

Infrared spectroscopic study of H₂O-D₂O mixed ice up to 100 GPa

Eriko Katoh and M. Song

*Core Research for Evolutional Science and Technology, Japan Science and Technology Corporation,
Kawaguchi, Saitama 332-0012, Japan*

H. Yamawaki, H. Fujihisa, M. Sakashita, and K. Aoki*

National Institute of Materials and Chemical Research, 1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan

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Infrared absorption spectra were measured for ice prepared from [H₂O]_{0.5}[D₂O]_{0.5} solution up to 100 GPa at 298 K and combined with those previously measured for pure H₂O and D₂O ices to complete the infrared data for the molecular and lattice vibrations. The isotopomeric molecular vibrations of H₂O, D₂O, and HDO in a molecular phase of ice VII existing between 2 and ~60 GPa showed pressure behavior very similar to that found for the corresponding isotopomers in H₂O ice, D₂O ice, and HDO-contaminated D₂O ice, respectively. The spectrum became featureless for an atomic phase of ice X appearing roughly at 100 GPa; the lattice vibrations related to proton motions were strongly disturbed by isotope mixing as expected. The spectral comparison between the mixed and pure ices for a pressure region of 60–100 GPa lead to an interpretation that hydrogen-bond symmetrization developed progressively in a translationally disordered intermediate phase.

In contrast to complex behavior at low pressures, the phase diagram of ice becomes simple at high pressures. The latest Raman measurement established boundary lines for a pressure region of 2–100 GPa for three dense ices:¹ a high-temperature molecular phase ice VII, a low-temperature molecular phase ice VIII, and an atomic phase ice X. Ice VII appearing at 2 GPa at room temperature has a crystal structure consisting of two interpenetrating networks in which rotationally disordered molecules are tetrahedrally connected by hydrogen bonding. The unit cell is described as a body-centered-cubic (bcc) lattice.^{2–4} The average positions of oxygen atoms are on the bcc sites with each oxygen atom covalently bonded to two hydrogen atoms occupying two of four tetrahedral sites. Ice VII has been predicted to transform at higher pressure into translationally disordered ice VII with protons showing bimodal distribution along the bonding axis as a result of enhanced tunneling transfer.^{5–9} This disordered structure gradually transforms into symmetric ice X with protons equidistant from the two bonded oxygen neighbors. Such sequential transformation can be understood in terms of progressive ordering of protons in the oxygen bcc lattice as schematically drawn in Fig. 1, having experimentally been investigated by Raman,¹ infrared,^{10–13} and x-ray diffraction^{14–16} measurements.

Vibrational spectroscopy has often been employed as a sensitive probe investigating the molecular structure and the bonding state in ice under pressure. H₂O (D₂O) molecule has three fundamental molecular vibrations: symmetric stretching, antisymmetric stretching, and bending modes. Among them, the stretching vibrations are particularly important. They are associated with proton motions along the hydrogen bonding axis, providing valuable information on the hydrogen bonding potential. Infrared (IR) absorption and Raman scattering measurements have revealed pressure-induced softening behavior^{10–13,17} and mode mixing^{12,13,18} for the stretching vibrations in ice VII. These spectral changes are interpreted as arising from deformation of the

hydrogen-bonding potential from a double towards single minimum shape, and hence as precursor to a phase transition into ice X. The transition into translationally disordered ice VII, an intermediate nonmolecular phase between molecular phase ice VII and atomic phase ice X, was observed at about 60 for H₂O ice^{1,10–13} and about 70 GPa for D₂O ice.^{10,13}

We present IR absorption spectra measured for a mixed ice containing the isotopomers of water H₂O, HDO, and D₂O. The spectra are compared with those measured previously for H₂O and D₂O ices and for HDO molecule contaminated in D₂O ice. Influence of isotope mixing on the hydrogen bonding in molecular and atomic phases of ice will be discussed.

