Dynamical Susceptibility of Proton in a Two-Morse Potential

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Dynamical susceptibility for a proton tunneling system is investigated by using the linear response theory and the mean field approximation. The double-minimum self-potential is constructed by a two-Morse potential, whose parameters are fixed to represent O-H stretching mode. Quantum mechanical calculations give a dynamic susceptibility showing a pronounced soft mode. The phase transitions for KDP and DKDP are described qualitatively, if an effective interaction between protons and a phenomenological damping factor are introduced. The temperature dependence of the dynamical susceptibility is discussed.

KEYWORDS: double-minimum potential, proton tunnel, dynamic susceptibility, soft mode, over-damped

1. Introduction

Structural phase transitions of second order in ferroelectrics and ferroelastics are usually classified into either order-disorder or displacive type.[1)] In the former type of crystals, a dielectric relaxation mode is observed at a few MHz regions around the transition point if the transition is second order. On the other hand, soft phonon modes are observable at GHz frequencies in typical displacive transitions. However, the soft phonon mode may couple with some relaxational degree of freedom, or the soft mode may become over-damped near the transition point. Therefore such a clear soft mode is hard to be observed in many cases. Although some theoretical studies have been devoted to distinguish these two transition types, the classification is not easy at many marginal cases.[2,3)]

KDP is a typical ferroelectric crystal, in which phosphate links each other via hydrogen bonding. Slater firstly noted that hydrogen can occupy randomly two positions between two oxygen atoms in the paraelectric phase, and that the ordering of the hydrogen was described in a statistic mechanical model.[4)] After the discovery of a remarkable isotope effect: the transition temperature rises about 100K if proton is replaced by deuteron, Blinc proposed a proton tunneling model.[5)] According to the model, the tunneling frequency was expected to slow down near the transition temperature.

Although a number of experimental studies have been devoted by many researchers, no clear soft mode was identified definitely. On the contrary, deformation of the phosphate tetra-

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hedron was detected in the Raman spectrum within the paraelectric phase, which was interpreted to indicate an order-disorder nature.[6] Some authors considered that a small structural difference between $H_2PO_4^+$ and $D_2PO_4^+$ induces the pronounced geometric isotope effect.[7]

On the other hand, quantum mechanical calculations on a hydrogen bonding system have been developed to support a proton tunneling state.[8] Moreover, an incoherent neutron scattering experiment has supported the coherent tunneling motion of proton in KDP.[9] Thus the proton tunneling picture should be reinvestigated carefully.[10]

Let's consider a particle within a double minimum potential, which is located on a lattice point. If an interaction between the particles is switched on, then an ordered state may be realized below a critical temperature T_c. The vibration mode of the particle becomes overdamped as the temperature closes to T_c, depending on the damping mechanism between the particle and the heat bath system.[11]

Onodera has analyzed the behavior of the classical particle in the following self-potential.[12]

$$V(x) = Ax^4 + Bx^2, \qquad (A > 0). \tag{1}$$

He calculated the single particle susceptibility $\phi(\omega)$ exactly by using the linear response theory.[13] The interaction between i-th and j-th particles

$$-\gamma x_i x_j \tag{2}$$

was taken into account through the mean field approximation. The dynamic susceptibility for frequency ω is expressed as

$$\chi(\omega) = \phi(\omega)/(1 - \gamma\phi(\omega)). \tag{3}$$

The system becomes unstable (so the phase transition takes place) if a pole of eq.(3) vanishes at a critical point. The spectrum of Raman spectroscopy is given by the imaginary part: $\chi''(\omega)$. If $B > 0$ in eq.(1), the system is apparently displacive. Even if $B < 0$ but the interaction is strong enough to induce the transition before the particle falls into the valley, then the transition nature is still displacive. On the contrary, if $B < 0$ and the potential barrier is higher than the thermal energy, the transition is order-disorder.

