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(NASA-CR-170300) EFFECT OF PRESSURE ON  
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EFFECT OF PRESSURE ON INFRARED SPECTRA OF ICE VII.

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ABSTRACT

The effect of pressure on the infrared spectra of H<sub>2</sub>O and D<sub>2</sub>O 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,  $\nu_{R}E_u^1$  and  $\nu_{R}E_u^2$ , one bending mode,  $\nu_{2A}^1$ , and various overtone bands are well resolved. The stretching modes,  $\nu_1$  and  $\nu_3$ , are poorly resolved due to overlap with diamond window absorption.  $\nu_{R}E_u^2$  shows a very strong shift to higher frequency with pressure, while  $\nu_1$  and  $\nu_3$  shift to lower frequencies and all other lines vary only slightly with pressure. Differences between the spectra of H<sub>2</sub>O and D<sub>2</sub>O are discussed.



From many experimental and theoretical points of view, liquid water and the many high pressure phases of ice are of special interest for understanding hydrogen-bonded systems.[1] Among the ices, ice VII and VIII have especially simple structures [2,3] which has made them attractive candidates for study not only by x-rays [2-8] but also by Raman spectroscopy, both at high pressures [8-11] and, for ice VIII quenched at low temperatures, near atmospheric pressure.[12] However, as far as we know, infrared (IR) spectra have been reported only for the liquid,[13] ice I,[14,15] and quenched samples of ice II, III, V, and VI.[16,17] Since the high symmetry of ice VIII, space group  $I4_1/amd$  ( $D_{4h}^{19}$ ) with proton ordering,[4] leads to mutually exclusive selection rules for Raman and IR spectra, these spectra complement each other for ice VIII.

The mutual exclusion rule does not hold for ice VII where, when one considers on the average structure, no correlations, and linear hydrogen bonds, O atoms occupy a body-centered cubic lattice,  $I432$  ( $O^5$ ), and the four protons are disordered with equal probability among 16 equivalent positions along the body diagonals.[3] However, the close similarities of the Raman spectra of ice VII and VIII show that strong correlations and short-range order persists in ice VII, at least at room temperature. One can expect, therefore, that the IR spectra of ice VII and VIII also will be similar. It thus appears reasonable for this first IR absorption study of ice under very high pressures to consider only ice VII and to avoid the additional experimental problems related to cooling of the high pressure cell in the spectrometer sample compartment.[10]

### EXPERIMENTAL

A modified Bassett-type [18] diamond (Type IIA with 0.6-mm culets) anvil high pressure cell with Inconel gaskets [19] was used for these studies. The sample of distilled H<sub>2</sub>O or, in some runs, 99.8% D<sub>2</sub>O was injected into the central 300- $\mu$ m diameter hole of the gasket by a syringe. Also included in the hole were one-to-three ruby splinters so the the pressure could be monitored by the ruby luminescence method; [19] the factor, 0.365 nm/GPa, was used to convert the shift of of the R<sub>1</sub> 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 Fig. 1. This spectrum shows the well-known structure of the absorption of type IIA diamonds [20] and a transmission of 0.04% in the 500-1500 cm<sup>-1</sup> region. The steep increases in transmission on both ends of this FTIR spectrum are artefacts 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 Fig. 1, as well as for the "sample" spectra, could be obtained by setting the resolution of the spectrometer to the largest bandpass,  $16\text{ cm}^{-1}$ , and by sampling and integrating for 4 hours. Longer exposure times with this sample and spectrometer enhanced artificial undulations in the spectra which are not visible in Fig. 1 but probably result from overflow in the memory of the FTIR computer. Perfect 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,  $3.7\text{ cm}^{-1}$  resolution, 80 minute scan for the  $200\text{-}4000\text{ cm}^{-1}$  range) by use of special collimating optics and specially adapted diamonds cells with larger ( $400\text{-}\mu\text{m}$  diameter) holes in the gaskets.[21] Similar observations were reported in an earlier IR absorption study of  $\text{CO}_2$  under pressure [22] performed with a diamond cell and a Nicolet 7199 FTIR spectrometer.

