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## Proton tunnelling and deuteration-induced phase transitions in hydrogen-bonded crystals

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**Abstract.** Experimental facts about appearance of new crystalline phases at low temperature related to deuterium substitution are collected and mechanisms of the isotope effect discussed. Compounds considered are (i) tri-alkali hydrogen selenates and sulphates, (ii) ammonium hexachlorometallates, (iii) bromo- and iodo-hydroxyphenalenone and (iv) chromium hydrogen dioxide. In (i), (iii) and (iv), linear O–H–O hydrogen bonds are involved. Proton tunnelling is the likely mechanism of the peculiar phase behaviour of (i). Definitely the tunnelling plays an essential role in (iii) but not in the extreme situation in (iv). In (ii), rotational tunnelling of an ammonium ion is the likely ingredient of the deuteration-induced phase transitions. The term proton cloud is introduced to describe the quantum mechanical distribution of the nucleus in the hydrogen bond and in the multi-valley rotational potential for an ammonium ion.

### 1. Introduction

Substitution of deuterons for protons in a substance containing hydrogen modifies its properties in various ways. Spectroscopic and spin-dependent properties change in a most obvious and predictable way and provide the basis for useful techniques in vibrational, NMR and neutron spectroscopies. By contrast, effects of deuterium substitution on thermodynamic properties are understood less well. By way of example, ordinary ice  $I_h$  melts at 273.15 K under 1 atm pressure and  $D_2O$  ice at 276.97 K, while the boiling points are 373.15 K and 374.59 K for the normal and heavy water, respectively. Ice  $I_h$  doped with a tiny amount of alkali hydroxide undergoes a phase transition to an ordered phase ice XI. The transition temperature is 72 K for  $H_2O$  and 76 K for  $D_2O$  [1, 2]. Thus the isotope effect on the phase behaviour is relatively small, a few per cent of the transition temperature even for ice in which the intermolecular force that binds the molecules together arises entirely from hydrogen bonding. The mechanism by which these temperatures change on deuteration is not understood at present. The enthalpy, entropy, free energy and other thermodynamic functions of a crystal depend on the normal mode frequencies of the crystal and hence on whether it is protonated or deuterated. However, as the transition temperature depends on the difference between the free energies of the two phases involved, the actual shift of the transition temperature depends on which of the phases is more affected by deuteration. In fact, both positive and negative changes of the transition temperature are known. An interesting case is that of methylammonium hexachlorostannate,  $(CH_3NH_3)_2SnCl_6$  where the transition temperatures (154.32 K and 154.96 K) of the protonated

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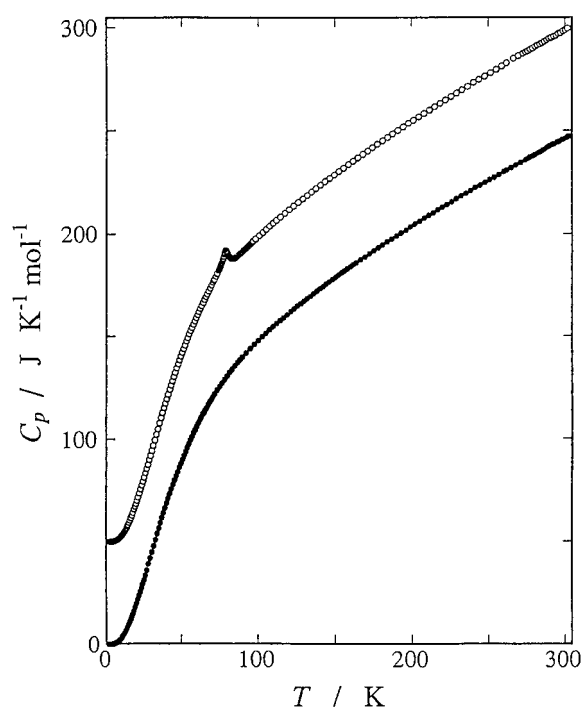
and fully deuterated crystals differ only by 0.41% [3, 4], even though the transition mechanism involves only the ordering of the position of hydrogen atoms [5]. For  $\text{CH}_3\text{NH}_3\text{I}$ , the transition temperature decreases from 166.1 K to 164.0 K on deuteration [6]. Having pointed out that the transition temperature is related to the molecular mass in a complicated way even for the simplest of the order–disorder systems, we will concentrate on the more drastic changes of the properties, namely phase transitions that occur only in the deuterated forms. In this article, an overview of this compact area of the isotope effect is presented along with a few new experimental results.

## 2. Deuteration-induced phase transitions

Phase transitions that occur only in deuterated compounds have been found more or less by chance. They are diverse in their chemical properties and structure. Some crystals of  $\text{A}_3\text{H}(\text{XO}_4)_2$  and  $(\text{NH}_4)_2\text{MCl}_6$  types undergo phase transitions when deuterated. Here A is potassium or rubidium cation, X sulphur or selenium and M one of the tetravalent ions Te, Pd, Pt or Pb. Other compounds behaving in a similar way are  $\text{C}_{13}\text{H}_6\text{BrOOH}$  (5-bromo-9-hydroxyphenalenone), chromium hydrogen dioxide, NaOH and  $\text{C}_{14}\text{H}_{10}$  (tolan, diphenylacetylene).

