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Infrared absorption by a tunneling proton in crystalline 5-bromo-9-hydroxyphenalenone

T. MATSUO¹(*), K. KOHNO¹, M. OHAMA¹, T. MOCHIDA²
A. IZUOKA³, and T. SUGAWARA³

¹ *Department of Chemistry, Graduate School of Science, Osaka University
1-1 Machikaneyama-cho, Toyonaka, Osaka 560-0043, Japan*

² *Department of Chemistry, Faculty of Science, Toho University
2-2-1 Miyama Funabashi, Chiba 274-8510, Japan*

³ *Department of Basic Science, Graduate School of Science and Arts
The University of Tokyo - 3-8-1 Komaba, Meguro-ku, Tokyo 153, Japan*

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Abstract. – 5-bromo-9-hydroxyphenalenone absorbs infrared radiation strongly at 83 cm^{-1} when cooled to 5 K. The absorption is attributed to a transition from the ground state to the first excited state of a tunneling proton in a double-well potential of the intramolecular hydrogen bond. The temperature dependence of the spectrum was studied in detail. The linewidth was exceptionally large. Two mechanisms of the broadening are discussed. The atomic motion in a deuterated crystal corresponding to the tunneling freezes at 34 K in a deuteration-induced phase transition. This is the first spectroscopic evidence for the absorption of radiation by a tunneling proton in a neat molecular crystal.

A proton (or any particle) moving in a symmetric double-well potential is in either a symmetric or an antisymmetric eigenstate formed by symmetric or antisymmetric combinations of the wave functions localized in each of the potential wells [1]. At the low energy end of the spectrum of such a Hamiltonian, the energy difference between the symmetric and antisymmetric states is known as the tunnel splitting. Figure 1 shows schematically a double-well potential and symmetric and antisymmetric wave functions of a proton moving in the hydrogen bond. This model is appropriate for the intramolecular hydrogen bond in the aromatic compound 5-bromo-9-hydroxyphenalenone (abbreviated BHP, $\text{C}_{13}\text{H}_6\text{BrOOH}$) whose molecular shape is shown in the figure. The oxygen-oxygen distance in the intramolecular hydrogen bond is 2.49 Å [2]. Also shown are the two terminal configurations of the hydrogen bond where the proton is localized in the left or right valley of the hydrogen bond. In the

(*) E-mail: matsuo@chem.sci.osaka-u.ac.jp

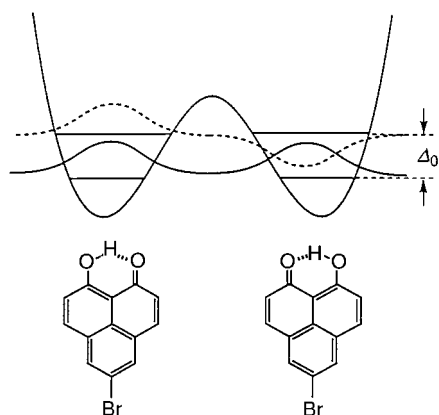


Fig. 1

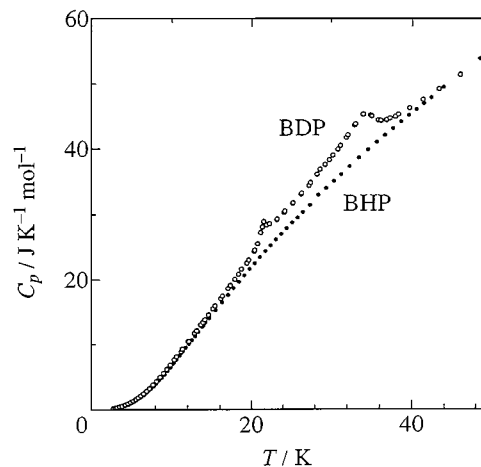


Fig. 2

Fig. 1. – Schematic representation of the double-well potential for a proton moving in the hydrogen bond of a 5-bromo-9-hydroxyphenalenone molecule. The energy levels and corresponding symmetric and antisymmetric wave functions are shown along with the two terminal states for the proton localized in one or the other potential well. The tunnel splitting is designated as Δ_0 .

