Proton-Lattice Interactions in Hydrogen-Bonded Ferroelectric Crystals

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The distortions of the lattice accompanying protonic order-disorder transitions, and the difference between the observed frequency of protonic or deuteronic intrabond motion and the one estimated on the basis of the rigid lattice model, seem to indicate that proton-lattice interactions are not negligible in the case of ferroelectric H-bonded crystals. In order to throw some light on this problem, the energy spectrum and polarizability of an isolated hydrogen-bonded proton, interacting with polar lattice vibrations in the presence of an electric field, have been studied both in the strong- and in the weak-coupling limits. The results obtained show that the intrabond tunneling frequency of a proton, interacting with the lattice, is in fact much smaller than the tunneling frequency of a bare proton in an undeformed lattice. In the case of strong proton-lattice interactions, the polarizability is anomalously large at relatively low field strengths and any small fluctuation in the lattice potential is accompanied by a trapping of the proton in an off-center position. Another specific consequence of proton-lattice interactions is an inherent distribution of dipolar relaxation times.

I. INTRODUCTION

THOUGH ferroelectric phenomena in hydrogen-bonded KH_2PO_4 type crystals have been extensively studied in recent years,[1] our understanding of the basic interactions that lead to ferroelectric transitions is still far from being complete, and no comprehensive theory yet exists.

In particular, model theories proposed so far[2] have considered the hydrogen-bonded protons to move in a completely rigid lattice potential, thus, neglecting proton-lattice interactions. On the other hand, it is well known[3] that the protonic order-disorder transition in KH_2PO_4 is accompanied by large displacements of the potassium and phosphorus ions, which account for nearly all of the spontaneous polarization of the crystal and which cannot be understood in terms of a rigid lattice model. Moreover, the observed protonic and deuteronic mobility[4–6] is much lower than the one estimated[6] on the basis of the rigid lattice model. This discrepancy in the order of magnitude of the protonic tunneling frequency, as well as the above-mentioned large lattice distortions, accompanying protonic order-disorder transitions in KH_2PO_4 type ferroelectric crystals, demonstrates that proton-lattice interactions are not at all negligible in ferroelectric, H-bonded crystals.

The same seems to be true for some nonferroelectric H—bonded crystals. Here, as well as in the case of ferroelectric crystals, infrared absorption[7,8] and dielectric relaxation spectra[9] have been observed, which are difficult to explain in terms of protonic motion in a rigid lattice potential.

In view of the complexity of the many-body problem in ferroelectric crystals, it seemed worthwhile to investigate first the energy spectrum and polarizability of a single, isolated hydrogen-bonded proton interacting with polar lattice vibrations in the presence of an electric field.

In Sec. II, the model Hamiltonian of the problem is defined. In view of the strong localization of the proton, the discrete structure of the lattice is taken into account explicitly.

In Sec. III, the energy spectrum and polarizability of a H bonded proton interacting with polar lattice vibrations are studied (i) in the strong coupling, low lattice frequency limit where protonic excitations induced by the zero-point fluctuations of the lattice field are neglected, and (ii) in the weak-coupling limit, where the proton lattice interactions are treated as a perturbation. A short discussion of the dielectric relaxation spectra of "dressed," H-bonded protons is added.

In the Appendix, the interaction parameters are explicitly evaluated for two simple lattice models, and a numerical example is given.

It is the explicit introduction of the concept of a "dressed" O—H—O dipole and the examination of some of the observable consequences of proton-lattice interactions that is the contribution of this paper.

II. THE HAMILTONIAN

We study the properties of the following Hamiltonian:

$$H=H_p+H_l+H_i=H_0+H_i, \tag{1}$$

where H_p stands for the energy operator of an O—H—O hydrogen-bonded proton, moving in a "rigid lattice" potential in the presence of a time-independent electric field F, H_l for the energy operator of the polar lattice

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vibrations in the absence of the proton, and H_i for the electrostatic "proton-lattice" and "electric field-lattice" interaction operators.

Experimental and theoretical investigations indicate that the potential energy surface of the proton in many H bonds has two minima.[3,4,10] Assuming interbond proton jumping[4] and band conductivity to be negligible for the phenomena treated in this paper, H_p is taken as

$$H_p=-(\hbar^2/2m)\Delta+V(\mathbf{r})-exF, \tag{2}$$

with $V(\mathbf{r})$ being a double minimum potential, which is symmetric about the center of the H bond [e.g., compare Eq. (43)]. It should be noted that in the absence of F, the whole Hamiltonian has the same symmetry.

