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# Proton order–disorder transition of ice investigated by far-infrared spectroscopy under high pressure

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**Abstract.** *In situ* high-pressure measurements of the far-infrared absorption spectra in ice VII and VIII covering the region of translational lattice modes are made by utilizing an infrared beam line of synchrotron radiation at the Institute for Molecular Science (Okazaki). Although the lattice dynamics are almost same for both the phases, large spectral changes are observed on the occasion of the proton order–disorder transition. In the proton disordered phase (ice VII), absorption spectra reflecting a density of states of lattice modes are obtained. The proton ordered phase (ice VIII) gives rise to an absorption peak due to the optical phonon at the Γ point. The anomalous pressure dependence of the phonon energy in ice VIII indicates the occurrence of a lattice instability below 2.7 GPa with decreasing pressure, which is supported by the recent neutron inelastic scattering experiments by Besson *et al*.

## 1. Introduction

Ice is one of the most typical and familiar hydrogen-bonded substances. There exist more than ten allotropic modifications which are classified into two groups: the proton ordered phase and disordered phase. Proton order–disorder transition problems have attracted plenty of research interest [1]. Though various kinds of measurement were performed with respect to the transition so far, *in situ* observation of far-infrared absorption spectra at high pressures has never been reported. The reason is that the intensity of usual far-infrared light sources is too weak to obtain enough signals for small-area samples loaded in a diamond anvil cell (DAC). In order to overcome the difficulty, we have utilized the far-infrared beam from synchrotron radiation.

The aim of the present study is to investigate the spectral change induced by the proton order–disorder transition between ice VII and VIII. Secondly, we have studied the pressure dependence of the optical phonon energy for the translational lattice mode in the proton ordered phase of ice VIII.

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## 2. Experimental method

As a far-infrared light source, we utilized the beam line 6A1 at the UVSOR facility in the Institute of Molecular Science. Ice VII was prepared by applying pressure higher than 2 GPa to distilled water or $D_2O$ (99.99% isotopic purity supplied by Aldrich Chemical Company) loaded in a DAC at room temperature. The DAC was settled into a cryostat equipped with a lever arm system which enables one to adjust the pressure outside the cryostat [2]. The VII–VIII transition was realized by cooling down the DAC. After passing through a Martin–Puplett interferometer, the infrared beam transmitted the sample in the DAC and was guided into a detector made of a Ge bolometer. Transmission spectra were obtained by the Fourier transformation method.

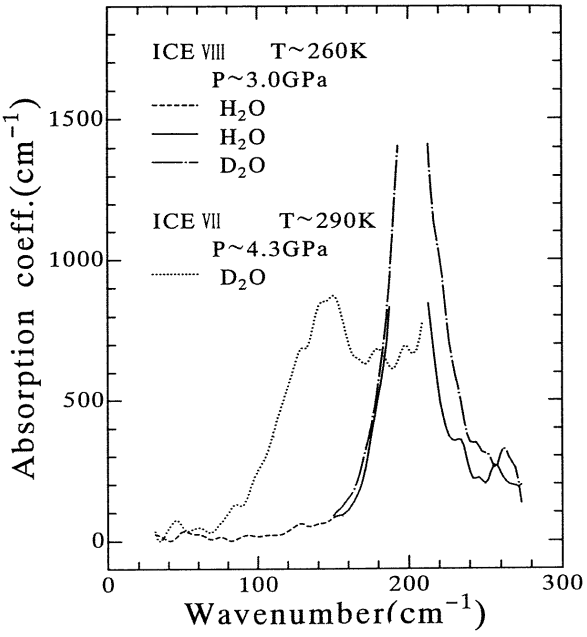


**Figure 1.** Far-infrared absorption spectra in ice VII and VIII.

## 3. Results and discussion

The dotted line in figure 1 shows the far-infrared absorption spectrum of $D_2O$ ice VII measured at 4.3 GPa and 290 K. The observed spectral range covers the lattice mode region. The chain line corresponds to $D_2O$ ice VIII obtained at 3.0 GPa and 260 K. The sample thickness larger than 20 $\mu$m for large absorption coefficients at a peak around 200 $cm^{-1}$ prevented observation of the top part of the absorption peak. Since ice VIII has complete translational symmetry even including the proton configuration, the selection rule for the wavenumber holds rigorously, which means only phonons with zero wavenumber are observable. Therefore, the absorption peak found for $D_2O$ ice VIII in figure 1 is attributed to the translational mode of the optical phonon at the $\Gamma$ point [3]. It is found that a large change of spectral shape occurs on the occasion of the proton order–disorder transition.

Although the centres of gravity for each water molecule in ice VII occupy lattice points of the crystal which belongs to the cubic $Pn3m$ space group [4], the proton configuration has no translational symmetry. The absorption coefficient $\alpha$ in such an orientationally disordered lattice is expected to be [5]

$$\alpha \propto \nu^2 D(\nu) \tag{1}$$

where $D(\nu)$ expresses a density of states for phonons. When a Debye type behaviour like

