

THEORETICAL MODELLING AND EXPLORATION OF NUCLEAR QUANTUM EFFECT ON THE HYDROGEN BONDS OF AMMONIUM DIHYDROGEN PHOSPHATE USING SINGLE-CRYSTAL NEUTRON DIFFRACTION

Dr. Jayaprakash

Jeppiaar Engineering College, TN. India

Abstract.

Potassium dihydrogen phosphate (KDP) family of hydrogen-bonded crystal constitutes an important family of crystals not only because of their immense importance in the field of nonlinear optics (NLOs) but also due to the fact that hydrogen bonds of these crystals provide us with a rare opportunity to understand the fundamental nature of hydrogen bonds, such as the effect of local chemical environment on the strength of hydrogen bonds and nuclear quantum effect on strong, moderate and weak hydrogen bonds. Keeping this aim in mind, we have undertaken detailed single-crystal neutron diffraction (SCND) investigations on ammonium dihydrogen phosphate (ADP) and KDP along with their deuterated analog crystals under ambient conditions. Fine differences in the hydrogen bonds of the above-mentioned crystals are analyzed in the light of a simple diabatic two-state theoretical model for hydrogen bonds. It is proposed that the presence of a partially covalent N–HN–O bond in ADP has a very significant effect on its O–H bond making it highly anharmonic. It is this higher bond anharmonicity in ADP that is most likely responsible for its larger NLO coefficient compared to KDP.

Keywords. Neutron diffraction; hydrogen bonds; deuteration.

1. Introduction

Ammonium dihydrogen phosphate (ADP) is a crystal known for a long time for its excellent electro-optic and nonlinear optic (NLO) properties [1–4]. ADP belongs to the family of hydrogen-bonded crystals having the general formula MY_2XO_4 , where $M = K^+, Rb^+$ or NH_4^+ , $Y = H$ or D and $X = P$ or As . The most important member of this crystal family is potassium dihydrogen phosphate (KDP) which is currently the only nonlinear material suitable for Pockels cells and frequency converters in high-power large-aperture laser systems, hence this crystal family is also sometimes known as the KDP family of

hydrogen-bonded crystals. In fact, ADP crystals were also considered for the nonlinear optical applications but the low transmittance in the near-infrared region affected by the N–H absorption band limited their application. Hence the KDP crystal and its deuterated analog potassium di deuterium phosphate (DKDP) were used primarily in most of the electro-optic applications. Recently, interest in ADP crystals has been revived due to the rising demand for a material with high fourth harmonic generation (FHG) efficiency that is required for the inertial confinement fusion facilities [5]. Compared to KDP and DKDP crystals, the ADP has a larger NLO coefficient and laser damage threshold and a shorter UV transmission cut-off [5,6]. According to a recent study, the conversion efficiency, the output energy and the angular bandwidth of the FHG of the ADP crystal are superior to those of KDP and DKDP crystals [7]. The crystals of the KDP family [8] have a tetragonal structure at room temperature and undergo a structural phase transition as the temperature is lowered below room temperature. The basic structural framework of these crystals is constructed by a network of zig-zag hydrogen-bonded chains of $[XO_2(OY)_2]^-$ anions along the ab planes, and the cations occupy the interspaces of the zig-zagged anionic chains and they interconnect the adjacent anionic networks along the c-axis. At room temperature, the O–H–O hydrogen bonds connecting the adjacent $[XO_2(OY)_2]^-$ anions are of the statistically symmetrical type $(X-O-Y_{1/2}-Y_{1/2}-O-X)$, with the hydrogen atom disordered between two equivalent minimum energy sites separated by a finite-energy barrier. The arrest of this hydrogen disorder as the crystal temperature is lowered is primarily responsible for structural phase transition in these crystals. The low-temperature phase is ferroelectric in nature for crystals in which the cation is an alkali ion (K^+ or Rb^+) whereas, for crystals containing ammonium cation (NH_4^+), the low-temperature phase is antiferroelectric in nature. For the former case, the interaction between the cation and anion is purely electrostatic, whereas for the latter case, due to the hydrogen bonding tendency of the ammonium ion, the nature of the interaction between the cation and anion is modified, and this most likely leads to the change in the nature of phase transition from ferroelectric to antiferroelectric [1]. The ADP undergoes an antiferroelectric phase change at 145 K whereas the KDP undergoes a ferroelectric phase change at 123 K.