The eigenfunctions of H_p in the absence of the field describe a nonlocalized state with the proton oscillating between the two potential minima in $V(\mathbf{r})$. The presence of a field results in a localization of the particle. In the case of a high intervening barrier—which is the case treated in this paper—the two lowest eigenfunctions can be approximated by a linear combination of wave functions localized in one or the other potential well, respectively,

$$\begin{aligned}\psi_1&=c_1\varphi_l(\mathbf{r})+c_2\varphi_r(\mathbf{r}),\\ \psi_2&=c_2\varphi_l(\mathbf{r})-c_1\varphi_r(\mathbf{r}),\end{aligned} \tag{3}$$

where

$$\langle\varphi_l|\,\varphi_l\rangle=\langle\varphi_r|\,\varphi_r\rangle=1.$$

As shown previously,[8]

$$c_{1,2}^2(F)=\tfrac{1}{2}[1\mp\mu F/(\beta^2+\mu^2F^2)^{1/2}], \tag{4}$$

where the overlap integrals

$$S=\langle\varphi_l|\,\varphi_r\rangle \tag{5}$$

are neglected, and where the symbols μ and β are defined as

$$\begin{aligned}\mu&=\langle\varphi_r|\,ex\,|\varphi_r\rangle,\\ \beta&=\langle\varphi_l|H_p|\,\varphi_r\rangle,\end{aligned} \tag{6}$$

with e standing for the effective charge of the proton.

In analogy to the procedure used in the treatment of electron-lattice interactions,[11–13] the polar vibrations of the lattice are divided in an "inert" and an "inertless" component, and H_i stands only for the interaction of the proton with the "inert" component. The interaction of the proton with the "inertless" component, which follows the motion of the proton adiabatically, is included in $V(\mathbf{r})$, whereas the interaction of the electric field with that component gives rise only to a constant, mass-independent term, which is omitted.

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The "inert lattice" in the "absence" of the proton is supposed to consist of a regular array of n polarizable ions. Each of the polar vibrations of the lattice can be described by a polarization vector

$$\mathbf{P}=(\cdots;\cdots;p_{ix},p_{iy},p_{iz};\cdots;\cdots), \tag{7}$$

where $(p_{ix}(t),p_{iy}(t),p_{iz}(t))$ is the dipole moment associated with the polar deformation of the ith ion. $\mathbf{P}$ is understood to be a vector in the $3n$-dimensional Hilbert space, where the scalar product of two vectors $\mathbf{P}$ and $\mathbf{P}'$ is defined by

$$(\mathbf{P},\mathbf{P}')=\textstyle\sum_{i,j}p_{ij}p_{ij}',\quad i=1,2,\cdots,n,\quad j=x,y,z. \tag{8}$$

Assuming that the potential energy of the polar lattice vibrations is a quadratic functional of $\mathbf{P}$, the inert part of the classical lattice Hamiltonian in the absence of the proton can be written as

$$H_l=\tfrac{1}{2}(\dot{\mathbf{P}},M\dot{\mathbf{P}})+\tfrac{1}{2}(\mathbf{P},K\mathbf{P}), \tag{9}$$

with M and K being time-independent, self-adjoint matrix operators. Since the kinetic energy is always positive and the system is assumed to be stable for $\mathbf{P}=0$, M and K are positive definite operators. Hence, $M^{1/2}$, $M^{-1/2}$, and $M^{-1/2}KM^{-1/2}$ exist and are, as well, positive definite and self-adjoint. The eigenvalues ω_k^2, $k=1,2,\cdots,3n$, of $M^{-1/2}KM^{-1/2}$ are thus all positive, and the corresponding eigenvectors $M^{1/2}\chi_k$ form a complete orthonormal system:

