Effect of Quantum Delocalization on
Temperature Dependent Double Proton Transfer
in Molecular Crystals of Terephthalic Acid

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Abstract

Double proton transfers (DPT) are important for several physical processes, both in molecules and in the condensed phase. While these have been widely studied in biological systems, their study in crystalline environments is rare. In this work, using Path Integral Molecular Dynamics simulations we have studied temperature dependent DPT in molecular crystals of terephthalic acid (TPA). In accordance with experimental reports, we find evidence for a double proton transfer induced order-to-disorder transition that is sensitive to the inclusion of nuclear quantum effects. Our simulations show that in addition to the presence of L and R tautomers of terephthalic acid, there
are a small but non negligible concentration of positive and negatively charged pairs of TPA molecules. At the onset of the transition at low temperatures, DPT likely occurs through a tunnelling mechanism while at room temperature, likely involves the dominance of activated hopping. Through an analysis of the electronic structure of the system using Wannier functions, we show that the H atom shuttling between the donor and acceptor O atoms involves a proton.

1 Introduction

Multiple hydrogen/proton transfer (MPT) reactions play a crucial role in a variety of important processes. The replication of DNA, one of the most fundamental biological processes, is prone to mutations, which are created by complex steps involving MPTs. MPTs also have a prominent role in enzyme catalysis as well as in other non-biological systems such as ionic liquids and organic solids. Moreover, the transfer of protons can also be coupled to changes in the underlying electronic structure of the system as seen in proton-coupled electron transfer reactions (PCET). PCET reactions are ubiquitous and diverse. For example, excited state proton transfer, has potential applications for use as a fluorescent probe in biological imaging and also for use as an organic opto-electronic material.

Majority of the MPTs are found in organic molecules like DNA base pairs and their analogues, porphyrin, porphycene, phthalocyanines, and carboxylic acids where the transfer of two protons generate tautomers. This special category of proton transfer induced tautomerization is classified as double proton transfer (DPT). Depending on the manner in which the two hydrogen atoms transfer, the overall process can have two mechanism, namely, stepwise or concerted. Typically, a stepwise proton transfer involves H atoms/protons moving individually resulting in ionic intermediates. For example, Zewail and coworkers reported the hydrogen atoms of 7-azaindole dimers, a prototypical system to the DNA base pair, transfer in a non-concerted manner generating ionic intermediate species. On the contrary, Kasha and coworkers interpret the transfer of protons to have a
concerted mechanism where the protons are transferred simultaneously resulting in a single non-ionic transition state. The stepwise process involves charged intermediates and in most cases, have higher activation barriers whereas the concerted pathway suffers from the small kinetic pre-factor of two atoms transferring at the same time. The competition between the two processes determine the rate of tautomerization and the proportion of tautomers, which are essential in enzymatic reactions and drug delivery.

The nuclei, due to their heavy mass, are typically treated as classical point like particles. However, recent studies have shown that the quantum fluctuations exhibited by them, either by the light ones like H or heavier ones like C and O, strongly influence the properties of many materials and different physical processes. Nuclear quantum effects (NQEs) in DPT are typically manifested through zero-point energy and tunnelling. While the zero-point energy fluctuations usually affect free energy barriers, tunnelling facilitates classically forbidden pathways at lower temperature. These manifestations in DPT are not only of fundamental interest in biological processes but are equally important in other chemical reactions. For example, Ivanov et al. and Wikfeldt et al. used path integral molecular dynamics (PIMD) simulations to capture NQEs in the dimer of formic acid and anti-ferroelectric squaric acid crystals respectively. They find the intermolecular DPT occurs through concerted proton transfer and is temperature dependent. Similarly, Cahlik et al. using a combination of low temperature STM, atomic force microscopy (AFM) and PIMD simulations, showed that the transferring hydrogen atoms in the one-dimensional quinonediimine molecular networks supported on Au(111) surface, are concerted. This promotes a delocalization of π-electrons along the molecular chain providing enhanced mechanical stability and giving rise to new states in the gap. In the study on intramolecular DPT in a single molecule of porphycene, Litman et al. using PIMD simulations report the hydrogen atoms tunnel concertedly at low temperatures (< 100 K) whereas a competition between the concerted and stepwise pathway is observed at high temperatures (100-300 K).

Although these studies have provided novel and invaluable information regarding the
nature of DPT, we note that most of these studies are primarily cases where the effect of crystal environment have been either ignored by taking single molecule and dimer or partially incorporated through a chain of molecules. However, a complete description of crystal field, much like solvent effects, is necessary. One of the discernible effect of crystal field is the non-degeneracy of the tautomers caused due to the induced asymmetry of the potential energy surface. The non-degeneracy manifests by modifying the rates of tautomerization which are critical in systems where the proton transfer processes are controlled by external stimuli such as electric field, light, heat, and stress.

