Overtone spectra and hydrogen potential of H$_2$O at high pressure

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The first overtones of the stretching and bending vibrations of H$_2$O and the first stretching overtone of D$_2$O were measured to pressures of 37 GPa at 300 K, encompassing the stability fields of water, ice VI, and ice VII. The successive disappearance of the overtone peaks in ice VII with increasing pressure indicates that the barrier height in the double minimum hydrogen potential decreases at a rate of 230 cm$^{-1}$ GPa$^{-1}$ to pressures of 32 GPa. The first overtone of the O-H stretching vibration splits and forms a doublet between 10 and 25 GPa, implying that the barrier height is near the energy of this overtone and that proton tunneling may occur at this energy level between 10 and 25 GPa. The frequency of the first stretching overtone of ice VII is also strongly influenced by quantum effects near the barrier top, as its frequency is larger than harmonic values. The hydrogen bonding potential in ice VII at high pressure is described using a semiempirical potential model that incorporates the observed rate of barrier height reduction and available O-H and O-O bond length data of ice VII under pressure. This model requires a rapid increase in O-H bond length between 40 and 60 GPa in order to reach a value of one half the O-O distance above 60 GPa, at which pressure the transition to ice X has been reported to occur. Up to 40 GPa, our model is consistent with the trend of O-H bond length observed in neutron diffraction data to 10 GPa. [S0163-1829(98)07837-0]

I. INTRODUCTION

The bonding properties of the hydrogen atom along the oxygen-oxygen axis in hydrogen bonded oxides have been successfully described with a double minimum (DM) potential function (e.g., Fig. 1). In such a potential, the two minima correspond to a hydroxyl bond forming with one oxygen and a hydrogen bond with the other, which may be described as either an O-H···O or O···H-O configuration. Typically, one of these configurations will be energetically favored, resulting in an asymmetric DM potential, with the local maximum between the minima keeping the proton confined within the deeper well (Fig. 1). The height of this DM barrier corresponds to the energy required for the proton to become delocalized between the oxygen atoms.

The DM potential has been spectroscopically characterized by measuring the energies of quantized bending and stretching O-H vibrations. The characterizations are based on marked differences in the DM system at vibrational energies below and above the DM barrier. At low vibrational energies, the protons are confined within a roughly harmonic local well, with near-evenly spaced and well-resolved absorption peaks. Much smaller spacings are exhibited between energy levels in the broad and anharmonic potential above the barrier, producing a quasicontinuum of states that results in absorption peaks which are broad and difficult to resolve. Thus, there is a transition in the spectroscopic properties of the DM system, from nearly harmonic and discrete absorption peaks at lower energies, to quasicontinuum absorption when vibrational energies exceed the barrier height.

The H$_2$O DM potential is altered by changes in the oxygen-oxygen separation ($d_{O-O}$), which decreases under pressure. At 300 K, H$_2$O remains a liquid up to ~1.0 GPa, at which pressure it solidifies to ice VI. Ice VI is stable at 300 K from 1.0 to 2.1 GPa, above which ice VII is the stable phase to 60 GPa. Above 60 GPa, neighboring oxygen atoms have been compressed closely enough together that the proton occupies the midpoint between them. The ordered cuprite-structured symmetrically hydrogen bound phase has been previously referred to as ice X, we follow this convention. The primary effect of pressure on the potential of H$_2$O up to 210 GPa is the transformation from a DM potential (present in water, and ices VI and VII) towards the single well potential of the O-H-O bond within symmetrically hydrogen bound ice. The mechanism of this fundamental change in the potential which occurs between ices VII and the symmetrically bonded form of ice is largely unconstrained, but must involve lowering of the DM barrier, and therefore this phase change probably represents a gradual evolution of the bonding properties of ice. Ultimately, when the barrier lies below the ground state of the stretching vibrations, the protons should be delocalized in the broad and anharmonic potential well, causing them to become statistically centered along the O-O axis.

Strong proton disorder is predicted to occur when the barrier disappears and the potential changes from a double well to a broad, flat-bottomed single well. This proton disordered structure differs from that generally proposed for ice X, which is characterized by proton ordering and likely has a nearly harmonic potential with a single distinct minimum.

