

A modeling of proton polaron spectra in crystals with a dense network of hydrogen bonds

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Abstract

In this chapter we model a possible behavior of the coefficient of absorption of proton polaron in a compound with a dense network of hydrogen bonds when a polaron interacts rather with local vibrating atoms than with the whole crystal lattice (i.e. crystal polarized optical phonons). Peculiarities of the manifestation of polarons in Raman and infrared spectra are discussed.

1. Introduction

Polarons can manifest themselves in experiments on conductivity. Namely, proton conductivity, which is characterized by a barrier of activation energy, directly points out to the presence of proton polarons in the crystal studied (see, e.g. Ref. 1).

In principle, the polaron formation means that a quasi-free proton strongly interacts with the crystal lattice, which results in a coupling of the proton with a few optical polar modes. Usually these modes fall with a range 1-100 cm^{-1} . However, this is correct rather for crystals with complicated structure [2] in which hydrogen bonds do not form a frame over the whole crystal. In the case of crystals in which hydrogen bonds form a dense network, a proton in the polaron state can be bound rather not with the whole crystal, but only with local atoms that participate in local vibrations whose frequencies vary from 1000 to 2000 cm^{-1} . If this takes place then such a polaron should be active in the appropriate spectral band of the Raman and infrared spectra.

The most power methods of investigation of the crystal structure and properties are the Raman and infrared spectroscopy, and the inelastic neutron spectra. In crystals with hydrogen bonds, especially O-H bonds active O-H stretching mode appears in the region between 1000 cm^{-1} to 2200 cm^{-1} displaying effects of different intensity in a wide temperature interval. These changes of intensity depend upon the polarization of the respective features. The differences in temperature sensitivity of components of the O-H stretching vibrations suggest a separation of the polarized spectra into groups dependent on tensor components. On cooling peaks in the spectra loose their intensity.

Infrared spectra reflect oscillations of polar molecules and their binding: the molecules absorb specific frequencies that are characteristic of their structure. The Raman effect occurs when a photon excites the molecule in either the ground rovibronic state or an excited rovibronic state; the molecule experiences an inelastic influence on the side of an incident photon and is transferred to a virtual high energy state for a short period of time.

There are libraries of tens of thousands of spectra of different compounds. But in newly synthesized compounds one may observe a few new maxima. Could they be associated with the formation of proton polarons? To answer the question we shall calculate the coefficient of absorption of the polaron and study it at different conditions, first of all as a function of temperature. In the polaron problem the energy of activation depends on temperature and decreases when the temperature is going down. Hence in Raman and infrared spectra the maximums associated with polarons have to increase with cooling.

2. The coefficient of absorption of polaron

A self-trapped state of hydrogen should be specified with a binding energy that significantly exceeds the thermal energy $k_B T$. Such a situation is typical for the theory of small proton polaron, when a proton strongly interacts with polar optical phonons and/or local polar oscillations of the crystal in general. The activation of a jump of the binding proton requires an activation energy E_{act} that can reasonable be associated with the mentioned binding energy of hydrogen. In the considered case the polaron is bound with local atoms rather than with the whole crystal lattice; nevertheless, in the present case we also anticipate that the inequality $E_{act} \gg k_B T$ should be hold.

Raman spectra record among other effects also inelastic light scattering by the proton polaron that is perceived by an incident laser light as a single quasi-molecule. So in the Raman spectra of the compound studied there should be maximums associated with the excitation of the polaron as the whole, i.e. like a “molecule” (the hydrogen joined with surrounded atoms), namely, the polaron gets excited to an excited level and then come back to one of the nearest based sublevels.

In a range of frequencies lower 2000 cm^{-1} there is a possible interaction of local vibrations with acoustic phonons. In such a case acoustic phonons may pump an additional energy to support the polaron state. Such kind of an interaction may result in a shift of the polaron maximum(s) with cooling in the Raman spectra.

Close to 2000 cm^{-1} the local mode-acoustic interaction should be weakening owing to a bigger difference in frequencies. Hence, in the vicinity of 2000 cm^{-1} the polaron might rather be active in infrared spectra. In this case the polaron will absorb a photon experiencing a transfer to an upper level in the polaron potential well.