## RESULTS

A typical set of spectra for  $\text{H}_2\text{O}$  ice VII ( $250\text{-}\mu\text{m}$  diameter,  $10\text{-}\mu\text{m}$  thick

sample) at room temperature and pressures between 3.0 and 14.4 GPa is shown in Fig. 2. Various systematic line shifts are evident in this presentation of the data. For quantitative evaluation, these transmittances were normalized with respect to the transmittance of the empty cell; and the normalized transmittance spectra are shown in Fig. 3, where additional computer smoothing corresponding to a band width of  $30 \text{ cm}^{-1}$  has been used to enhance the prominent features of the spectra.

Several spectra features are well resolved in the range from 400 to  $1800 \text{ cm}^{-1}$ . Between  $1800$  and  $2600 \text{ cm}^{-1}$ , 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  $4000 \text{ cm}^{-1}$ , although the reduced primary intensity of the spectrometer at the upper end of this range introduces some noise in the spectra. Nevertheless, the changes observed in this region of the spectra are qualitatively consistent with what one expects from the Raman measurements.[8,9] Similar results for a sample of  $\text{D}_2\text{O}$  ice VII of almost the same thickness ( $\sim 13 \mu\text{m}$ ) are shown in Fig. 4. A detailed evaluation of the line shifts observed from these and other samples is given in Fig. 5 for  $\text{H}_2\text{O}$  ice VII and in Fig. 6 for  $\text{D}_2\text{O}$  ice VII. Both Fig. 5 and 6 include 0-GPa IR data for liquid water [13] and, at 7 GPa, Raman data for quenched ice VIII with their respective assignments.[12]

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<sub>2</sub>O and D<sub>2</sub>O ice VII are given on the right-hand sides of Fig. 5 and 6. These mode assignments, the pressure dependences of the frequencies of the modes, and the corresponding mode-Grüneisen parameters are presented in Table I, where an average bulk modulus of 43 GPa [8] is used to evaluate the mode-Grüneisen parameters.

#### DISCUSSION

Two  $\nu_r E_u$  rotational modes and one  $\nu_2 A_{2u}$  molecular bending mode are well resolved in all of the spectra and assigned in Table I. This assignment is supported not only by the similarity to the liquid water [13] and Raman [12] data but also by the frequency ratios,  $\nu(\text{H}_2\text{O})/\nu(\text{D}_2\text{O})$ , of about 1.3 as shown in Table I. Isotopic differences in mode-Grüneisen parameters are not observed with the present experimental precision, but the data in Table I may suggest slightly smaller values for D<sub>2</sub>O.

The most striking result of the present investigation is the strong increase of  $\nu_r E_u^2$  and  $\nu_2 A_{2u}^1$  under pressure. In fact, one can expect these modes to become degenerate when the hydrogen bonds become symmetric at higher pressures.

Both the much stronger absorption and larger line widths of H<sub>2</sub>O with respect to D<sub>2</sub>O 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.[14] The same effect may also explain the appearance of one additional line at about  $1450 \text{ cm}^{-1}$  in  $\text{H}_2\text{O}$ , which is assigned tentatively to the Raman-active mode  $\nu_2^2 A_{1g}$  of ice VIII. This mode may be weakly allowed by disorder in ice VII. Some overtone bands also are well resolved in the  $\text{D}_2\text{O}$  spectra. These include a  $\nu_2^2 A_{1g} + \nu_R E_u^2$  overtone near  $1480 \text{ cm}^{-1}$ , and  $\nu_2^2 B_{1g} + \nu_R E_u^2$  overtone at  $1700 \text{ cm}^{-1}$ , and, between  $2600$  and  $3600 \text{ cm}^{-1}$ , various combinations of  $\nu_1$  and  $\nu_3$  with  $\nu_R$  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.[11]

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CAPTIONS

Fig. 1. FTIR spectrum of the empty diamond-anvil high pressure cell obtained with  $16 \text{ cm}^{-1}$  bandwidth and  $33 \text{ cm}^{-1}$  broad smoothing.

Fig. 2. FTIR spectra of the diamond cell with  $\text{H}_2\text{O}$  ice VII at several pressures.

Fig. 3. IR transmission of  $\text{H}_2\text{O}$  ice VII at several pressures.

