Observation of Fano Interference in High-Pressure Ice VII

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Infrared absorption spectra of ice VII have been measured up to 100 GPa at room temperature. The OH stretching peaks, which showed a rapid shift to low frequency with an enormous line broadening with increasing pressure, were found to interfere with the OH bending and librational peaks at very high pressures above 40 GPa. Appearance of such *Fano*-type interference in absorption line shape indicates that the OH stretching modes form a continuous (or quasicontinuous) energy band in their excitation state. The formation of the energy continuum is closely related to the conversion from double- to single-minimum shape in the hydrogen-bond potential, and hence considered to be a signature of the onset of hydrogen-bond symmetrization.

The hydrogen-bond symmetrization in ice has been one of the major subjects in chemistry and physics over a half century. The energy potential for the proton motion along the hydrogen-bonded O-O axis in ice can be described with a double-minimum potential. As oxygen atoms in a crystal lattice are pushed closer by applying pressure, the central potential barrier separating the two minima will gradually be depressed and eventually the potential may converge into a single-minimum shape at a sufficiently high pressure [1]. Hydrogen-bonded protons initially located at about one-third of the O-O distance will relocate to the symmetric midpoints; the picture of ice as a molecular crystal breaks down entirely.

The microscopic mechanism of the hydrogen-bond symmetrization has repeatedly been investigated previously using semiempirical methods [1–4] and very recently using *ab initio* quantum-mechanical methods [5,6], whose predicted transition pressures range from 35 to 80 GPa. Some experimental evidence was reported in the early 1980s suggesting a transition into symmetric ice around 50 GPa; it was an anomaly in the longitudinal sound velocity observed in the ice-VII phase at room temperature [7] or the appearance of a new lattice vibrational peak observed in the ice-VIII phase at 100 K [8,9]. The latest Raman measurement, however, indicated that the low-temperature transition in ice VIII was into a known high-pressure phase of ice VII [10,11]. The hydrogen-bond symmetrization has not been confirmed yet.

We have measured infrared absorption spectra of ice VII to 110 GPa at 298 K using a diamond anvil cell [12] in order to explore the hydrogen-bond symmetrization. Thin ice films were prepared by condensation of evaporated water on the top face of one diamond anvil with an attached metal gasket with a hole 20 μm in depth and 50 μm in diameter, which was previously cooled in a liquid nitrogen bath. Then solidified xenon or tetrachloromethane was charged in the gasket hole. The former is transparent over the whole wave-number region measured, while the latter is also transparent in the region

for the molecular vibrations of H_2O above 1000 cm^{-1}. Spectral measurement was made at room temperature with a microscope FT-IR spectrometer. Pressure was determined using the ruby fluorescence technique [13]. The highest pressures reached with xenon and tetrachloromethane were 85 and 110 GPa, respectively. Both pressure media provided the same results.

The OH stretching peaks show the most drastic pressure change among the observed vibrational peaks (Fig. 1). The peak positions rapidly shift from about 3000 to near 2000 cm^{-1} with an enormous peak broadening, while the pressure increases from 18 to 45 GPa. The extending tail already intrudes into the low-frequency region below 700 cm^{-1}, the measuring low-frequency limit of the detector. Although determination of the peak position and width becomes hard, the backgrounds continuously rising around 700 cm^{-1} suggest further peak shifts to low frequency on compression beyond 60 GPa. The HOH bending vibrational peak, which stays at nearly the same position of 1550 cm^{-1}, disappears gradually about 45 GPa, whereas the librational peak shows a monotonic shift to high frequency.

