^{17}O NQR and the Mechanism of the Phase Transition in KH_2PO_4 Type H-bonded Systems *

R. Blinc
J. Stefan Institute, E. Kardelj University of Ljubljana, Ljubljana, Yugoslavia

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^{17}O quadrupole and ^{17}O-proton magnetic dipolar coupling data are used to discriminate between three alternative phase transition driving mechanisms in KH_2PO_4 type H-bonded systems: (i) the proton order-disorder model; (ii) the P (or Se) ion order-disorder model, and (iii) the PO_4 (or SeO_3) orientational order-disorder model.The data for $KH_3(SeO_3)_2$, CsH_2PO_4 and KH_2PO_4 definitely exclude models (ii) and (iii) and agree with the predictions of model (i).

I. Introduction

There are two basic questions which have to be answered before we can hope to understand the nature of phase transitions in hydrogen bonded ferroelectrics. These two questions are:

i) What is the exact position of the proton in the O–H– –O bond? Is the proton located in the centre or in an off-centre site or is there more than one equilibrium site?

(ii) What is the driving force of the phase transition? Is the transition connected with a displacement of the proton from the centre of the H-bond or do we deal with an order-disorder transition if there is more than one proton equilibrium site per H-bond? Do we perhaps deal with a case where the protons are not involved at all in the phase transition?

Neutron diffraction is often inconclusive in answering these two questions. It is very hard to distinguish with scattering techniques between a centrally located proton in an O–H–O bond and a proton moving between two symmetrically located off-centre positions, O–H– – –O and O– – –H–O.

Since the proton does not have a quadrupole moment, the problem has to be approached by ^{17}O ($I = 5/2$) nuclear quadrupole resonance (NQR) spectroscopy. This technique is rather sensitive since even small proton displacements produce large changes in the electric field gradient (EFG) tensors at the oxygen sites and thus large changes in the ^{17}O NQR frequencies. If the proton is centrally located, O–H–O, both oxygens are equivalent and we expect just one set of ^{17}O NQR lines ($\nu_{1/2\to3/2}$, $\nu_{3/2\to5/2}$, $\nu_{1/2\to5/2}$) per hydrogen bond. If the proton is located in an off-centre site the two oxygens in an O–H– –O bond are non-equivalent and we expect two sets of NQR lines per hydrogen bond. If the protons are dynamically disordered between off-centre sites, the observed ^{17}O electric field gradient tensor should be an average of the EFG tensors for the two separate off-centre sites. In addition the ^{17}O spin-lattice relaxation times should be much shorter than for static protons. Phase transitions involving an ordering of protons into one of the two possible equilibrium sites or the displacement of the proton from a central into an off-centre position are thus connected with a *doubling* of the ^{17}O NQR lines at the transition temperature T_c. In the first of these two cases the paraelectric ^{17}O EFG tensor is an *average* of the two ferroelectric ones whereas no such relation exists in the second of the above two cases where the transition is a displacive one.

Some recently studied representative cases are collected in Table 1. In the following we shall dicuss in more detail the relation between the ^{17}O NQR spectra and the phase transition mechanism in some KH_2PO_4 type H-bonded systems.

II. Phase Transition Mechanisms in KH_2PO_4

Structural phase transitions in KH_2PO_4 and other hydrogen-bonded crystals are generally considered to be triggered by the ordering of protons in the

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Reprint requests to Prof. R. Blinc, J. Stefan Institute, Dept. of Physics, F-5, 61111 Ljubljana, Jamova 39, POB 53, Yugoslavia.

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Table 1. ^{17}O quadrupole coupling constants and asymmetry parameters in some H-bonded ferroelectrics and ferroelastics.