In the original theory by Onodera, the particle could not climb over the potential barrier in the order-disorder case.[12] Therefore no relaxation mode was represented in his expression, although the relaxation mode for the order-disorder transition is expected to increase its intensity as the temperature approaches to T_c. In order to consider the pure relaxation mode, Onodera has proposed a modification recently within his classical approach.[14]

Meanwhile, the climbing over the barrier is represented as a tunneling effect in quantum mechanics. To investigate the difference between the displacive and the order-disorder type transitions, the quantum mechanical treatment is inevitable. Above all, proton in KDP will

behave as a quantum particle.

In this article we calculate the Schrödinger equation for proton in a double-minimum potential, and obtain the dynamic susceptibility explicitly to discuss the continuous crossover form displacive to order-disorder behavior. We also discuss the well-known isotope effect in KDP from the framework of quantum tunneling of proton.

2. Formalism

Both in quantum and classical mechanics, the dynamic susceptibility is given by eq.(3), if the bilinear interaction eq.(2) is treated with the mean-field approximation. The relaxation function is given by[13)]

$$\Phi(t) = \int_0^\beta d\lambda \mathrm{Tr}(\rho x(-\mathrm{i}\hbar\lambda)x(t)). \tag{4}$$

Here $\beta = 1/k_\mathrm{B}T$ is the inverse thermal energy, and the canonical density matrix ρ is related to the single particle Hamiltonian $\mathcal{H}$ with $\rho = \exp(-\beta\mathcal{H})/Z$, where $Z = \mathrm{Tr}\ \exp(-\beta\mathcal{H})$. The time development is shown by $x(t) = \exp(\mathrm{i}t\mathcal{H}/\hbar)x\exp(-\mathrm{i}t\mathcal{H}/\hbar)$. Performing the Laplace transformation

$$\Xi(\omega) = \int_0^\infty \Phi(t)\exp(-\mathrm{i}\omega t)dt, \tag{5}$$

we get the single particle susceptibility as

$$\phi(\omega) = \Phi(0) - \mathrm{i}\omega\Xi(\omega). \tag{6}$$

Once the energy eigen values and wave functions are calculated from the Schrödinger equation $\mathcal{H}|j\rangle = \epsilon_j|j\rangle$, the canonical correlation function is given by the following relation:

$$\begin{aligned}\Phi(t) = \frac{1}{Z}\sum_{j,k}\frac{\exp(-\beta\epsilon_k) - \exp(-\beta\epsilon_j)}{\epsilon_j - \epsilon_k} \\ \times |\langle j|x|k\rangle|^2\exp(\mathrm{i}t(\epsilon_k - \epsilon_j)/\hbar).\end{aligned} \tag{7}$$

Here, let's consider a two-level system. The quantum relaxation function is

$$\Phi(t) = \frac{2x_0^2}{\hbar\omega_1}\tanh(\beta\hbar\omega_1/2)\cos\omega_1 t, \tag{8}$$

where

$$x_0^2 = |\langle 0|x|1\rangle|^2, \qquad \hbar\omega_1 = \epsilon_1 - \epsilon_0.$$

The isolated system does not suffer any damping. But real system has many degrees of freedom, and the relaxation function should damp. According to the method of Langevin's equation with random forces,[15)] a damping term Δ would be introduced in the continued fraction expansion form as[16)]

$$\Xi(\omega) = \Phi(0)/(\mathrm{i}\omega + \omega_1^2/(\mathrm{i}\omega + \Delta)).$$

From eq.(6), the single particle susceptibility is

$$\phi(\omega) = \Phi(0)\omega_1^2/(-\omega^2 + \omega_1^2 + \mathrm{i}\omega\Delta),$$

which coincides with that of the usual damped-harmonic oscillator. The pole of the dynamical susceptibility $\chi(\omega)$ is

$$\omega = \pm\sqrt{\omega_1^2(1-\gamma\Phi(0)) - (\Delta/2)^2} + \mathrm{i}\Delta/2.$$

In the high temperature approximation, the static single particle susceptibility

$$\Phi(0) = x_0^2/k_\mathrm{B}T$$

increases with decreasing temperature. Therefore poles become pure imaginary below some temperature, and one of the pole becomes zero at a critical temperature T_c, which is given by $1 = \gamma\Phi(0)$. Then the static susceptibility diverges to induce the phase transition. Within the high temperature approximation, T_c is given by $T_\mathrm{c} = \gamma x_0^2/k_\mathrm{B}$.