$$(\chi_k,M\chi_{k'})=\delta_{kk'}. \tag{10}$$

Expressing the polarization vector $\mathbf{P}$ in terms of normal modes,

$$\mathbf{P}=\textstyle\sum_k P_k(t)\chi_k, \tag{11}$$

and inserting (11) into (9), we get

$$H_l=\tfrac{1}{2}\textstyle\sum_k(\omega_k^2P_k^2+\dot{P}_k^2), \tag{12}$$

where the normal coordinates P_k are given by

$$P_k(t)=(\mathbf{P},M\chi_k). \tag{13}$$

Introducing the dimensionless normal coordinates $q_k=(\omega_k/\hbar)^{1/2}P_k$ and replacing $\dot{P}_k$ by $-i(\hbar\omega_k)^{1/2}\partial/\partial q_k$, the quantum lattice Hamiltonian is obtained as

$$H_l=\tfrac{1}{2}\sum_k\hbar\omega_k\left(q_k^2-\frac{\partial^2}{\partial q_k^2}\right), \tag{14}$$

with ω_k being the frequency of the kth polar lattice mode.

The proton, moving slowly between the two potential minima in $V(\mathbf{r})$, interacts electrostatically with the polar lattice modes. Using expansion (11), the electrostatic proton-lattice interaction Hamiltonian

$$H_i=\left(\mathbf{P},\frac{e}{4\pi\epsilon_0}\operatorname{grad}_{\mathbf{r}'}|\mathbf{r}-\mathbf{r}'|^{-1}-\mathbf{F}\right) \tag{15}$$

can be written as

$$H_i=\sum_k V_k q_k. \tag{16}$$

Here the coefficients V_k are given by

$$V_k=(\hbar/\omega_k)^{1/2}\left(\chi_k, \frac{e}{4\pi\epsilon_0}\,\mathrm{grad}_{r'}|\mathbf{r}-\mathbf{r}'|^{-1}-\mathbf{F}\right), \tag{17}$$

and the $3n$-dimensional vectors $\mathrm{grad}_{r'}|\mathbf{r}-\mathbf{r}'|^{-1}$ and $\mathbf{F}$ are defined as

$$\begin{aligned}&\mathrm{grad}_{r'}|\mathbf{r}-\mathbf{r}'|^{-1}\\&=(\cdots;\cdots;\partial|\mathbf{r}-\mathbf{r}_i'|^{-1}/\partial x_i',\ \partial|\mathbf{r}-\mathbf{r}_i'|^{-1}/\partial y_i',\\&\qquad\times\partial|\mathbf{r}-\mathbf{r}_i'|^{-1}/\partial z_i';\cdots;\cdots);\qquad(18)\\&\mathbf{F}=Fe_1,\quad e_1=(1,0,0;1,0,0;\cdots;\cdots;1,0,0).\end{aligned}$$

In case of the dielectric continuum model essentially the same treatment is applicable. The vector $\mathbf{P}$ becomes a 3-dimensional vector, the components of which are functions of the continuous variable $\mathbf{r}$. Accordingly, in the definition (8) of the scalar product, the summation over the discrete variable $\mathbf{r}_i$ has to be replaced by an integration over the continuous variable $\mathbf{r}$.

III. ENERGY SPECTRUM

A. Strong-Coupling Case

Let us first investigate our Hamiltonian

$$H=-\frac{\hbar^2}{2m}\Delta+V(\mathbf{r})-exF+\sum_k V_k q_k+\tfrac{1}{2}\sum_k \hbar\omega_k\left(q_k^2-\frac{\partial^2}{\partial q_k^2}\right), \tag{19}$$

in the strong-coupling, low-lattice-frequency limit, using a variational method.[11–13]

We treat two distinct cases:

In the first, the intrabond proton tunneling frequency β is larger than the lattice frequencies, but smaller than the spacing $h\nu_0$ of the unperturbed protonic energy levels in case of an infinitely high intervening potential barrier: $\hbar\omega_k<\beta<h\nu_0$. The lattice cannot follow the motion of the proton at all and responds to the charge density of the proton averaged over the two sites.

In the second case, the lattice frequencies are larger than the intrabond tunneling frequency: $\beta<\hbar\omega_k<h\nu_0$. The lattice cannot follow the motion of the proton within one well, but is able to respond to the slower proton motion between the two wells. Thus, in this case, the lattice interacts with the charge density of the proton averaged only over one site.