Let us consider the behavior of the proton polaron theoretically. In the polaron problem, the initial Hamiltonian can be written as follows [2]

$$\hat{H} = \hat{H}_0 + \hat{H}_{\text{tun}} \quad (1)$$

$$\begin{aligned} \hat{H}_0 = & \sum_l E_l \hat{a}_l^+ \hat{a}_l + \sum_{\alpha, \mathbf{q}} \hbar \omega_{\alpha \mathbf{q}} \left(\hat{b}_{\alpha \mathbf{q}}^+ \hat{b}_{\alpha \mathbf{q}} + \frac{1}{2} \right) \\ & - \sum_l \hat{a}_l^+ \hat{a}_l \sum_{\alpha, \mathbf{n}} \hbar \omega_{\alpha \mathbf{q}} \left[u_{l\alpha}(\mathbf{q}) \hat{b}_{\alpha \mathbf{q}}^+ + u_{l\alpha}(\mathbf{q}) \hat{b}_{\alpha \mathbf{q}} \right] \end{aligned} \quad (2)$$

$$\hat{H}_{\text{tun}} = \sum_l M_{l,l'} \left(\hat{a}_l^+ \hat{a}_{l'} + \hat{a}_{l'}^+ \hat{a}_l \right) \quad (3)$$

where \hat{H}_0 is the Hamiltonian that includes the bond energy E_l of a proton in the l th equilibrium position between oxygen atoms O ... O (i.e. E_l is the energy of an inner proton polaronic configuration – the l th level – in the one-minimum proton potential well) the energy of the lattice phonons, and the interaction of the proton with the lattice and its optical phonons; \hat{H}_{tun} is the tunneling Hamiltonian that provides for proton transfer between positions l and l' in the same O ... O bonding. \hat{a}_l^+ (\hat{a}_l) is the Fermi operator of creation (annihilation) of hydrogen atom in the l th position; $\hat{b}_{\alpha\mathbf{q}}^+$ ($\hat{b}_{\alpha\mathbf{q}}$) is the Bose operator of creation (annihilation) of the lattice polarized optical phonons, which belong to the α th branch, with the energy $\hbar\omega_{\alpha\mathbf{q}}$ and the wave vector \mathbf{q} ; $u_{l\alpha}(\mathbf{q}) = u_{(\alpha)} \exp(i\mathbf{q} \cdot \mathbf{l})$, where $u_{(\alpha)}$ is the dimensionless value that characterizes the displacement of the pair of oxygen atoms O ... O, which form the hydrogen bond, from their initial equilibrium position due to the appearance of the hydrogen atom between them. The transfer matrix element in expression (3) is determined as

$$M_{l,l'} = \int d\mathbf{r} \psi_l^* W \psi_{l'} \quad (4)$$

where W is the potential in the hydrogen bond, which specified two possible position of a hydrogen atom; ψ_l and $\psi_{l'}$ are wav functions of the hydrogen atom, which are localized at the aforementioned positions.

The operator of proton transfer density between the two different positions in the hydrogen bond is

$$\hat{j} = \frac{1}{i\hbar V} \left[\hat{H}_{\text{tun}}, \sum_l R_l \hat{a}_l^+ \hat{a}_l \right] \quad (5)$$

where R_l is the position/coordinate of hydrogen and V is the effective volume occupied by the hydrogen atom in the O ... O bond.

The equation of motion for the statistical operator, which describes the system studied, is

$$i\hbar \frac{\partial \hat{\rho}}{\partial t} = [\hat{H}, \hat{\rho}] \quad (6)$$

Putting for the undisturbed statistical operator

$$\hat{\rho}_0 = \frac{\exp(-\hat{H}_0 / k_B T)}{\text{Tr} \exp(-\hat{H}_0 / k_B T)} \quad (7)$$

The correction to $\hat{\rho}_0$ caused by the interaction Hamiltonian (3) is

$$\hat{\rho}_{\text{tun}} = -\frac{i}{\hbar} \int_{-\infty}^t d\tau e^{-i\frac{t-\tau}{\hbar} \hat{H}_0} [\hat{H}_{\text{tun}}, \hat{\rho}_0] e^{i\frac{t-\tau}{\hbar} \hat{H}_0} \quad (8)$$