System		$e^2 q Q/h$ [kHz]	$\eta = \frac{V_{XX} - V_{YY}}{V_{ZZ}}$
I. KH_2PO_4			
$T > T_c$:			
Disordered:		-5115 ± 5	0.572 ± 0.003
$T < T_c$:			
Close:	$^{17}O-H--O$	-5845 ± 5	0.718 ± 0.003
Far:	$^{17}O----H-O$	-4690 ± 10	0.310 ± 0.002
II. CsH_2PO_4			
$T > T_c$:			
Ordered:	$^{17}O-H(1)---O$	6500	0.75
Disordered:	$^{17}O-H(2)---O$	5300	0.57
$T < T_c$:			
	$^{17}O-H(1)--O$	6500	0.75
Close:	$^{17}O-H(2)---O$	6100	0.70
Far:	$^{17}O---H(2)-O$	4600	0.30
III. $PbHPO_4$			
$T > T_c$:			
Disordered:		5200	0.52
$T < T_c$:			
Close:	$^{17}O-H--O$	5800	0.65
Far:	$^{17}O--H-O$	4800	0.29
IV. $C_4H_4O_2$			
$T > T_c$:			
Disordered:		6250	0.73 ($T = 130\,°C$)
$T < T_c$:			
Close:	$C-{}^{17}O-H--O$	7575	0.145
Far:	$C={}^{17}O---H-O$	7325	0.320
V. $KH_3(SeO_3)_2$			
$T > T_c$:			
Ordered:	$^{17}O(1)-H(1)--O(3)$	8190	0.25
	$O(1)-H(1)--{}^{17}O(3)$	7480	0.741
Disordered:	$^{17}O(2)-H(2)--O(2)$	7440	0.601 ($T = -50\,°C$)
$T < T_c$:			
	$^{17}O(1)-H(1)--O(3)$	8190	0.25
	$O(1)-H(1)--{}^{17}O(3)$	7480	0.80
Close:	$^{17}O(2)-H(2)--O(2)$	7650	0.72
Far:	$^{17}O---H(2)-O(2)$	7510	0.42

double minimum potentials of the O$-$H$--$O hydrogen bond network [1]. The most characteristic property of this class of phase transitions is the existence of a large isotope effect in the transition temperature T_c when protons are replaced by deuterons [1]. Typically T_c increases by a factor 1.5$-$2. The isotope effect in T_c is generally connected with a slowing down of the hydrogen bond dynamics by an order of magnitude as shown by dielectric spectroscopy [2] and a negative pressure coefficient [3] of the transition temperature, $dT_c/d_p < 0$. When the applied hydrostatic pressure exceeds a critical value, ferroelectric or antiferroelectric ordering does not take place $-$ presumably due to tunelling $-$ and the system remains a quantum paraelectric at all temperatures [1, 3].

The above features are generally predicted by the Ising model in a transverse tunelling field (JMTF) Hamiltonian [1, 4] which describes both the tunnelling motion of the protons in the O$-$H$--$O bonds as well as the interactions between these bonds. Whereas the model gives a satisfactory qualitative description of the above mentioned phenomena even in the simple molecular field (MFA) or random phase approximation (RPA) the supporting evidence is still more indirect than direct.

If the collective proton tunnelling mode predicted by the JMTF Hamiltonian were a well defined propagating excitation, the experimental observation of the dispersion curve of the soft proton mode – and the experimental verification of this model – would have been straightforward. In the deuterated system, on the other hand, the real part of the collective tunnelling – soft mode – frequency would be close to zero zero and only a critical slowing of the non-propagating fluctuations – corresponding to the hopping motion of deuterons between the two wells – would be observed as $T \rightarrow T_c$.

Such a clear cut distinction is however unfortunately not possible.

The observed Raman and neutron spectra of KH_2PO_4 – and other H-bonded ferroelectrics – are at normal pressures overdamped. KH_2PO_4 becomes underdamped only at relatively high hydrostatic pressures [1, 5]. Except for KH_2PO_4 no other high pressure investigation of the H-bond dynamics seems to have been carried out so far and no determination of the proton soft mode dispersion in the underdamped regime exists as yet.