To further constrain the pressure induced changes of the DM potential in ice VII, we have measured the overtone bands in H$_2$O and D$_2$O under compression using infrared spectroscopy. The bonding properties of D$_2$O are similar to those of H$_2$O, but the vibrational levels lie at lower energies and thus offer additional information on the DM potential. The infrared absorption peaks we characterize in this study are the asymmetric stretching overtone band 2 $v_3$ in H$_2$O and D$_2$O, and a combination of the fundamental stretching and bending vibrations $v_3 + v_2$ in H$_2$O. As the DM barrier drops with pressure, we expect it to pass through these vibrational
Infrared spectra were measured on a Bruker IFS66V Fourier transform infrared spectrometer using a CaF$_2$ beam splitter, tungsten filament source, and an InSb detector with a frequency range from $\sim$11000 to 1700 cm$^{-1}$. The spectra were collected under vacuum to reduce water vapor contamination of the spectra, and no focussing optics other than the characteristic focus of the spectrometer were utilized. All spectra are reported with a resolution of 4 cm$^{-1}$. Samples of distilled H$_2$O and of 99.8% D$_2$O were loaded as liquid at 300 K into a diamond-anvil cell and contained by a steel gasket. Both modified Mao-Bell and Merrill-Bassett type diamond-anvil cells were used; the diamonds were usually equipped with 500 $\mu$m diameter culets, and characteristic sample diameters were about 150 $\mu$m. We measured spectra of liquid water, ice VI, and ice VII of four H$_2$O and five D$_2$O samples under pressure, up to a maximum of 37 GPa. Spectral fringing was present in many of these samples, and was particularly severe in the D$_2$O samples. The ruby fluorescence technique was used to determine the pressure$^{21}$ with the pressure at three to five separate ruby grains being monitored at high pressures. Due to the narrow pressure stability fields of water and ice VI at 300 K, pressure measurements were conducted with a typical accuracy of $\pm 0.1$ GPa for the spectra below 3 GPa, while the higher pressure spectra have typical errors of $\pm 1.0$ GPa.

III. RESULTS

Figures 2(a) and 2(b) show infrared spectra of H$_2$O to $\sim 31$ GPa, while Fig. 2(c) shows the infrared spectra of D$_2$O to $\sim 29$ GPa. Previous assignments of solid H$_2$O and D$_2$O overtone spectra exist for the ice I$_h$ structure, although there is some disagreement on the precise location of 2$\nu_3$.$^{26}$ Haas and Horning$^{27}$ assigned a broad band ($\sim 400$ cm$^{-1}$ width) centered at $\sim 6500$ cm$^{-1}$ to 2$\nu_3$ excitations of individual H$_2$O molecules in the ice I$_h$ structure, and used bandwidth data to calculate the height of the DM barrier in this structure (Fig. 1). However, Kroh and Ron$^6$ reassigned the 6500 cm$^{-1}$ band to a nonbound overtone of O-H stretching vibrations; this combination of fundamental vibrations on neighboring molecules (i.e., $\nu_3 + \nu_3$) is less affected by anharmonicity or near-barrier effects of the DM potential than are single molecule (bound) overtones.$^6$–$^{13}$ The reassignment of the 2$\nu_3$ bound overtone to a narrower peak ($\sim 250$ cm$^{-1}$ width) at 6000 cm$^{-1}$ suggests a grouping of levels near the barrier top, and therefore the barrier top was predicted to be near this energy (Fig. 1).$^6$ Although this ambiguity exists for ice I$_h$, the spectra of compressed water, ice VI, and ice VII are all less complex in the overtone region than that of ice I$_h$, and the region between 7800 cm$^{-1}$ and 5500 cm$^{-1}$ in H$_2$O (between 6000 and 4000 cm$^{-1}$ in D$_2$O) is dominated by a single...
FIG. 3. Mode shifts of $2\nu_3$ and $\nu_3 + \nu_2$ of H$_2$O and D$_2$O within the stability fields of water, ice VI, and ice VII; the relevant stability fields are indicated. The solid line is a mode shift predicted from a harmonic potential, calculated with data from Ref. 9. The error bars on the $2\nu_3$ peak of H$_2$O ice VII between 4 and 11 GPa indicate the broadening (full width at half-maximum) of this peak; between 15 and 25 GPa two distinct peaks are observed for this vibration.

