, where an average bulk modulus of 43 GPa [*Walrafen et al.*, 1982] is used to evaluate the mode-Grüneisen parameters.

### DISCUSSION

Two $v_r E_u$ rotational modes and one $v_2 A_{2u}$ molecular bending mode are well resolved in all of the spectra and assigned in Table 1. This assignment is supported not only by the similarity to the liquid water [*Walrafen*, 1966] and Raman data [*Wong and Whalley*, 1976] but also by the frequency ratios, $v(H_2O)/v(D_2O)$, of about 1.3 as shown in Table 1. Isotopic differences in mode-Grüneisen parameters are not observed with the present experimental precision, but the data in Table 1 may suggest slightly smaller values for $D_2O$.

The most striking result of the present investigation is the strong increase of $v_R E_u^3$ and the decrease in the difference

TABLE 1.  Mode Assignment, Wavenumbers, Pressure Derivatives, Mode-Grüneisen Parameters and Isotope Ratios for $H_2O$ and $D_2O$ Ice VII

| Mode Assignment Related to Ice VIII | $H_2O$ | | | $D_2O$ | | | |
|---|---|---|---|---|---|---|---|
| | $v/cm^{-1}$ at 5 GPa | $\partial v/\partial P,$ $cm^{-1}$ $GPa^{-1}$ | $\gamma$ | $v/cm^{-1}$ at 5 GPa | $\partial v/\partial P,$ $cm^{-1}$ $GPa^{-1}$ | $\gamma$ | $vH_2O/vD_2O$ |
| $RE_u^2$ | 710 (80) | 15 (5) | 0.9 (3) | 540 (60) | 7 (5) | 0.6 (4) | 1.31 (13) |
| $RE_u^3$ | 1090 (30) | 37 (7) | 1.4 (3) | 790 (30) | 21 (6) | 1.1 (3) | 1.38 (4) |
| $RA_{2u}^1$ | 1680 (60) | −2 (5) | −0.1 (2) | 1230 (30) | −2 (4) | −0.1 (2) | 1.37 (8) |

between $v_R E_u^3$ and $v_2 A_{2u}^1$ under pressure. In fact, one can expect these modes to become degenerate when the hydrogen bonds become symmetric at higher pressure [*Holzapfel*, 1972].

Both the much stronger absorption and broader line widths of $H_2O$ with respect to $D_2O$ can be explained by the larger amplitudes of the proton motion than of deuteron motion and, in addition, by shorter lifetimes of the proton vibrational modes due to higher tunneling probabilities [*Haas and Hornig*, 1960]. The same effect may also explain the appearance of one additional line at about 1450 $cm^{-1}$ in $H_2O$, which is assigned tentatively to the Raman-active mode $v_2 A_{1g}^2$ of ice VIII. This mode may be weakly allowed by disorder in ice VII. Some overtone bands also are well resolved in the $D_2O$ spectra. These include a $v_2 A_{1g}^2 + v_R E_u^2$ overtone near 1480 $cm^{-1}$, a $v_2 B_{1g}^2 + v_R E_u^2$ overtone at 1700 $cm^{-1}$, and, between 2600 and 3600 $cm^{-1}$, various combinations of $v_1$ and $v_3$ with $v_R$ and translational modes. The different pressure dependences of the individual modes lead almost to a cancellation in the pressure dependences of the overtone bands.

In addition to this qualitative support of the present understanding for the lattice dynamics of ice, the data reported herein will be very valuable for a quantitative lattice dynamical model of ice VIII based primarily on recent Raman measurements on ice VIII over an extended pressure range that will be reported elsewhere (K. R. Hirsch, personal communication, 1983).

REFERENCES

Adams, D. M., and S. K. Sharma, Selection of diamonds for infrared and Raman spectroscopy, *J. Phys.*, E10, 680–682, 1977.
Adams, D. M., and S. K. Sharma, Spectroscopy at very high pressures. 23:Mid-IR ultramicroscopy with a gasketed diamond anvil cell, *Appl. Opt.*, 18, 594–595, 1979.
Bassett, W. A., T. Takahashi, and P. W. Stock, X-ray diffraction and optical observations of crystalline solids up to 300 kbar, *Rev. Sci. Instrum.*, 38, 37–42, 1967.
Bertie, J. E., and F. E. Bates, Mid-infrared spectra of deuterated ices at 10 K and interpretation of the OD stretching bands of ices II and IX, *J. Chem. Phys.*, 67, 1511–1518, 1977.
Bertie, J. E., and E. Whalley, Infrared spectra of ices II, III, and V in the range 4000–350 $cm^{-1}$, *J. Chem. Phys.*, 40, 1646–1659, 1964.
Bertie, J. E., H. J. Labbe, and E. Whalley, Absorptivity of ice I in the range 4000–30 $cm^{-1}$, *J. Chem. Phys.*, 50, 4501–4520, 1969.