Asymmetric deformation in peak shape is another drastic change observed in the high-pressure spectra. This is demonstrated for the bending peak and more clearly for the librational peak when these peaks overlap with the broadened stretching peak. The librational peak, for instance, begins to deform at about 40 GPa, whereby its peak position just slides up the extending tail of the stretching peak. As seen in the spectrum measured at 18 GPa, a librational peak located sufficiently far from the stretching peak does not suffer from deformation, and the peak shape is well fitted with a Lorentzian function as usual. Around 85 GPa, the molecular rotational peak grows a sharpened asymmetric shape with a dip in the low-frequency side and an extending tail in the other side. This kind of interference phenomenon in absorption shape has been known as Fano interference [16], and will be discussed again later.
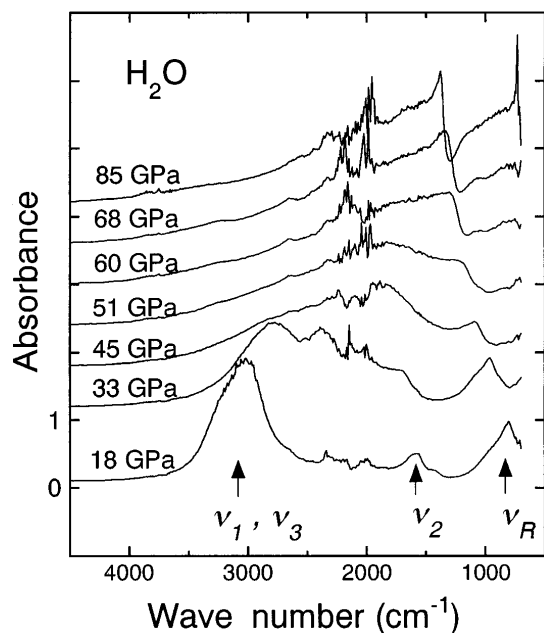
FIG. 1. Infrared absorption spectra of ice VII, in which oxygen atoms comprise a body centered cubic lattice with disorder protons [14]. Three infrared-active intramolecular vibrations, a symmetric bond stretching (ν_1), an asymmetric bond stretching (ν_3), and a bond bending vibration (ν_2), were observed. In addition, one librational vibration (ν_R) was able to be seen at pressures above 18 GPa [15]. Large noises ranging from 2000 to 2400 cm^{-1} were due to incomplete cancellation of the strong absorption of the diamond anvils in background subtraction procedures.

The observed peak frequencies are plotted as a function of pressure in Fig. 2. The stretching frequency decreases very rapidly at rates of 20 to 30 cm^{-1} GPa^{-1}, intersecting the bending and librational frequencies, respectively, at about 50 and 70 GPa. In order to demonstrate the unusual peak broadening, the full width at half maximum of the peak height is presented by a vertical bar attached to each data point. The broadening seems to be accelerated above 30 GPa, and the width increases beyond 3000 cm^{-1} at higher pressures. The unperturbed peak frequencies for the asymmetrically deformed peaks were determined by fitting the observed spectra with Fano functions [16]. The librational frequency thus obtained shows a monotonic increase from 800 to 1400 cm^{-1} as the pressure increases from 20 to 110 GPa. The bending frequency shows pressure-insensitive behavior.

Fano interference has been interpreted in terms of the interaction of a discrete energy state with a continuous (or quasicontinuous) energy continuum [16]. Consider two excitation processes from a ground state to one single discrete state and to a continuous band as displayed in the schematic energy diagram [Fig. 3(a)], in which the single-state energy level is assumed to be within the continuous band. When there is no interaction between the two energy states, two excitations occur independently without
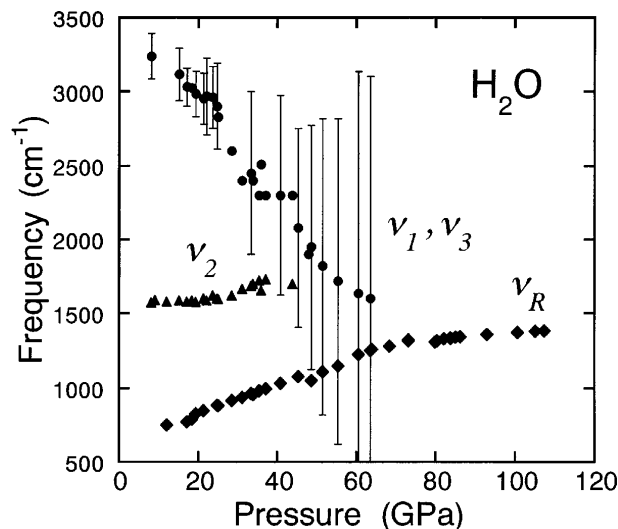

FIG. 2. The observed peak frequencies are plotted as a function of pressure. The full width at half maximum of the peak height is presented by a vertical bar for the stretching vibration. The peak frequencies of the interfering librational mode were obtained by fitting the observed spectra with Fano functions.

any interference and the overall absorption spectrum can be obtained simply by summing up the individual spectra. Interaction V will modulate their unperturbed energy states and cause an asymmetric interference in the absorption line. This interference model was first applied to explain the asymmetric shape of electronic absorption spectra [16] and later extended to asymmetric vibrational [17] or coupled electronic-vibrational spectra [18]. We found exactly this kind of interference phenomenon in the absorption spectra of highly pressurized ice, and notably that the stretching vibration was responsible for the formation of a continuous energy band. One example of absorption spectra fitted with a Fano function is demonstrated in Fig. 3(b).