## 3. $\text{A}_3\text{H}(\text{XO}_4)_2$

The unexpected behaviour of  $\text{Rb}_3\text{H}(\text{SeO}_4)_2$  and  $\text{Rb}_3\text{D}(\text{SeO}_4)_2$  was first reported by Gesi who measured their dielectric permittivity [7]. He found that the dielectric constant of the H compound increases smoothly as the temperature decreases down to 4 K while that of the D compound undergoes a maximum at 92 K. We measured the heat capacities of the two compounds [8] and confirmed the phase transition in  $\text{Rb}_3\text{D}(\text{SeO}_4)_2$  and its absence in  $\text{Rb}_3\text{H}(\text{SeO}_4)_2$ . The transition temperature was 95.4 K by the calorimetry. The measurement was extended to 2 K, further confirming the absence of a transition in the H compound [9]. An interesting result of the low temperature thermal measurements is that the heat capacity of the H compound is larger than that of the D compound at temperatures below 50 K. Because of the very small difference of the molar masses of the H and D compounds, the expected difference in the heat capacity is very small. For that matter it should be in the opposite sense to the experiment results if one considers only the molar mass difference. The experimental result that the heat capacity of the H compound is larger shows that there is an additional degree of freedom in the H compound. This was explained by assuming an extra energy level possibly related to tunnelling motion of the proton on the hydrogen bond. Structurally, the centre of symmetry in  $\text{Rb}_3\text{H}(\text{SeO}_4)_2$  is preserved at 4 K [10]. The protons may be in a static disorder. But it could also be in a quantum mechanical symmetric ground state. In view of the temperature dependence of the dielectric permittivity, the tunnelling ground state is likely to be the case. For the sulphate pair  $\text{Rb}_3\text{H}(\text{SO}_4)_2$  and  $\text{Rb}_3\text{D}(\text{SO}_4)_2$  [11], as the heat capacity curves plotted in figure 1 show, the phase behaviour is the same as in  $\text{Rb}_3\text{H}(\text{SeO}_4)_2$  and  $\text{Rb}_3\text{D}(\text{SeO}_4)_2$  with a slightly lower transition temperature of 78.5 K in  $\text{Rb}_3\text{D}(\text{SO}_4)_2$ . The low temperature behaviour is also the same as that of the selenate pair: the heat capacity of  $\text{Rb}_3\text{H}(\text{SO}_4)_2$  is larger than that of  $\text{Rb}_3\text{D}(\text{SO}_4)_2$  at temperatures below 40 K as figure 2 shows. By fitting a Schottky heat capacity function to the experimental excess heat capacity we obtained  $520 \text{ J mol}^{-1}$  for the energy of the tunnel level. In  $\text{Rb}_3\text{D}(\text{SO}_4)_2$  the deuterium bond is ordered at this low temperature, so that there is no possibility of the tunnelling motion for the deuterium atom. At higher temperature the symmetry may not be fully restored [12–14]. There appears to be a

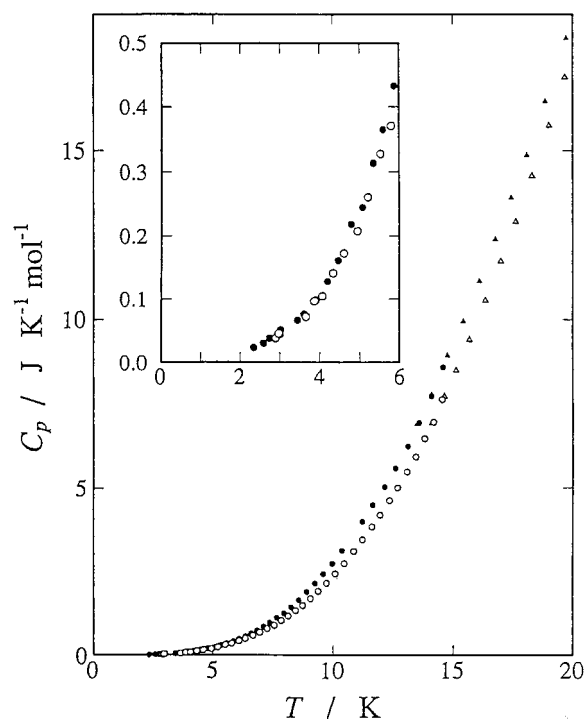


**Figure 1.** The heat capacities of  $\text{Rb}_3\text{H}(\text{SO}_4)_2$  and  $\text{Rb}_3\text{D}(\text{SO}_4)_2$  showing a gradual transition in the latter at 78.5 K and none in the former [11]. See also [8, 9].

subtle effect that breaks the symmetry of the crystal. The relation of this effect to the isotope effect is not known and need be studied further.