These fascinating reports prompted us to undertake a theoretical study on the nature of DPT. Therefore, in this work we investigate DPT in molecular crystals of terephthalic acid (TPA). The choice provides a more realistic and less complicated system to understand the nature of DPT and how it is modulated by the environment. TPA is also used as a commercial precursor in the polymer industry. Moreover, the molecules of TPA are used as ligands for synthesizing metal-organic frameworks and supramolecular complexes catering to a wide range of applications. More recently, Karothu and coworkers observed that the application of thermal/mechanical stimulus on the crystals of TPA results in a polymorphic phase transition. This behaviour is referred to as thermosalient/mechanosalin effect and has important applications in the design of transducers.

TPA exhibits three crystalline forms, namely, form I, II and III of which form I is found to be stable till 500 K. When form I is heated from low temperature to room temperature, it is known to undergo a continuous order-disorder transition. From their neutron diffraction studies, Fischer and co-workers determined the onset of disorder in the H positions to be around 80 K. Their results were further corroborated by temperature dependent Raman studies by Fjaer and coworkers. The temperature dependence of the disorder is examined using solid state nuclear magnetic resonance (SS-NMR). From the dipolar lineshapes they find the proton to dynamically exchange in an asymmetric double well potential. Also, the temperature dependent study of the spin-lattice relaxation rates (T1)
shows characteristic asymmetry with a steeper slope in the high temperature region (T > 100 K) suggesting that the proton transfer mechanisms are different at low (T < 100 K) and high (T > 100 K) temperatures. The slopes of this plot correspond to the barrier associated with proton transfer. From the slope of the curve in the low temperature regime (T < 100 K), they obtained an activation energy of 8 meV, while that in the high temperature regime (T > 100 K) yield an activation energy of 27 meV. Similar conclusions were also derived by Meier and coworkers\textsuperscript{55} from their temperature dependent inelastic neutron scattering studies.

Using Born Oppenheimer Molecular dynamics (BOMD) simulations and Path Integral Molecular Dynamics (PIMD) simulations coupled to the Generalized Langevin Equation based thermostat (PIGLET) we have studied the temperature dependent behavior of NQEs on the DPT in form I of TPA. Our findings suggests that NQEs involves a dominant tunnelling DPT mechanism at low temperatures (< 100 K) whereas at room temperature (300 K), it is most probably the zero-point energy fluctuations that increases the shuttling process by decreasing the activation barrier. In both scenarios, as expected, the hydrogen atom shuttles more like a proton rather than a neutral atom. Moreover, we observed that NQEs, in addition to creating neutral tautomers, also create a small but non-negligible amount of charged intermediates at both low and high temperatures. The rest of the manuscript is divided as follows: in Section 2 we provide the details of the BOMD and PIMD simulations. The results are presented and discussed in Section 3. Finally, we conclude in Section 4 with some outlook and perspectives.

2 Methods

Since form I is a stable polymorph of TPA between 70 and 300 K\textsuperscript{50,51} the temperature range of interest in this study, we have restricted our calculations to form I. The crystal structure of this form was taken from the Cambridge Crystallographic Data Centre under the de-
position number 1269122 and is optimized using the Broyden–Fletcher–Goldfarb–Shanno\(^5\) (BFGS) algorithm where the electronic structure was calculated using the Quickstep\(^5\) module, which is a Gaussian and Plane wave (GPW) based implementation of Density Functional Theory, in the open source CP2K\(^5\) package. The electronic exchange and correlation are approximated within the generalized gradient approximation (GGA) framework proposed by Becke-Lee-Yang-Parr\(^59,60\) (BLYP). van der Waals interactions have been included using the Grimme’s D3 dispersion correction.\(^6\) The electron-ion interactions were described by the norm-conserving, separable, dual-space Gaussian-type pseudopotentials of Goedecker, Teter, and Hutter\(^62\) (GTH). The triple-zeta valence polarisation (TZVP) basis set was used to expand the electronic wavefunctions. The charge density was expanded on a grid with a plane wave cutoff of 450 Ry. The electronic calculations were done using a 2×2×5 supercell. Brillouin zone integrations have been performed using only the Γ-point.

The BOMD simulations of TPA crystals were performed at 70, 100, 200 and 300 K using a canonical sampling through velocity rescaling\(^63\) (CSVR) thermostat as implemented in the CP2K package. In order to study the effect of NQE, we have performed PIMD simulations at the same temperatures. These simulations were carried out using the i-PI\(^64\) and CP2K software, where i-PI propagates the nuclear motion and CP2K calculates the electronic forces and energy. A coloured noise Generalised Langevin Equation based thermostat (GLE) is coupled to PIMD simulation\(^65\) (PIGLET) to accelerate the convergence with respect to the number of beads. The converged number of beads for the PIGLET simulation at 70 K was estimated to be 16 (the results of the convergence tests are shown in Section 2 of the Supporting Information (SI)). For the higher temperature simulations we have used, for consistency, the same number of beads. The parameters for the diffusion and drift matrices of the coloured noise thermostat were generated from the online repository (\texttt{http://gle4md.org/}) such that the maximum physical frequency lie close to 4000 cm\(^{-1}\) for all temperatures. The equations of motion in the various molecular dynamics simulations were integrated with a time step of 0.5 fs. The BOMD and PIGLET simulations were performed for 35 ps and 20
ps respectively. The analysis were done using the last 30 ps and 18 ps of the BOMD and PIGLET trajectories respectively.

