

RAMAN SPECTRA OF THE HIGH PRESSURE PHASES OF ICE IN THEIR REGION OF STABILITY

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ABSTRACT

The Raman spectra of Ices Ih, II, III, V, VI and IX of H_2O , D_2O and 2% D_2O in H_2O in their regions of stability (pressure and temperature) were measured in the range of $4000 - 10 \text{ cm}^{-1}$.

A high pressure (up to 6.5 k bar) and low temperature (down to 140K) Raman cell was used, specially designed for this purpose. Better quality Raman spectra have been obtained than the ones reported for quenched polymorphous ices at atmospheric pressure, particularly in the lattice vibrational region.

Raman spectra of Ices II and V were measured in a wide range of temperatures and pressures. The temperature dependence of Ice VI was followed, and an attempt was made to detect Ice VI–Ice VI' transition.

Special emphasis was given to the Ice III–Ice IX disorder–order transition, and the results were compared with dielectric measurements.

INTRODUCTION

A special high pressure low temperature liquid Raman cell was designed in this laboratory for studies of water and different phases of ices. Preliminary results for some of the phases of ice were reported in 1976 (ref.1).

Apart from this, almost all the other Raman spectra of the high pressure phases of ice reported so far (see eg refs. (2) and (3) and the references therein) were recorded as quenched ices at atmospheric pressure and at 77K. (Recently some diamond anvil cell work on ices VII and VIII has been published). We have recorded Raman spectra of six of the high pressure phases of ice in their regions of stability. High quality Raman spectra have been obtained, which is especially noticeable in the lattice vibration region where the Raman spectra could be recorded as low as 10 cm^{-1} . Some temperature and pressure dependent studies within individual phases have been made.

EXPERIMENTAL METHODS

The high pressure phases of Ice were made in the special-purpose high pressure,

low temperature Raman cell mentioned above; detailed description of this cell will be given elsewhere. It has three mm thick sapphire windows for laser in, laser out and collection at 90° of the Raman scattering.

H_2O ices were made from redistilled, deionized water. D_2O ices were made from 99.8% D_2O . Temperature was controlled by varying the flow rate of cold nitrogen gas through cooling channels in the cell, and measured by a thermocouple. A ruby crystal was mounted inside the Raman cell and its R_1 fluorescent frequency allowed us to calculate the pressure with an accuracy of ± 0.2 k bar.

The Raman spectra were recorded with a Spex Ramalog 5M system with a Spectra Physics argon ion laser. All the spectra were calibrated against the standard emission lines of neon or the plasma lines from the laser.

The spectral slitwidth for the whole Raman region (from 4000 – 10 cm^{-1}), was between 3 – 4 cm^{-1} . For a dilute solution of HDO in H_2O a spectral slitwidth of about 2 cm^{-1} was used when studying the isolated O-D stretching bands.

RESULTS AND DISCUSSION

Raman spectra of ices Ih, II, III, IX, V and VI of H_2O are shown in fig.1, and

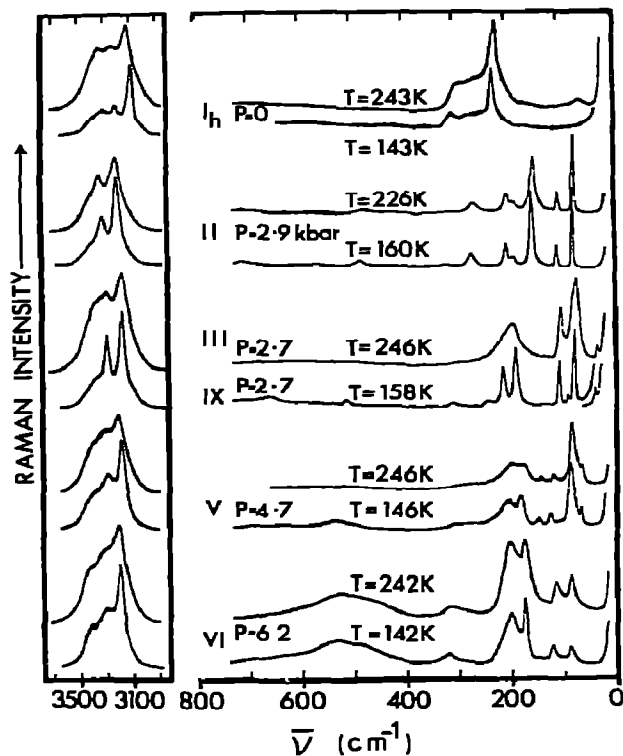


Fig.1. Raman spectra of O-H stretching modes and lattice modes of ice phases I, II, III, IX, V and VI at the temperatures and pressures indicated.