(i) $\hbar\omega_k<\beta<h\nu_0$

In this case, where the lattice interacts with the charge density of the proton, averaged over both sites, a Hartree-type wave function

$$\Psi(\mathbf{r},\cdots,q_k,\cdots)=\psi_1(\mathbf{r})\phi(\cdots,q_k,\cdots) \tag{20}$$

is indicated for the investigation of the ground state.[11–13] Here ψ_1 depends only on the protonic coordinates and ϕ on the coordinates of the polarization field. We assume that both ψ_1 and ϕ are normalized,

$$\langle\psi_1|\psi_1\rangle=\langle\phi|\phi\rangle=1. \tag{21}$$

Minimizing the expectation value $\langle\Psi|H|\Psi\rangle$ with respect to ϕ under the restraint $\langle\phi|\phi\rangle=1$, we obtain a solution for ϕ in the form[11]

$$\phi=\prod_k \phi_{n_k}(q_k-q_{k,1}),\quad q_{k,1}=-\langle\psi_1|V_k|\psi_1\rangle/\hbar\omega_k, \tag{22}$$

the $\phi_{n_k}(q_k-q_{k,1})$ being displaced harmonic oscillator wave functions.

Substituting this solution into $\langle\Psi|H|\Psi\rangle$ and putting all displaced lattice oscillators in their ground states, $n_k=0$, we obtain

$$\langle\Psi|H|\Psi\rangle=\mathcal{G}(\psi_1)+\tfrac{1}{2}\sum_k\hbar\omega_k, \tag{23}$$

with

$$\mathcal{G}(\psi_1)=\langle\psi_1|H_p|\psi_1\rangle-\tfrac{1}{2}\sum_k\hbar\omega_k q_{k,1}^2. \tag{24}$$

The protonic part of the ground-state wave function has now to be determined by minimizing the functional $\mathcal{G}(\psi_1)$ with respect to ψ_1.

Since we are interested in the effects of strong proton-lattice interactions in the presence of a field F, we take for the protonic part of the trial wave function an eigenfunction of H_p in the presence of an arbitrary field u, which is considered as a variational parameter:

$$\psi_1=c_1(u)\varphi_l(\mathbf{r})+c_2(u)\varphi_r(\mathbf{r}). \tag{25}$$

Here $c_1(u)$ and $c_2(u)$ are given by Eq. (4), with u taking the place of F. In this way, the effect of the induced lattice displacements on the motion of the proton is replaced by an effective field u which has to be determined self-consistently. The treatment of the problem, taking into account the changes in the shape of φ_l and φ_r—which are small anyway in the case of high intervening barriers—is reserved for a subsequent paper.

Inserting (25) into (24), and noting that the ground-state energy does not depend on the particular direction of F, the functional $\mathcal{G}(\psi_1)$ becomes a functional of u:

$$\mathcal{G}(u)=-\frac{\beta^2+\mu^2u(1+B)F}{(\beta^2+\mu^2u^2)^{1/2}}-A_-\frac{\mu^2u^2}{\beta^2+\mu^2u^2}-A_+-DF^2, \tag{26}$$

with

$$D=\tfrac{1}{2}\sum_k\omega_k^{-2}(\chi_k,e_1)^2.$$

Here B stands for

$$B=\sum_k B_k, \tag{27}$$

with

$$B_k=\frac{e(\chi_k,e_1)}{8\pi\epsilon_0\mu\omega_k^2}\left(\chi_k,\ \mathrm{grad}_{r'}\int\frac{\varphi_l^2(\mathbf{r})-\varphi_r^2(\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}\right),$$

and $A_\pm$, which is a measure of the strength of the proton-

lattice interaction, for

$$A_{\pm}=\sum_k A_{k,\pm},$$

with

$$A_{k,\pm}=\frac{1}{2}\left(\frac{e}{8\pi\epsilon_0\omega_k}\right)^2\left(\chi_k,\ \mathrm{grad}_{\mathbf{r}'}\int\frac{\varphi_l^2(\mathbf{r})\pm\varphi_r^2(\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}\right)^2. \tag{28}$$

In deriving expression (26), overlap integrals have been neglected.

It should be stressed that the expression (26) contains just one effective parameter A_-, which determines the change in the polarization behavior of the proton due to proton-lattice interactions. B, namely, amounts just to a renormalization of the O—H dipole moment: Instead of the field F, the proton "sees" the field $(1+B)F$. In the following A_-, B, and D will be treated as parameters which have to be evaluated for each particular crystal lattice we are interested in (cf., Appendix).

