

## Isotope Effects and Fermi Resonance in Hydrogen Bonds: A New Model

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A new and simple numerical model of O—H—O hydrogen bond dynamics is presented. The model accurately reproduces the well-known dependence of the O—H stretching mode on the hydrogen bond length. Other general properties of hydrogen bonds are also reproduced: The Ubbelohde effect and anomalously low isotope shifts. A specific comparison of the model calculations with the observed pressure dependence of the stretching mode in ice VII provides a strong support for the model. A Fermi resonance is predicted to be a major feature of all O—H—O hydrogen bonds of about 2.6 Å length. [S0031-9007(98)07939-3]

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Hydrogen-bond compounds, such as water, are omnipresent and play a central role in many industrial and most biochemical processes. They are crucial for the existence of life itself, and are of interest across the whole range of scientific disciplines, from physics to chemistry and biology. In these compounds, the presence of the H bond imparts many unusual properties. Perhaps the most interesting issue is the large isotope effects produced by deuteration of the bonds. These include the Ubbelohde effect, where the O-O distance ( $R$ ) increases upon deuteration, and also changes at the phase-transition temperature ( $T_c$ ) of some ferroelectrics. Furthermore, deuteration is also known to seriously reduce the reaction rate of many biochemical processes [1].

H-bonded compounds have attracted much interest for many years, and many experimental and theoretical studies have been published. Novak [2] tabulated the O-H fundamental stretching excitation energies ( $\nu_{\text{OH}}$ ) of several compounds as a function of  $R$ . He demonstrated a strong empirical relationship, which appears to hold true despite the widely different properties of individual compounds (see Fig. 1). The  $\nu_{\text{OH}}$  data in the figure show that the rate of increase of  $\nu_{\text{OH}}$  is greatest for the strongest H bonds, and occurs in the range  $2.40 < R < 2.60$  Å. Moreover, the isotopic energy shifts ( $\nu_{\text{OH}}/\nu_{\text{OD}}$ ) show anomalously low values ( $1 \pm 0.1$ ) only over a very limited range of  $R$ , close to 2.5 Å.

There have recently been several systematic neutron-scattering studies of important H-bond systems, such as  $\text{KH}_2\text{PO}_4$  [3] and  $\text{KHCO}_3$  [4]. This work has provided new information about their structures and vibrational spectra. In the case of  $\text{KH}_2\text{PO}_4$ , a complete description of the neutron results in terms of a vibrational potential function was possible [3]. The large isotope effect on the ferroelectric transition,  $T_c(\text{D})/T_c(\text{H})$ , was theoretically

explained in terms of a hydrogen-lattice (or hydrogen-electric dipole moment) interaction [5–8]. In this Letter, we present a model which quantitatively describes the following: first, the isotope effects observed in H-bonded compounds; second, the functional relationship of  $\nu_{\text{OH}}$  and  $R$ ; and third, the pressure dependence of the changes recently reported for ice VII [9–11].

We consider a simple system of O—H—O bonds in which the oxygens are fixed at a separation of  $R$  and the hydrogen interacts with the lattice system through the oxygens. The Hamiltonian can be written as [7,8]

$$H = H_p + H_q + H'_{pq}, \quad (1a)$$

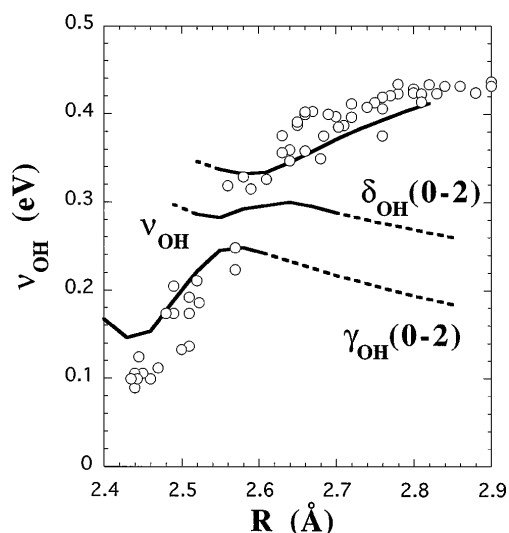


FIG. 1. Variation in the hydrogen stretching mode energy ( $\nu_{\text{OH}}$ ) on the hydrogen-bond length ( $R$ ). The open circles are the experimental values summarized by Novak. The solid lines are the calculated values of  $\nu_{\text{OH}}$ . The dotted lines are the calculated values of  $\gamma_{\text{OH}}(0-2)$  and  $\delta_{\text{OH}}(0-2)$ .