$$D(\nu) \propto \nu^2 \tag{2}$$

is substituted into equation (1), the relationship $\alpha \propto \nu^4$ is obtained. The data points in the wavenumber region lower than 140 $cm^{-1}$ in figure 1 are replotted on a logarithmic scale as shown by solid circles in figure 2. The broken line exhibits a relation as $\alpha \propto \nu^{4.7}$. The deviation of the exponent from 4 could be ascribed to an increased exponent for $D(\nu)$, since equation (2) is valid only for the low wavenumber region for the acoustic modes. The peak around 150 $cm^{-1}$ for the dotted line in figure 1 is therefore interpreted as a peak for the density of states. This interpretation is also supported by the inelastic neutron scattering for ice VIII at ambient pressure at 25 K [6]. Kolesnikov *et al* [6] reported the peak found at 119 $cm^{-1}$ corresponds to the maximum of a density of states for the acoustic mode. We have measured the pressure coefficient of a Raman active translational mode. Six data points taken from the low wavenumber region of figure 2 in [1] gives a slope of 13.3 $cm^{-1}$ $GPa^{-1}$. The Raman measurement also gave a temperature coefficient as $-0.05$ $cm^{-1}$ $K^{-1}$. Adopting these values of the coefficients, we convert the peak wavenumber 119 $cm^{-1}$ into the conditions of our observation (4.3 GPa and 290 K) as $119 + 13.3 \times 4.3 - 0.05 \times (290 - 25) = 163$ $cm^{-1}$. The value roughly coincides with our peak value 150 $cm^{-1}$. These arguments indicate that the far-infrared absorption spectrum of ice VII in figure 1 results from the fact that all the phonon modes become infrared active over the entire Brillouin zone on account of the proton disorder [5].

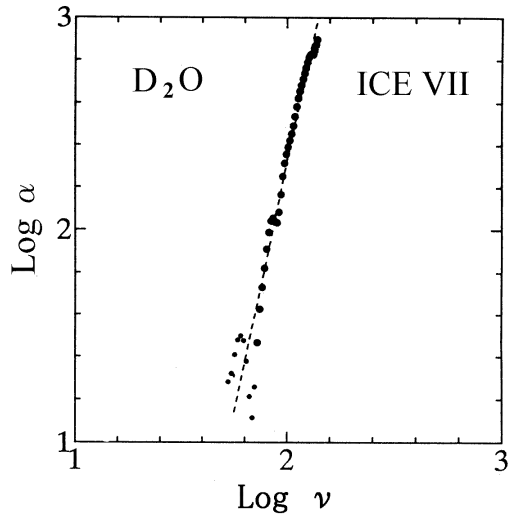


**Figure 2.** Logarithmic plots of absorption coefficient $\alpha$ against wavenumber $\nu$ in ice VII. Data taken from figure 1 in the wavenumber region below 140 $cm^{-1}$ are plotted. Relationship $\alpha \propto \nu^{4.7}$ is shown by a broken line.

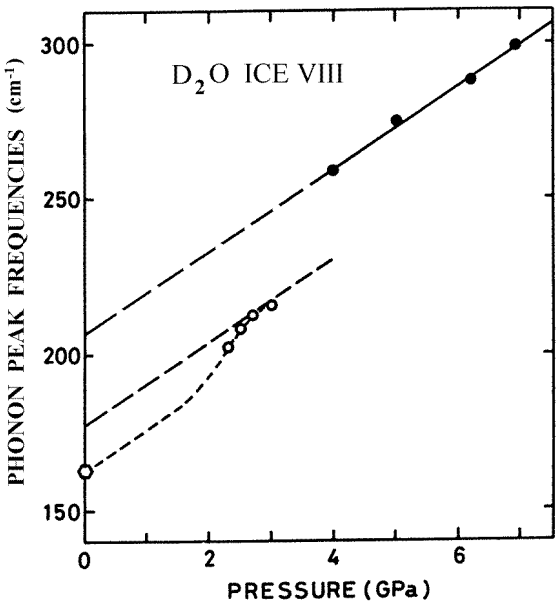


**Figure 3.** Pressure dependence of phonon peak frequencies for the translational lattice modes in ice VIII. Open circles correspond to the infrared active mode measured at 260 K. Closed circles exhibit the Raman active mode measured at 100 K. The hexagonal mark is taken from the data for pressure retrieved ice VIII at ambient pressure after Tay *et al* [3].

Figure 3 exhibits the pressure dependence of peak wavenumbers of the far-infrared absorption and Raman spectra in ice VIII denoted by open circles and closed circles, respectively. Since the true absorption peak was not observed as explained above, we define it by the centre of the absorption band. The hexagonal mark at zero pressure was taken from the datum by Tay *et al* who observed the far-infrared absorption peak in pressure retrieved ice VIII at 100 K and ascribed it to the $\nu_{Tx,Ty}(E_u)$ lattice mode [3]. Since both the infrared absorption peak and the Raman peak belong to the translational mode, their pressure coefficients are expected to be almost the same. A broken line in the figure is drawn under such expectation. It is not reasonable to connect the hexagonal mark and four open circles with a straight line, because such a line gives too large a pressure coefficient compared with the Raman mode. More rigorously, since the absolute phonon energy of the infrared active mode is smaller than that of the Raman mode, the pressure coefficient also should be smaller for the infrared mode. It is found that the pressure dependence of the phonon energy for the infrared active mode tends to deviate downwards from the linear dependence around 2.7 GPa with decreasing pressure. It has been long believed that ice VIII is able to be retrieved at ambient pressure below 125 K as the metastable phase. However, the anomalous pressure dependence of the infrared active phonon shown in figure 3 indicates that some kind of structural anomaly is involved below 2.7 GPa in ice VIII. Recently, neutron diffraction studies by Besson *et al* [7] revealed an isostructural phase transformation below 2 GPa related to a weakening of the bonds between the two $D_2O$ sublattices of ice VIII. Such an interpretation well fits to our observation in figure 3.

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