In general, let's introduce damping terms for every transitions, then eqs.(5) and (7) gives the following equation:

$$\begin{aligned}\Xi(\omega) = \frac{2}{Z}\sum_{j=0}\sum_{k=j+1}|\langle j|x|k\rangle|^2\frac{\exp(-\beta\epsilon_j)-\exp(-\beta\epsilon_k)}{\epsilon_k-\epsilon_j} \\ \times\frac{\Delta_{jk}\omega_{jk}^2 - \mathrm{i}\omega(\omega^2-\omega_{jk}^2+\Delta_{jk}^2)}{(-\omega^2+\omega_{jk}^2)^2+\omega^2\Delta_{jk}^2}.\end{aligned} \tag{9}$$

We write the real and imaginary parts as $\chi(\omega) = \chi' - \mathrm{i}\chi''$, $\Xi(\omega) = \Xi' - \mathrm{i}\Xi''$, then the spectrum is given by

$$\frac{\chi''}{\omega} = \frac{\Xi'}{(1-\gamma(\Phi(0)-\omega\Xi''))^2 + (\gamma\omega\Xi')^2}. \tag{10}$$

At the transition temperature, the static susceptibility $\chi(0)$ diverges, which depends both energy eigen values ϵ_j and the transition matrix $\langle j|x|k\rangle$. If the damping terms Δ_{jk} are given properly, the spectrum can be constructed explicitly from eqs.(9) and (10).

3. Two-Morse Potential and the Energy Levels

In order to investigate the transition of a proton-tunneling system concretely, we adopt a two-Morse potential which has been considered frequently; [17]

$$U(x) = 2D\{\mathrm{e}^{-2ad}\cosh 2ax - 2\mathrm{e}^{-ad}\cosh ax\}, \tag{11}$$

The parameters are selected to be[18]

$$D = 2.2\ \mathrm{eV}, \qquad a = 3.8\ \mathrm{\AA}^{-1}, \qquad d = 0.29\ \mathrm{\AA}, \tag{12}$$

which may be suitable for the proton potential in KDP. Here D and a are chosen so that the stretching mode of the O-H bond can be reproduced in the one-Morse potential. In the paraelectric phase of KDP, the neutron diffraction analysis revealed a double-peak density