The doublet persists up to 22 GPa where the lower frequency component of the doublet becomes un-resolvable. With further compression the higher frequency component becomes very broad (~550 cm$^{-1}$ width) by 25 GPa, and is unresolved near 30 GPa.

Such splitting was not definitively observed for the $2\nu_3$ overtone in D$_2$O, although spectral fringing could have obscured this feature [Fig. 2(c)], particularly at pressures above 13 GPa. Notably, the $2\nu_3$ overtone in D$_2$O was observed to broaden above 13 GPa, and is unresolved above 22 GPa. Similarly, the $\nu_3 + \nu_2$ peak in H$_2$O begins to broaden dramatically above 15 GPa and becomes difficult to resolve above 28 GPa [Fig. 2(b)]. This combination band does not appear to split under compression. A third peak near 4005 cm$^{-1}$ is also present in the H$_2$O spectra from 2 to 11 GPa [Fig. 2(b)] and has a slightly positive shift of ~2 cm$^{-1}$ GPa$^{-1}$ within ice VII. This peak may be produced by a combination of the O-H stretching vibration with a lattice vibration.

IV. DISCUSSION

Changes in barrier height with pressure. In H$_2$O, both the $2\nu_3$ and $\nu_3 + \nu_2$ peaks broaden and disappear over a range of pressures: between 4 and 25 GPa for $2\nu_3$, and from 15 to 28 GPa for $\nu_3 + \nu_2$ (Fig. 2). In D$_2$O, $2\nu_3$ broadens and disappears over the range between 13 and 22 GPa. Additionally, Aoki et al. observed the stretching fundamental $\nu_3$ to broaden and essentially disappear between 18 and 45 GPa. We attribute the broadening and disappearance of these peaks to the lowering of the DM barrier with pressure below the energies of these peaks. The origin of the wide pressure intervals in which the peaks broaden and disappear is twofold: the negative mode shifts of the overtone peaks under pressure increases the range over which their energies lie close to the barrier top. This effect is amplified by near-barrier quantum effects which cause the energy levels in a DM potential to be attracted to the barrier top. Further increases in these pressure intervals may be caused by relatively low frequency lattice vibrations interacting with molecular vibrations to create energy bands centered about the discrete molecular vibrations. The combination of these effects makes it difficult to ascertain the exact pressure at which the barrier drops below the energy of a given vibration. We can, however, approximate the pressure at which the barrier height equals the vibrational energies as the middle of the pressure range over which the vibrational peaks broaden and disappear. Using this technique, we find the barrier height above the ground state to be 6440 (±50) cm$^{-1}$ [0.800(6) eV] at 14 (±2) GPa from the H$_2$O $2\nu_3$ peak, and 4750 (±25) cm$^{-1}$ [0.590(3) eV] at 21 (±2) GPa from the $\nu_3 + \nu_2$ peak. The D$_2$O $2\nu_3$ peak coincides with the barrier top at 4600 (±50) cm$^{-1}$ [0.570(6) eV] and 18 (±2) GPa. Using the data of Aoki et al., $\nu_3$ is found to coincide with the barrier top at 32 (±2) GPa, with an energy above the ground state of 2550 (±70) cm$^{-1}$ [0.317(9) eV]. While recognizing that this method for barrier-height determination is empirical, we note that our derived results are internally consistent and produce a zero-pressure intercept for the initial barrier height of ~1.4 eV (Fig. 4), in good accord with previous estimates of the barrier height in ice I. For comparison, ab initio Hartree-Fock calculations on ice VIII yield a zero pressure value for the barrier height of 2.2 eV, which decreases to less than 0.5 eV at 32 GPa.