IR absorption spectra were measured at pressures up to 100 GPa at 298 K with a diamond-anvil cell (DAC). Ice films were prepared by freezing a solution of H₂O (50%) and D₂O (50%) in a sample chamber of DAC cooled below 293 K in advance. The detailed procedures for sample preparation, DAC handling, and IR measurement have been described elsewhere.¹³

The IR spectra observed consist of the peaks related to stretching, bending and rotational vibrations of the iso-

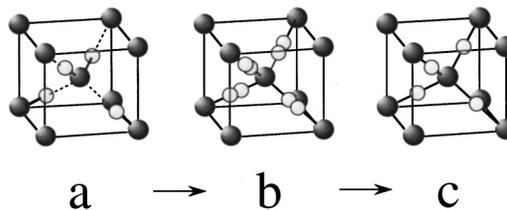


FIG. 1. Crystal structures of high-pressure dense ices. Oxygen atoms are represented by large spheres and hydrogen atoms by small spheres. Oxygen atoms form bcc lattices (a) with rotationally disorder in molecular orientation for ice VII, (b) with bimodal proton distribution due to tunneling transfer for translationally disordered ice VII, and (c) with ordered protons at the bond midpoints for ice X.

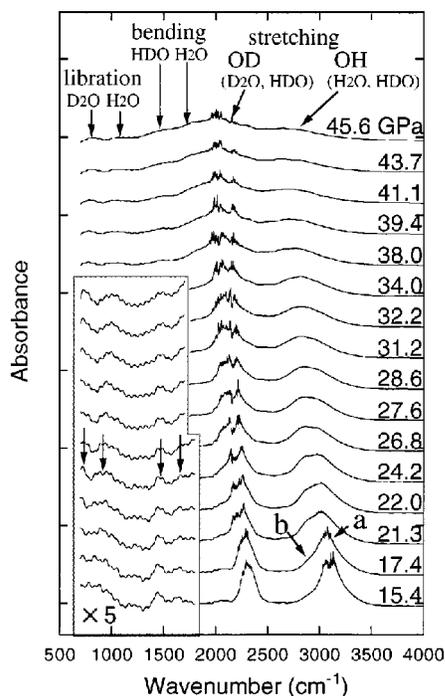


FIG. 2. IR spectra measured for H₂O-D₂O mixed ice up to 50 GPa. The absorption bands observed are those related to stretching, bending, and librational vibrations of the isotopomers of H₂O, HDO, and D₂O. Arrows *a* and *b* in a 17.4-GPa spectrum represent the OH stretching and the overtone of the HDO bending peaks, respectively, which show resonance behavior at higher pressures.

isomers H₂O (25%), HDO (50%), and D₂O (25%) as shown in Fig. 2. A 15.4-GPa spectrum shows intense peaks at ~ 2300 and ~ 3100 cm^{-1} assigned to the OD and OH stretching modes, respectively. Each peak involves the contributions from two isotopomers; the peak at ~ 3100 cm^{-1} , for example, can be deconvoluted into the OH stretching components of H₂O and HDO molecules. The stretching peaks move to low frequency with increasing pressure, becoming broadened significantly. We find a peak separation in the OH stretching region at pressures of 20–30 GPa and an alternation in relative intensity between the separated peaks with further increase in pressure to 40 GPa. The OD stretching peaks merge into diamond absorption bands extending between ~ 1900 and ~ 2600 cm^{-1} . Large noise in the diamond region is attributed to insufficient absorption correction, interfering with observation of the whole peak shape for the OD stretching. Approximate peak positions are hence determined by eyes. Several peaks appear in a low frequency region below 2000 cm^{-1} as shown in the magnified spectra. The peaks showing slight shift to high frequency in a region of 600 – 1000 cm^{-1} are assigned to the librational vibrations of H₂O and D₂O molecules. Those steadily remaining around 1500 cm^{-1} are assigned to the bending vibrations of HDO and H₂O molecules.^{18,19}

IR frequencies measured for the mixed ice (solid circles) are plotted as a function of pressure along with those of H₂O ice (solid lines),¹³ D₂O ice (dotted lines),¹³ and HDO molecule contaminated in D₂O ice (dashed lines)¹⁸ in Fig. 3. For the mixed ice, each molecular species is found to show frequency shift with pressure close to that of the corresponding molecular species of pure ices or HDO impurity. The OD