It has been as well shown that a quantitative description of the statics and dynamics of H-bonded systems requires a cluster approximation and that the MFA and RPA treatments are not adequate. In some systems like $KH_3(SeO_3)_2$ [6] and CsH_2PO_4 [7] the apparent proton tunnelling frequency is much smaller than kT_c and within the MFA therefore cannot be responsible for the observed isotope shift of T_c. Whereas this can be in principle understood in the dynamic cluster approximation [7] as being due to a renormalization of the proton frequency by short range order effects, some doubt has been nevertheless cast on the up till now generally accepted mechanism for ferroelectric phase transitions in H-bonded systems and alternative models [7, 8] have been suggested.

The possible phase transition mechanism for KH_2PO_4 and other H-bonded ferroelectrics proposed so far are:

(i) The proton O–H– –O order-disorder model orignally introduced by Slater [6] for KH_2PO_4 and later extended to include long range forces [8] and tunnelling effects [1, 9]. This model involves two equilibrium sites for the H-atoms in the H-bonds and a phonon-like behaviour of the heavy atoms.

(ii) The P order-disorder model [10] involving a Jahn-Teller type distortion of the PO_4 group and two equilibrium sites for the P ions along the $z \parallel c$ direction.

(iii) The orientational order-disorder model of H_2PO_4 dipoles [11, 12] recently introduced by Tokunaga and Tatsuzaki where rigid H_2PO_4 groups of C_2 site symmetry make a librational flip-flop motion between two equilibrium orientations. The S_4 site symmetry above T_c is here the result of averaging between the two H_2PO_4 configurations with C_2 site symmetry realized below T_c. The average time required for a H_2PO_4 dipole to make a flip-flop motion is supposed to be larger than the inverse of the PO_4 internal vibrational frequencies and the momentary selection rule for the internal PO_4 modes is that of C_2.

It is the purpose of this paper to compare the predictions of the above models for KH_2PO_4, CsH_2PO_4 and $KH_3(SeO_3)_2$ with recent ^{17}O nuclear quadrupole resonance data in order to discriminate between the various alternative phase transition mechanisms.

III. $KH_3(SeO_3)_2$

$KH_3(SeO_3)_2$ – abbreviated as H-KTS – undergoes a ferroelastic phase transition [13] at $T_c = 211$ K whereas the deuterated analogue D-KTS undergoes a similar transition at $T_c = 303$ K. Above T_c all four SeO_3 sites per unit cell are chemically equivalent. Below T_c there are two chemically non-equivalent sets of SeO_3 sites per unit cell. The phase transition is associated with an instability of the B_{3g} transverse acoustic phonon at the Γ point. The acoustic instability was proposed to be driven by a coupled proton-lattice optic soft mode involving O(2)– –H(2)– – –O(2) proton tunnelling as well as a tilting of the SeO_3 groups around the crystal a-axis [13]. A recent inelastic neutron scattering study [6] showed that the effective frequency of the coupled proton-lattice optic mode which interacts with the acoustic mode is only about 12 cm^{-1} and thus by more than an order of magnitude smaller than kT_c. This mode is overdamped and the characteristic frequency factor is only 40% higher than in D-KTS. Such a low proton soft mode frequency, which moreover does not greatly decrease on deuteration, is incompatible with the simple RPA treatment of the JMTF Hamiltonian and indicates either a different transition mechanism or the necessity of a dynamic cluster approximation in the treatment of the proton-optic lattice mode coupling.

Similarly as in KH_2PO_4 the following alternative basic phase transition mechanisms are a priori possible:

(i) The proton order-disorder model in the O(2)−H(2)−−O(2) bonds as the basic driving force of the transition.

(ii) The Jahn-teller distortion of the SeO_3 groups resulting in two Se equilibrium sites and a Se order-disorder model.