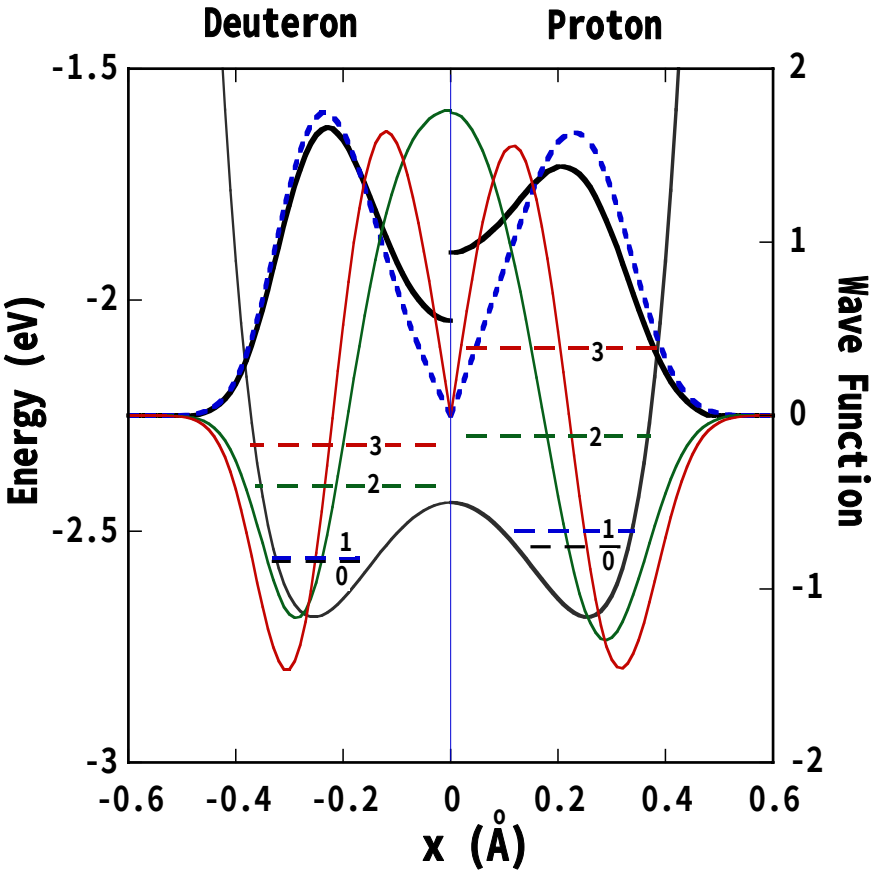

Fig. 1. The wave functions and the eigen energies for the two-Morse potential with D=2.2, a=3.8 and d=0.29. The right and left halves are for proton and deuteron, respectively. The ground and first-excited state wave functions are indicated by bold solid and broken curves, respectively. The second and third excited states are also drawn by gray curves. Horizontal broken lines indicate eigen energies E_n ($n = 0$: ground state, $n \geq 1$: excited states).

distribution of hydrogen: the peak splitting was reported as 0.32 and 0.44Å for KDP and DKDP, respectively,[19] which is reproduced approximately from the above value of d.

The Schrödinger equation is solved numerically to give eigen values and wave functions as shown in Fig. 1. The peak splitting of the ground state wave function is 0.41 and 0.46Å for proton and deuteron, respectively. Even if proton and deuteron are situated in the same potential function, the density distribution differs a little because of the mass effect in the zero-point energy. The energy levels for deuteron are always lower than those for proton. The tunneling gap (the energy difference between ground and first excited states) of deuteron is 7.3 meV and much smaller than 34 meV of proton. The wave functions for energy levels above the potential barrier are similar between deuteron and proton. The absolute value of eigen energy is plotted in Fig. 2. The eigen energies depend on the splitting parameter d drastically. The

minimum value of the potential and the barrier height $U(0) = 2D\{\exp(-2ad) - 2\exp(-ad)\}$, are also plotted. The potential barrier disappears if $d < 0.1824$. The ground state energy becomes below $U(0)$ if $d > 0.2421$ (proton) or 0.2284 (deuteron). The first excited state also below $U(0)$ if $d > 0.2724$ (proton) or 0.2522 (deuteron). In a range of $0.26 < d < 0.3$, the feature represented in Fig. 1 does not suffer any essential change.

4. Interactions and Spectrum

Now let's introduce interactions eq.(2). With a choice of $\gamma = 0.45$ eV/Å^2, the transition temperature is $T_c = 101.5$ K and 246 K for proton and deuteron, respectively. These values can be compared to the transition temperatures 122 K (KDP) and 229 K (DKDP). The damping term is assigned arbitrarily as $\Delta = 0.005$ eV $= 40.3$ cm^{-1}. The spectral function $\chi''(\omega)/\omega$ can be calculated from eqs.(9) and (10).

Figure 3 displays the calculated spectrum for (a) proton and (b) deuteron. For proton, the transition line $0 \rightarrow 1$ between ground state and first excited state at 274 cm^{-1} increases its intensity with decreasing temperature. The frequency softens rapidly with approaching the transition temperature. The transition lines around $1500 \sim 2000$ cm^{-1} change their frequency little. However, transitions from the excited states weaken their intensity at low temperature, because the occupation probability decreases following the Bose factor.