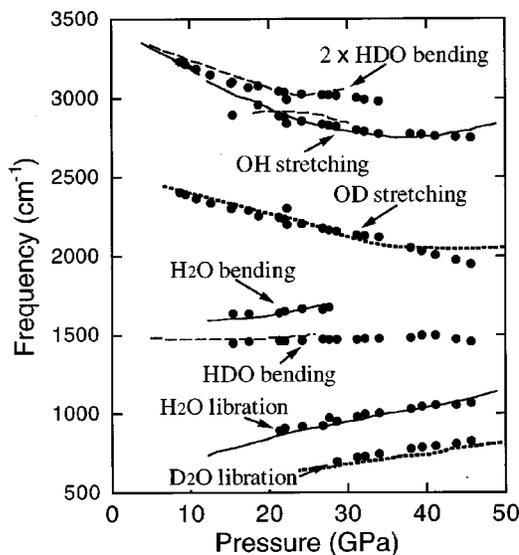


FIG. 3. IR peak frequencies measured for H₂O-D₂O mixed ice (solid circles), H₂O ice (solid lines, Ref. 13), D₂O ice (dotted lines Ref. 13), and HDO molecule contaminated in D₂O ice (dashed lines, Ref. 18) at pressures up to 50 GPa.

stretching frequencies, for example, of the mixed and pure D₂O ice are exactly on the same line for the whole pressure region measured.²⁰ One can hence make vibrational mode assignment immediately; they are overtone of HDO bending, OH stretching of H₂O and HDO, OD stretching of D₂O and HDO, H₂O bending, HDO bending, H₂O libration, and D₂O libration as labeled in Fig. 3.

The spectra measured at 60, 80, and 100 GPa are drawn along with those of H₂O and D₂O ices¹³ in Fig. 4. At 60 GPa, pure ices lose definite peaks originating from the molecular vibrations, showing significantly broadened bands with peak tops at approximately 1250 and 1750 cm^{-1} for H₂O ice and 850 and 1300 cm^{-1} for D₂O ice. Further increase in pressure changes the spectral feature gradually but dramatically. An intense, sharp peak appears at 1350 cm^{-1} in H₂O ice and at 1000 cm^{-1} in D₂O ice at 80 GPa. Three dominant peaks are observed in a 100-GPa spectrum: two H₂O-ice peaks and one D₂O-ice peak. By contrast, the spectrum of the mixed ice remains featureless even at 100 GPa. The absorption bands become slightly narrow but still broad compared to those of pure ices. The peak tops, however, are located at 810 , 1140 , and 1410 cm^{-1} well corresponding to those of pure ices as seen in the top spectra.

No significant change due to isotope mixing was observed for the vibrational states of water molecules in ice below 60 GPa. As described previously, the H₂O, HDO, and D₂O isotopomers in the mixed ice show frequency shift with pressure close to that found for pure H₂O and D₂O ices and contaminated HDO molecule. In ice VII each molecule is connected by hydrogen bonding to four neighboring molecules tetrahedrally arranged (see Fig. 1); the surrounding molecules are H₂O, HDO, or D₂O isotopomers in the mixed ice and H₂O species alone in pure H₂O ice. If the hydrogen bonding state depended on the partner molecular species, the vibrational frequencies of the mixed ice should be modified to some degree from those of pure ices. Both mixed and pure ices show quite similar pressure behavior in vibrational fre-

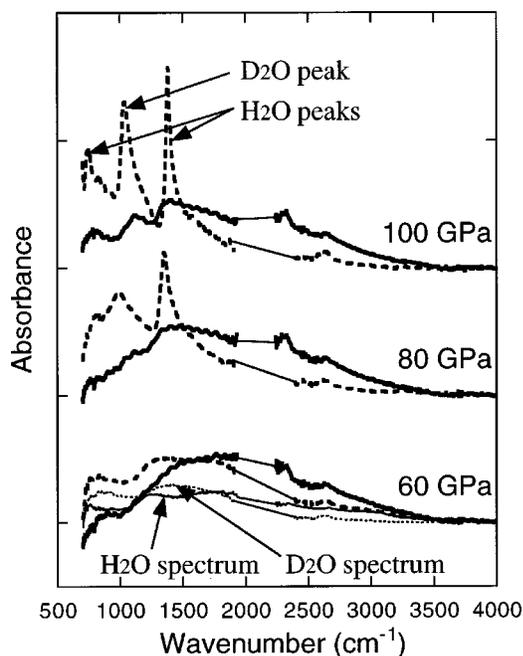


FIG. 4. IR absorption spectra of ices measured at 60, 80, and 100 GPa: spectra of H₂O-D₂O mixed ice (thick solid lines), sum spectra of H₂O and D₂O ices [thick dashed lines (Ref. 13)]. For the 60-GPa spectrum, the individual spectra of H₂O ice (thin solid line) and D₂O ice (dotted line) are additionally presented to demonstrate their contribution to the sum spectrum. The region of 1900–2400 cm⁻¹ is significantly noisy owing to insufficient correction for the diamond absorption. We omit the data and fill in the blank with solid lines.

quency over a wide pressure range as demonstrated by the OD stretching modes of D₂O and HDO species. They keep decreasing in frequency along the same line in spite of a large change in frequency by ~500 cm⁻¹ for a pressure increase from 2 and 50 GPa (Fig. 3). We hence conclude that the molecular vibrations are influenced little by hydrogen-bonded partners and dominated by hydrogen-bond length.