Expressions (5) and (8) allow one to calculate the flow of protons/hydrogen atoms, or transfer density of hydrogen atoms/protons (the dimensionality is $\text{s}^{-1}\text{m}^{-2}$)

$$I = \text{Tr}(\hat{\rho}_{\text{tun}} \hat{j})/V \quad (9)$$

In the explicit form

$$I_{\alpha} = 2^{3/2} \pi^{1/2} \hbar^{-2} n \delta r |M|^2 \sinh \frac{|E_l| - |E_r|}{k_B T} \exp(-E_{\text{act},\alpha} / k_B T) \times \left\{ |\Delta_{\alpha}|^2 \omega_{\alpha}^2 \text{cosech}[\hbar \omega_{\alpha} / (2k_B T)] \right\}^{-1/2} \quad (10)$$

where n is the concentration of hydrogen atoms in the crystal, $\delta r = R_l - R_r$ is the distance between two equilibrium positions of hydrogen atom in the hydrogen bond, and $|\Delta_{\alpha}|^2 = |u_{\alpha l} - u_{\alpha r}|^2$ is the coupling constant of the hydrogen with the crystal lattice; $M = |M_{lr}|$ is the resonance integral (4); the activation energy is

$$E_{\text{act},\alpha} = k_B T |\Delta_{\alpha}|^2 \tanh \frac{\hbar \omega_{\alpha}}{4k_B T} - \frac{3}{2} (|E_l| - |E_r|) \quad (11)$$

Thus, we have derived the expression (10) that describes the motion of hydrogen from one equilibrium position to another in the hydrogen bond, which is caused by the difference in the bound energy of the hydrogen, E_l and E_r in these two positions.

What is the energy spectrum of such hydrogen bond? The easiest way is to construct the Green function for a hydrogen/proton located between the pair of oxygen atoms $\text{O} \cdots \text{O}$. The singularity of Green function discloses the spectrum of the system of interest, which in our case is associated with the spectrum of the $\text{O} - \text{H} \cdots \text{O}$ bound in the OADH crystal. The equation for the Green function in Fourier presentation is [2] (see, also e.g. Refs. 3 to 5)

$$G = G^{(0)} + G^{(0)} \tilde{t} G \quad (12)$$

where $G^{(0)}$ is the one-particle Green function and \tilde{t} is the transfer matrix. In the first approximation Eq. (12) is simplified as below

$$G = G^{(0)} + G^{(0)^2} \tilde{t} \quad (13)$$

The coefficient of absorption $K(\omega)$ can immediately be derived from this equation,

$$K_{\alpha}(\omega) = |\mu_{\alpha}|^2 \frac{\gamma}{(\omega - \omega_{\alpha})^2 + \gamma^2} + |\mu_{\alpha}|^2 \left[\frac{\gamma}{(\omega - \omega_{\alpha})^2 + \gamma^2} \right]^2 \langle \langle \hat{a}_l^+ \hat{a}_r \rangle \rangle_{\alpha} \quad (14)$$

where $|\mu_{\alpha}|^2$ is the function proportional to the magnitude of an induced dipole moment of a proton polaron, which provides the transition of the polaron to an excited level. The transfer matrix \tilde{t} includes only contribution from the non-diagonal product of Fermi operators $\hat{a}_l^+ \hat{a}_r$,

i.e. correlator $\langle\langle \hat{a}_l^+ \hat{a}_r \rangle\rangle_\alpha$. The correlator is calculated as the average by quantum mechanical and thermodynamic operators, i.e. \hat{a}_l^+ and \hat{a}_r and the statistical operator (7), and hence it is directly associated with are the transfer density of protons (10), namely,

$$\begin{aligned} \langle\langle \hat{a}_l^+ \hat{a}_r \rangle\rangle_\alpha &= 2^{3/2} \pi^{1/2} \hbar^{-2} |M|^2 \sinh [(|E_l| - |E_r|)/(k_B T)] \\ &\times \exp(-E_{\text{act},\alpha}/(k_B T)) \left[|\Delta_\alpha|^2 \omega_\alpha^2 \text{cosech}(\hbar\omega_\alpha/(2k_B T)) \right]^{1/2} \end{aligned} \quad (15)$$

where we add the index α to the correlator, which specifies the α th optical branch that interacts with the hydrogen.