For deuteron, the $0 \rightarrow 1$ transition line around 59 cm^{-1} softens and the intensity strengthens with decreasing temperature. The tunneling mode becomes over-damped below room temperature. Since the transition temperature is rather high, $1 \rightarrow 2$ and $0 \rightarrow 3$ transitions do not change so much, however, the $2 \rightarrow 3$ transition around 712 cm^{-1} weakens because of the Bose factor.

5. Discussion

Our model of a phase transition consists of protons which are embodied in the two-Morse potential eq.(11) and are interacting with each other by bilinear coupling eq.(2). Though the two-Morse potential for proton was considered already by Lowrence and Robertson,[17] they did not take the interaction into account to discuss the phase transition. Our model parameters D and a are similar to theirs as discussed in our previous report.[18]

The characteristics of the phase transition depend on the potential parameters D, a and d in eq.(12), as well as the interaction parameter γ. In our previous report,[18] the parameter d was either 0.27 for proton or 0.28 for deuteron, in order to reproduce the nuclear density distribution determined from the neutron diffraction measurement.[19] In this report, we have adopted the same parameter d=0.29 for both proton and deuteron to stress the tunneling effect clearly, and we have extended to the multi-level system (up to the sixth excited state), rather than the two-level system, in discussing the spectral function and the transition point.

Here we demonstrate the transition temperature T_c as a function of d and γ. Figure 4

plots how T_c changes with the splitting distance d for $\gamma = 0.45$ and 0.5 (proton) or for $\gamma = 0.4$ and 0.45 (deuteron). Stronger γ, higher is the T_c. With decreasing d, T_c decreases because the potential minimum becomes shallow and the potential barrier low. At a critical d, T_c vanishes logarithmically.[18] The interaction $\gamma = 0.45$ is one of the choice that the T_c for deuteron system is about 100 K higher than that for proton. At low temperature in the paraelectric phase, the static susceptibility deviates from the Curie-Weiss law and can be well expressed by the Barrett equation.[18] This is also a quantum effect.

It has been observed that the oxygen-oxygen distance of KDP shrinks and the double peak sprit of proton distribution also decreases at high pressure.[20] Therefore we can image that d decreases with pressure. Even if the interaction parameter does not depend on pressure, the transition temperature decreases with pressure. The similar phase diagram, especially the sudden drop of T_c near 0 K has been observed experimentally both in KDP and DKDP.[21] Though the details of the pressure-temperature phase diagram of the real crystal are different a little with Fig. 4, our simple model is successful, qualitatively. Thus we consider that tunneling is essential in a proton system with a double minimum potential.

Next we comment on the spectral function $\chi''(\omega)/\omega$. Our theoretical treatment is within the framework of the linear response theory,[13,15] according which Tokunaga also calculated the spectral function.[22] But he treated the quantum two-level system represented by spin variables. In this report, we have considered the multi-level system and demonstrated the softening of the tunneling mode from the numerical calculation explicitly.

Whether the proton tunneling mode is under-damped or over-damped depends on the damping (line width) parameter Δ introduced phenomenologically. The coupling between proton and PO_4 tetrahedron will be the main origin of the damping in KDP. It is reported that ν_2 mode of PO_4^{3-} is 420 cm^{-1} comparable to the proton tunneling frequency, so the proton motion will suffer a serious damping. Near T_c, the tunneling frequency becomes soft, and the coupling with the phonon modes (external modes) induces another damping against the proton system.

The oscillator strength for proton may be weaker than that for PO_4. Such a situation may make it difficult to observe the proton tunneling mode by means of usual Raman spectroscopy. Any way, the tunneling mode is expected to exist below 200 cm^{-1}. If the low temperature suppress the damping of the phonon mode and the high pressure makes the proton mode a little hard, then the proton-PO_4 coupled vibration mode may be observable under such conditions.[23]

