

## EFFECT OF PRESSURE ON INFRARED-SPECTRA OF ICE VII.

W.B. Holzapfel\*, B. Seiler and M.F. Nicol

Department of Chemistry and Biochemistry  
University of California  
Los Angeles, California 90024

The ability to identify high pressure solid phases of water, ammonia, methane, and their compounds by vibrational spectroscopy is an essential prerequisite for studies of phase equilibria under conditions relevant to icy planets and satellites. Raman spectra of many high pressure phases of ice have been reported (1-5); however, infrared (IR) spectra of water under high pressure have been reported only for the liquid and ice I. (6-8) Although spectra of samples of ice II, III, V, and VI quenched at atmospheric pressure have been reported, (9-10) as far as we know, IR spectra have not been reported for the higher pressure phase of ice (VII and VIII); and little is known about how the infrared absorption frequencies of these ices vary with compression.

This report describes, therefore, what we believe to be the first measurements of the infrared spectra of the high pressure solid phases of ices under high pressures. The close similarity of the Raman spectra of ice VII and VIII suggests that their IR spectra also may be similar. Thus, this initial study considered only ice VII to avoid the additional experimental problems related to cooling a high pressure cell in a spectrometer sample compartment.

A modified Bassett-type (11) diamond (Type IIa) anvil high pressure cell with Inconel gaskets was mounted for these studies in the sample compartment of a commercial Fourier transform-IR spectrometer (Nicolet MX-1) by a translational stage which allow precise x-y adjustments perpendicular to the optical axis of the instrument. Distilled H<sub>2</sub>O or, in some runs, 99.8% D<sub>2</sub>O was injected into a 0.3-mm diameter hole of the gasket by a syringe. The ruby fluorescence method was used to measure pressure with the factor, 0.365 nm/PGa used to convert the shift of the R<sub>1</sub> ruby luminescence line to pressure. The initial thickness of the prepresses gasket was typically 0.03 mm; however, in some runs, the thickness as small as 0.01 mm were used.

Reasonable signal-to-noise ratios for "background" spectra and for "sample" spectra were obtained by setting the spectrometer to the largest band pass, 16 cm<sup>-1</sup>, and by sampling and averaging for 4 hours. Two  $\nu_R E_u$  rotational modes and one  $\nu_2 A_{2u}$  molecular bending modes were well resolved in all spectra. The  $\nu_1$  and  $\nu_3$  stretching modes were more difficult to resolve because diamond absorptions interfered at these frequencies.

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The most dramatic effect of pressure on the IR spectra of ice VII is the strong increase of the frequency of the  $\nu_R E_u^2$  mode from  $1090 \text{ cm}^{-1}$  at 5 GPa by  $37 \text{ cm}^{-1}/\text{GPa}$  for  $\text{H}_2\text{O}$  and from  $790 \text{ cm}^{-1}$  by  $21 \text{ cm}^{-1}/\text{GPa}$  for  $\text{D}_2\text{O}$ . The differences between these  $\nu_R E_u^2$  modes and the  $\nu_2 A_{2u}$  modes of the two isotopic species decrease by correspondingly strong amounts as the hydrogen bonds become more symmetric, since these modes should be degenerate for ice VII with symmetric hydrogen bonds. The changes of the hydrogen bonds with pressure also shift the stretching modes to lower frequencies, while other bands shift only to minor degrees. The absorption bands are both more intense and broader in  $\text{H}_2\text{O}$  ice VII than in  $\text{D}_2\text{O}$  ice VII. This is attributed to a combination of factors. The H motions have larger amplitudes than the D motions and the H vibrations have shorter lifetimes because of higher tunneling probabilities.

In addition to their value for identifying the occurrence of ice VII at high pressure, these spectra provide qualitative support for the present understanding of the lattice dynamics of the ices. Together with available Raman data, these IR data will be valuable for constraining quantitative lattice dynamical models of ice VII and VIII that will be reported elsewhere. (4)

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