In order to estimate the full height of the barrier above the bottom of the lower minimum, we calculate the zero point energy using a harmonic model at each of the pressures for

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which we constrain the barrier height. Thus, the ground state energy was assumed to be equal to one half the energy of the $v_3$ vibration (e.g., Ref. 24), and we utilize the results on the pressure shift of the $v_3$ fundamental of Ref. 9 to approximately constrain this value. For D$_2$O, no data on the fundamental stretching vibration at pressure are available, so the zero point energy was assumed to equal one quarter the energy of $2v_3$. The predictions of this simple harmonic model may be aliased by near-barrier quantum effects on the mode shift of $v_3$ (or that of $2v_3$ for D$_2$O). However, these barrier interactions likely introduce an overestimate of no more than $\sim 20\%$ for the ground state energy at our highest pressure, and therefore introduce an uncertainty of only $\sim 8\%$ in our estimate of the barrier height at 32 GPa. The barrier heights we determine from this simple model are shown in Fig. 4, and show a linear decrease in barrier height with pressure. The estimated change in barrier height is 230 cm$^{-1}$ GPa$^{-1}$ (0.029 eV GPa$^{-1}$). If the simple linear model of Fig. 4 is extrapolated to higher pressures, the pressure at which the potential barrier is inferred to disappear is 47 (±5) GPa. There have been experimental indications that a shift in bonding in ice may occur near this pressure based on Brillouin$^{25}$ and Raman measurements,$^{26}$ as well as from theoretical results which predict barrier disappearance at 45–49 GPa.$^{27,28}$ However, more recent Raman measurements$^{29,30}$ and infrared measurements$^{9–11}$ indicate that the onset of strong proton tunneling (as opposed to barrier disappearance) probably occurs near 60 GPa in H$_2$O. Thus, it is likely that a simple linear extrapolation of the barrier height trend of Fig. 4 produces an underestimate of the actual pressure at which symmetrization of the hydrogen atoms occurs in ice. Indeed, Hartree-Fock calculations indicate that the barrier height may become significantly less pressure dependent above about 35 GPa.$^{23}$

Mode shifts. In Fig. 3, our results on the $2v_3$ overtone are compared with a purely harmonic prediction in which the first overtone lies at twice the frequency of the fundamental (derived from the $v_3$ data of Aoki et al.).$^{9}$ Clearly, the observed mode shift does not agree with the harmonic prediction; nor can it be modeled with a standard anharmonic potential, as the $2v_3$ peak in ice VII lies at energies greater than two times the fundamental stretching vibration. The pressure induced change from a nearly harmonic potential to one in which $2v_3$ lies at greater than twice the frequency of the fundamental under increasing pressure indicates that the energy levels are perturbed by proximity to the DM barrier.$^3$ Mode shift variations that have been attributed to near-barrier effects have been reported for $v_3$ between 25 and 40 GPa.$^{11}$ Such perturbation of energy levels near a DM barrier maximum has been the subject of considerable theoretical effort.$^{3,7,22,31–36}$ Our results are in agreement with the prediction that the energy levels are attracted towards the barrier, thus producing the observed deviation from normal harmonic behavior. It is this behavior that likely produces the relatively high frequency and small pressure shift of the high frequency component of the $2v_3$ band above 10 GPa (Fig. 3).

The $2v_3$ and $v_3 + v_2$ peaks decrease markedly in frequency between the spectra taken at 1.0 and 1.8 GPa in H$_2$O [Figs. 2(a) and 2(b)], as does the $2v_3$ peak in D$_2$O between 0.3 and 1.5 GPa [Fig. 2(c)]. These negative shifts, which occur abruptly as the initially liquid sample freezes to ice VI, imply that the hydrogen bonding in ice VI is significantly stronger than the average hydrogen bonding within compressed water, as O-H vibrational frequencies typically decrease with stronger hydrogen bonding.$^7$ When H$_2$O (D$_2$O) converts from ice VI to ice VII, both $2v_3$ and $v_3 + v_2$ shift positively. These shifts are consistent with differences in the oxygen-oxygen separation ($d_{O-O}$) of these two phases: in ice VI at 1.1 GPa, $d_{O-O}$ is 2.774 Å, while in ice VII at 2.4 GPa, $d_{O-O}$ is 2.890 Å.$^{37}$ Thus, the larger oxygen-oxygen distances generated by the ice VI to ice VII transition cause the $v_3$ stretching vibration to increase in frequency: this behavior is consistent with observations on the behavior of $v_3$ in a wide range of hydrogen-bonded solids with oxygen-oxygen separations above $\sim 2.45$ Å.$^7$