Minimizing the ground-state energy (26) with respect to the variational parameter u, $d\vartheta/du=0$, the self-consistency equation for u is obtained as

$$u=(1+B)F+2A_-u/(\beta^2+\mu^2u^2)^{1/2}. \tag{29}$$

Any change in F results according to Eq. (29) in a change in u and in $q_{k,1}$. Inserting (22) into (11), the time average value of the lattice distortion due to proton-lattice and electric field-lattice interactions, is obtained as

$$\mathbf{P}=-\sum_k\hbar^{-1/2}\omega_k^{-3/2}\langle\psi_1|V_k|\psi_1\rangle\chi_k. \tag{30}$$

It should be noted that in the absence of an external or internal field F, the true ground state of H must have the symmetry of $V(\mathbf{r})$, and hence a nonvanishing value of u is not allowed.

On the other hand, Eq. (29) shows that if the condition $2A_->\beta$ is fulfilled, i.e., if the strength of the proton-lattice interaction exceeds a critical value, determined by the tunneling frequency of the proton in the ground state, even the smallest F will result in a relatively large u. Thus, the system is inherently unstable, if $2A_->\beta$, and any small asymmetric fluctuation Δ in the hydrogen-bond potential is immediately accompanied by a self-trapping of the proton, i.e., a nonzero value of u:

$$u_{F=0,\Delta\approx0}=\mu^{-1}(4A_-^2-\beta^2)^{1/2}. \tag{31}$$

The protonic part of the "true" ground-state wave function corresponds thus in the presence of small fluctuations Δ to a localized, "self-trapped" state— though $F=0$—and permanent "O—H" dipoles are thus created. The ground-state energy E_1 of such a self-trapped state in the absence of F is obtained in the limit of $\Delta\approx0$ as

$$E_1=-\beta^2/4A_--(A_++A_-)+\tfrac{1}{2}\sum_k\hbar\omega_k, \tag{32a}$$

if the condition $2A_->\beta$ is fulfilled.

The "self-trapped" ground state evidently corresponds to a lower energy that the state of the bare proton in the undeformed lattice,

$$E_1=-|\beta|+\tfrac{1}{2}\sum_k\hbar\omega_k, \tag{32b}$$

since the constants $A_\pm$ are always positive.

Excited "dressed" proton states $\Psi(p,\cdots,n_k,\cdots)=\psi_p(\mathbf{r})\times\prod_k\phi_{n_k}(q_k-q_{k,p})$ can be calculated in a similar fashion, using trial wave functions ψ_p which are mutually orthogonal.

Using a trial wave function

$$\psi_2=c_2(u)\varphi_l(\mathbf{r})-c_1(u)\varphi_r(\mathbf{r}),$$

orthogonal to the ground state, the energy of the first excited state is obtained in the case $2A_->\beta$ and $F=0$ as

$$E_2=3\beta^2/4A_--(A_++A_-)+\tfrac{1}{2}\sum_k\hbar\omega_k. \tag{32c}$$

The introduction of proton-lattice coupling, thus, reduces the resonance energy splitting of the ground-state doublet from 2β to the smaller value β^2/A_- and, hence, decreases the intrabond tunneling frequency of the proton.

(*ii*) $\beta<\hbar\omega_k<h\nu_0$

In this case, where the lattice interacts with the charge density of the proton, averaged only over one well, a ground-state trial wave function

$$\begin{aligned}\Psi_1&=c_1(u)\Psi_l+c_2(u)\Psi_r,\\ \Psi_i&=\varphi_i(\mathbf{r})\prod_k\phi_{n_k}(q_k-q_{k,i}),\\ q_{k,i}&=-\langle\varphi_i|V_k|\varphi_i\rangle/\hbar\omega_k,\quad i=l,r,\end{aligned} \tag{33}$$

is indicated. This function is a linear combination of states where the proton is localized on one site and is surrounded by suitable displaced lattice oscillators.