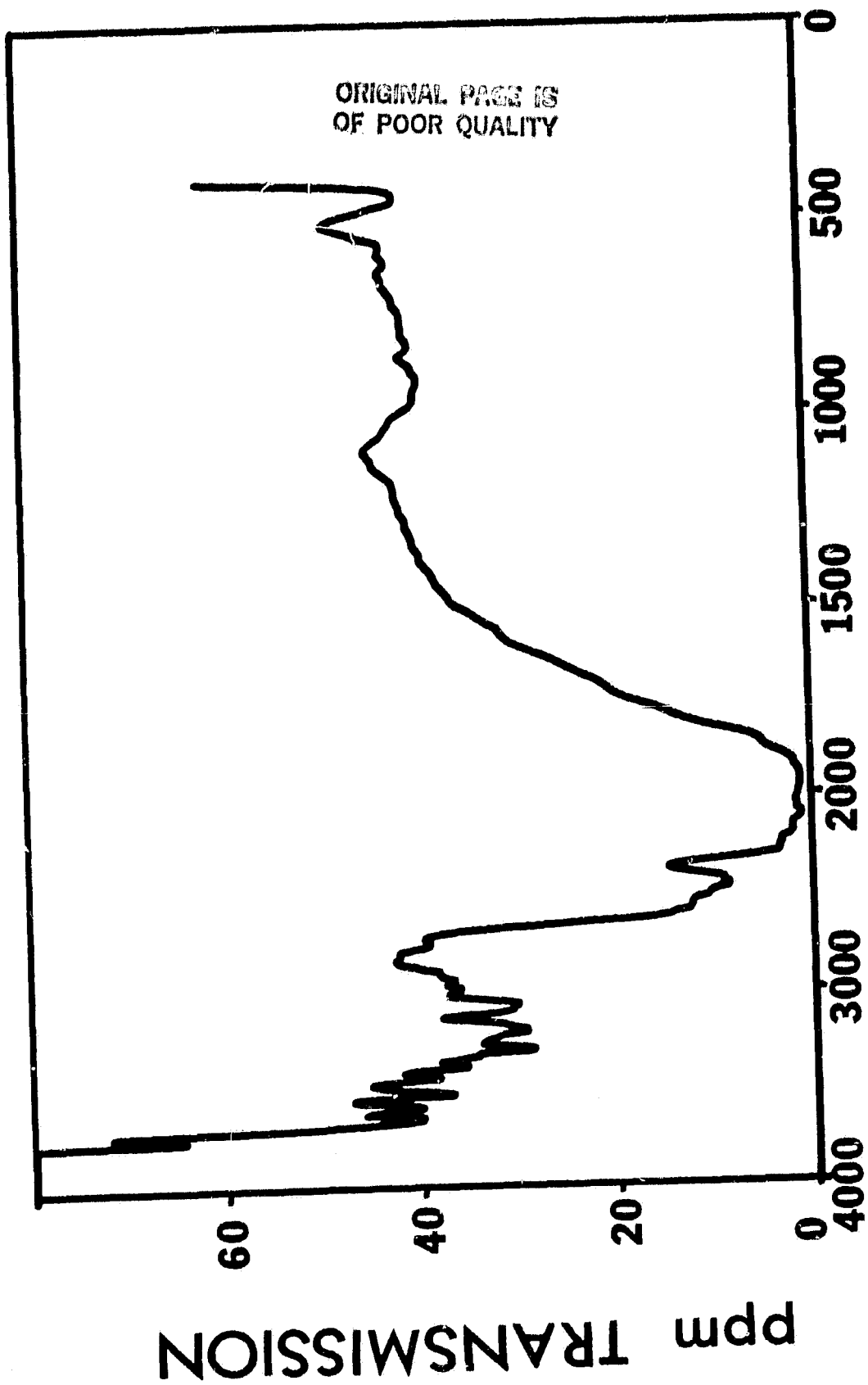
Fig. 4. IR transmission of  $\text{D}_2\text{O}$  ice VII at several pressures.

Fig. 5. Effect of pressure on the wavenumbers of the IR absorption bands of  $\text{H}_2\text{O}$  ice VII at room temperature: ●, bands that are IR active in ice VIII; ○, a band that is IR active only in ice VII; I, schematic representation of bandwidths; #, wavenumbers and assignments of Raman active bands of quenched ice VIII (Ref. 12); ◆, wavenumbers and assignments of IR absorption of liquid water at ambient pressure and  $25^\circ \text{C}$  (Ref. 13).