Fig. 2. – The heat capacity curves of 5-bromo-9-hydroxyphenalenone $C_{13}H_6BrOOH$ (BHP) and 5-bromo-9-deuteroxyphenalenone $C_{13}H_6BrOOD$ (BDP) at low temperature, showing two phase transitions in the deuterated crystal and none in the protonated one [3].

classical limit, the tunnel splitting is zero and the pair of states are degenerate, representing classical two-state disorder.

Tunnel states and deuteration-induced phase transition. – Figure 2, reproduced from ref. [3], presents the heat capacity curves of BHP and its analog 5-bromo-9-deuteroxyphenalenone (BDP). There are two peaks in the heat capacity of BDP showing the occurrence of phase transitions. The integrated transition entropy ($= 6.8 \text{ J/K mol}$) is consistent with a two-state disorder in the high-temperature phase. The smooth heat capacity of the natural species shows the absence of this type of ordering for the protonic system. The difference resulting from the deuterium substitution has been explained by the different energies of the tunnel levels for the proton and deuteron, moving in the essentially same intramolecular hydrogen bond. There has been controversy as to whether or not a well-defined nuclear tunneling state exists in a solid where the proton is embedded in a collection of other degrees of freedom possessing comparable energies [4]. It has been argued that coupling with other degrees of freedom such as phonons and neighboring hydrogen bonds is so strong that an isolated tunneling state cannot be a correct description of a proton in a crystalline environment even as a qualitative approximation to the actual situation. A description based on single-atom tunnel states is likely to be incorrect for KH_2PO_4 and KD_2PO_4 [5], both of which undergo a phase transition. However, phase transitions induced by deuterium substitution are understood by assigning an essential role to the mass-dependent kinetic energy of the proton (and deuteron) in the free energy of the crystal [6-9].

The dielectric properties of BHP change in an essential way on deuteration of the intramolecular hydrogen bond [10]. For BHP the dielectric permittivity increases smoothly with decreasing temperature approaching a constant value at 4 K, whereas for BDP it follows the

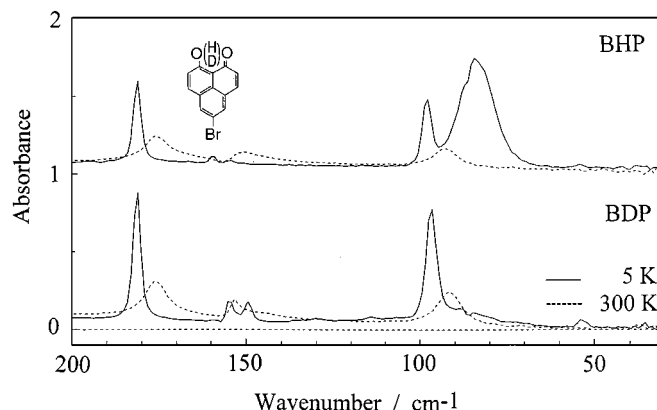


Fig. 3. – Infrared transmission spectra of 5-bromo-9-hydroxyphenalenone $C_{13}H_6BrOOH$ (BHP) and 5-bromo-9-deuteroxyphenalenone $C_{13}H_6BrOOD$ (BDP). The intense absorption at 83 cm^{-1} occurs only for BHP at low temperature, and is assigned to the transition between the tunneling states. The absorption at 96 and 181 cm^{-1} is due to molecular or lattice vibrations.

Curie-Weiss law at higher temperatures and undergoes two anomalous regions as the dipole reorientation freezes at the two phase transitions. The dielectric behavior of BHP suggests the importance of the quantum fluctuation and tunneling while that of BDP is more or less classical with a complication related to the occurrence of an incommensurate phase [11, 12].

For impurity dipoles isolated in a matrix, tunneling states have been identified spectroscopically in the millimeter-wave region [13]. In the present letter, we report an experiment that shows the first direct observation of infrared absorption by a spectroscopic transition between tunnel levels of a proton in a neat molecular crystal (as opposed to a doped system).

Far-infrared spectrum. – BHP was prepared by the method described in ref. [2] and deuterated by recrystallization from a two-phase mixture of deuterium oxide and dichloromethane. Only the proton on the hydrogen bond is deuterated by this method. The infrared spectra were recorded on a BIORAD far-infrared spectrometer equipped with an Oxford Instruments spectroscopic cryostat. The spectral resolution was 2 cm^{-1} . The temperature of the sample was measured to an accuracy of plus or minus 1 K with a thermocouple attached to the polyethylene sheet on which the powder crystal mixed in paraffin was spread. The temperature difference between the thermocouple and the sample was negligible since they were thermostated in the same helium gas atmosphere.