The splitting of the $2v_3$ peak within ice VII. A variety of DM potential shapes have been proposed for various hydrogen-bonded compounds.$^{3,8,38–41}$ For some materials, a splitting of the first O-H stretching overtone has been observed when the DM barrier lies close in energy to $2v_3$.$^{4,8}$ This splitting has been attributed to proton tunneling between the two minima in a DM potential,$^{4,8}$ consistent with a range of theoretical studies.$^{3,22,31,32}$ However, except for a few special cases, it has been shown that this splitting is predicted only for symmetric DM potentials,$^3$ while the majority of hydrogen bonded solids (including most of the ice polymorphs) have asymmetric DM potentials.$^{3,13}$

In our experiments, samples of H$_2$O were found to exhibit splitting of the $2v_3$ peak within a range of pressures between 4 and 25 GPa [Figs. 2(a) and 3]. The possibility that this doublet arises from differing mode shifts of the $2v_3$ and $v_3$ components within the stretch overtone is improbable, as the fundamental stretching peak does not exhibit splitting over the same pressure range.$^{11}$ Also, the pattern of splitting and mode shifts do not resemble a Fermi-resonance type phenomenon, as has been observed between the $v_3$ and $2v_2$ vibrations of HDO molecules in a D$_2$O ice VII matrix between 20 and 30 GPa.$^{42}$ Splitting of $v_3$ in H$_2$O has been reported between 25 and 45 GPa,$^{11}$ a pressure range in which barrier interactions are likely to be important for this vibrational level (e.g., Fig. 4 and Ref. 11). An assignment of the doublet to coupled ($2v_3$) and uncoupled overtones (such as
FIG. 5. (a) Modeled potential energy surface of the hydrogen bond within ice VII and symmetric ice expressed in equipotentials with a contour spacing of 0.5 eV. The circles are observed O-H bond length under pressure; data to 10 GPa are from Ref. 36, and those above 60 GPa are from Ref. 13. Solid lines show the trend of these experimental data. (b) Cross sections of the potential energy surface at the pressures for which DM barrier heights were determined, with the relevant transitions labeled.

\[ V(r) = D_0 \left[ 1 - \exp\left( -n \left( r - d_{O-H}\right)^2/(2r) \right) \right] + C_0 \times \left[ 1 - \exp\left( -n \left( d_{O-O} - r - d_{O-H}\right)^2/(2C(d_{O-O} - r)) \right) \right] + 259.5/(d_{O-O})^6 - 7.87 \times 10^6 \exp\left[ -5.0d_{O-O} \right]. \]  

Here, \( r \) is interatomic distance, \( D_0 \) is the dissociation energy, \( d_{O-H} \) and \( d_{O-O} \) are oxygen-hydrogen and oxygen-oxygen equilibrium separations, respectively, and \( C \) is a fit parameter which scales the relative strength of the two oxygen-hydrogen interactions. The parameter \( n \) is related to the force constant \( k \) of the oxygen-hydrogen bonds by

\[ n = kd_{O-H}/D_0. \]  

At ambient pressures, experimental values for \( D_0 \), \( d_{O-O} \), \( d_{O-H} \), and \( n \) are available for \( \text{H}_2\text{O} \); \(^{39} \) Eq. (1) was used to calculate the ice \( I_n \) DM potential curves in Fig. 1. However, the pressure dependences of the parameters \( C, n, d_{O-O}, \) and \( d_{O-H} \) must be evaluated in order to construct a model of the hydrogen potential in \( \text{H}_2\text{O} \) under compression. At ambient pressures, a value of 0.85 for \( C \) is required to reproduce the depth of the second well in the DM potential. \(^{2} \) This parameter should converge on unity at high pressure as the O-O distance shortens and the DM potential becomes more symmetric. \(^{31} \) Our observation that the \( 2v_3 \) overtone splits to form a doublet within the pressure range from 4 to 24 GPa indicates that the DM potential of ice VII approaches symmetry in this pressure range. Therefore, we impose that \( C \) increases linearly from 0.85 at zero pressure to 1.0 at 17 GPa, the pressure at which the splitting of \( 2v_3 \) is most pronounced. At higher pressures we assume that the potential remains symmetric and \( C \) is kept constant at 1.0.