The key to understand the differences between the KDP and ADP crystals and their deuterated analogs lies in the study of the minute differences in hydrogen bonding networks within their crystallographic frame since it is well recognized that hydrogen bonding plays the most important role in determining the physical properties of crystals belonging to the KDP family [9– 11]. To understand hydrogen bonding in both KDP and ADP crystals, the neutron diffraction has been proven to be the method of choice [12,13] with its well-known advantage of locating the hydrogen atom precisely within the crystalline environment. Hydrogen bonding in KDP crystals has been studied extensively for a very long time by various techniques including neutron diffraction [12], but the only room-temperature single-crystal neutron structure for ADP available in the literature was reported way back in 1958 [13] using a limited data set of 64 non-equivalent (0kl) reflections.

Moreover, no detailed report of single-crystal neutron diffraction (SCND) investigations on deuterated ammonium dihydrogen phosphate (DADP) was found in the literature. Hence, in order to investigate the minute differences in the hydrogen bonding network of these crystals,



we have undertaken detailed SCND investigations on ADP, DADP, KDP and DKDP crystals under similar ambient conditions. We present here not only a detailed comparison between the crystal structure of ADP and DADP but also look at the differences between the pro crystal electron densities of ADP, DADP, KDP and DKDP. The procrystal electron density distribution of a crystal is constructed by superimposing the averaged electron density distributions of ground-state neutral atoms at the positions that the atoms occupy in the crystal [14,15]. The difference between a procrystal electron density distribution $\rho(r)_{\text{pro}}$ and the actual crystal electron density $\rho(r)$ is relatively small and thus a close connection is expected to exist between the properties of $\rho(r)$ and $\rho(r)_{\text{pro}}$.

A simple diabatic two-state Hamiltonian [16,17] is used to obtain the energy surface for O–H–O hydrogen bonds of ADP, DADP, KDP and DKDP, and a comparison of these energy surfaces throws light on how the O–H–O bond can be finely tuned by manipulating its local environment which in turn affects the overall physical properties of the crystal [18–24]. Recent insitu molecule vibration spectral investigations [23,24] for the early crystal formation stages of both KDP and ADP demonstrated how the formation of O–H–O hydrogen bonds between phosphates plays the primary role in initiating crystallization in these crystals. Numerous studies on important advances such as morphology and structure studies of KDP and ADP crystallites in water and ethanol solutions have been undertaken to understand crystal growth in this family of compounds [25–27]. Studies on the rapid growth of ADP crystals [21,28] have shown that the hydrogen bonds play a key role in determining the crystal morphology of these crystals. All these studies point towards the importance of hydrogen bonds in crystal belonging to KDP family. It is highly desirable to understand how the changes in the local environment affect the hydrogen bond energy surfaces as this is the most common mechanism employed by nature to bring about changes in the phases of hydrogenous materials such as the proteins, etc. Hence, we have undertaken this study with an intention to not only understand the hydrogen bonding in KDP family but also to reveal the basic nature of different types of hydrogen bonds (weak, moderate and strong hydrogen bonds) and their influence on one another.

2. Experiment

AR-grade ADP and KDP salts are used to obtain large ADP and KDP [29] crystals from aqueous solution, and DADP and DKDP crystals were obtained after repeated recrystallization from heavy water solutions. Crystals so obtained were characterized using DSC and powder X-ray diffraction. Table 1 enumerates a few properties of these crystals. The change in transition temperature T_c on deuteration indicates that the deuteration level in DADP and DKDP is >85%.