Mode mixing is found for the stretching vibration of HDO species in the mixed ice as well as that contaminated in D₂O ice. An intense peak is observed at 3070 cm⁻¹ with a shoulder peak on the low frequency side at 17.4 GPa (Fig. 2). The main peak (arrow *a*) involves those of the OH stretching vibrations of both H₂O and HDO molecules, and the shoulder peak (arrow *b*) likely arises from an overtone of the bending vibration of HDO molecule. An increase in pressure inverts gradually the peak intensity for the two peaks owing to mixing of the vibrational modes. The peak originally assigned as the overtone of bending mode is converted into stretching one at about 40 GPa eventually. Such mode mixing has been observed for the OH stretching and the overtone

of bending modes of HDO molecule contaminated in D₂O ice.¹⁸ The modulated frequencies (dashed lines in Fig. 3) exhibit clearly anticrossing behavior at pressures of 20–30 GPa. This is typical of mode mixing often called as Fermi resonance. The peak frequencies of the corresponding vibrational modes in the mixed ice also show anticrossing in the approximately same pressure range but its repulsive feature is less clear. The resonance feature is slightly smeared out in the mixed ice spectra owing to peak broadening.

The featureless spectrum of the mixed ice at 100 GPa is attributed to site disordering of the centered H and D atoms. The atomic phase of pure H₂O ice above 100 GPa has a Cu₂O structure with H atoms at the bond midpoints.¹⁶ The H(D) atoms oscillate around the equilibrium positions located at the minimum of a single-well potential, forming normal modes for the lattice vibrations. Two IR-active *T*_{1u} modes have been assigned to the IR peaks observed for the atomic phase ice X.^{10–13} A 100-GPa spectrum of mixed ice shows significant degradation of the lattice peaks dominated by H(D) motions, indicating destruction of H₄(D₄) tetrahedrons and consequently related normal vibrations by isotope mixing. The lattice mode dominated by oxygen motions (Raman active *T*_{2g} mode) should not essentially be influenced by isotope mixing. The comparison of the pure- and mixed-ice spectra thus allows reconfirmation of the mode assignment for the IR-active lattice peaks and hence the transition into the atomic phase around 100 GPa.

The featureless spectrum of pure ices at 60 GPa can now be attributed to H(D) atoms disordered translationally along the hydrogen bonds by tunneling transfer. The sluggish transition with pressure to the atomic or ordered X phase is demonstrated as gradual growth of the IR peaks (see Fig. 4 and Ref. 13). The recent Raman measurement succeeded in detecting a lattice vibrational peak of ordered ice X.¹ The peak was identified as the *T*_{2g} mode of oxygen bcc lattice, appearing at about 80 GPa and becoming dominant in the spectrum at pressures above 100 GPa. The Raman data on the lattice vibration suggested presence of an intermediate disordered phase between the molecular and atomic phases at a pressure region from 60 to roughly 80 GPa in qualitative agreement with the theoretical prediction.⁷ The mixed ice involves disordering arising from both translational motion and isotope mixing in the intermediate phase. The disordering due to mixing still remains in the atomic phase as seen in the IR spectrum measured at 100 GPa. The changes in IR spectra of the mixed and pure ices can consistently be interpreted in terms of presence of the intermediate disordered phase.

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*Author to whom correspondence should be addressed. Email address: aoki@home.nimc.go.jp

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- ²⁰The stretching frequencies of pure ices tend to deviate from those of mixed ice above 35 GPa. The deviation were produced in procedure for determining the peak positions of the stretching modes which were resonanced with underlying combinations modes (Ref. 13). For pure ices, the resonanced peaks were well separated and their positions were individually determined using a conventional fitting program. For the mixed ice, the center position of unseparated, resonanced peaks was roughly determined by eye.