Acoustic phonons have also to affect the vibrating hydrogen (bound with O), which has to affect the coefficient of absorption $K(\omega)$. Namely, due to the local and acoustic vibrations the frequency of polaron changes in the first approximation as follows $\omega \rightarrow \omega \cdot (1 + \delta\nu)$, where the correction $\delta\nu$ is caused by the interaction of local oscillations with acoustic phonons, $\delta\hat{\nu} = \kappa \hat{B}^+ + \kappa^* \hat{B}$; here, κ is the dimensionless function of the phonon-phonon interaction and \hat{B}^+ (\hat{B}) is the Bose operator of creation (annihilation) of an acoustic phonon. Thermodynamic averaging results in

$$\begin{aligned} \delta\nu &= \langle \kappa \hat{B}^+ + \kappa^* \hat{B} \rangle = \left\langle \frac{\exp\{-\hbar\Omega(\hat{B}^+ \hat{B} + 1/2)/(k_B T)\}}{\text{Tr} \exp\{-\hbar\Omega(\hat{B}^+ \hat{B} + 1/2)/(k_B T)\}} (\kappa \hat{B}^+ + \kappa^* \hat{B}) \right\rangle \\ &= \frac{1}{2} |\kappa|^2 \exp\left\{ \frac{1}{2} \coth \frac{\hbar\Omega}{k_B T} - \frac{1}{2} + \frac{1}{2} |\kappa|^2 \right\} \end{aligned} \quad (16)$$

Thus the introduction of the interaction with acoustic phonons changes the expression for the coefficient of absorption (14) preserving only linear terms by $\delta\nu$ as follows

$$\begin{aligned} K_\alpha(\omega) &= |\mu_\alpha|^2 \frac{\gamma}{(\omega + \delta\nu - \omega_\alpha)^2 + \gamma^2} + \\ &+ |\mu_\alpha|^2 \left[\frac{\gamma}{(\omega + \delta\nu - \omega_\alpha)^2 + \gamma^2} \right]^2 \langle\langle \hat{a}_l^+ \hat{a}_r \rangle\rangle_\alpha \end{aligned} \quad (17)$$

where the contribution on the side of acoustic phonons $\delta\nu$ is defined in expression (16) and the polaron correlator $\langle\langle \hat{a}_l^+ \hat{a}_r \rangle\rangle_\alpha$ is determined in expression (15). Anharmonism associated with the introduction of acoustic should also influence the correlator (15), however, this adds secondary effects that weakly influence the final result.

Let us calculation a numerical value of the absorption coefficient $K_\alpha(\omega)$ (17) at temperatures 300 and 10 K. Let the maximum of polaron be found at 1300 cm^{-1} at 300 K and at 1400 cm^{-1} at 10 K and let the maximum in an acoustic band be found at 50 cm^{-1} . Fig. 1 exhibits the behavior of the coefficient $K(\nu_\alpha)$ where $\nu_\alpha = \omega_\alpha/(2\pi)$ near the frequencies $\nu_\alpha = 1400 \text{ cm}^{-1}$ and $\nu_\alpha = 1300 \text{ cm}^{-1}$, respectively. The values of the parameters are shown in the legend to Fig. 1. As is seen, the maximum 1400 cm^{-1} shifts when the temperature is going down, which is caused by the interaction with the 50 cm^{-1} acoustic mode. Note the value of

the coefficient K_a is growing when the temperature decreases, which is typical for the polaron problem.