Figure 3 compares the far-infrared spectra of the protonated and deuterated compounds at 5 and 300 K. One notices a very strong absorption at 83 cm^{-1} for BHP at low temperature. The BDP spectrum has no corresponding peak. The peaks at 96 and 181 cm^{-1} occurred for both and are assigned to intra- or intermolecular vibrations. These peaks broadened and shifted to lower frequencies at higher temperature, following the usual temperature dependence of slightly anharmonic vibrations. The weak peaks at 153 cm^{-1} in the low-temperature spectrum of BDP arose from the lowered crystal symmetry accompanying the deuteration-induced phase transitions at 21.3 K and 33.9 K [3]. In contrast to these more or less normal types of behavior of the vibrational transitions, the temperature dependence of the intense absorption in BHP at 83 cm^{-1} is unusual. As fig. 3 shows, the absorption at 5 K is six to seven times more intense than the neighboring vibrational transition at 96 cm^{-1} and disappeared entirely at 300 K. Figure 4 shows the temperature evolution of the absorbance in this frequency range. One

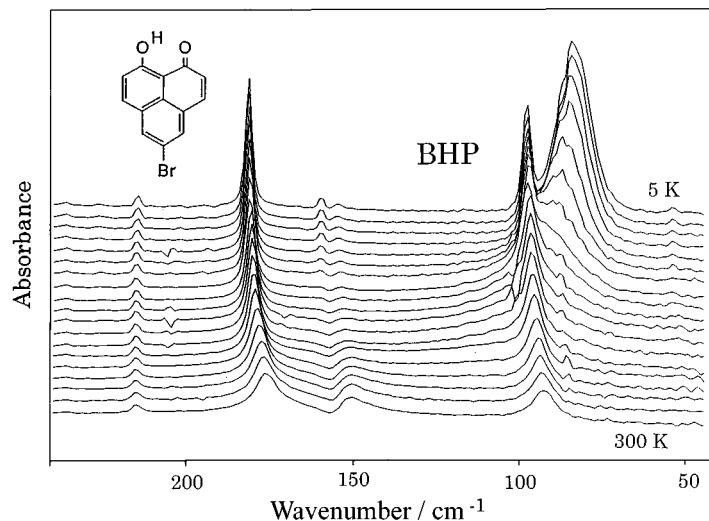


Fig. 4. – Temperature evolution of the infrared absorbance of 5-bromo-9-hydroxyphenalenone $C_{13}H_6BrOOH$ (BHP). The sample temperature was 5 K for the top spectrum and 300 K for the bottom spectrum. The temperature was 15, 25, 35, 45, 55, 65, 75, 85, 95, 105, 115, 130, 150, 180, 210, 240 and 270 K for those in between. The tunnel absorption at 83 cm^{-1} lost its intensity rapidly as the temperature increased. The absorptions at 96 and 181 cm^{-1} followed the normal temperature dependence of a slightly anharmonic molecular vibration.

notices drastic decrease of the absorbance of the 83 cm^{-1} peak at temperatures between 50 and 100 K. The temperature range corresponds to a substantial decrease of the ground-state population as a result of thermal excitation to the energy level at 83 cm^{-1} . This indicates that the 83 cm^{-1} level is isolated and not followed up by the usual equidistant rungs of levels of a harmonic oscillator.

We have thus found two unusual properties of the absorption at 83 cm^{-1} of BHP: it occurs only in the protonated compound (entirely absent from the spectrum of the deuterated compound), and its intensity decreases drastically at higher temperatures. From the mass dependence, we attribute the 83 cm^{-1} absorption to the transition between the ground and excited states of a tunneling proton. The transition should be infrared active in agreement with the experiment since it occurs between symmetric and antisymmetric states.

Evidence for low-lying energy states has been found in the heat capacity of BHP. The heat capacity of BDP is smaller than that of BHP between 70 and 150 K [3]. We recall that the normal effect of deuterium substitution is to decrease lattice and molecular vibrational frequencies and hence to increase the heat capacity. The opposite deuteration effect found in the heat capacities of these compounds has been attributed to extra energy levels present only in BHP. The inverse isotope effect (*i.e.*, a larger heat capacity for the non-deuterated compound) occurs also in other compounds that undergo phase transitions only in the deuterated forms: $Rb_3D(SeO_4)_2$ [14], $(ND_4)_2TeCl_6$ [15], $(ND_4)_2PbCl_6$ [16] and NaOD [17]. This can be understood by the presence of extra energy levels in the protonated compounds. Indirect evidence for the tunneling in BHP has also been obtained from the H-D phase diagram [18] and dielectric measurements [2, 10].