Minimizing the expectation value $\langle\psi_1|H|\psi_1\rangle$ with respect to the variational parameter u, we obtain u as

$$u=(1+B)(\beta/\beta_d)F, \tag{34a}$$

with

$$\beta_d=\langle\Psi_l|H|\Psi_r\rangle=\beta\exp(-2\sum_k A_{k,-}/\hbar\omega_k). \tag{34b}$$

Inserting this value for u into

$$\langle\Psi_1(n_k=0)|H|\Psi_1(n_k=0)\rangle,$$

the ground-state energy E_1 and the energy of the first excited state E_2 [corresponding to $\Psi_2=c_2(u)\Psi_l-c_1(u)\Psi_r$] are obtained as

$$E_{1,2}=-(A_++A_-)-DF^2\mp[\beta_d^2+\mu^2(1+B)^2F^2]^{1/2}+\tfrac{1}{2}\sum_k\hbar\omega_k, \tag{35a}$$

and $c_{1,2}$ as

$$c_{1,2}^2(F)=\tfrac{1}{2}\{1\mp\mu(1+B)F[\beta_d^2+\mu^2(1+B)^2F^2]^{-1/2}\}. \tag{35b}$$

The above treatment is appropriate as long as $(E_2-E_1)<\hbar\omega_k$. Hence, we get for its validity, in the case $F=0$, the condition $\beta_d<\hbar\omega_k<h\nu_0$ which is less restrictive than the one assumed before: $\beta<\hbar\omega_k<h\nu_0$.

It should be pointed out, that in contrast to Eq. (29), Eq. (34a) does not have a nonzero solution for u in the absence of F and, hence, the ground-state wave function (33) automatically has always the correct symmetry. On the other hand, here as well as in the former case, even the smallest F will result in a large u, i.e., in a localization of the particle.

The resonance matrix element β_d between two "dressed" protonic states Ψ_l and Ψ_r is always smaller than the corresponding resonance matrix element β between two "bare" protonic states. The reduction is the larger, the greater the strength of the interaction $A_{k,-}$, and the lower the frequency of the normal mode ω_k, interacting with the proton.

The intrabond tunneling frequency of the proton, dressed in a self-consistent polarization cloud, may be thus much smaller than the tunneling frequency of a bare proton in an undeformed lattice. Strong proton-lattice interactions, thus, drastically reduce the mobility of the protons, since the whole lattice ought to "tunnel" through the potential barrier together with the proton.

In this connection it should be noted that the frequency of the deuteron intrabond motion in KD_2PO_4, as obtained from magnetic resonance data,[4] is much smaller than the one estimated on the basis of the rigid lattice model. The temperature dependence of the deuteron motion[4] shows further that the contribution of tunneling to the deuteron mobility is negligible within the investigated temperature region ($T=200$–$300°K$), and that the deuteron—in spite of the low potential barrier—behaves like a classical particle with a large effective mass. Similarly, the frequency of the protonic ground-state doublet transition in[6] KH_2PO_4 is much lower than the one calculated within the rigid-lattice model[6] on the basis of neutron diffraction data.[3] Moreover, no double minimum effects at all have been observed in the vibrational spectra of triglycine sulphate,[5] where proton-lattice interactions seem to be particularly strong, though the rigid lattice model predicts very large resonance matrix elements due to the shortness of the O—H—O bond ($R_{0\ldots0}=2.43$ Å). The introduction of proton-lattice coupling and the corresponding reduction of the resonance matrix elements may explain all above discrepancies.

B. Weak-Coupling Case

Since the protonic excitations, induced by the zero-point fluctuations of the lattice field, have so far been neglected, the above treatments are essentially static. Let us now investigate the dynamic aspects of proton-lattice interactions in the weak-coupling limit, using second-order perturbation theory. Since the two lowest eigenvalues of H_p form a closely spaced doublet, separated by a large gap from higher vibrational states, we will consider only protonic excitations induced within the doublet and neglect the contribution of higher excitations.

The matrix elements of H_i with respect to the eigenfunctions of H_0 are

$$\langle\psi_p\prod_k\phi_{n_k}|H_i|\psi_{p'}\prod_k\phi_{n'_k}\rangle=\frac{1}{\sqrt{2}}\sum_k\langle\psi_p|V_k|\psi_{p'}\rangle \times[(n_k+1)^{1/2}\delta_{n_{k'},n'_{k-1}}+n_k^{1/2}\delta_{n_k,n'_{k+1}}]\prod_{k',k'\neq k}\delta_{n_{k'},n'_{k'}}, \tag{36}$$

and the ground-state energy E_1 is obtained in the dynamic case as

$$E_1=E_1^{(0)}+E_1^{(2)} \tag{37}$$

with

$$E_1^{(0)}=-(\beta^2+\mu^2F^2)^{1/2}+\tfrac{1}{2}\textstyle\sum_k\hbar\omega_k \tag{38}$$

being the lowest eigenvalue of H_0, and $E_1^{(2)}$ being the energy shift due to proton-lattice interactions:

$$E_1^{(2)}=-\tfrac{1}{2}\sum_k\left(\frac{\langle\psi_1|V_k|\psi_1\rangle^2}{\hbar\omega_k}+\frac{\langle\psi_1|V_k|\psi_2\rangle^2}{2(\beta^2+\mu^2F^2)^{1/2}+\hbar\omega_k}\right). \tag{39}$$