So far we have calculated proton (deuteron) motion within the given double-minimum potential constructed by placing two Morse potential functions back to back. The Morse potential for proton is supplied by the neighboring oxygen of PO_4. According to the detailed structural analysis, the Debye-Waller factor of oxygen is $U_{11} \approx 0.007$ Å^2 (0.011 Å^2 for DKDP)

at just above T_c.[19] Since the zero-point motion of oxygen is estimated to be $U_{11} \approx 0.006$ Å^2 from the extrapolated value at $T \to 0$, oxygen of KDP is almost in the ground state. In DKDP, the thermal amplitude of oxygen is estimated to be about 0.03 Å. Here let's inquire Fig. 2 again. Even if the oxygen moves thermally around the mean position, the splitting distance d will be in the range of $0.26 < d < 0.31$. Then the ground state of proton (deuteron) is still below the potential barrier and the tunneling frequency is several hundred (proton) or dozen (deuteron) cm^{-1}. The essential features do not change at all; the difference between the deuteron and the proton system stems from the quantum mechanical mass effect. A further discussion is out of the scope of this report.

Our model system does not take into account of PO_4 and K cation explicitly. The interaction between proton and PO_4 is only considered through the effective interaction between protons; the mean field approximation does not matter to the details of the interactions. Our theory depends also on the linear response theory. Since both treatments are quite general frameworks of the theory, microscopic details do not change qualitatively. The isotope effect in KDP can be explained by the tunneling motion of proton.

In summary, we considered a quantum mechanical motion of proton in a double-minimum potential. Even if the double well is so deep that the particle energy is not enough to climb over the barrier classically, the quantum particle can tunnel the wall. The relaxational behavior of the order-disorder case is described with introducing the phenomenological damping in the quantum mechanical susceptibility. Whether the motion is displacive or order-disorder would not be decided by a simple classical consideration. The displacive system changes to the order-disorder one continuously if the tunneling gap decreases as the potential splitting d increases (see Fig. 2). The actual criterion would depend on the damping mechanism of the quantum system via the coupling to the heat bath system. If the quantum motion is slow enough to loss the quantum coherency, the spectral function changes from the resonance type to the pure relaxational one to represent the stochastic nature. The quantum effect is most remarkable in a hydrogen-bonding system, however, any atom within a shallow double-minimum potential should be analyzed by quantum mechanics, especially at low temperature.

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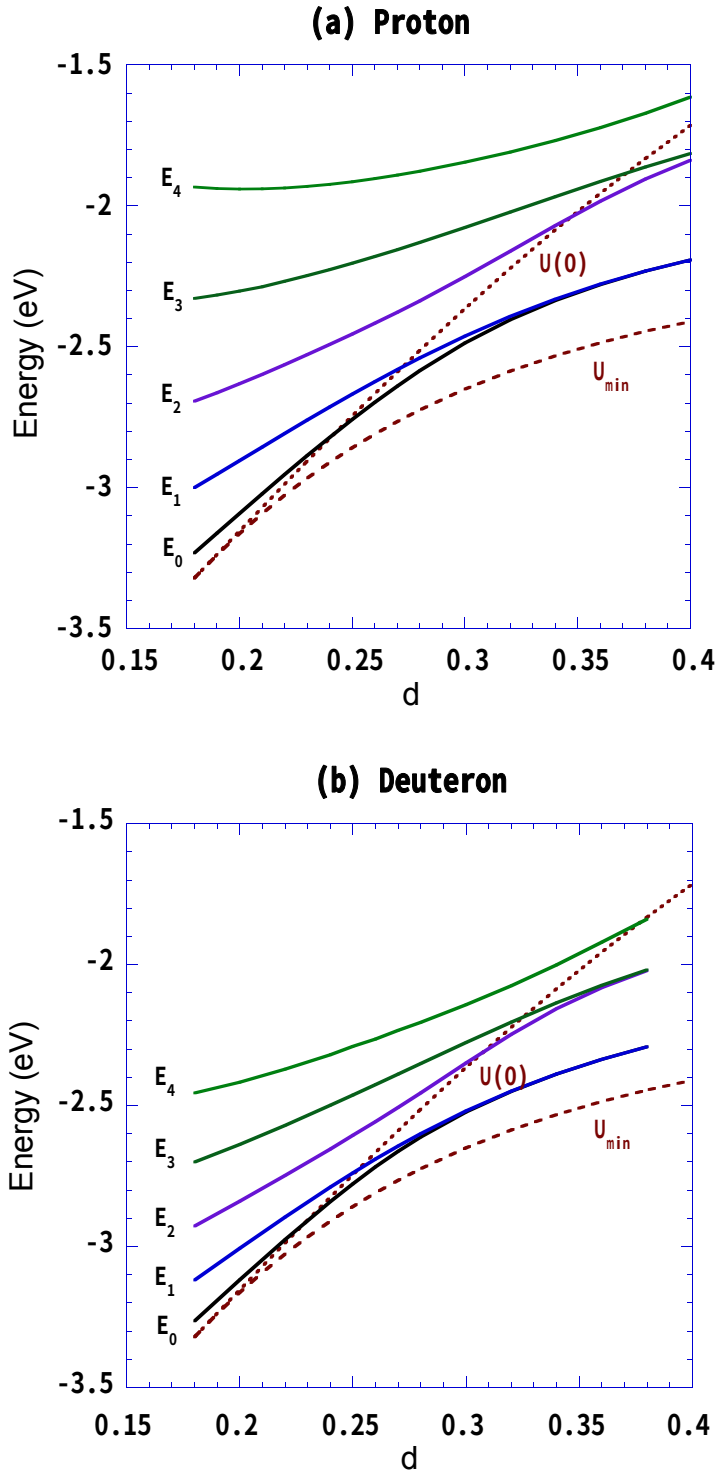