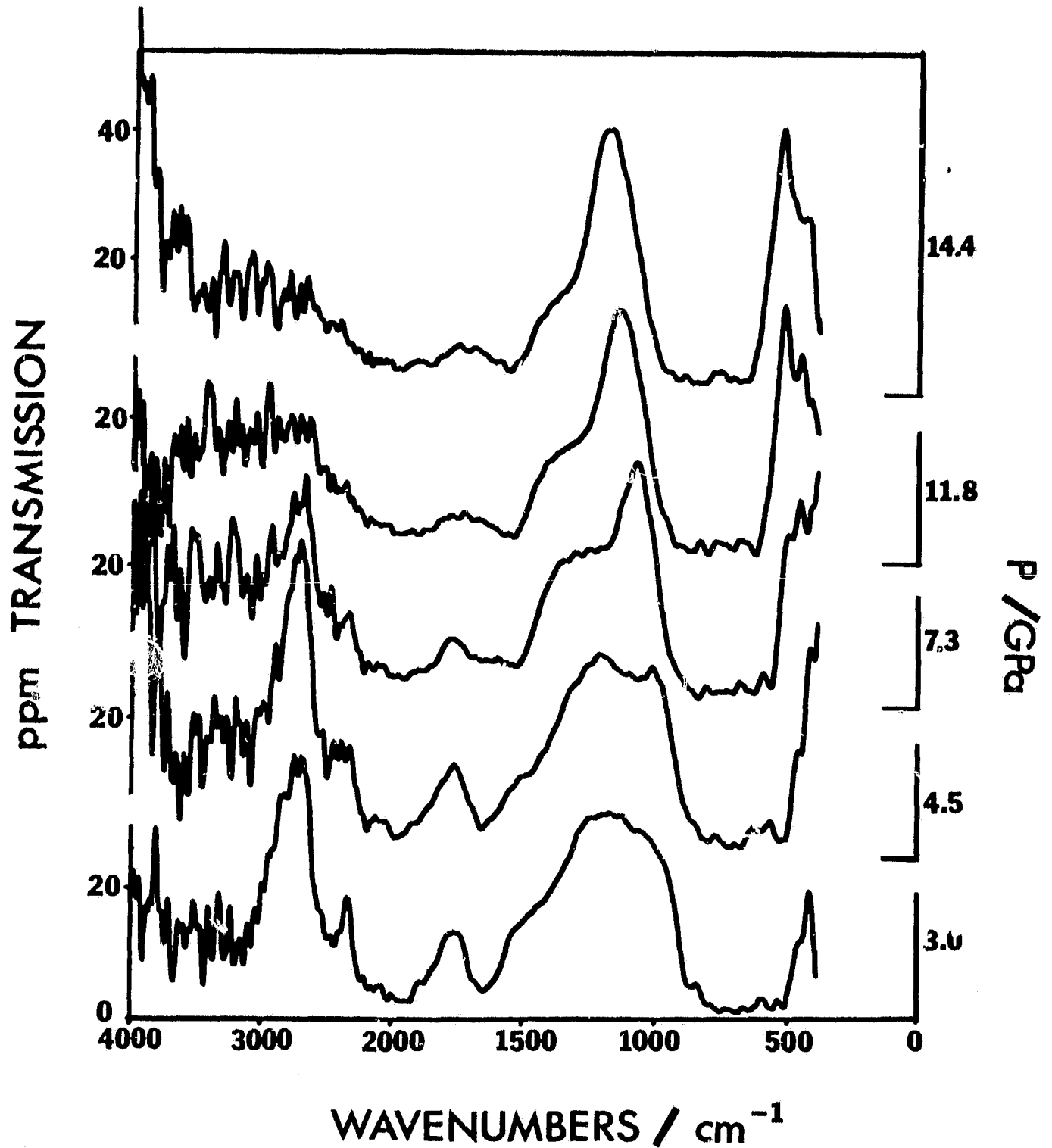
Fig. 6. Comparable plot to Fig. 5 for  $\text{D}_2\text{O}$ , except: ○, data for overtone bands.

TABLE I: Mode assignment, wavenumbers, pressure derivatives, mode-Grüneisen parameters and isotope ratios for H<sub>2</sub>O and D<sub>2</sub>O ice VII.