(iii) The existence of flip-flop motion of SeO_3 groups between two orientations resulting in an orientational order-disorder model.

The mechanism (i) of course corresponds to the standard model accepted so far. The SeO_3 groups are linked by two types of hydrogen bonds. The O(1)−−−H(1)−O(3) bonds are ordered and the protons are located near the O(3) oxygens. The O(2)−H(2)−−O(2) hydrogen bonds are supposed to be disordered with the protons moving between two equilibrium sites above T_c and ordered below T_c. If this model is correct one expects no change in the ^{17}O NQR spectra a T_c for the O(1)−−H(1)−O(3) hydrogen bonds and a splitting of the ^{17}O NQR spectra of the O(2)−H(2)−−O(2) bonds into two components corresponding to a "far" (^{17}O−−H(2)−O) and a "close" (^{17}O−H(2)−−O) proton site. The ^{17}O electric field gradient (EFG) tensor above T_c should be a dynamic average over these two sites

$$V(T > T_c) = \tfrac{1}{2}\,[V_{\text{close}} + V_{\text{far}}]\,, \qquad (1)$$

as above T_c the proton motion between the two equivalent sites in the O(2)−H(2)−−O(2) bond should be fast as compared to the NQR splitting between these two sites.

According to model (ii) the ^{17}O quadrupole coupling of all three oxygen sites in the SeO_3 groups should change at T_c as a result of the freezing out of the Se motion.

According to model (iii) – involving an orientational freeze out of rigid SeO_3 groups – there should be no change in the magnitude of the ^{17}O quadrupole coupling at any oxygen site. There should be however a change in the direction of the principal axes of the ^{17}O EFG tensor which is not observable in pure NQR.

The experimental data obtained by a ^{17}O-proton double resonance technique [14] are shown in Figure 1. At T_c there is no change in the quadrupole coupling tensor for the O(1) and O(3) oxygens but a splitting into two components for the O(2) oxygens. Models (ii) and (iii) are thus clearly ruled out by the ^{17}O quadrupole coupling data. The results are completely consistent with model (i) involving an order-disorder transition of the O(2)−H(2)−−−O(2) hydrogens.

It should be noted that in case of a displacive transition where the proton would be centered above T_c and displaced to on off-centre site below T_c, the ^{17}O EFG tensor would be strongly T-dependent above T_c in contrast to the experimental data. In addition, the paraelectric EFG tensor would not be an average of the two low temperature ($T < T_c$) ones. The ^{17}O−H magnetic dipolar coupling data [14] can as well discriminate between the proton order-disorder and the displacive type of transition.

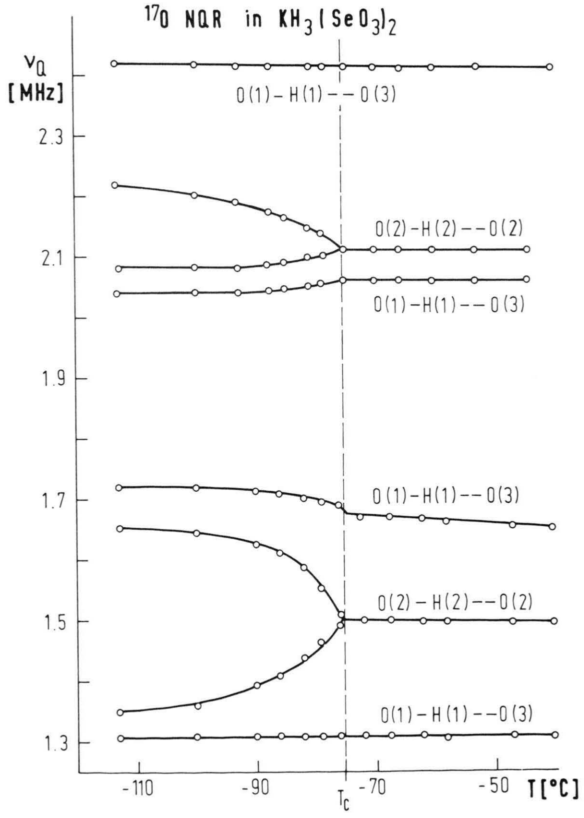

Fig. 1. Temperature dependence [14] of the ^{17}O NQR transition frequencies in $KH_3(SeO_3)_2$.