How can the OH stretching vibration form an energy continuum? Let us first start from a harmonic oscillation model, and in turn see how anharmonicity alters the characteristics of the harmonic vibration. The harmonic oscillation model leads to a quantized energy series $h\nu(1/2 + n)$, and a selection rule $\Delta n = \pm 1$ for transitions between them [19]. These results can be applied to the proton motions in ice at relatively low pressures, in which each minimum of the double-well potential is approximately described with a quadratic expression. Allowed transitions from the ground to the first excitation state result in a rather narrow absorption peak.

A drastic change in the vibrational state will take place when the central potential barrier decreases to an energy level comparable to the first excitation state of the OH stretching vibration. The proton motions originally confined in one minimum will step out to extend over the flattened double-well potential. Apparently, the harmonic
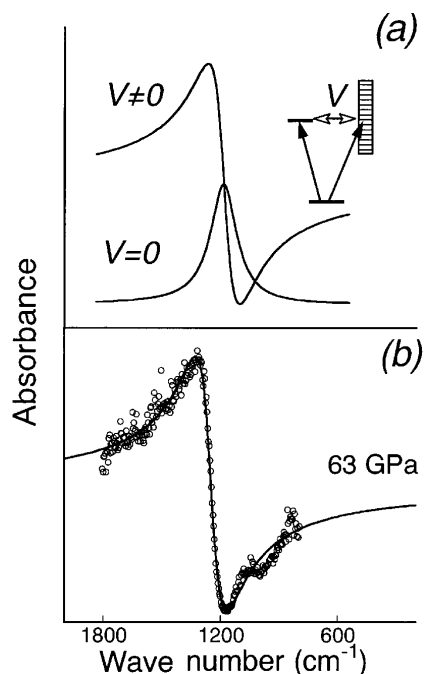
FIG. 3. (a) A model for analyzing interference phenomena in absorption. A single discrete state interacts with a continuous (or quasicontinuous) band through V, producing an asymmetric absorption peak described by $(q + \varepsilon)^2/(1 + \varepsilon^2)$: q is a lineshape parameter and $\varepsilon = (\omega - \omega_0)/\Gamma$, where ω_0 is an unperturbed vibrational frequency and Γ is a linewidth parameter. In the case of ice, discrete and continuum energy states correspond to the librational and OH stretching vibrational states, respectively. (b) One typical example of spectra fitted with Fano functions. A librational peak measured at 63 GPa was well reproduced with the optimized parameters of $q = 1.01$, $\omega_0 = 1250$ cm^{-1}, and $\Gamma = 80$ cm^{-1}.

oscillation model is no longer adopted. There is no theoretical investigation available for consideration of such enormously anharmonic proton motions. However, it is intuitively speculated that the introduced anharmonicity alters the characteristics of the harmonic vibration. First, the delocalization of proton motion reduces the energy intervals in the excitation levels and probably creates a quasicontinuous excitation band. Second, the selection rule for excitation breaks down and any excitation to the quasicontinuous band will become allowed. These alternations seem to give a qualitative explanation for the formation of an energy continuum and hence the appearance of Fano interference in ice.

In the present study, clear evidence for the transition to the symmetric hydrogen bond was not obtained up to 110 GPa. The symmetrization transition point should be detectable, for instance, as a minimum in the stretch-

ing frequencies plotted as a function of pressure, since the pressure dependence of the stretching frequency turns from a negative to a positive slope through the conversion in the potential shape [4,6]. This has been believed to be unambiguous evidence for the symmetric transition. The infrared absorption spectra showed a rather complicated behavior: Fano-type interference phenomena in the absorption peak shape. The observed spectral features indicate that the hydrogen-bond potential already loses the original double-minimum shape and possibly converts into a single-minimum-like potential in the measured pressure range to 110 GPa. To extract the nature of hydrogen-bond symmetrization from the observed spectra, more quantitative theoretical studies of the anharmonic vibrational motions of protons in highly densified ice will be required.

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