$$H_p = -(\hbar^2/2m)(d^2/d^2X) + U_{\text{unperturb}}(X), \quad (1b)$$

$$H_q = -(\hbar^2/2M)(d^2/d^2q) + (1/2)M\omega^2q^2, \quad (1c)$$

and

$$H'_{pq} = \lambda qx, \quad (1d)$$

where  $X = (x, y, z)$ .  $H_p$  and  $H_q$  are the Hamiltonian of the hydrogen and the lattice systems, respectively, in which the O—H—O bond is decoupled from the lattice system.  $m$  is the hydrogen mass.  $q$  and  $M$  are the coordinate in the lattice system and the effective mass of the lattice, respectively.  $H'_{pq}$  is an interaction term between the hydrogen and the lattice systems. Here, the lowest order of the combination of  $q$  and  $x$  is assumed.  $x$  is a coordinate of the hydrogen along the H bond, and the coefficient  $\lambda$  is a constant.

According to Sugimoto and Ikeda [6], as well as Ikeda and Yamada [7,8], we adopt the adiabatic approximation. In this case, the wave functions of the hydrogen and lattice,  $\varphi(X; q)$  and  $\Theta(q)$ , as well as their eigenenergies,  $E$  and  $\epsilon$ , can be derived from the following equations:

$$\begin{aligned} [-(\hbar^2/2m)(d^2/d^2X) + U_{\text{unperturb}}(X) + \lambda qx]\varphi(X; q) \\ = E(q)\varphi(X; q), \end{aligned} \quad (2a)$$

and

$$[-(\hbar^2/2M)(d^2/d^2q) + G(q)]\Theta(q) = \epsilon\Theta(q). \quad (2b)$$

A modified lattice potential,  $G(q)$ , is defined as, using the ground-state energy of hydrogen,  $E_0(q)$ , obtained from Eq. (2a),

$$G(q) = (1/2)M\omega^2q^2 + E_0(q). \quad (3)$$

The unperturbed hydrogen potential function,  $U_{\text{unperturb}}(X)$ , was given as [6,8]

$$\begin{aligned} U_{\text{unperturb}}(x, y, z) = \frac{f}{2}(\alpha_1^2 + \alpha_2^2) + \frac{g}{2}(\beta_1^2 + \beta_2^2) \\ + V([(x - x_1)^2 + y^2 + z^2]^{1/2}) \\ + V([(x - x_2)^2 + y^2 + z^2]^{1/2}), \end{aligned} \quad (4)$$

where  $x_1$  and  $x_2$  are the oxygen positions, at  $x = \pm R/2$ , and  $\alpha_{1,2}$  and  $\beta_{1,2}$  are the bending angles of the hydrogen defined with respect to both oxygens (1 and 2), respectively.  $V(r)$  is the Morse potential defined as  $V(r) = V_0[e^{-2a(r-r_0)} - 2e^{-a(r-r_0)}]$ .

The ground-state wave function of the lattice,  $\Theta_0(q)$ , is extended around a stable lattice point,  $q_c$ , which is fixed according to the condition that a minimum in  $G(q)$  occurs at  $q = q_c$ . Generally, the ground-state energy of the hydrogen, as obtained from Eq. (2a), decreases as  $q$  increases. Even if all parameters in  $U_{\text{unperturb}}(X)$  are identical, the large mass ratio of H to D has important effects. The ground-state energy of the D isotopomers,  $E_0(q; D)$ , changes more rapidly with  $q$  than that of the H isotopomers,  $E_0(q; H)$ . This difference in their dependence on  $q$  of  $E_0(q; H)$  and  $E_0(q; D)$  gives different stable lattice points for the H and the D isotopomers,  $q_c(H)$  and  $q_c(D)$ , respectively.