The data [14] fully support the order-disorder mechanism. Of course the ^{17}O results by themselves can not descriminate between proton tunnelling between the two sites above T_c and classical hopping above the potential barrier. The distance between the two proton equlilibrium sites in the O(2)−H(2)−−O(2) bond, derived from the proton-^{17}O dipolar coupling [14], is however so small that for any reasonable model of the H-bond potential proton tunnelling should prevail. The estimated values of the proton tunnelling integral are all much larger than the value 12 cm^{-1} observed by neutron scattering [6] thus emphasizing the importance of the renormalization of the bare O−H−−O proton tunnelling frequency by "ice-rules" and short range order effects *before* the proton mode is coupled to the optic-lattice mode and the combined proton-lattice mode is taken to interact with the acoustic mode. The theory of the isotope effect in this system thus still has to be worked out.

IV. CsH_2PO_4

CsH_2PO_4 [15] undergoes a ferroelectric phase transition at $T_c = 154$ K whereas the transition in CsD_2PO_4 takes place at $T_c = 264$ K. There are two different types of O−H−−O bonds in the structure. The asymmetric O−H(1)−−O bonds link the PO_4 groups along the *a*-axis and are ordered even above T_c. The short O−H(2)−−O bonds are assumed to be disordered above T_c and become ordered below T_c. The standard explanation of the isotope effect in T_c is the existence of a soft proton tunnelling mode similar as in H-KTS and KH_2PO_4. A recent theoretical study [15] has however discovered some inconsistencies in this simple picture and gave an anomalously low value for the proton tunnelling frequency similarly as in H-KTS [5].

In view of that it seemed worthwhile to reinvestigate the possible phase transition mechanisms:

(i) Proton ordering in the O−H(2)−−O bonds.

(ii) Jahn-Teller distortion of the PO_4 groups resulting in two P equilibrium sites and a P order-disorder model.

(iii) The existence of flip-flop motion of PO_4 groups between two orientations resulting in an orientational order-disorder model.

The way these three models reflect in the ^{17}O data is the same as in KTS.

The experimental ^{17}O NQR frequencies [16] are shown in Figure 2. There is no change at T_c in the ^{17}O quadrupole coupling for the asymmetric O−H(1)−−O hydrogen bonds, but a splitting into two components for the O−H(2)−−O oxygens in agreement with the proton order-disorder model (i). Model (ii), involving an order-disorder transition of the P ions and model (iii), involving an orientational order-disorder transition of rigid H_2PO_4 dipoles are again clearly ruled out. The same is true for a model involving a displacive transition where the O−H(2)−−O proton would be centered above T_c and displaced to an off-centre site below T_c. In such a case the ^{17}O−H(2)−−O EFG tensor would be strongly T-dependent above T_c and the paraelectric ^{17}O EFG tensor would not be the average of the two ferroelectric ones.

The discrepancies noted in (15) thus do not seem to be due to a phase transition mechanism different from the O−H(2)−−O proton order-disorder one