Replacing ω_k with the limiting lattice frequency ω and noting that E_0 is an even function of F, the above sums can be evaluated giving

$$E_1^{(2)}=-(A_++A_-)-DF^2-B\mu^2F^2(\beta^2+\mu^2F^2)^{-1/2} +A_-\beta^2(\beta^2+\mu^2F^2)^{-1/2}[(\beta^2+\mu^2F^2)^{1/2}+\hbar\omega/2]^{-1}. \tag{40}$$

Here $A_\pm$, B, and D are given by Eqs. (28), (27), and (26) with $\omega_k=\omega$.

In the absence of the field F, Eqs. (37), (38), and (40) yield

$$E_1=-|\beta|+\tfrac{1}{2}\textstyle\sum_k\hbar\omega_k-A_-\hbar\omega(\hbar\omega+2\beta)^{-1}-A_+, \tag{41}$$

and the ground-state energy of the proton, interacting with polar-lattice waves, is again lower than the ground state of a bare proton in a rigid lattice.

C. Polarization Behavior

Let us now investigate the polarization behavior of an H-bonded proton, interacting with the lattice. The polarization in the state $\Psi(p;\cdots,n_k,\cdots)$ is obtained as $P(p;\cdots,n_k,\cdots)=-\partial E(p;\cdots,n_k,\cdots)/\partial F$ and the polarizability as $\alpha(p;\cdots,n_k,\cdots)=P(p;\cdots,n_k,\cdots)/F$.

The ground-state polarization is obtained in the case $\beta<\hbar\omega_k<h\nu_0$ as

$$P=2DF+\mu^2(1+B)^2F[\beta_d^2+\mu^2(1+B)^2F^2]^{-1/2}. \tag{42}$$

As a consequence of the introduction of proton-lattice coupling and the corresponding reduction of the resonance matrix element, $\beta_d\leqslant\beta$, we obtain with increasing static field F a rapid build up of an anomalously large polarization, which approaches the saturation value at relatively low-field strengths. The polarization is larger for a deuterium than for a hydrogen-bonded crystal, thus showing the correct dependence on the mass of the hydrogen isotope.[2]

Essentially the same behavior is obtained in the other two cases, treated above. It should be mentioned, that in the weak-coupling dynamic case the correction term due to proton-lattice interactions goes monotonically to zero as the lattice frequencies increase.

Strong proton-lattice interactions may as well result in a freezing out of the dielectric relaxation spectra at sufficiently low temperature due to immobilization of the O—H—O dipole moment by self-trapping in the ground state.[14] The necessary small, asymmetric deformation of the O—H—O potential, which is strongly enhanced by the effect of proton-lattice interaction, may be provided, e.g., by short-range interactions between the O—H—O dipoles. A diminishing of the amount of dielectric absorption with decreasing temperature has in fact been observed in a variety of solids with long H bonds and a correspondingly small β.[9]

Another specific consequence of strong proton-lattice interactions is an inherent distribution of dipolar relaxation times, leading to broader dielectric loss vs frequency curves than expected on the basis of the Debye model with a single relaxation time. This effect, which has been observed in a variety of H-bonded solids,[9,14,15] can be easily understood in terms of a classical model: At the time, when the external polarizing field is removed, the effective lattice potentials will not be exactly the same for all O—H—O dipoles, and any class of dipoles in a given effective potential will relax exponentially, with its own relaxation time.

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APPENDIX

In order to get a notion for the dependence of the coupling parameter A_- on the lattice structure, let us consider two specific models.