For  $A = \text{potassium}$  and  $X = \text{selenium}$ , the protonated compound ( $\text{K}_3\text{H}(\text{SeO}_4)_2$ ) undergoes a phase transition at 20–23 K and the deuterated one at 104 K [15]. The excess heat capacity of the D compound (figure 3) is typical of a gradual phase transition of an order–disorder type. The entropy change is  $4.2 \text{ J K}^{-1} \text{ mol}^{-1}$ , a value consistent with a twofold disorder in the high temperature phase. But the excess heat capacity of  $\text{K}_3\text{H}(\text{SeO}_4)_2$  is very unusual in its temperature dependence (figure 4). The anomaly is so broad that one recognizes its presence only by comparing with the heat capacity of  $\text{K}_3\text{D}(\text{SeO}_4)_2$ . (At 23 K the heat capacity of the latter is essentially the vibrational heat capacity, the effect of the transition at 104 K being negligible at this low temperature.) With the help of the reported dielectric anomaly [16], one convinces oneself of the occurrence of a phase transition at 23 K. The excess heat capacity of  $\text{K}_3\text{H}(\text{SeO}_4)_2$  has an appreciable magnitude above the transition temperature in contrast to the excess heat capacity of  $\text{K}_3\text{D}(\text{SeO}_4)_2$  (see figure 3). This was explained as a Schottky heat capacity due to a tunnelling proton on the hydrogen bond [17,18].

There are two opposing effects operating in this hydrogen bond system. One is the interaction between hydrogen bonds that favours an ordered state at low temperature and the other the tunnelling energy of a single hydrogen bond that favours a delocalized state. The relative importance of the two energies depends on the compound (H or D, chemical properties of the other ions) and the temperature. In  $\text{K}_3\text{H}(\text{SeO}_4)_2$  both energies appear to be equally important at low temperature, but the tunnelling energy becomes dominant above the transition temperature where the ordering interaction averages out to zero. The result is a two level Schottky heat capacity with an excess contribution that decays slowly with



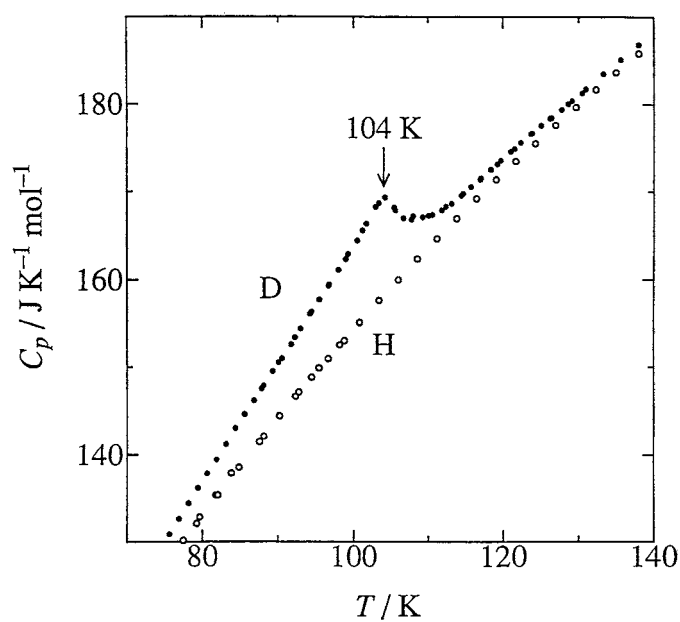
**Figure 2.** The heat capacities of  $\text{Rb}_3\text{H}(\text{SO}_4)_2$  and  $\text{Rb}_3\text{D}(\text{SO}_4)_2$  at low temperature. The protonated compound has significantly larger heat capacity below  $\sim 40$  K [11]. See also [8, 9].

increasing temperature. The Schottky level determined by fitting the excess heat capacity with the theoretical curve was  $430 \text{ J mol}^{-1}$  above the ground state.