As the bonding characteristics between the oxygen and hydrogen are expected to change under compression, a pressure dependence of the effective force constant \( k \) is also expected. In particular, pressure induced shifts in the polarizability of the oxygen ion are well known in a range of compounds (e.g., Ref. 44), and although explicit functions of \( k \) versus pressure are not available, we assume that \( k \) (and therefore \( n \)) will monotonically increase with pressure as ice VII densifies. An increase in the force constant within simple structures is usually reflected in a positive mode shift of stretching frequencies, whereas stretching frequencies in ice VII exhibit negative mode shifts with pressure. \(^{9,11} \) However, these negative mode shifts do not imply that the force constant associated with a hypothetical isolated O-H ion must weaken with pressure, as the frequencies of these vibrations are produced by the effects of two O-H bonds directed along the O-O axis. Rather, the negative mode shifts are related to the transformation of the DM potential towards a single minimum potential (or, equivalently, the increase in strength of the hydrogen bond until it becomes equal in strength to the hydroxyl bond). This enhanced hydrogen bond strength generates an associated pressure-induced increase in the anharmonicity of the hydroxyl potential well, thus lowering the frequency of the hydroxyl stretch. Indeed, once the symmetrically bound phase has been accessed, the O-H stretching frequency shifts positively with pressure. \(^{10,11} \)

Oxygen-oxygen separations \( d_{O-O} \) are available to 128 GPa (Refs. 14 and 45) [calculated using Eq. (A1) of Ref. 1] in ices VII and the symmetrically bound phase, as are oxygen-hydrogen separations \( d_{O-H} \) to 10 GPa in the low-temperature ice VIII phase \(^{23,46} \), which is essentially an ordered form of the ice VII structure. \(^{47} \) Within the stability field of the symmetrically bound phase (above 60 GPa) \( d_{O-H} \) is simply equal to one half of \( d_{O-O} \), and accordingly \( d_{O-H} \) is...
known between 60 and 128 GPa. Presently available $d_{O-H}$ values are shown in Fig. 5(a). Using the lower pressure (to 10 GPa) and higher pressure (above 60 GPa) dependences of $d_{O-H}$ as constraints, we assumed different possible models for the 10 to 60 GPa pressure dependence of $d_{O-H}$ in Eq. (1), and then fit the resulting potentials to the observed barrier heights of Fig. 4 by scaling $n$ [Fig. 5(b)]. This iterative procedure produced different pressure dependences of $n$ for each pressure dependence of $d_{O-H}$, and it was found that pressure dependences of $d_{O-H}$ which departed from the lower pressure trend at less than $\sim 35$ GPa were not consistent with a monotonic increase in $n$. Such low pressure deviations from the trend of Nelmes et al.\textsuperscript{46} invariably required a decrease in $n$ at pressures above $\sim 32$ GPa, after a rapid increase up to this pressure. However, pressure dependences of $d_{O-H}$ which followed the lower pressure trend until near the barrier disappearance were found to be consistent with a simple linear increase in $n$. Our preferred model for the hydrogen potential is shown in Fig. 5, and incorporates a linear increase of $n$ at a rate of 0.37 Å$^{-1}$ GPa$^{-1}$. The rate of change of $d_{O-H}$ determined by neutron diffraction in ice VIII [4 × 10$^{-4}$ Å GPa$^{-1}$ (Ref. 46)] to 10 GPa is shown in Fig. 5(a), as well as the trend of $d_{O-H}$ above 60 GPa.\textsuperscript{11,14} In addition to reproducing the change in barrier height of Fig. 4 and reasonably accurately simulating the known changes in O-H bond distance under pressure, this model also forms an approximately harmonic single well potential by 60 GPa [Fig. 5(a)], consistent with the observed symmetrization of hydrogen bonding near this pressure;\textsuperscript{39–41} a flat-bottomed well is, however, produced at pressures above about 47 GPa. Notably, our semiempirical model precludes neither an abrupt change in the pressure dependence of $d_{O-H}$ above 40 GPa, nor a more gradual change in the slope of $d_{O-H}$ at 40 and 60 GPa; rather, our model is simply designed to reproduce the known features of hydrogen bonding in H$_2$O under high pressures, within the framework of a potential model commonly used for hydrogen bonded systems.