Fig. 2. Eigen energy E_n as a function of the potential splitting d; (a) proton and (b) deuteron. The potential barrier $U(0)$ and the minimum $U_{\min}$ are also plotted.

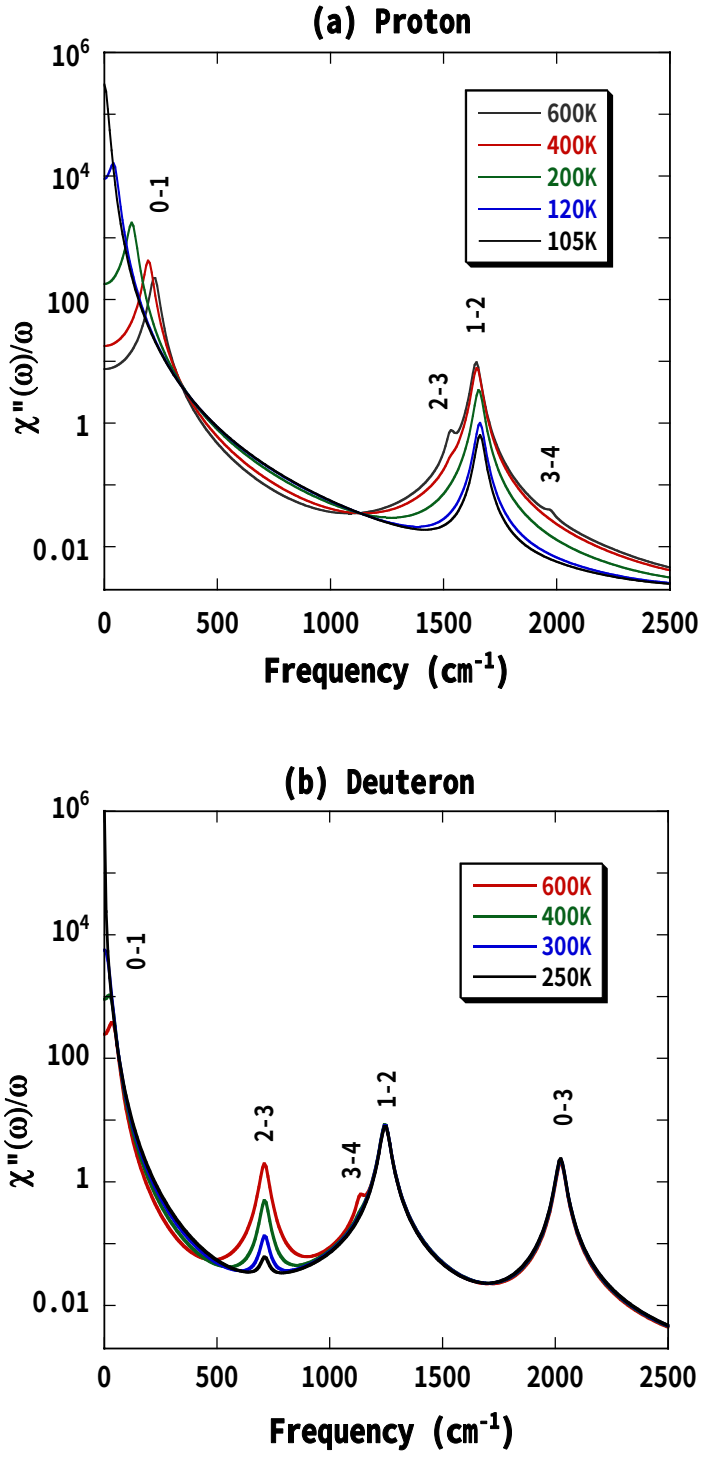

Fig. 3. Spectrum for proton (a) and deuteron (b). In proton system, with decreasing temperature from 600 K to 105 K, the 0-1 transition line (tunneling mode) decreases its