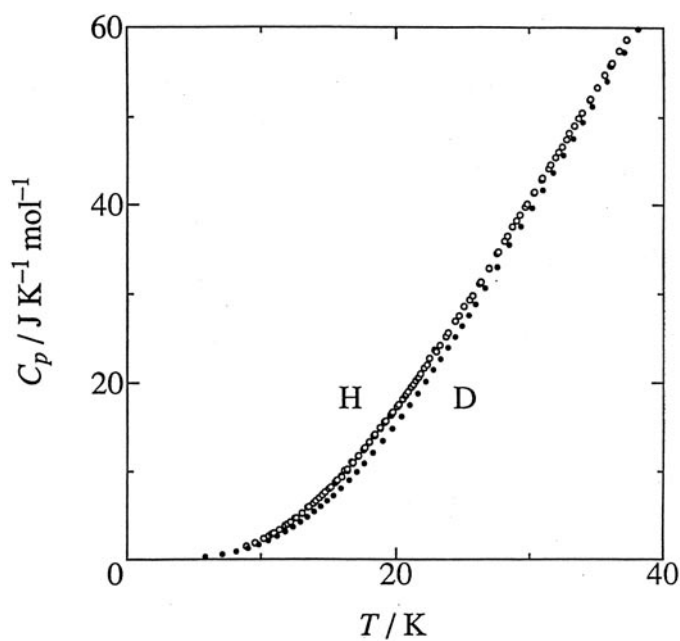
Recently we determined the crystal structure of  $\text{K}_3\text{H}(\text{SeO}_4)_2$  and  $\text{K}_3\text{D}(\text{SeO}_4)_2$  by neutron diffraction using HRPD at Rutherford Appleton Laboratory [19]. The oxygen–oxygen distance was  $249.5(1) \text{ pm}$  in the former and  $253.2(2) \text{ pm}$  in the latter. Thus the deuterium bond is significantly longer than the hydrogen bond. Other structural parameters being the same, the unit cell dimensions also reflect the smaller size of the hydrogen bonded dimer of selenate ions in  $\text{K}_3\text{H}(\text{SeO}_4)_2$ . The two positions occupied by a proton on the hydrogen bond are separated by  $32.0(10) \text{ pm}$  in  $\text{K}_3\text{H}(\text{SeO}_4)_2$  and by  $55.0(4) \text{ pm}$  in  $\text{K}_3\text{D}(\text{SeO}_4)_2$ . Thus the two stable positions occupied with a 50% probability in a classical picture are less distinct in  $\text{K}_3\text{H}(\text{SeO}_4)_2$  than in  $\text{K}_3\text{D}(\text{SeO}_4)_2$ . Whatever the reason for this H–D difference, this leads to a smaller transition temperature in the protonated compound, because a smaller polarity reversal is associated with the motion of a proton than with the motion of a deuteron on the hydrogen/deuterium bond. The origin of the isotope effect has been discussed from a similar point of view based on single crystal x-ray diffraction data [20]. Advanced quantum chemical calculations beyond the Born–Oppenheimer approximation have been proposed for description of a delocalized nuclear wave function of a proton [18, 21, 22].

#### 4. $(\text{NH}_4)_2\text{MCl}_6$

In this type of cubic crystal, the ammonium ion is situated at  $(1/4, 1/4, 1/4)$  of an fcc unit cell where the cation is surrounded by 12 chloride ions. The symmetry of the site  $T_d$  is the same



**Figure 3.** The heat capacities of  $\text{K}_3\text{H}(\text{SO}_4)_2$  and  $\text{K}_3\text{D}(\text{SO}_4)_2$  showing the excess part of the latter [15].



**Figure 4.** The heat capacities of  $\text{K}_3\text{H}(\text{SO}_4)_2$  and  $\text{K}_3\text{D}(\text{SO}_4)_2$  showing the excess part of the former [15].

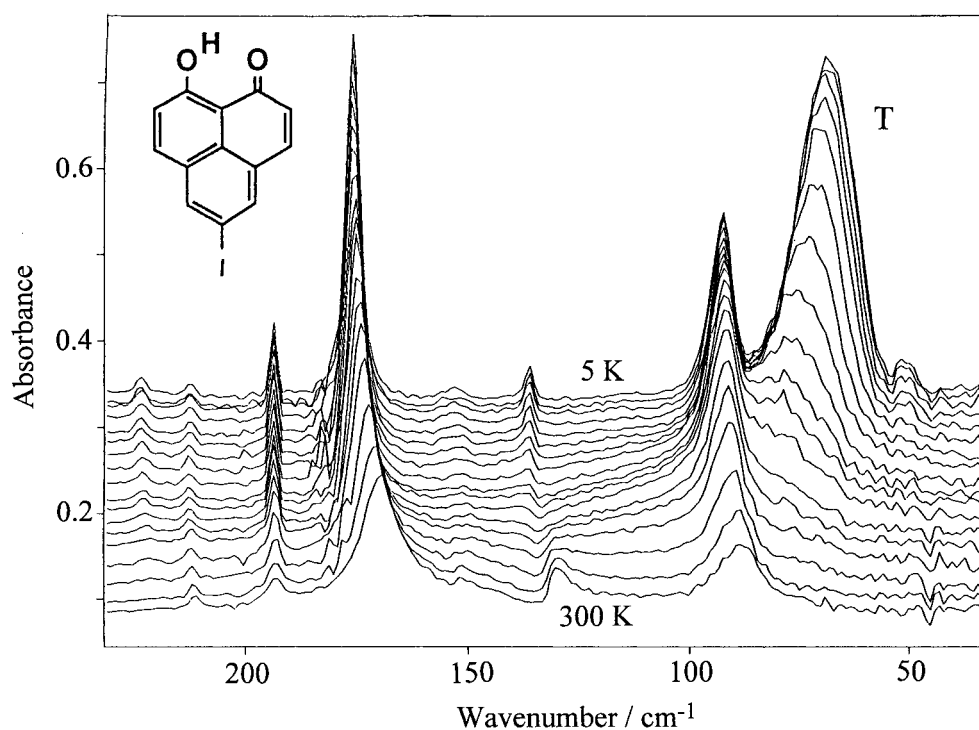
as that of an ammonium ion. Therefore an ammonium ion may occupy the site in a unique orientation without disorder. At the first glance this appears to be the case in  $(\text{NH}_4)_2\text{PtCl}_6$  and  $(\text{NH}_4)_2\text{PdCl}_6$  as these compounds do not undergo a phase change down to the lowest