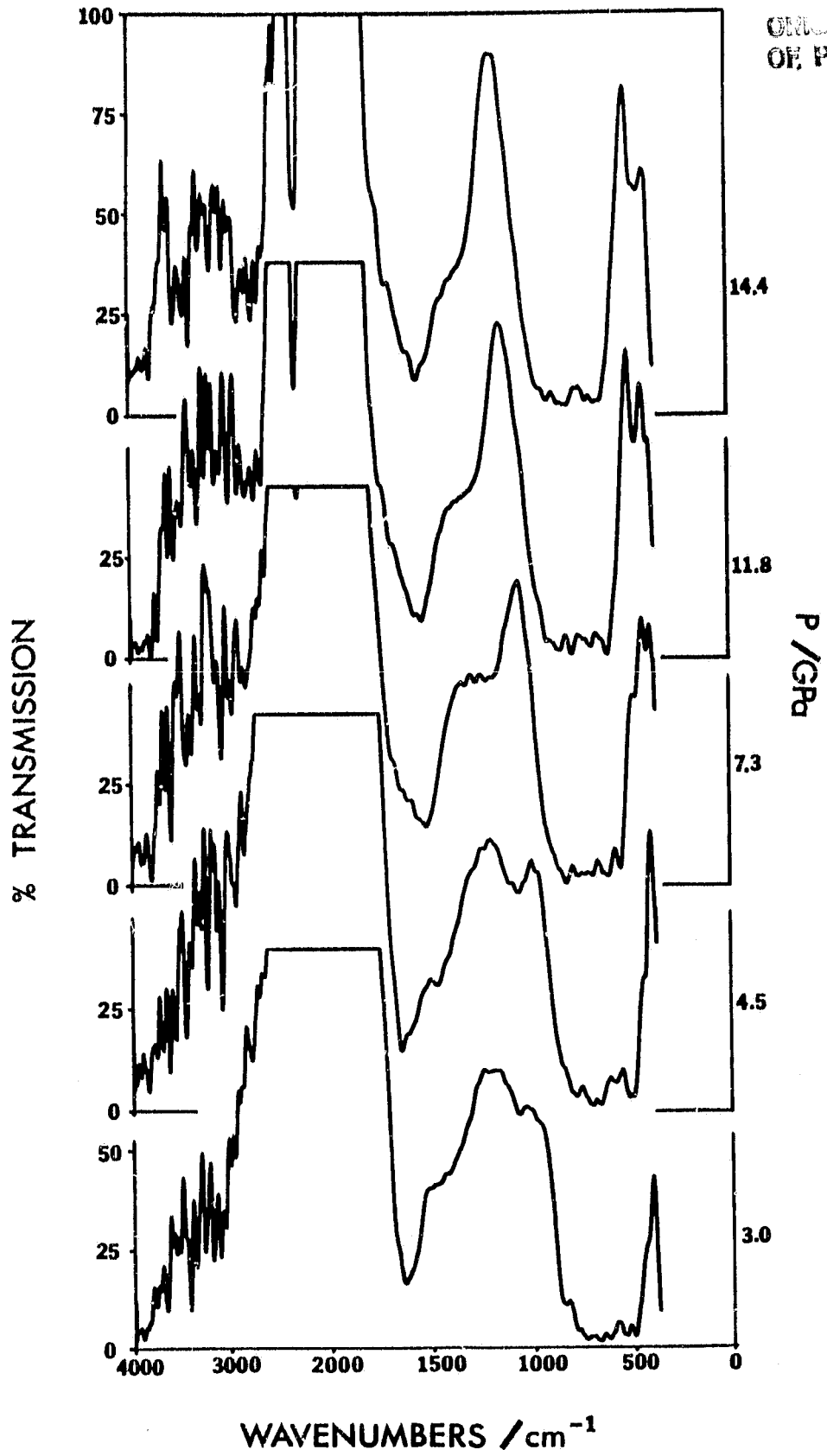
| Mode Assignment Related to Ice VIII | H <sub>2</sub> O              |   |          | D <sub>2</sub> O              |   |          | $\frac{\nu_{\text{H}_2\text{O}}}{\nu_{\text{D}_2\text{O}}}$ |
|-------------------------------------|-------------------------------|---|----------|-------------------------------|---|----------|---|
|                                     | $\nu/\text{cm}^{-1}$ at 5 GPa | $\frac{\partial \nu}{\partial P}$ $\text{cm}^{-1} \cdot \text{kbar}^{-1}$ | $\gamma$ | $\nu/\text{cm}^{-1}$ at 5 GPa | $\frac{\partial \nu}{\partial P}$ $\text{cm}^{-1} \cdot \text{kbar}^{-1}$ | $\gamma$ |   |
| $\nu_R E_u^2$                       | 710 (80)                      | 15 (5)  | 0.8 (3)  | 540 (60)                      | 7 (5)   | 0.5 (4)  | 1.31 (13)   |
| $\nu_R E_u^3$                       | 1090 (30)                     | 37 (7)  | 1.2 (3)  | 790 (30)                      | 21 (6)  | 1.0 (3)  | 1.38 (4)  |
| $\nu_R A_{2u}^1$                    | 1680 (60)                     | -2 (5)  | -0.1 (2) | 1230 (30)                     | -2 (4)  | -0.1 (2) | 1.37 (8)  |