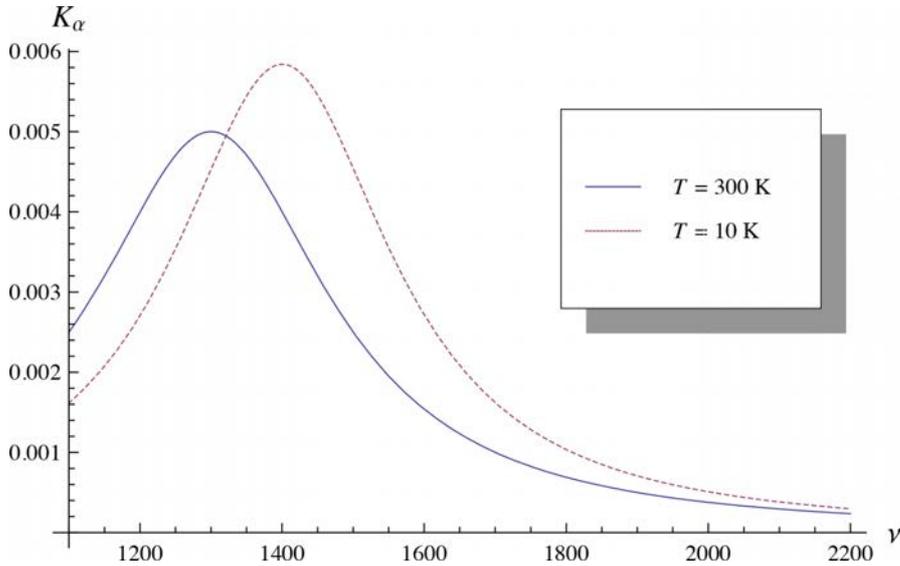


Fig. 1. Calculated band at the maximum 1300 cm^{-1} by expression (17). $|\mu_a|^2 = 0.1$; $|\Delta|^2 = 11$; $\gamma = 200 \text{ cm}^{-1}$; $\varepsilon = |E_l| - |E_r| = 0.1 \text{ cm}^{-1}$; $|\kappa|^2 = 1.4$ and $\Omega/(2\pi) = 50 \text{ cm}^{-1}$.

The behavior of band 2200 cm^{-1} is different, because this is a case of a higher frequency when the appropriate local mode is not affected by acoustic phonons. In this case the intensity of the maximum, i.e. the coefficient of adsorption (17), practically does not depend on acoustic component $\delta\nu$ when the temperature is decreasing. Fig. 2 demonstrates that in the case of the high frequency mode 2200 cm^{-1} , the full polaron effect is not manifested at a low temperature, 10 K. This is because its power is not enough: the intensity of the maximum does not increase with decrease of T . However, in this case we may anticipate that the hydrogen atom being in the polaron state becomes to interact also with a polar environment, which will result in a broadening of the absorption band (i.e., $\gamma = 200 \text{ cm}^{-1}$ may increase, for example, to $\gamma = 600 \text{ cm}^{-1}$).

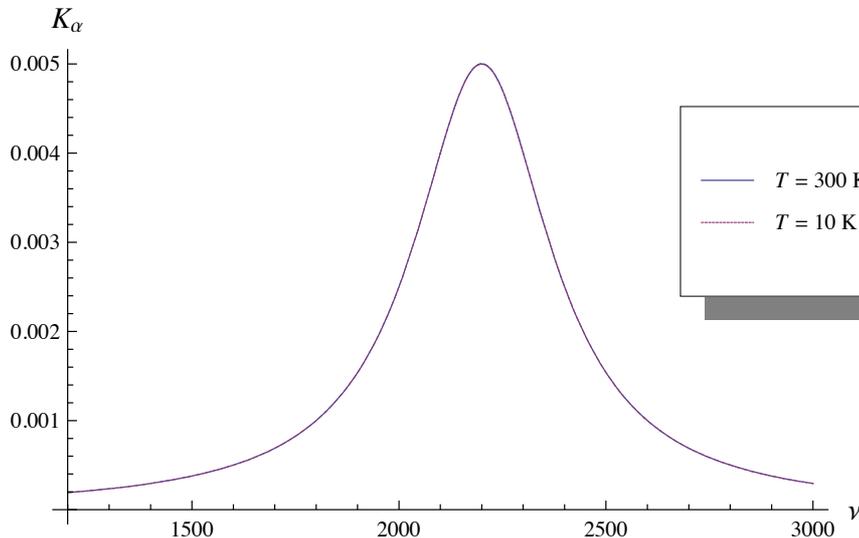


Fig. 2. Calculated band of absorption of OADH at the maximum 2200 cm^{-1} by expression (17). $|\mu_a|^2 = 0.1$, $|\Delta|^2 = 30$, $\gamma = 200\text{ cm}^{-1}$, $\varepsilon = |E_l| - |E_r| = 0.1\text{ cm}^{-1}$.

The behavior of each band is asymmetric and each band drops faster at a higher frequency wing. The shape of the curve $K_\alpha(\nu)$ is sensitive to the parameters $|\Delta|^2$, γ and $|\kappa|^2$.

Nevertheless, in addition to recorded spectra one should study the proton conductivity of the crystal in question at which the energy of activation (11) has to manifest itself directly. This additional characteristic will allow one to estimate correctly the major parameters of the polaron, first of all the polaron coupling constant $|\Delta|^2$.

3. Conclusion

The modeling of proton polaron spectrum would be applicable to a specific compound with a wide net of hydrogen bonds. Of course new effects may also manifest themselves; by the polaron effect must be dominated in all the spectra.

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