temperature [23, 24]. When deuterated, they undergo first order phase transitions at  $\sim 30$  K [23–25]. The transition entropies being  $10\text{--}15\text{ J K}^{-1}\text{ mol}^{-1}$ , the phase at ambient temperature is clearly disordered. Therefore it is not obvious that the H ammonium ion occupies the  $T_d$  site without disorder. For  $(\text{NH}_4)_2\text{TeCl}_6$  and  $(\text{NH}_4)_2\text{PbCl}_6$ , the cubic phase changes into a trigonal phase at  $\sim 80$  K in a gradual transition related to rotation of the hexachloro anions [26–31]. The deuterated forms of these crystals undergo further transitions at lower temperature [27–32]. The trigonal distortions are small, leaving the environment of the ammonium ion essentially the same as in the cubic phase. Thus these four ammonium compounds (the Pd, Pt, Te and Pb complex salts) behave in the same way with respect to the deuterium-related phase change (the Te compound is more complicated with two deuteration-related phase transitions).

The mechanism of the phase transitions may be described qualitatively as follows. Following the above argument we assume that the direction along the threefold axis is unstable for the N–H(D) bond of the ammonium ion. There are stable orientations off the threefold axis (three pairs of them by symmetry) [33, 34]. We assume further that the barrier separating these minima is low. For an  $\text{ND}_4$  ion the six orientations are relatively distinct because of its large moment of inertia. At low enough temperature, the interactions between neighbouring  $\text{ND}_4$  ions become significant in comparison with the entropic term  $-kT \ln 6$  in the free energy and result in a phase transition from the orientationally disordered state to an ordered one. In the  $\text{NH}_4$  compounds, the rotational wave functions of the  $\text{NH}_4$  ion centred at respective energy minima are more delocalized. The six states are less distinct, producing a region of considerable overlap in the directions of the threefold axis of the crystal. The eigenstates are formed by linear combinations of the localized states. If the ground state made up of the symmetric combination of the six orientational states is more stable than the classically ordered state (which is stabilized by interaction with neighbouring ammonium ions) there will be no phase transition in the natural ammonium compounds. A deuteration-induced phase transition will be realized if the tunnelling stabilization and inter-ionic stabilization energies are of such magnitude that the former exceeds the latter in the  $\text{NH}_4$  crystal and in the reverse relation in the  $\text{ND}_4$  crystal. If the inter-ionic orienting interaction prevails both in the H and D crystals, they will both undergo a phase change. This occurs in  $(\text{NH}_4)_2\text{SeCl}_6$  and  $(\text{ND}_4)_2\text{SeCl}_6$  [35]. In the opposite situation where the tunnelling stabilization is greater in both H and D compounds, there will be no phase transition in either of the isotopic pair. This is probably the case in  $(\text{NH}_4)_2\text{SnCl}_6$  and  $(\text{ND}_4)_2\text{SnCl}_6$ . Structural aspects of this argument have been discussed in [36].

##### **5. $\text{C}_{13}\text{H}_6\text{BrOOH}$ (5-bromo-9-hydroxyphenalenone) and $\text{C}_{13}\text{H}_6\text{IOOH}$ (5-iodo-9-hydroxyphenalenone)**

These organic molecules have short symmetric intramolecular hydrogen bonds in them. The O–O distance 249 pm [37] is comparable with those in the diselenate ion discussed above. The molecular structure is inset in figure 5.  $\text{C}_{13}\text{H}_6\text{BrOOD}$  undergoes phase transitions at 21.3 and 33.9 K while the protonated compound does not [38, 39]. In this compound a proton tunnelling state has been identified spectroscopically [40]. The upper level of the tunnel-split pair lies at  $83\text{ cm}^{-1}$  above the ground state in the bromine compound. In the iodine compound  $\text{C}_{13}\text{H}_6\text{IOOH}$ , the tunnelling level occurs at  $68\text{ cm}^{-1}$  [41]. As shown in figure 5, the absorption (marked T for tunnelling) is extremely strong. It does not occur in  $\text{C}_{13}\text{H}_6\text{BrOOD}$  or  $\text{C}_{13}\text{H}_6\text{IOOD}$ . As the series of spectra recorded at different temperatures shows this absorption became quickly weaker as the temperature increased. The behaviour is quite distinct from the temperature dependence of other absorption lines (inter- and intra-molecular phonon bands) in the spectra. The difference arises from the difference in the level schemes: for the phonon