Ikeda *et al.* [8] adjusted the parameter values in Eq. (4) as well as the values of  $\lambda q_c(H)$  and  $\lambda q_c(D)$  to reproduce the excitation energies observed in both  $\text{KH}_2\text{PO}_4$  and  $\text{KD}_2\text{PO}_4$ . All of the parameters in  $U_{\text{unperturb}}(X)$  were identical for both compounds. Those were  $V_0 = 2.3$  eV,  $a = 3.0 \text{ \AA}^{-1}$ ,  $r_0 = 0.98 \text{ \AA}$ ,  $f = 0.34$  eV, and  $g = 1.32$  eV [8]. The values of  $\lambda q_c(H)$  and  $\lambda q_c(D)$  were  $0.8 \text{ eV \AA}^{-1}$  for  $\text{KH}_2\text{PO}_4$  and  $1.07 \text{ eV \AA}^{-1}$  for  $\text{KD}_2\text{PO}_4$ , respectively [8]. With those values, the values of  $\frac{1}{2}M\omega^2\lambda^{-2}$  can be estimated for both  $\text{KH}_2\text{PO}_4$  and  $\text{KD}_2\text{PO}_4$ , since the values of  $\lambda q_c(H)$  and  $\lambda q_c(D)$  can be derived using the  $\lambda q$  dependences of  $E_0(q; H)$  and  $E_0(q; D)$  calculated from Eq. (2a) as well as a condition of  $[dG(q)/dq]_{q=q_c} = 0$ . The estimated values of  $\frac{1}{2}M\omega^2\lambda^{-2}$  were  $0.11 \text{ \AA}^2 \text{ eV}^{-1}$  for  $\text{KH}_2\text{PO}_4$  and  $0.115 \text{ \AA}^2 \text{ eV}^{-1}$  for  $\text{KD}_2\text{PO}_4$ , respectively. This indicates that the value of  $\frac{1}{2}M\omega^2\lambda^{-2}$  is also almost identical in both salts.

The shape of  $U_{\text{unperturb}}(X)$  in Eq. (4) is given as a function of  $R$ , which introduces a strong  $R$  dependence to all of the quantities such as  $E_0(q; H)$  and  $E_0(q; D)$  as well as  $\lambda q_c(H)$  and  $\lambda q_c(D)$ . Novak suggests, as shown in Fig. 1, that the stretching excitation energy of the hydrogen is independent of the details of the molecular structure surrounding the bond. From this suggestion as well as the above conclusion on their  $\text{KH}_2\text{PO}_4$  studies, we expect that all of the parameters in  $U_{\text{unperturb}}(X)$  and  $\frac{1}{2}M\omega^2\lambda^{-2}$ , which actually determine the value of the stretching excitation energy through Eqs. (2a), (2b), and (3), are identical for both the H and the D isotopomers of all of the compounds under consideration. With this assumption, and using the values determined in the  $\text{KH}_2\text{PO}_4$  studies for all of the parameters in  $U_{\text{unperturb}}(X)$  as well as  $\frac{1}{2}M\omega^2\lambda^{-2}$ , the values of  $\lambda q_c(H)$  and  $\lambda q_c(D)$  can be calculated for various bond lengths ( $R$ ). In these calculations, we used  $\frac{1}{2}M\omega^2\lambda^{-2} = 0.11 \text{ \AA}^2 \text{ eV}^{-1}$  for both the H and the D isotopomers.