Block, S., and G. Piermarini, The diamond cell stimulates high pressure research, *Phys. Today*, 29, 44–55, 1976.
Englehardt, H., and E. Whalley, The infrared spectrum of ice IV in the range 4000–400 $cm^{-1}$, *J. Chem. Phys.*, 71, 4050–4051, 1979.
Hanson, R. C., and L. H. Jones, Infrared and Raman studies of pressure effects on the vibrational modes of solid $CO_2$, *J. Chem. Phys.*, 75, 1102–1112, 1981.
Haas, C., and D. F. Hornig, Inter- and intramolecular potentials and the spectrum of ice, *J. Chem. Phys.*, 32, 1763–1769, 1960.
Hirsch, K. R., and W. B. Holzapfel, Diamond anvil high pressure cell for Raman spectroscopy, *Rev. Sci. Instrum.*, 52, 52–55, 1981.
Holzapfel, W. B., On the symmetry of the hydrogen bonds in ice VII, *J. Chem. Phys.*, 56, 712–715, 1972.
Holzapfel, W. B., and H. G. Drickamer, Effect of pressure on the volume of the high pressure (VII) phase of $H_2O$ and $D_2O$, *J. Chem. Phys.*, 48, 4798–4800, 1968.
Holzapfel, W. B., R. S. Hawke, and K. Syassen, Raman studies on ice VII and VIII, in *Proceedings of the 4th International Conference on High Pressure*, edited by J. Osugi, pp. 344–347, Phys.-Chem. Soc. Japan, Kyoto, 1975.
Kamb, B., Structures of the forms of ice, *Acta Crystallogr.*, A25, S117, 1969.
Kamb, B., and B. L. Davis, Ice VII, the densest form of ice, *Proc. Natl. Acad. Sci USA*, 52, 1433–1439, 1964.
Lippencott, E. R., C. E. Weir, and A. van Valkenburg, Infrared studies of dense forms of ice, *J. Chem. Phys.*, 32, 612–614, 1960.
Marckmann, J. P., and E. Whalley, Vibrational spectra of the ices, Raman spectra of ice VI and VII, *J. Chem. Phys.*, 41, 1450–1453, 1964.
Olinger, B., and P. M. Halleck, Compression and bonding of ice VII and an empirical linear expression for the isothermal compression of solids, *J. Chem. Phys.*, 62, 94–99, 1975.
Schubert, G., D. J. Stevenson, and K. Ellsworth, Internal structure of the Galilean satellites, *Icarus*, 47, 46–59, 1981.
Stevenson, D. J., Interiors of the giant planets, *Annu. Rev. Earth Planet. Sci.*, 10, 277–295, 1982.
Walrafen, G. E., Raman spectral studies of water structure, *J. Chem. Phys.*, 40, 3249–3256, 1966.
Walrafen, G. E., M. Abebe, F. A. Maner, S. Block, G. J. Piermarini, and R. J. Munro, Raman and x-ray investigation of ice VII to 36.0 GPa, *J. Chem. Phys.*, 77, 2166–2174, 1982.
Weir, C. E., S. Block, and G. J. Piermarini, *J. Res. Natl. Bur. Stand. Sect. C*, 69, 275, 1965.
Whalley, E., The hydrogen bond in ice, in *The Hydrogen Bond*, edited by P. Schuster, G. Zundel, and C. Sandorfy, pp. 1425–1470, North-Holland, Amsterdam, 1976.
Whalley, E., The detailed assignment of the O-H stretching bands of ice I, *Can. J. Chem.*, 55, 3429–3441, 1977.
Wong, P. T. T., and E. Whalley, Raman spectrum of ice VIII, *J. Chem. Phys.*, 64, 2359–2366, 1976.

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