**Figure 5.** Far infrared absorption spectra of  $C_{13}H_6IOOH$  at temperatures between 5 and 300 K [41]. See also [40]. The strongest peak marked T at  $68\text{ cm}^{-1}$  is assigned to the tunnelling transition. The peaks at  $178$  and  $95\text{ cm}^{-1}$  (in the 5 K spectrum) and other weaker ones (except the  $130\text{ cm}^{-1}$  absorption) are due to intra- and inter-molecular phonon absorption. The weak peak at  $130\text{ cm}^{-1}$  is stronger at higher temperature and may be assigned to a hot band of the proton tunnelling mode [18].

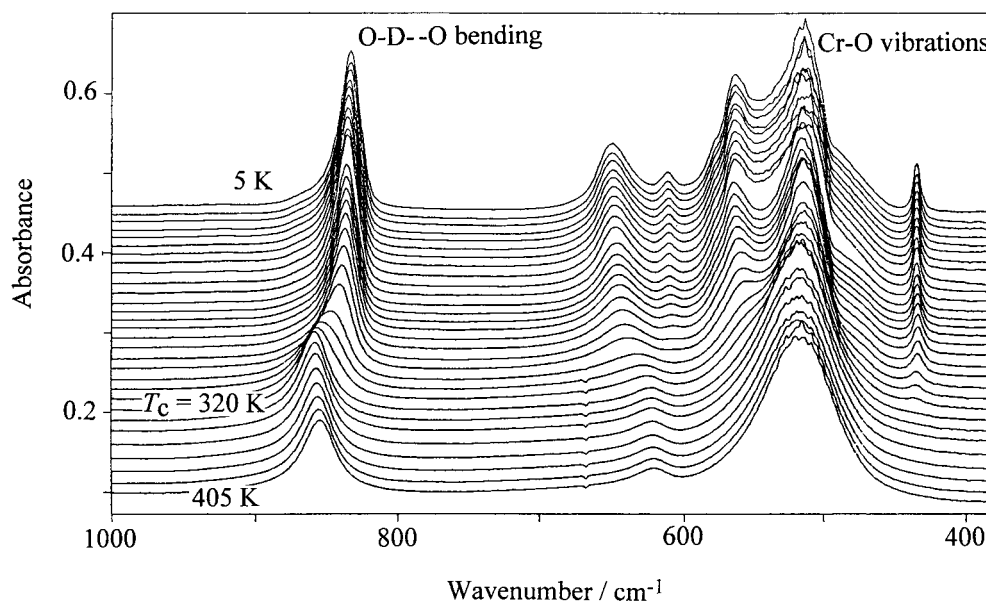
lines there are infinite series of levels at the same intervals whereas the tunnelling levels are only a pair of states. Hence the absorbance becomes weaker as the upper level become more and more populated at higher temperatures. The same temperature dependence has been found for the  $83\text{ cm}^{-1}$  absorption in  $C_{13}H_6BrOOH$  [40]. As to the temperature dependence of the phonon lines, the fully harmonic vibration is an idealization. The anharmonicity is evident in the actual spectra as red shift, broadening and weaker intensities of most of the absorption peaks at higher temperature shown in figure 5. However, the difference between the tunnelling transition at  $68\text{ cm}^{-1}$  and the other peaks cannot be missed. The uniquely strong intensity at low temperature, the large width and the blue shift at higher temperature are distinct features shared by the tunnel lines in  $C_{13}H_6BrOOH$  and  $C_{13}H_6IOOH$ .

The possibility of the tunnelling states playing an essential role in the isotope effect in the phase behaviour was first proposed in 1959 [42] to explain the large increase of the ferroelectric transition temperature in  $KD_2PO_4$ . However, after the initial success in explaining thermal and dielectric properties, the tunnel model has somewhat lost credibility as attempts to find the tunnel levels directly by spectroscopic methods failed. The present results restore the original idea that tunnel states exist as quantum mechanical eigenstates even in a crystalline environment where a large number of other degrees of freedom co-exist with comparable energies. As further evidence for the tunnel level, a neutron inelastic scattering peak occurs at the same energy in  $C_{13}H_6BrOOH$  as the infrared peak [43]. The scattering peak, totally absent from the spectrum of  $C_{13}H_6BrOOD$  has been identified with the tunnel level.