energy, and finally the mode becomes over-damped. In deuteron system, as temperature decreases from 600 K to 250 K, the 0-1 transition line (tunneling mode) decreases its energy, and the mode becomes over-damped below room temperature.

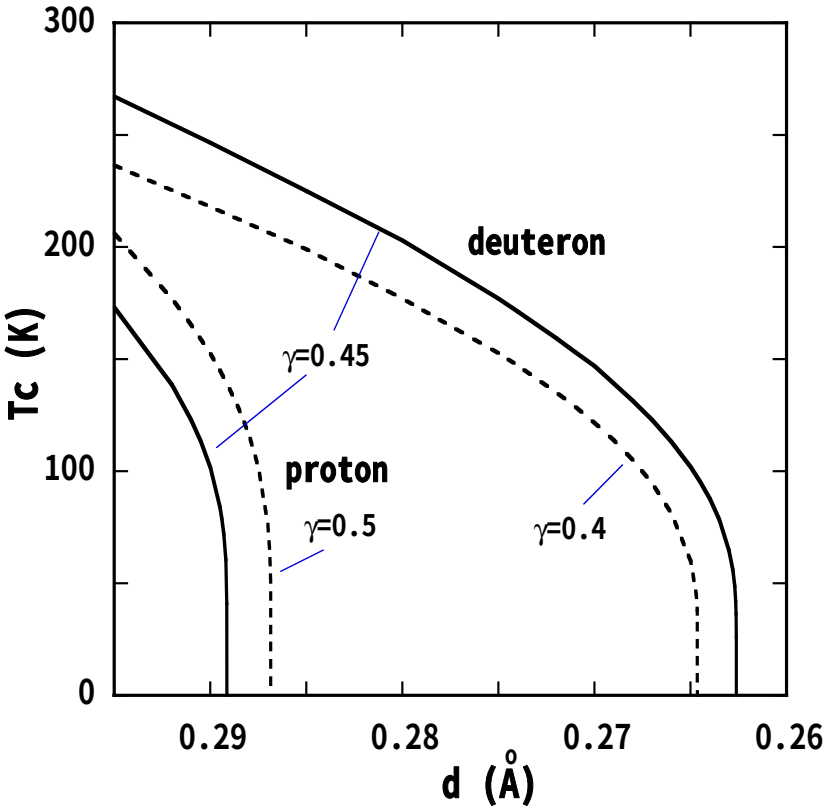

Fig. 4. Parameter dependence on the transition temperature T_c.

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