Four-circle single-crystal neutron diffractometer with BF₃ point detector [30] located at Dhruva reactor at Trombay was used to collect the complete SCND data for the crystals DKDP and DADP. The crystal structures of KDP and ADP collected on the same instruments under similar conditions have been reported in our earlier paper [29]. Table 2 gives details of the data collection as well as structure

refinement. Table 3 gives the final refined coordinates and table 4 gives a comparison between the various structural parameters of ADP, DADP, KDP and DKDP. The procrystal densities of ADP, KDP, DADP and DKDP were obtained using their respective refined atomic coordinates and anisotropic thermal parameters in the program PRIOR developed by van Smaalen et al. [32]. The program models the procrystal electron density as a superposition of the electron densities of free, non-interacting atoms placed in their refined positions and convoluted with the refined thermal motion. Such a model describes the major part of the electron density very well, but it does not account fully for the effects of bonding on the electron density. Figure 1 shows the procrystal electron densities in the specified plains of KDP, ADP, DADP and DKDP.

Table 1. Cell parameters and transition temperatures of the crystals.

Crystal	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	Vol. (Å) ³	<i>T_c</i> (K)
ADP	7.511(3)	7.511(3)	7.556(5)	426.2(4)	145
DADP	7.521(2)	7.521(3)	7.555(5)	427.3(3)	231
KDP	7.460(1)	7.460(1)	6.980(5)	388.4(3)	122
DKDP	7.469(1)	7.469(1)	6.975(2)	389.1(4)	213

Table 2. Data collection and structure refinement details.

Diffractometer	Four-circle single-crystal neutron diffractometer				
Radiation type	Neutron				
Wavelength	0.995 Å				
Temperature	295 K				
Software	SHELXL [31]				
	ADP	DADP	KDP	DKDP	
$\sin \theta/\lambda$	0.70	0.70	0.69	0.69	
<i>h, k, l</i> range	<i>h</i> = -10-10 <i>k</i> = -5-7 <i>l</i> = -10-6	<i>h</i> = -6-10 <i>k</i> = -10-10 <i>l</i> = -10-7	<i>h</i> = 0-10 <i>k</i> = 0-10 <i>l</i> = 0-9	<i>h</i> = 0-10 <i>k</i> = 0-10 <i>l</i> = 0-9	
No. measured	191	227	169	169	
No. independent	191	227	169	169	
Obs (<i>I</i> > 2σ(<i>I</i>)) ref.	158	202	148	134	
No. of parameters	28	28	19	19	
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.075, 0.221, 1.146	0.066, 0.160, 1.321	0.056, 0.158, 1.144	0.059, 0.150, 1.258	
Δρ _{max} , Δρ _{min} (e/Å)	0.109, -0.154	0.718, -1.107	0.083, -0.092	1.063, -0.939	

Table 3. Final refined coordinates of ADP, DADP, KDP and DKDP.

		ADP	DADP	KDP	DKDP
P	<i>x/a</i>	0.000	0.000	0.000	0.000
	<i>y/b</i>	0.000	0.000	0.000	0.000
	<i>z/c</i>	0.000	0.000	0.000	0.000
N/K	<i>x/a</i>	0.000	0.000	0.000	0.000
	<i>y/b</i>	0.000	0.000	0.000	0.000
	<i>z/c</i>	0.500	0.500	0.500	0.500
O	<i>x/a</i>	0.0839(6)	0.0833(4)	0.0819(3)	0.0806(4)
	<i>y/b</i>	0.1466(6)	0.1467(4)	0.1483(3)	0.1487(4)
	<i>z/c</i>	0.1159(6)	0.1151(4)	0.1262(4)	0.1258(6)
H _O /D _O	<i>x/a</i>	0.230(2)	0.218(1)	0.224(1)	0.219(1)
	<i>y/b</i>	0.143(2)	0.144(1)	0.147(1)	0.147(1)
	<i>z/c</i>	0.119(3)	0.117(1)	0.118(2)	0.122(1)
H _N /D _N	<i>x/a</i>	0.017(2)	0.017(1)		
	<i>y/b</i>	0.111(2)	0.114(1)		
	<i>z/c</i>	0.576(4)	0.571(1)		

The former has a partial covalent character with charge delocalization, whereas the latter has no charge delocalization and the interaction is purely electrostatic in nature. Unlike the case of a strong O–H–O hydrogen bond, the charge delocalization in N–HN–O and N–DN–O hydrogen bonds is comparable with no significant effect of deuteration.