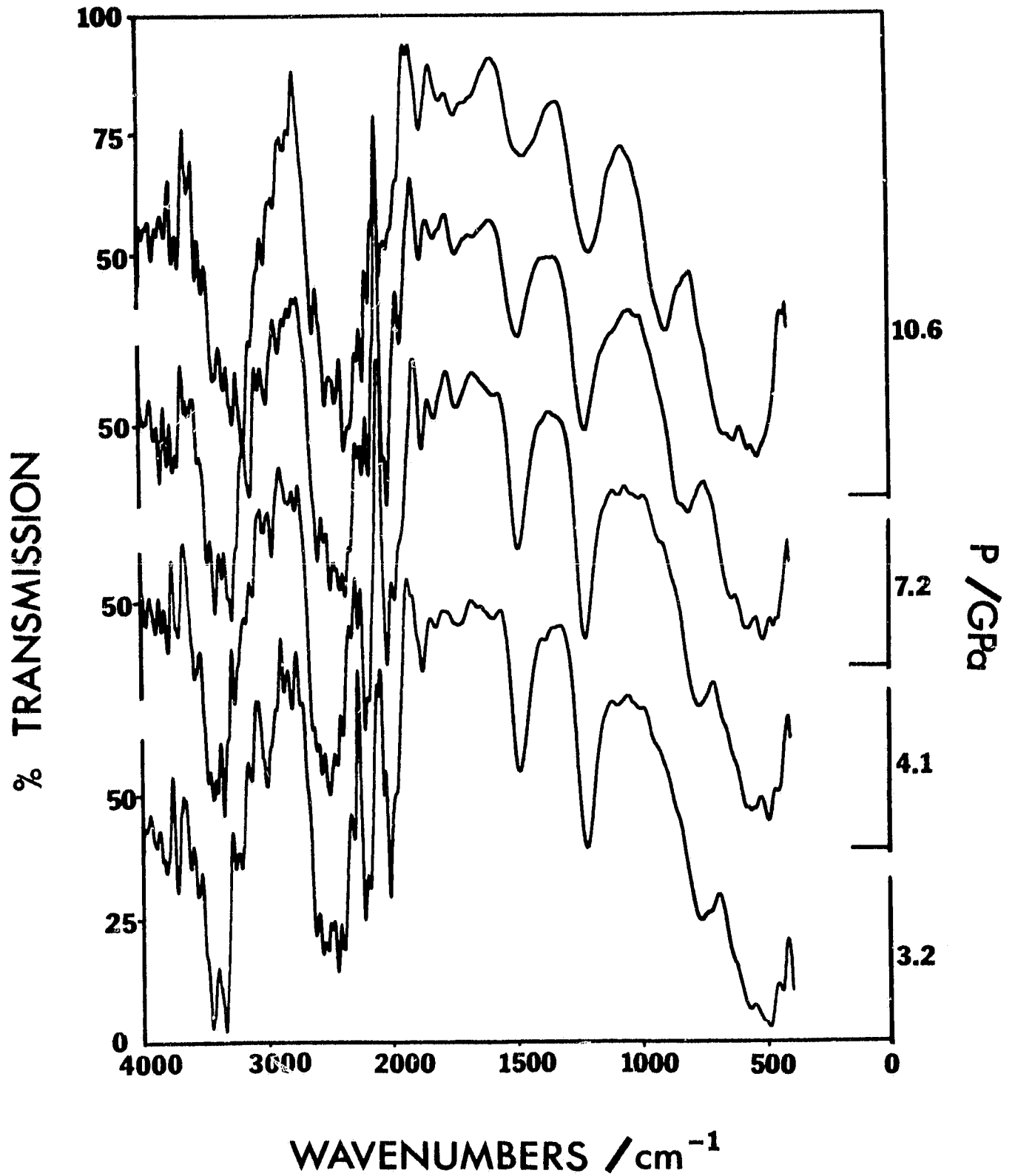
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