Our predicted pressure dependence of $d_{O-H}$ is in excellent agreement with a previous theoretical calculation based on the pressure induced change in the proton order-disorder transition temperature (between ices VII and VIII); this analysis also predicts the onset of a rapid increase in $d_{O-H}$ at 40 GPa.\textsuperscript{1} Our pressure dependence of $d_{O-H}$ also agrees with the empirical dependence of $d_{O-H}$ on $d_{O-O}$ found in a wide range of hydrogen bond crystals which have an O-H $\cdot$ O bond angle of more than 170°.\textsuperscript{7} For hydrogen bound crystals with $d_{O-O}$ values of approximately 2.50 Å or larger, $d_{O-H}$ is nearly constant, while for those crystals with $d_{O-O}$ values shorter than $\sim 2.50$ Å, $d_{O-H}$ rapidly increases with decreasing $d_{O-O}$, although there is some variation in the rate of increase.\textsuperscript{7} In ice VII at 40 GPa, $d_{O-O}$ has been compressed to 2.48 Å,\textsuperscript{14} and therefore our model follows closely the empirical (ambient pressure) trend at the shorter $d_{O-O}$ distances induced by higher pressures. Furthermore, our model suggests that the departure of $d_{O-H}$ from the trend of Nelmes et al.\textsuperscript{46} occurs at a pressure below that at which the barrier disappears [Fig. 5(a)], suggesting the onset of strong proton disorder before this pressure. Previous semiempirical calculations agree well with this prediction, as strong tunneling (and consequently disorder) was found to be necessary to explain the empirical relationship between $d_{O-H}$ and $d_{O-O}$ in a wide range of hydrogen bound crystals.\textsuperscript{7} Specifically, the average rate of increase of $d_{O-H}$ with values of $d_{O-O}$ below the transition value of 2.50 Å was found to be too slow in a classical model, but excellent agreement with observations was produced when tunneling effects were included.\textsuperscript{7}

V. SUMMARY

Infrared absorption spectra of H$_2$O and D$_2$O to 37 GPa indicate that the central barrier in the ice VII DM potential lowers with pressure. This decrease in barrier height is manifested by barrier interaction effects which are observable in the spectra: these include broadening and disappearance of absorption peaks as the barrier passes through the energy of each peak, peak shifts to greater than harmonic values caused by energy level perturbation near the barrier top, and splitting of the first O-H stretching overtone, a phenomenon which could be caused by proton tunneling across the central barrier (Figs. 2 and 3). The pressure dependence of the barrier height to 32 GPa is determined to be $-230$ cm$^{-1}$ GPa$^{-1}$ (0.029 eV GPa$^{-1}$) from the pressures and frequencies at which absorption peaks disappear in the H$_2$O and D$_2$O spectra (Fig. 4). With this new constraint, a semiempirical model\textsuperscript{38–41} is adapted to characterize the pressure induced changes in the DM potential of the ice VII as it evolves towards a single well potential (Fig. 5).\textsuperscript{10,11} Using a linear increase with pressure of the force constants of the hydrogen-bonded system, this model produces a rapid increase in O-H bond length between 40 and 60 GPa. This shift from the lower pressure trend of O-H length observed in neutron diffraction data to 10 GPa (Ref. 46) generates expansion of the O-H distance to one-half the O-O distance at 60 GPa [Fig. 5(a)].\textsuperscript{11} This simple model thus reproduces all observed effects of pressure on the hydrogen potential in ice VII, and provides a testable prediction of the behavior of the O-H bond length between 10 and 60 GPa.

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\textsuperscript{1}Ph. Pruzan, J. Mol. Struct. 322, 279 (1994).