3. Deuteration effect

Deuteration has a significant effect on the crystal structure and hydrogen bonds, and the change in bond length X–H on substitution of hydrogen by deuterium is termed as a primary isotope effect. Crystals, where X–H bonds are also involved in hydrogen bonds such as the X–H–Y, there is an additional effect called the secondary isotope effect where X–Y distance changes on substitution of hydrogen (H) by deuterium (D).

An important observation from table 4 is that the change in O–H bond length on the deuteration of ADP (0.082 Å) is nearly four times that of the change in O–H bond length on the deuteration of KDP (0.022 Å), i.e. the primary isotope effect on O–H bonds of ADP is significantly larger than that of KDP. This

shows that O–H covalent bonds in these two crystals are not identical. Potential energy for a covalent bond such as O–H bond is most often represented by a Morse potential function

$$V_J(r) = D_J[e^{-2a_J(r-r_{oJ})} - 2e^{-a_J(r-r_{oJ})}],$$

Where D_J is the bond dissociation energy, r_{oJ} is the equilibrium bond length and a_J is a parameter dependent on the force constant of the bond, i.e. on the bond stiffness. The Morse potential is asymmetric, and the asymmetry in the bond potential energy is due to its finite bond stiffness. Due to this asymmetry of the bond potential energy and the quantum nature of H atom, the minimum of the potential energy does not coincide with the position of the H atom in the H–O bond defined as the maximum of the probability density for H.

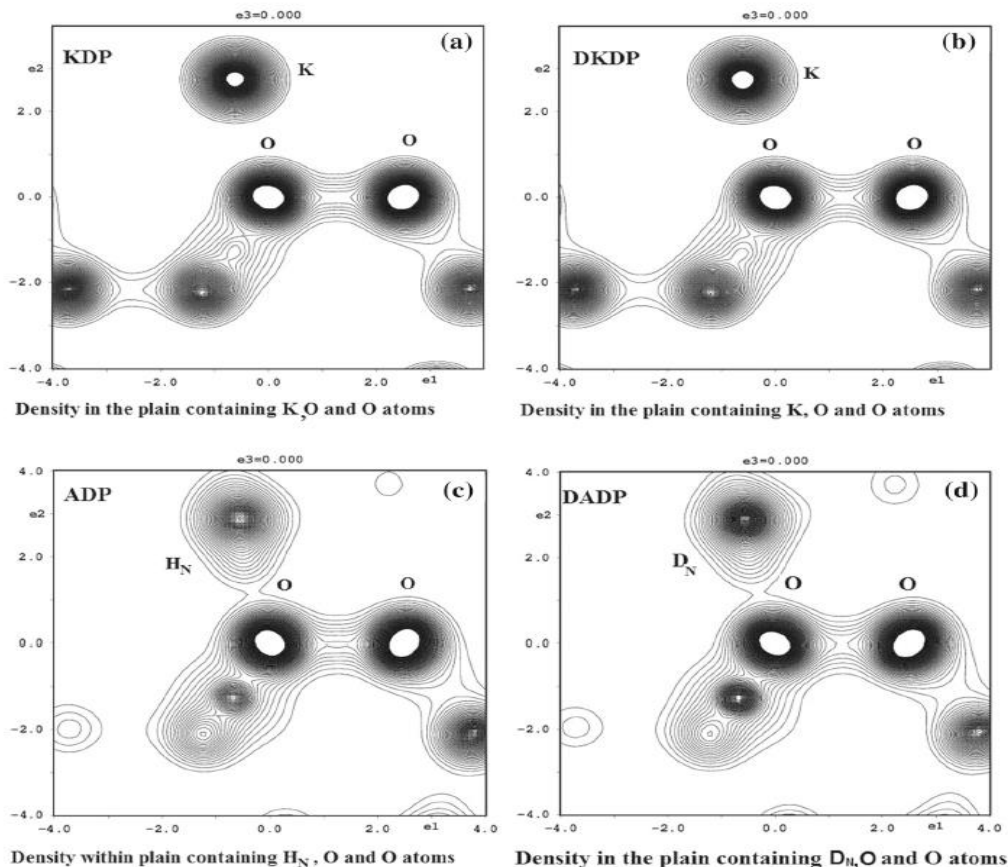


Figure 1. Procrystal electron densities in the specified planes of KDP, ADP DADP and DKDP.