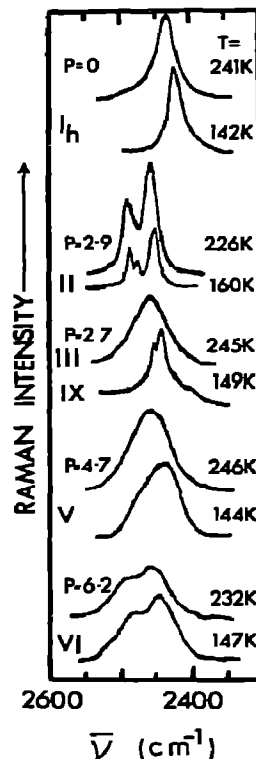


Fig.2. Raman spectra of the isolated O-D modes in ice phases I, II, III, IX, V and VI formed from 2% D_2O in H_2O at the temperatures and pressures indicated.

the Raman spectra of the isolated O-D stretching vibrations of the corresponding ices of 2% D₂O in H₂O are shown in fig.2. (Raman spectra of ices formed from pure D₂O and from 2% H₂O in D₂O have also been recorded.)

Ices I, II, V and VI are shown in their high temperature region of stability, and at low temperature (between 140K and 150K).

Ice III is presented in the same way, but in this case at the same pressure and lower temperature, the ordered form of ice III, Ice IX, exists.

Ice II and ice V

The observed ratios of H₂O to D₂O frequencies for Ice II in the translational lattice vibration region are between 1.025-1.045. In the rotational region these ratios are about 1.375 and in the OH stretching region they are 1.359 and 1.338. (Isotopic shifts for the other ice structures have been measured, and the ratios are similar to those for ice II give above.)

The frequencies of the bands in Ices II and V of H₂O and D₂O were followed in a range of temperatures and pressures. For H₂O ice the translational lattice modes of phase II showed decrease in frequency with increasing temperature that were typically -0.006 cm⁻¹/K, whereas the rotational modes shifted faster, about -0.2 cm⁻¹/K and the O-H stretching modes showed reverse shifts of about +0.2 cm⁻¹/K. The corresponding pressure induced shifts were about + 2.4 cm⁻¹/k bar, + 3 cm⁻¹/k bar and -5.9 cm⁻¹/k bar. Ice V showed shifts with the same signs, but the magnitudes were generally slightly smaller in the lattice mode region, but larger in the O-H stretch region.

Pressure and temperature dependence of the Raman frequencies of Ice Ih have recently been published (ref.4), and those results were similar to those given above for ices II and V.

The Raman frequencies of quenched samples of Ice II have been followed in a temperature range of 100K to 30K (ref.3) where the average variation was about 0.1 cm⁻¹/K in the OH stretching vibration region.

During a low temperature experiment (which lasted about 4-5 hours at 140K) ice V did not transform into ice II although it was well into the region of stability of ice II.

Ice VI

Temperature dependence for ice VI was also followed at p=6.3 k bar. The average slope in the lattice vibrational region (dv/dT) is -0.047 cm⁻¹/K and in the O-H stretching vibration region (dv/dT) is +0.173 cm⁻¹/K.

While cooling ice VI under a pressure of not more than 6.5 k bar, the spectrum was carefully studied in order to detect any changes which could indicate the formation of phase VI'. (Quoted in the literature as "partially disordered", ref. (5).) There were not any significant changes in the Raman spectrum of Ice

VI beyond the expected sharpening of the bands on cooling. (In particular the band at 155 cm^{-1} (in H_2O) sharpened considerably.) This does not conflict with the previous experiments (ref. 6) since they indicated a very slow transition from phase VI to phase VI' over a time period much longer than that of our experiment.

Ice III - ice IX transition

The Ice III to Ice IX transition (disorder-order transition) was optically recorded for the first time during these experiments. (See fig. 1 and fig. 2.) The transition started at about 183K (for H_2O), and was completed by about 168K. Sharp bands in the ice IX structure indicate an ordered structure which agrees with the X-ray structural data and neutron diffraction data.

Temperature dependence for Ice III (H_2O) has been followed in the range of temperatures between 236K and 186K.

The Ice III to Ice IX transition was studied at different constant pressures at a cooling rate of 1K/min. We observed the Ice III to Ice IX transition only if the pressure was kept between about 2.5 and 3.2 k bar. At pressures outside that range Ice II appeared.

The Raman spectra of 2% D_2O in H_2O shown on fig. 2 are the first reported Raman frequencies of the uncoupled O-D frequencies. They are similar to the uncoupled O-D frequencies obtained from the infrared spectra of reclaimed samples (ref. 7).

A more detailed description of this work is being prepared in the form of a PhD thesis (B. Sukarova) which will form the basis of a later publication.

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