The tunnel splitting for the deuterium, if it occurs at all, is smaller than that of the proton and may be below the experimental range of our spectrometer (30 cm^{-1}). Such strong mass-dependence is consistent with the general properties of a tunneling system [1]. For the

deuterated crystal at low enough temperature where the assumed small tunnel splitting may be observed unhindered by broadening and other secondary effects, the molecules are already ordered, thus excluding the possibility of tunneling motion.

The temperature dependence, width and intensity of the absorption by tunneling. – We notice in fig. 4 an increased absorbance at 150 cm^{-1} for the spectra taken at higher temperatures. This can be assigned to a hot band arising from the population of the first excited level being further excited to the second excited level. Recent calculation of the energy of the several lowest levels for a proton in a double-well potential supports the possibility of a hot band occurring at this frequency [19].

The wave number of the absorption maximum increased from 83 cm^{-1} at 5 K to about 89 cm^{-1} at 65 K (fig. 4). Although the shift could not be evaluated at higher temperatures because of broadening, this behavior is clearly different from that of a vibrational transition and supports a non-vibrational origin of the 83 cm^{-1} absorption.

The full width (about 16 cm^{-1}) of the 83 cm^{-1} absorption is substantially larger than that of the vibrational transitions (ca. 3 cm^{-1}) at 96 cm^{-1} and 181 cm^{-1} . The width deserves a further discussion of its origin since it occurs at low temperature (5 K) and is independent of temperature below 20 K. Easy explanations of the broadening that invoke disorder or other thermal effects are thus excluded. A mechanism of broadening may be found in the fluctuating interaction (electric or otherwise) due to neighboring protons. The interaction is random and fluctuates because the protons in neighboring molecules are tunneling from one minimum to the other on their own hydrogen bonds, even though they are ordered in the ground state. In this model, the width (16 cm^{-1}) gives a measure of the strength of the intermolecular interaction. Another mechanism of broadening is the interaction via the transition moment of the infrared absorption [20]. The magnitude of this interaction is proportional to the square of the transition moment and thus to the integrated intensity of the absorption. Randomness and hence broadening are introduced through the dependence of the interaction energy on the shape and size of the crystallites in which the absorbing dipoles are embedded. This mechanism relates the large intensity and width of the tunneling transition in an essential way. At present we cannot choose one over the other of the two mechanisms.

The strong intensity of the 83 cm^{-1} absorption is consistent with the tunneling model. One expects a large transition dipole matrix element between a pair of tunnel states for which the wave functions have large amplitude away from the coordinate origin. In comparison, the wave functions of a harmonic oscillator are more compactly concentrated at the center, giving a relatively small transition moment. As a related point, fluorescence spectroscopy has given tunneling frequencies of comparable magnitude for the present molecule in the gas phase and its non-brominated analog $\text{C}_{13}\text{H}_7\text{OOH}$ isolated in a rare-gas matrix [21,22].

It should be clear that the tunneling motion discussed here is different from the rotational tunneling of a methyl group about the C_3 axis or methane molecules and ammonium ions from one stable orientation to another in a crystalline environment [23]. Rotational tunneling of that type, well established by neutron scattering, calorimetry and nuclear magnetic resonance, involves nuclear spin coordinates and permutation of the protons by spatial rotation. The tunneling discussed here is simpler conceptually, involving only the spatial coordinate and no exchange of protons.

In a wider perspective, the present result gives an example of quantum effect on the motion of an atom confined in a weak and broad potential valley. The situation is similar in the ammonium compounds which undergo phase transitions only in the deuterated forms [15,16] and in a proton glass [24]. Recently, quantum delocalization was found to be important in the atomic motion and excitation spectrum in amorphous silicon [25]. The silicon atoms are situated in a variety of environments ranging from tight to slack as was originally proposed in

the two-level system description of glasses [26,27]. A slackly bound silicon atom behaves in the same way as the hydrogen atom in the present compound.

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