The calculated values are shown in Fig. 2(a), where it can be seen that both  $\lambda q_c(H)$  and  $\lambda q_c(D)$  increase with  $R$ . Using these values, the effective hydrogen potentials  $[U_{\text{unperturb}}(X) + \lambda q_c(H)x]$  were calculated and are shown in an inset of Fig. 2. It can be seen in the figure that a notable asymmetry occurs for large values of  $R$ . Figure 2(a) shows that  $\lambda q_c(D) \geq \lambda q_c(H)$  for all  $R$ , but that they differ significantly only over a small region of  $R$ ,  $2.43 < R < 2.60 \text{ \AA}$ . Intriguingly, this is just the range in  $R$  for which the  $\nu_{\text{OH}}/\nu_{\text{OD}}$  ratio shows its largest anomaly. This suggests that the D isotopomer lattices are always more distorted than those of the H isotopomers. Moreover, a critical value of  $R$ ,  $R_c$ , can be defined as the O—H—O length at which the value of  $\lambda q_c$  becomes zero [see Fig. 2(a)]. The values of  $R_c$  are  $2.45 \text{ \AA}$  for H isotopomers and  $2.43 \text{ \AA}$  for D isotopomers, respectively. In recent Raman measurements on  $\text{KH}_2\text{PO}_4$ , at high pressures, the  $\nu_4$  mode (a  $\text{PO}_4$  deformation) disappears at about 3 GPa [12]. We associate this disappearance with a reduction of the O—O distance, under pressure, to a

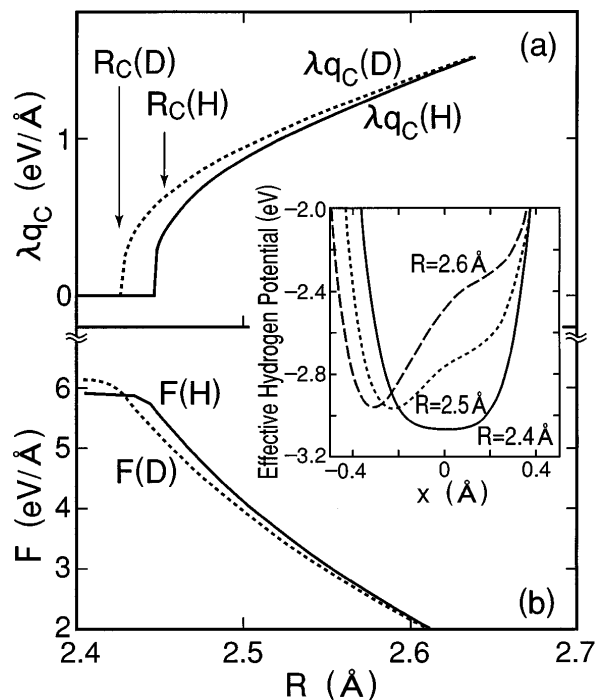


FIG. 2. Variation of several important parameters of the model with the bond length. (a)  $R$  dependences of asymmetry parameters  $\lambda q_c(H)$  and  $\lambda q_c(D)$ . (b)  $R$  dependences of attractive forces  $F(H)$  and  $F(D)$ .  $\lambda q_c(H)$  and  $F(H)$  are shown by the solid lines in (a) and (b), respectively.  $\lambda q_c(D)$  and  $F(D)$  are shown by the dotted lines, respectively. In the inset, the shapes of the effective hydrogen potential with  $R = 2.4$ , 2.5, and 2.6 Å are displayed along the bond axis;  $x = 0$  is the center of the bond. The solid line, dotted line, and dashed line show the calculated values at  $R = 2.4$ , 2.5, and 2.6 Å, respectively.

critical length ( $R_c$ ) of 2.45 Å; also, a local distortion of the  $\text{PO}_4$  tetrahedron is removed. The  $R$  dependence of  $\lambda q_c(H)$  explains this experimental result rather well.

The total energy of the hydrogen and the lattice systems at a given stable point ( $q_c$ ) can be approximated by  $G(q_c)$  of Eq. (3). The total energy of H isotopomers and D isotopomers are denoted as  $G(q_c, H)$  and  $G(q_c, D)$ , respectively. The value of  $G(q_c, D)$  is always lower than that of  $G(q_c, H)$ , and the  $R$  dependence of the isotopomers arises mainly from the different  $\lambda q_c(H)$  and  $\lambda q_c(D)$  variations. Using these  $R$  dependences, the bonding strength ( $F$ ) can be determined as

$$F = dG(q_c)/dR, \quad (5)$$

where the attractive force is defined to be positive. The bonding strengths of the H and D isotopomers are denoted as  $F(H)$  and  $F(D)$ , respectively.