Table 5. Raman vibration frequency of O–H and O–D covalent bonds of ADP, DADP, KDP and DKDP.

	$\Omega(\text{O-H})(\text{cm}^{-1})$	$\Omega(\text{O-D})(\text{cm}^{-1})$	$\Omega(\text{O-H})/\Omega(\text{O-D})$	χ	Cal- $\Omega(\text{O-H})(\text{cm}^{-1})$	Cal- $\Omega(\text{O-D})(\text{cm}^{-1})$
KDP	1806.2	1342.5	1.345	0.08	1812.4	1382.2
ADP	1704.5	1367.9	1.246	0.16	1707.3	1345.5

As the quantum nature of D is much smaller than that of H, the difference between the minimum of the potential energy and the position of D atom in the D–O bond is defined as the maximum of the probability density for D, which is much less. As a result, O–H bond lengths are usually different from O–D bond lengths, and the magnitude of this difference depends directly on the asymmetry of the bond potential energy. The larger primary isotope effect on O–H bond in ADP compared to the primary isotope effect on O–H bond in KDP is an indication that the O–H bonds in ADP are less stiff and hence weaker compared to those in KDP. The formation of a partially covalent N–HN–O bond in ADP leading to the charge redistribution between the ammonium ion and O atom most likely affects the O–H bond, making it more anharmonic.

It is very interesting to point out that the secondary isotope effect is defined as $\Delta R = R_{\text{eq}}(\text{H}) - R_{\text{eq}}(\text{D})$. Here, R the O–O distance, is higher in KD P compared to that in ADP. This is evident from a larger increase in O–O distance on deuteration of KDP (0.022 Å) compared to that of ADP (0.012 Å). It is known that the secondary isotope effect in X–H–X type hydrogen bonds depends on the X–X distance (R). Theoretical treatment of hydrogen bonds using the simple diabatic two-state Hamiltonian showed that the secondary isotope effect R is a nonmonotonic function of R. It reaches a maximum value of about 0.1 Å for $R \approx 2.5\text{Å}$, and drops towards zero on either side, i.e. for very weak and very strong hydrogen bonds, the secondary isotope effect is not significant and it is only hydrogen bonds of intermediate moderate strengths that the secondary isotope effect is significant. Hence, we can say that smaller secondary isotope effect in ADP compared to that in KDP is an indication of a stronger O–H–O hydrogen bond in ADP.

Another way of studying the effect of deuteration is to compare the O–H and O–D vibration frequencies. We have recorded the Raman spectra of KDP, DKDP, ADP and DADP. Table 5 lists the O–H and O–D stretch frequencies for these crystals. It is observed that the ratio (O–H)/(O–D) is higher for KDP compared to ADP. This is once again a consequence of the higher anharmonicity of a O–H bond in ADP, and the theoretical value of the ratio

$$\frac{\Omega(\text{O-H})}{\Omega(\text{O-D})} = \sqrt{2} \left(\frac{1 - 2\chi}{1 - \chi\sqrt{2}} \right).$$

Here χ is the bond anharmonicity factor, and the estimated value of χ for ADP is nearly twice that of KDP. Hence, we conclude that the presence of N–HN–O bond in ADP has a very significant effect on the O–H bond making it highly anharmonic. It is this higher bond anharmonicity in ADP which is most likely responsible for its higher polarisability, resulting in a larger NLO coefficient compared to KDP. It will be worthwhile to calculate the nonlinear optical coefficients of both KDP and ADP utilizing the structural parameters reported in this paper, and applying a method similar to that used by Kumar and Yadav [34].