## 6. HCrO<sub>2</sub> and DCrO<sub>2</sub>

These paramagnetic compounds undergo magnetic ordering at 20–25 K. The deuterated crystal undergoes a further phase transition at 320 K, which the normal compound does not. The evidence for the transition is given in figure 6 where infrared spectra taken at temperatures between 5 and 405 K are plotted. The experimental detail will be published in a separate paper [44]. One notices a rapid change of the temperature dependence of the absorption frequency at 835 to 860 cm<sup>-1</sup> as the transition temperature 320 K is traversed from below. The shift is opposite to the normal red shift at higher temperature. This absorption arises from the bending mode of the deuterium bond. The blue shift means a stronger deuterium bond in the high temperature phase. Fading out of some of absorption in the Cr–O vibrations (400–700 cm<sup>-1</sup>) reflects a higher symmetry of the crystal structure above the transition point. A similar measurement on HCrO<sub>2</sub> showed only gradual shift of the frequencies due to anharmonicity. The number of absorption lines in the Cr–O vibration region is the same as in the high temperature phase of DCrO<sub>2</sub> reflecting the same higher symmetry down to the lowest temperature (5 K) for HCrO<sub>2</sub>.



**Figure 6.** Infrared spectra of DCrO<sub>2</sub> showing anomalous shift of the frequencies due to a phase transition at 320 K [44].

The heat capacity measurement confirmed the phase transition in DCrO<sub>2</sub> and its absence in HCrO<sub>2</sub> [44]. Interestingly both compounds are completely transparent in the far infrared region (400 to 20 cm<sup>-1</sup>) where the tunnelling absorption as well as a number of phonon absorptions is found in C<sub>13</sub>H<sub>6</sub>BrOOH and C<sub>13</sub>H<sub>6</sub>IOOH. The absorption peaks in the mid-infrared region (figure 6) are completely assigned to O–H stretching, O–H–O bending and vibrations involving O and Cr, leaving none assignable to the tunnelling transition. The same is true with the spectrum of the deuterated compound. It is unlikely that a tunnelling line occurs anywhere in the absorption spectra of HCrO<sub>2</sub> or DCrO<sub>2</sub>. Therefore we conclude that there is a mechanism of a phase transition that occurs only in the deuterated crystal and that does not involve proton tunnelling. Our infrared measurement extends only to 20 cm<sup>-1</sup>. But there will

be no tunnelling absorption below this frequency. A tunnel splitting of such a small magnitude should not affect a phase transition that occurs at 320 K. If the only difference between the H and D compounds were a tunnel splitting smaller than  $20 \text{ cm}^{-1}$ , a phase transition should also occur in the H compound. Since this is not the case, other explanations have to be sought. A most probable one for the difference between the two compounds is that the hydrogen/deuterium bond is the single minimum type in  $\text{HCrO}_2$  and double minimum type in  $\text{DCrO}_2$ .

## 7. Other systems

$\text{NaOD}$  undergoes a phase transition at 153.2 K which  $\text{NaOH}$  does not [45]. The heat capacity of  $\text{NaOH}$  is larger than that of  $\text{NaOD}$  at low temperature. These suggest the existence of extra energy levels in the protonated crystal as in  $\text{Rb}_3\text{H}(\text{SeO}_4)_2$ ,  $(\text{NH}_4)_2\text{TeCl}_6$  and  $\text{C}_{13}\text{H}_6\text{BrOOH}$ . For hydrazinium hydrogen oxalate, a tunnel splitting of  $135 \text{ cm}^{-1}$  was derived from the heat capacity [46], though there has been no evidence for a phase transition due to deuteration. The crystal structure suggests a possibility for the tunnelling state [47]. A deuteration-induced phase transition has been found in an organic crystal tolan (dimethylacetylene)  $\text{C}_{14}\text{H}_{10}$  [48]. Also some organic conductors behave in a similar way [49, 50]. The deuteration effect in these may involve a different mechanism.

## 8. Some general considerations

The compounds that undergo a phase transition when deuterated are very diverse chemically. However, with the exceptions of tolan [48] and the organic conductor group [49, 50], they share a common structural feature that the hydrogen atoms are confined in a two- or multi-valley potential surface characterized by low barriers. In the classical limit the multiple valley represents disorder. The disorder is removed by a phase transition at low enough temperature where the interaction energy between the disorder units exceeds the thermal energy. In the quantum case, it costs an amount of energy to localize the disorder unit. Given a certain magnitude of mutual stabilization energy for an assembly of disorder units, a phase transition may or may not occur depending on the magnitude of the energy required for localization. Because of the larger localization energy for protonated systems, the normal protonated compounds may remain in the delocalized state to zero kelvin, while the deuterated compounds conforming more or less to classical description undergo ordering transitions. This mechanism has been formulated using the Pauli spin matrices [51–53] for O–H–O hydrogen bonds. A similar formulation will be possible for the description of the phase transitions in the ammonium compounds where the three-dimensional rotation of an ammonium ion will complicate the mathematics [54].