The calculated values of  $F(H)$  and  $F(D)$  are shown in Fig. 2(b). Here, it can be clearly seen that  $F(H)$  and  $F(D)$  decrease monotonically with  $R$ ;  $F(H) < F(D)$  at  $R < 2.43$  Å;  $F(H) > F(D)$  at  $2.43 < R < 2.6$  Å; and  $F(H) \approx F(D)$  at  $R > 2.6$  Å. These results explain two characteristics of hydrogen-bonded compounds rather well: first, the H-bond strength becomes weaker as  $R$

increases; second, the bond strength of H bonds is generally greater than that of the respective D bonds, except at the very shortest bond lengths. This is related to the well-known Ubbelohde effect, and the hydrogen-bond lengths generally increase upon deuteration. Ichikawa [13] has summarized the changes in the bond length caused by deuteration in ferroelectric hydrogen-bonded compounds, and showed that these characteristic changes occurred in the limited range  $2.43 < R < 2.6$  Å. He also speculated that a reversal of these effects might be possible for  $R < 2.43$  Å. Our calculations are consistent with his work.

In order to successfully calculate the  $R$  dependence of the stretching excitation energies across a wide range of  $R$  ( $2.4 < R < 2.9$  Å), higher order bending terms,  $\zeta(\alpha_1^4 + \beta_1^4 + \alpha_2^4 + \beta_2^4)$ , have been additionally introduced into Eq. (4). Here,  $\zeta = 5$  eV. Although the values of  $\lambda q_c(H)$  and  $\lambda q_c(D)$  were recalculated in this wide range, those remained consistent to the previous ones in the range  $2.4 < R < 2.65$  Å. Using those new values of  $\lambda q_c(H)$  obtained in the wide range, we calculated the  $\nu_{\text{OH}}$  energies, fundamental bending energies,  $\delta_{\text{OH}}(0-1)$  and  $\gamma_{\text{OH}}(0-1)$ , and their overtones,  $\delta_{\text{OH}}(0-2)$  and  $\gamma_{\text{OH}}(0-2)$ . The calculated values, as a function of  $R$ , are compared with Novak's summary of the experimental data in Fig. 1. In this figure, the lines are solid where the hydrogen vibrational displacement vectors lie approximately parallel to the O—H—O direction, and are dotted so as to represent vibrational displacements perpendicular to the O—H—O direction. As can be seen from the figure, our calculated values are totally consistent with the observed data. We believe that this emphasizes the overall correctness of our model of all H-bonded compounds. Further, for values of  $R \approx 2.6$  Å, a strong Fermi resonance is predicted between the fundamental of the stretching vibration and the overtones of the bending modes. Thus, at  $R \approx 2.6$  Å, the character of the  $\nu_{\text{OH}}$  mode changes continuously to that of  $\gamma_{\text{OH}}(0-2)$  and, at  $R \approx 2.65$  Å, it is transformed into  $\delta_{\text{OH}}(0-2)$ . This Fermi resonance is predicted as a general feature of any H-bonded compound with  $R \approx 2.6$  Å.

Recent IR work on the pressure dependence of the vibration in ice VII has produced clear evidence for this Fermi resonance [9–11], and our model calculations have been verified by several results from this body of experimental work. The hydrogen-bond length ( $R$ ) was determined from the pressure dependence of the molar volume [14], assuming the bcc structure. The variation in  $\nu_{\text{OH}}$  and other excitations against  $R$  is shown in Fig. 3 along with our calculated values; again, the agreement is excellent and completely explains a series of Fermi resonances of  $\nu_{\text{OH}}$  and  $\gamma_{\text{OH}}(0-2)$  as well as  $\nu_{\text{OH}}$  and  $\delta_{\text{OH}}(0-2)$ . We believe that these two comparisons demonstrate that the Fermi resonance is indeed a general phenomenon in compounds with H-bond lengths of  $R = 2.6$  Å.