The N–HN–O hydrogen bond of ADP is much weaker compared to O–H–O, and it is observed that the secondary isotope effect on this hydrogen bond is negligible ($R(N-O) = 0.004\text{\AA}$). The main effect of deuteration on this hydrogen bond is an increase in hydrogen bond angle $\angle N-HN-O$ by about 3.8° , i.e. N–DN–O hydrogen bonds of DADP are more linear than the N–HN–O bonds of ADP. It was earlier demonstrated by Li et al [35] that the effect of isotope substitution on the H-bonding interaction quantitatively comes down to a delicate interplay between the covalent bond stretching and intermolecular bond bending. With Xin-Zheng Li's argument, the effect of isotope substitution on the N–HN–O bonds of ADP can be summed up as follows: the decrease in the amplitude of bending vibrations, due to the heavier mass of D atom, leads to a more linear and hence a stronger N–DN–O bond in DADP. The larger deviation of ND₄ in DADP from the ideal tetrahedral geometry compared to NH₄ in ADP is a direct consequence of a stronger N–DN–O bond in DADP compared to N–HN–O bonds in ADP. The fact that N–HN–O hydrogen bond of ADP is strengthened on deuteration is most likely responsible for the reported larger shift of the N position in DADP T_c compared to that in ADP [36].

4. Diabatic two-state Hamiltonian for hydrogen bonds

We have compared the O–H–O hydrogen bonds of ADP, KDP, DADP and DKDP using the simple effective two-diabatic state Hamiltonian for a hydrogen bond between a donor D and an acceptor A. The hydrogen bond, according to this model, can be represented as a state intermediate between the D–H–A and D–H–A states, whereas D–H and H–A are normal covalent bonds that can be represented by Morse potential function $V_J(r)$ and the potential energy surface of D–H–A hydrogen bonds is made of double Morse potential and has the following electronic energy eigenvalues:

$$\epsilon_{\pm} = \frac{1}{2} [V_X(r) + V_Y(R-r)] \pm \frac{1}{2} [(V_X(r) - V_Y(R-r))^2 + 4\Delta(R)^2]^{1/2},$$

where

$$\Delta_{XY}(R, \phi) = \Delta_1 \cos \phi \frac{R - r \cos \phi}{r} e^{-b(R-R_1)}.$$

$V_X(r)$ and $V_Y(r)$ are the Morse potentials of the isolated D–H and A–H bonds, respectively, and R , r and ϕ are the D–A distance, D–H distance and D–H–A angle, respectively. This hydrogen bond model has essentially two free parameters, b and 1 , and the value of these parameters for O–H–O hydrogen bonds is approximated as $1 = 0.4D(\text{O–H})$ and $b = 2.2\text{\AA}^{-1}$ [16].

We calculated the energy surfaces \pm for O–H–O hydrogen bonds using the experimentally obtained R values for KDP, DKDP, ADP and DADP (figure 2). The one-dimensional Schrödinger equations for the motion of a nucleus (proton or deuteron) of reduced mass M in the minimum energy potentials – were solved using the FINDIF program [37] to get low-lying vibrational eigenstates E_{1+} and E_{0-} . The Morse potential parameter aJ is tuned so as to match the calculated value of $\text{Cal}-(\text{O–H})$ and $\text{Cal}-(\text{O–D})$ defined as $(E_{1+} - E_{0-})$, with the experimentally obtained (O–H) and (O–D) values. As expected, the value of aJ , which is the measure of bond stiffness, came out to be smaller for ADP than for KDP (figure 2).