In case of the dielectric continuum model, A_- is easily evaluated, if we assume $\omega_k=\omega$, i.e., an Einstein model. Describing the shape of the hydrogen-bond potential by

$$\begin{aligned} V(\mathbf{r})&=\tfrac{1}{2}k[(x+l)^2+y^2+z^2], \quad x<0 \\ &=\tfrac{1}{2}k[(x-l)^2+y^2+z^2], \quad x>0 \end{aligned} \tag{43}$$

and taking

$$\varphi_{l,r}=(\gamma/\pi)^{3/4}\exp\{-\tfrac{1}{2}\gamma[(x\pm l)^2+y^2+z^2]\}, \qquad \gamma=(mk)^{1/2}/\hbar,$$

A_- is explicitly obtained as

$$A_-=\frac{e^2}{32\pi\epsilon_0}\left(\frac{1}{n^2}-\frac{1}{\epsilon}\right)\left((2\gamma)^{1/2}-\frac{1}{l}\int_0^{l(2\gamma)^{1/2}}e^{-x^2}dx\right), \tag{44}$$

with n^2 and ϵ being the high- and low-frequency dielectric constants of the medium.[11]

In contrast to A_- which increases with increasing mass of the particle, B is mass independent in case of the homogeneous continuum model.

Due to the strong localization of the protonic wave functions, the continuum model is a rather inadequate approximation and expression (44) is not very useful for a quantitative estimate of the magnitude of A_-.

Therefore, let us consider a case with the simplest possible discrete structure of the lattice. In this model, the proton, moving in a double minimum potential $V(\mathbf{r})$, interacts with two identical oscillating "lattice" dipoles $[(p_{l,x}=e_d x_l, 0, 0)$ and $(p_{r,x}=e_d x_r, 0, 0)]$, located on the x axis in a distance $\pm d$ from the center of the H-bond potential. Writing the polarization vector $\mathbf{P}$ as

$$\mathbf{P}=e_d\begin{pmatrix}x_l\\x_r\end{pmatrix}, \tag{45a}$$

and assuming

$$M=m_d e_d^{-2}\begin{Vmatrix}1&0\\0&1\end{Vmatrix}, \quad K=e_d^{-2}\begin{Vmatrix}k&-k'\\-k'&k\end{Vmatrix}, \tag{45b}$$

we obtain χ_1 and χ_2 as

$$\chi_1=[e_d/(2m_d)^{1/2}]\begin{pmatrix}1\\1\end{pmatrix}, \quad \chi_2=[e_d/(2m_d)^{1/2}]\begin{pmatrix}1\\-1\end{pmatrix}, \tag{46a}$$

and the frequencies of the two normal "lattice" modes as

$$\omega_{1,2}^2=(k\mp k')/m_d. \tag{46b}$$

Here m_d stands for the effective mass of the oscillating "lattice" dipole, k for the corresponding force constant and k' for the interaction force constant between the two dipoles p_{lx} and p_{rx}.

Inserting the above expressions for χ_k into Eq. (28), and expanding $|\mathbf{r}'-\mathbf{r}|^{-1}$ in powers of $\mathbf{r}'$, we obtain $A_{k,-}$ explicitly as

$$A_{1,-}=\frac{e_d^2\mu^2}{(2\pi\epsilon_0)^2\omega_1^2 m_d d^6}, \quad A_{2,-}=0, \tag{47a}$$

if terms higher than $(1/d)^6$ are neglected. Within the same model

$$B_1=\frac{e_d^2}{\pi\epsilon_0\omega_1^2 m_d d^3}, \quad B_2=0, \quad D=\frac{e_d^2}{\omega_1^2 m_d}. \tag{47b}$$

In order to get a feeling for the order of magnitude of $A_{k,-}$ let us evaluate $A_{1,-}$ assuming $\omega/2\pi=300$ cm^{-1}, $d=1.25$ Å, $m_d=16\times1.67\times10^{-27}$ kg, $e_d=e=1.6\times10^{-19}$ A sec, $\mu=1.6\times10^{-19}$ A sec 0.15 Å. We get $A_{1,-}=744$ cm^{-1}, showing that the magnitude of $A_{k,-}$ in polar crystals may well lie in the 10^2 cm^{-1} range, and is thus definitely not negligible. The corresponding values of B_1 and D are: $B_1=5.5$, $D=1.5\times10^{-17}$ (m/V)^2 cm^{-1}.

[14] R. Fuchs and A. von Hippel, Technical Report 156, Lab. Ins. Res., Massachusetts Institute of Technology, 1960 (unpublished).
[15] R. M. Hill (private communication).