Using the values of  $\lambda q_c(D)$ , we have also calculated the  $R$  dependence of  $\nu_{\text{OD}}$  for deuterated compounds. Again, a Fermi resonance is predicted, in this case

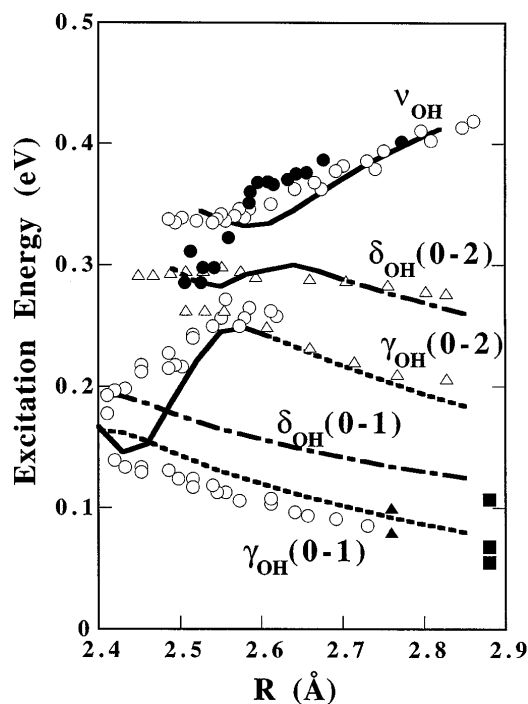


FIG. 3. Variation in the observed excitation energies in ice VII and the calculated values of  $\nu_{\text{OH}}$ ,  $\gamma_{\text{OH}}(0-1)$ ,  $\delta_{\text{OH}}(0-1)$ ,  $\gamma_{\text{OH}}(0-2)$ , and  $\delta_{\text{OH}}(0-2)$  along with the bond length. The solid lines, dotted lines, and dot-dashed lines are the calculated values. The solid lines indicate that the hydrogen vibrational displacement vectors lie approximately parallel to the O—H—O direction. The dotted lines and the dot-dashed lines present those vectors perpendicular to the O—H—O direction. The closed circles, open circles, and open triangles are experimental values observed by Aoki, Goncharov, and Struzhkin, respectively. Those experimental values were taken from Fig. 2 in Ref. [9], Fig. 4 in Ref. [10], and Fig. 2 in Ref. [11], respectively. ( $\blacktriangle$ ) and ( $\blacksquare$ ) indicate the observed values in ice Ih and ice VIII, respectively [15].

at  $R = 2.55 \text{ \AA}$ . In calculations on both the H and the D isotopomers, we have shown the existence of characteristic hydrogen-bond lengths ( $R_f$ ) at which a Fermi resonance is predicted. Here, we should emphasize that  $R_f$  for the D isotopomers is smaller than that for the H isotopomers. From the calculated values of  $\nu_{\text{OH}}$  and  $\nu_{\text{OD}}$ , we find that the ratio  $\nu_{\text{H}}/\nu_{\text{D}}$  remains about 1.4 for both ranges of  $R < 2.43 \text{ \AA}$  and  $R > 2.6 \text{ \AA}$ , but falls drastically to about 1 for  $2.43 < R < 2.45 \text{ \AA}$ . This agrees well with Novak's work [2] and, in our model, stems from the fact that the H and the D isotopomers have different hydrogen potentials over the range  $2.43 < R < 2.6 \text{ \AA}$ . This, in turn, arises because  $\lambda q_c(\text{H})$  differs greatly from  $\lambda q_c(\text{D})$  over this range.

We have succeeded, using a new and simple model, to explain some of the unusual properties of hydrogen-bond compounds, in general. As first suggested by Novak, the

shape of the hydrogen potential in O—H—O bonds is independent of the details of the molecular structure surrounding the bond. Therefore, the origin of the hydrogen-lattice interaction term ( $H'_{pq} = \lambda q x$ ) must come from the nature of the oxygen atoms within the bond. Present considerations imply that it is strongly related to the distortion of the electron distribution around the oxygen atoms in the bond. Since  $\lambda q_c(\text{D}) > \lambda q_c(\text{H})$ , a stronger effective distortion occurs in the D potentials and produces a larger asymmetry in O—D—O bonds. Such strong distortions will always depress the ground-state energy of deuterium. This results in a reduced rate for deuterium transfer along the O—D—O (cf. O—H—O) bonds, and thus depresses the reaction rate of D isotopomers beyond that expected from simple mass considerations [16].

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