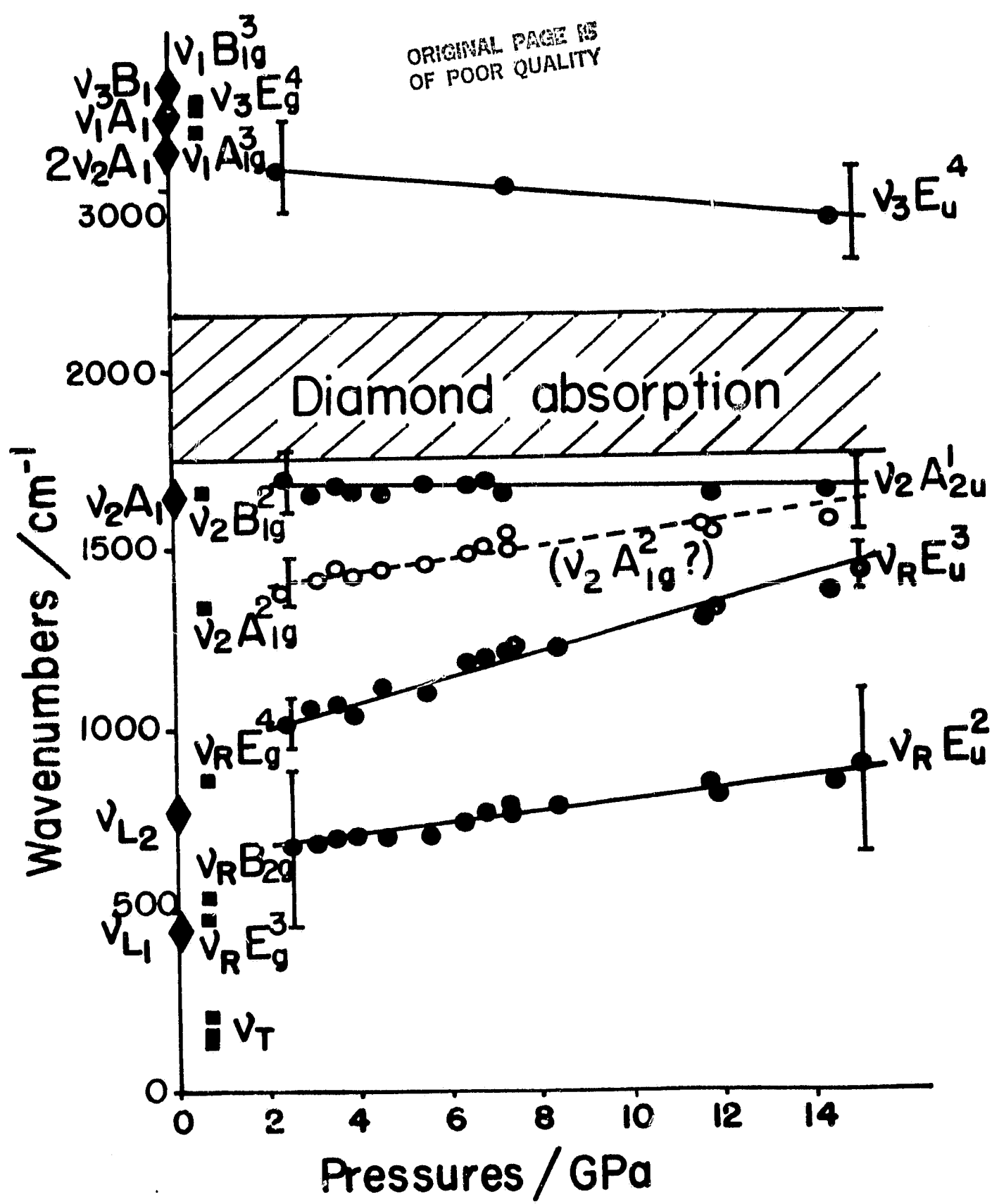


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