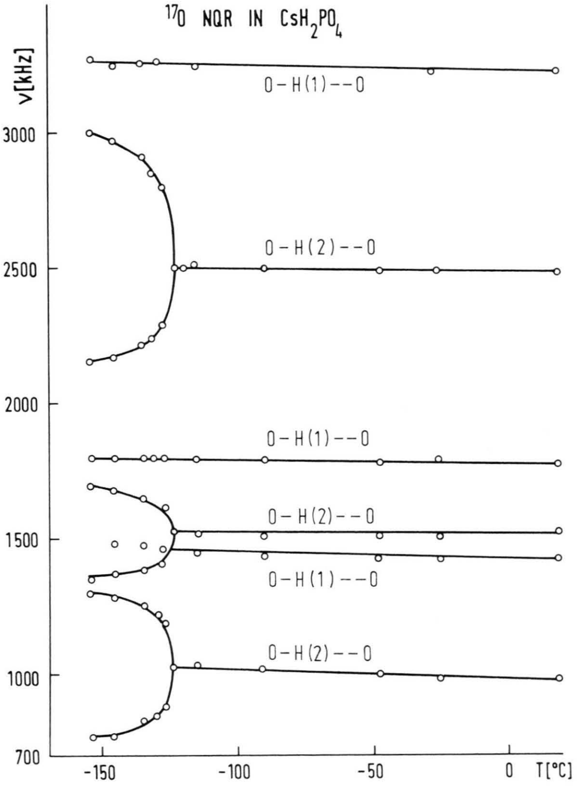

Fig. 2. Temperature dependence [16] of the ^{17}O transition frequencies in CsH_2PO_4.

but rather due to the details of the "Slater-rules" in this system and the proper way of making a dynamic "cluster" approximation [17].

V. KH_2PO_4

In contrast to H-KTS and CsH_2PO_4 all O−H−−O hydrogen bonds are equivalent in KH_2PO_4 thus making it more difficult to discriminate by ^{17}O NQR between models (i) and (ii) than in KTS or CsH_2PO_4.

The proton double minimum type order-disorder model (i) predicts that all ^{17}O sites are equivalent above T_c whereas all ^{17}O lines should split into two components below T_c. This is due to the fact that below T_c the proton can be found either in a "far", ^{17}O−−−H−O or in a "close", ^{17}O−H−−O, position with the same probability, whereas above T_c the proton moves fast between these two positions resulting in an effective time averaged ^{17}O electric field gradient.

According to the P order-disorder model (ii) all ^{17}O sites should be again equivalent above T_c if the P atom jumps rapidly enough between the two equilibrium sites whereas the ^{17}O spectrum should significantly change below T_c where the P freezes out into one of the two equilibrium sites. The details of the ^{17}O spectrum depend on the direction of the P motion. It is however quite plausible that the P motion is such that two oxygens are equally "close" and two equally "far" from the P ion. In this case we get a doubling of the ^{17}O NQR lines below T_c similarly as in the proton order-disorder model (i).

According to the PO_4 orientational order-disorder model (iii) there should be no change in the magnitude of the ^{17}O quadrupole coupling at T_c but only a change in the direction of the principal axes of the ^{17}O EFG tensor.

The temperature dependence of the ^{17}O NQR spectra [18] is shown in Figure 3. The presence of only three ^{17}O lines − $\nu_{1/2\to 3/2}$, $\nu_{3/2\to 5/2}$, $\nu_{1/2\to 5/2}$ − demonstrates that all PO_4 oxygen sites in the unit cell are indeed chemically equivalent above T_c so that the PO_4 group is not distorted on the NQR time scale. Below T_c each ^{17}O NQR line splits into two components. The H_2PO_4 orientational order-disorder model (iii) [11, 12] is thus definitely excluded by the ^{17}O NQR data. The above data by themselves however cannot definitely discriminate between models (i) and (ii).

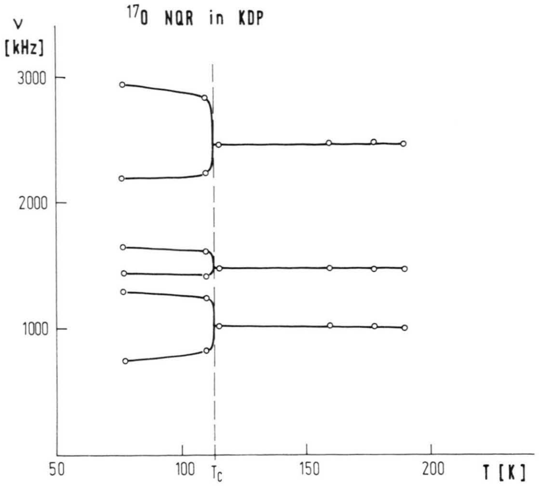

Fig. 3. Temperature dependence [18, 20] of the ^{17}O transition frequencies in KH_2PO_4.

