

H. J. Hall

Infrared Studies of Dense Forms of Ice

E. R. LIPPINCOTT, *Department of Chemistry, University of Maryland,
College Park, Maryland*

AND

C. E. WEIR AND A. VAN VALKENBURG, *National Bureau of
Standards, Washington, D. C.*

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THE structures of the dense forms of ice have been of considerable interest since the complexity of the system was revealed by Bridgman.¹ McFarlan² produced the various forms under pressure, cooled the system to a temperature sufficiently low that the pressure could be released without reversion to Ice-I, and obtained x-ray patterns in the metastable state at 1 atm. He found Ice-II and Ice-III to be orthorhombic and to contain distorted oxygen tetrahedra. Data for the higher pressure forms IV, V, and VI were obtained but were not worked out because of their low symmetry.

Recently a high pressure infrared cell using two type-II diamonds in a "squeezer" design has been constructed here.³ Preliminary infrared patterns differing considerably from that of Ice-I have been obtained and, since these patterns may be of interest, they are reported here. In these studies the specimen was cooled by passing cold nitrogen gas through the supporting steel block, temperatures being measured by a thermocouple placed close to the diamonds. Temperature was controlled by adjusting the flow of gas and in any run varied not more than $\pm 0.5^\circ\text{C}$. From observations on cooling near 0°C it was concluded that the tempera-

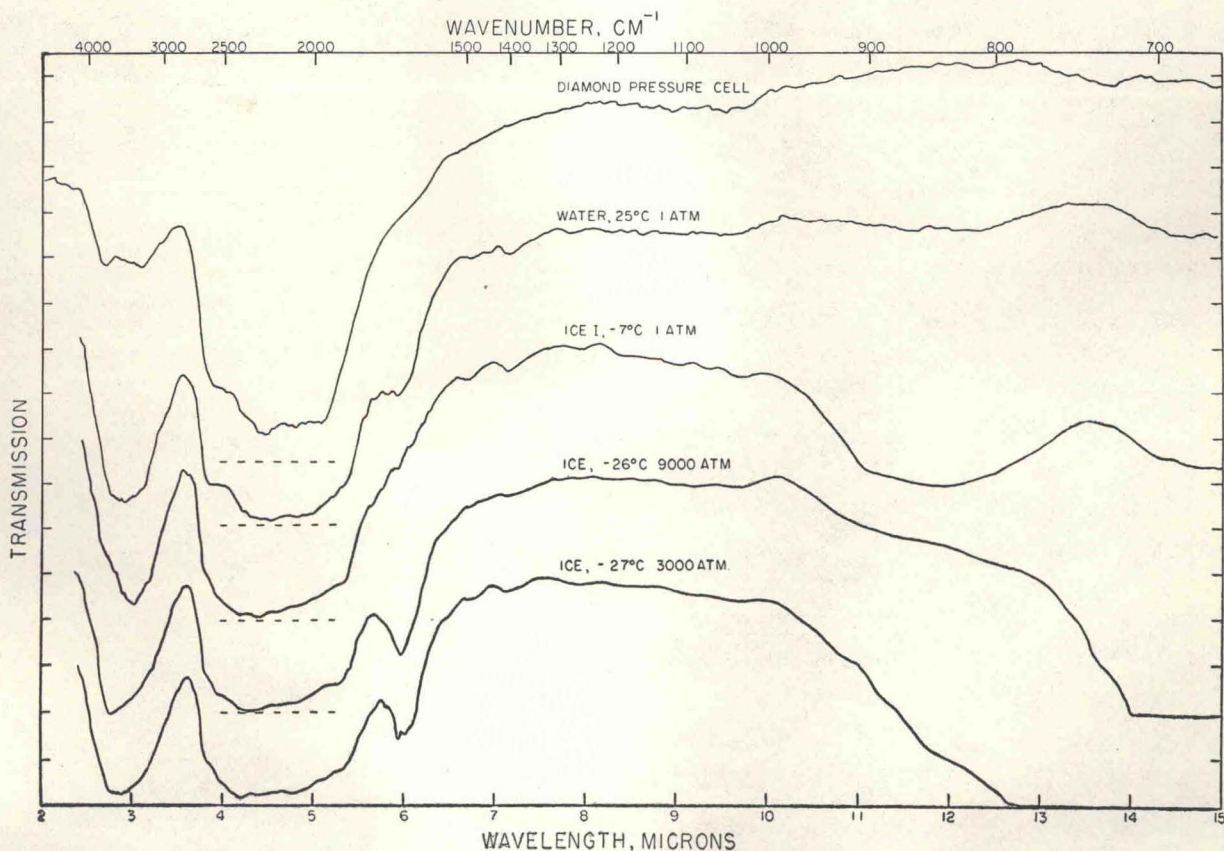


FIG. 1. Infrared patterns for water and ice in the diamond pressure cell. Curves are displaced vertically to avoid overlapping. The zero line for each curve is indicated by the broken line immediately below each curve between 4 and 5 μ . For the bottom curve the abscissa represents the zero line.

ture of the specimen was not more than 5°C above that registered by the couple.

Spectra obtained are shown in Fig. 1 as recorded successively for liquid water at room temperature and 1 atmos; Ice-I at -7°C and 1 atmos; ice at -26°C and 9000 atmos, obtained by cooling the previous specimen and then compressing; and ice at -27°C and 3000 atmos, obtained by decompressing from 9000 atmos. A pattern of the diamond cell alone is included for comparison. In view of the metastability of the forms of ice reported previously,^{1,2} and also observed here, the phases present at the elevated pressures are not certain. The run at 9000 atmos is in the Ice-VI field while the 3000-atmos run is in the Ice-II field but so close to the II-III transition line that the temperature differential between specimen and thermocouple might place the run in the Ice-III field.

In Ice-I the band centered at 3200 cm⁻¹ corresponds to the hydrogen bonded O—H stretching mode and the 1630 cm⁻¹ band on the shoulder of the diamond band to the H—O—H bending mode. The broad band centered near 850 cm⁻¹ corresponds to a libration mode of the molecule. When liquid water is frozen the formation of the strong hydrogen bonds of Ice-I is accom-

panied by a shift of the stretching band to lower frequencies, a marked apparent decrease in intensity of the bending band and an increase in intensity of the libration band.⁴ In the spectrum at 9000 atmos the peak stretching frequency has shifted to 3600 cm⁻¹, the bending band has a greatly increased intensity but has not shifted appreciably, and the libration band is either missing or has shifted to lower frequencies. These results are consistent with the interpretation that the hydrogen bonds responsible for the open structure of Ice-I have collapsed and, in the close-packed structure of the dense ice, hydrogen bonding produces a minor effect on the vibration modes. Presumably, weak hydrogen bonds still exist in the dense ice but with the O—H···O angle deviating considerably from 180°.

The spectrum at 3000 atmos is in many respects intermediate between that of Ice-I and that at 9000 atmos. It is not certain that the splitting of the bending band is real because of low intensities associated with frosting of the apparatus in this run.

¹ P. W. Bridgman, *The Physics of High Pressure* (G. Bell and Sons, Ltd., London, 1952), pp. 242, 426.

² R. L. McFarlan, *J. Chem. Phys.* **4**, 60, 253 (1936).

³ Weir, Lippincott, Van Valkenburg, and Bunting, *J. Research Natl. Bur. Standards* **63A**, 55 (1959).

⁴ P. A. Giguère and K. B. Harvey, *Can. J. Chem.* **34**, 798 (1956).