The minimum energy potentials – have asymmetric double-well form with a finite barrier at the centre of O–O. It is important to point out that the height of the energy barrier at the centre of O–O is higher for KDP (6.69 kcal/mol) than for ADP (5.30 kcal/mol) indicating that

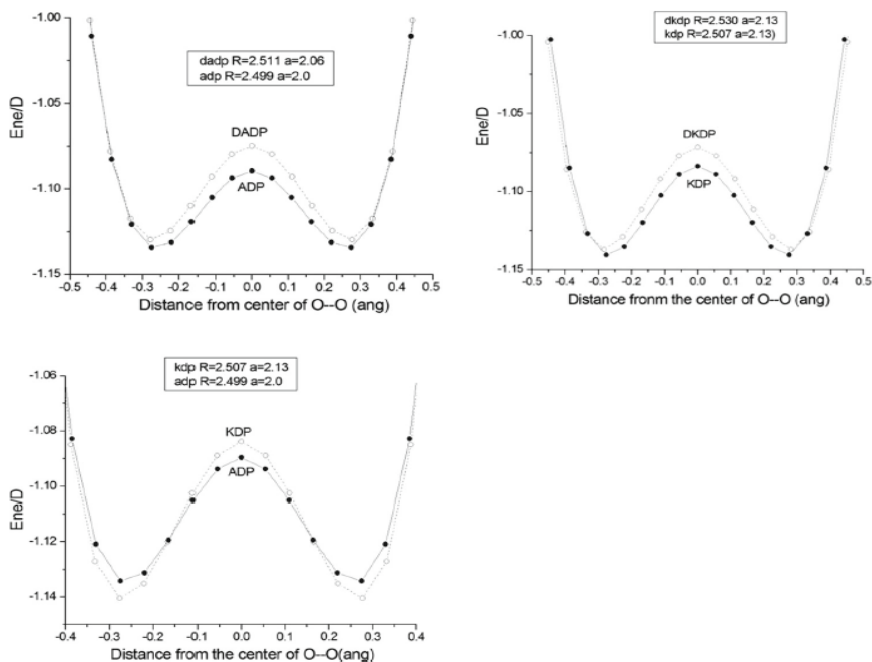


Figure 2. Energy surface for O–H–O hydrogen bonds of KDP, DKDP, ADP and DADP.



5. Conclusion

We have performed the SCND investigation on ADP, DADP, KDP and DKDP crystals under identical conditions to elucidate the subtle differences in the hydrogen bond network of these crystals which are known to play a defining role in determining the physical properties of these crystals. These structural differences are incorporated in a simple effective two diabatic state Hamiltonian to get the potential energy surfaces for the O–H–O hydrogen bonds of these crystals.

References

- [1] S Koval, J Lasave, R L Migoni, J Kohanoff and N S Dalal, *Ferroelectrics – characterization and modeling* edited by M Lallart (InTech, New York, 2011) Chapter 21
- [2] D Eimerl, *Ferroelectric* 72, 95 (1987)
- [3] D Xue and S Zhang, *Chem. Phys. Lett.* 301, 449 (1999)
- [4] D Xue and S Zhang, *J. Phys. Chem. Solids* 57, 1321 (1996)
- [5] S Ji, F Wang, L Zhu, X Xu, Z Wang and X Sun, *Sci. Rep.* 3, 1605, <https://doi.org/10.1038/srep01605>
- [6] X Feng, L Zhu, F Li, F Wang, W Han, Z Wang, Q Zhu and X Sun, *RSC Adv.* 6, 33983 (2016)
- [7] S Ji, F Wang, M Xu, L Zhu, X Xu, Z Wang and X Sun, *Opt. Lett.* 38, 1679 (2013)
- [8] V Hugo Schmidt, *Ferroelectrics* 72, 157 (1987)
- [9] D Xu and D Xue, *J. Crystal Growth* 310, 2157 (2008)
- [10] D Xu and D Xue, *J. Crystal Growth* 286, 108 (2006)
- [11] D Xu and D Xue, *Phys. B Condens. Matter* 370, 84 (2005)
- [12] Z Tun, R J Nelmes, W F Kuhs and R F D Stansfield, *J. Phys. C* 21, 245 (1988)
- [13] L Tenzer, B C Frazer and R Pepinskiv, *Acta Crystallogr.* 11, 505 (1958)
- [14] L Palatinus and S van Smaalen, *Acta Crystallogr.* A58, 559 (2002)
- [15] L Palatinus and S van Smaalen, *Acta Crystallogr.* A61, 363 (2005)