Spatial extension of the nuclear wave function discussed here may be described as proton cloud. For a typical hydrogen atom vibrating at a frequency of  $3000 \text{ cm}^{-1}$ , the mean square zero point amplitude  $\langle x^2 \rangle^{1/2}$  is 7.4 pm using the relation for the ground state harmonic wave function

$$\langle x^2 \rangle = \hbar / (2m\omega)$$

where  $m$  is the mass of a proton and  $\omega$  the angular frequency of the vibration. For  $\text{Rb}_3\text{H}(\text{SeO}_4)_2$  at 4 K, the ‘thermal’ parameter of the hydrogen atom is essentially the zero point vibrational amplitude. From  $U_{iso}(\text{H}) = 150(30) \text{ pm}^2$  [10] we obtain 12(2) pm for the mean square amplitude. Similar values have been obtained from the data on  $\text{K}_3\text{H}(\text{SeO}_4)_2$  and  $\text{K}_3\text{D}(\text{SeO}_4)_2$  [19]. At twice this separation where the amplitude should be still appreciable if the wave function were truly Gaussian, the other half of the wave function is centred for the tunnelling

ground state. We may call this probability distribution a proton cloud in analogy with the electron cloud.

The electron cloud analogy can be carried on further to explain the shorter O–O distance in the hydrogen bond than in the deuterium bond. The symmetric and antisymmetric states of a proton in a double minimum potential are split by the tunnelling energy. The magnitude of the splitting depends on the height and thickness of the barrier and the mass of the tunnelling particle. The ground state energy decreases as the two minima come closer. This exerts in effect an attractive force between the two oxygen atoms. The situation is analogous to the bonding orbital (as opposed to the anti-bonding one) in the molecular orbital theory of chemical bonds. The tunnelling stabilization is greater for a proton than for a deuteron because the smaller mass of the proton has a more extended wave function. Thus the effective attraction is greater for a proton bond. The attraction arising from this effect (i.e. proton/deuteron exchange force) competes with other forces in the crystal to determine the equilibrium positions of the atoms. Assuming the non-hydrogen-bond parts are the same, one expects a shorter O–O distance in the proton bond than in the deuteron bond in agreement with most of the geometric isotope effects known experimentally [19, 20, 55–58]. Recent non-Born–Oppenheimer calculations [17, 18, 21, 22] of the electronic and nuclear wave functions take this into account. On the experimental side, precise determination of the temperature dependence of structural parameters (positions and thermal parameters) and lattice constants at low temperature is of interest in this respect.

In  $C_{13}H_6BrOOH$ , the proton exchange attraction operates in the rigid framework of the aromatic hydrocarbon. The effect on the O–O distance will be minimal in this case, as born out by the experiment [59]. The other extreme situation is probably realized in  $HCrO_2$ . Here all the hydrogen bonds are parallel to each other. They connect planes of edge-sharing units of  $CrO_6$ . It appears that the hydrogen bonds are allowed to determine their own length in unison with each other and without being subject to intervention from other building blocks of the crystal. The O–O distance in  $DCrO_2$  is longer than that in  $HCrO_2$  by 10 pm [55–58]. The effect (5 per cent of the O–O distance) is so large that it may no longer be adequate to describe the situation in terms of the tunnelling. This appears to tell us that if the nucleus is stationary the stable configuration of a hydrogen bond is asymmetric as realized in  $DCrO_2$ . In  $HCrO_2$  the proton exchange attraction is so strong that the double minima have merged into a single minimum. This explains the unusually high temperature of the phase transition in  $DCrO_2$  with no corresponding phase change in  $HCrO_2$ . The notion of the proton cloud is closely related to that of proton polarizability conceived by Zundel [60, 61]. He used the idea to explain the very strong continuum of absorption extending from  $\sim 400$  to  $3500\text{ cm}^{-1}$  in the infrared spectra of acidic and alkaline solutions. The idea interpolates between the vibrational polarization of a charged harmonic oscillator and the classic orientational polarization of a polar molecule. The phase transitions discussed in the present article may be regarded as energetic and structural consequences of the interaction of protons and deuterons through their proton or deuteron polarizabilities. The interaction may involve additional complications due to steric effects and chemical bond forces that are absent from the usual electrostatic van der Waals attraction between normal electronically polarizable molecules. But unlike the solutions originally discussed using this concept, the crystals are much simpler and better characterized structurally. This means on the one hand that consequences of the interaction are observed more clearly in the structural parameters, in thermal and dielectric properties and as distinct spectroscopic energy levels rather than the absorption continuum of the solution systems. On the other hand, it also means that the combination of the parameter values under which deuteration-induced phase changes occur is rather limited, giving us only a few substances behaving in this interesting way. For the phase transitions in the ammonium compounds, the

analogy with proton polarizability may be somewhat contrived, since the ordering forces are rotational and are mediated by hexachloro anions. However, their character as phase transitions occurring in systems halfway between classical and quantum mechanical is essentially the same as those occurring in the linear hydrogen bonded crystals.

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