A discrimination between these two models is however possible on the basis of the ^{17}O-proton magnetic dipolar fine structure [19, 20] of the ^{17}O NQR lines revealed by a double irradiation [19] technique. In the P order-disorder model no change in the ^{17}O−H magnetic dipolar fine structure is expected on going through T_c whereas a significant change is predicted by the proton order-disorder model. The P-^{17}O dipolar fine structure is negligible in comparison with the proton one in both models.

The experimental data [19, 20] indeed show a significant change in the ^{17}O−H magnetic dipolar fine structure at T_c as predicted by the proton order-disorder model. The ^{17}O−H distance for the "close" proton site below T_c is found as $R_{O-H} = 1.05 \pm 0.01$ Å. Above T_c the proton spends equal times at the "close" ($R^{cl}_{O-H} = 1.05$ Å) and at the "far" ($R^{far}_{O-H} = 1.48$ Å) equilibrium site so that the magnetic dipolar interaction is characterized [18] by an effective ^{17}O−H distance

$$T > T_c\colon \langle R_{OH}\rangle_w^{-3} = \tfrac{1}{2}[(R^{cl}_{OH})^{-3} + (R^{far}_{OH})^{-3}] = [1.19 \pm 0.02\ \text{Å}]^{-3} \qquad (2)$$

which in fact corresponds to the observed [19] dipolar structure above T_c. The distance between the two proton equilibrium sites in the O−H−−O bond thus amounts to 0.43 Å, i.e. to a value which should result in a large "bare" proton tunnelling frequency. If the proton would be above T_c situated halfway between the two oxygens this would lead to another value of the effective O−H distance

$$T > T_c: \langle R_{\mathrm{OH}} \rangle_{\mathrm{symm}} = 1.265\ \text{Å} \tag{3}$$

in poor agreement with the experimental value 1.19 Å [19, 20]. Thus only model (i) is consistent with the ^{17}O quadrupole coupling and ^{17}O−H magnetic dipolar splitting data.

VI. Conclusions

The ^{17}O NQR and ^{17}O−H magnetic dipolar splitting data clearly show that the double well type O−H(2)−−O proton order-disorder is the driving mechanism in the ferroelastic phase transition in KTS and the ferroelectric phase transition in CsH_2PO_4, whereas the O−H−−O double well type proton order-disorder drives the ferroelectric phase transition in KH_2PO_4. The PO_4 orientational order-disorder model and the P double well order-disorder model are in particular definitely ruled out by the experimental data. It should be stressed that K, Rb, Cs and P NMR [1] investigations did as well not provide any evidence for the existence of a double well potential for the heavy atoms in the $z \parallel c$ directions but that deuteron NMR [1] provided clear cut evidence for a double well potential for deuteron motion. This result agrees with the ^{75}As NQR data [1] which provided direct evidence for the six Slater H_2AsO_4 configurations [1]. It also agrees with the results of a recent high resolution neutron diffraction study [21] of KH_2PO_4 and KD_2PO_4 which showed no sign of a two-site distribution for the heavy atoms and supported the simple two-site (pseudo-spin) behaviour of the H-atoms coupled to a more phonon-like behaviour of the K and P ions.

More refined theories are needed to explain the apparent inconsistencies in the Raman data [11, 12] and the influence of the "Slater" – or "ice" rules [1] – on the proton dynamics and isotope effects on replacing hydrogen by deuterium [2].

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