3 Results and Discussion

3.1 Crystal Structure of TPA

Each TPA molecule consists of a benzene ring with two carboxyl group at each of the para positions of the benzene ring (Figure 1(a)). In the crystalline form, the molecules are arranged in chains that are formed through double hydrogen bonding between the hydroxyl OH groups of the -COOH group of one TPA unit with the oxygen of the -COOH group in the neighbouring TPA unit. Two such chains are further bound together by weak H bonds between the H atoms of the phenyl group and the O atoms of the -COOH group to give rise to a two-dimensional sheet. These two-dimensional sheets are stacked on top of each other to give rise to the three-dimensional crystal structure. Depending upon how two such sheets are stacked, TPA exists in three polymorphs, namely form I, II and III, where, in case of the most stable form I (see Section 1 of the supporting information), the TPA molecules of one sheet are on top of those in the sheet below it, as shown in Figure 1(a).

Form I of the TPA crystallizes in the triclinic structure with the chain axis parallel to the \( a \) lattice vectors where the lattice parameters at 0 K are 9.62 Å \((a)\), 7.61 Å \((b)\), 3.62 Å \((c)\), 73.80° \((\alpha)\), 105.07° \((\beta)\) and 139.44° \((\gamma)\). The lattice parameters obtained from our calculations are given in Table S1 of the Supporting Information showing consistency with previous reports.\(^{50,51}\) At this temperature, all the TPA molecules are in the trans configuration (Figure 1(a)) and has two types of hydrogen bonded interactions, (i) a pair of O-H\(\cdots\)O bonds parallel to the chain direction (highlighted by a black square in Figure 1(a)), with a shorter heavy atoms separation of 2.63 Å and (ii) a pair of C-H\(\cdots\)O bonds\(^{66}\) perpendicular to the chain direction (highlighted by a yellow square in Figure 1(a)) with heavy atoms separation \(d_{C-O}\) of 3.36 Å and 3.46 Å where the shorter (longer) heavy atom separation is due
to the interaction of the benzene hydrogen with the lone pair of the more (less) acidic $sp^3$ $(sp^2)$ hybridized acceptor (donor) oxygen. On the basis of the heavy atom separation, the O-H···O is categorised as a strong hydrogen bond (sHB) whereas the C-H···O falls under the category of weak improper hydrogen bond (wHB). Clearly, DPT processes are observed along the O-H···O sHB.

In this study, we refer to these intra chain DPT junctions throughout the crystals as the L-tautomer as shown in Figure 1(a). When both the two protons bonded to the donor oxygen ($O_D$) atoms in these L-tautomers are transferred to the respective acceptor oxygen ($O_A$) atoms along the hydrogen bonds, we end up with their R tautomeric form shown in Figure 1(b). In this tautomeric state the pair of O-H···O bonds remain same. However, the corresponding heavy atom separations are 3.42 Å ($d_{C-O_D}$, where donor O has become $sp^2$ hybridized) and 3.38 Å (where acceptor O has become $sp^3$ hybridized). The dissimilar pair of C-H···O wHBs for the L and R-tautomers is responsible for lifting the degeneracy between the two tautomers by 19 meV/DPT junction. As a result, the associated DPT process occurs through an asymmetric double well potential which is discussed in Section 4 of the supporting information.

### 3.2 Finite Temperature NQE on strong hydrogen bonds

In order to analyze the proton transfer events, we define the following proton transfer coordinates ($\delta_{1,2}$) as shown in Figure 1(c), where, $\delta_{1,2}$ is the difference between H-bond length between the acceptor oxygen atom ($O_A$) and the transferring hydrogen atom ($d_{O_A-H}$) and the covalent bond length between the donor oxygen atom ($O_D$) and the same transferring hydrogen atom ($d_{O_D-H}$). At 0 K, in the L-tautomer of form I, the protons are bonded to the donor oxygen atoms and exhibits the ordered state resulting in a negative value of $\delta_{1,2}$. Fluctuations of the $\delta_{1,2}$ between positive and negative values indicate the occurrence of proton transfer events.

*Double Proton Transfer.* The dependency between $\delta_1$ and $\delta_2$ provides insight into the under-
Figure 1: Crystal structure of form I of TPA using ball and stick representation. Top view showing the stacking of the TPA chains where all the DPT junctions are in (a) L and (b) R tautomeric state. The black (yellow) square highlights the strong (weak) intermolecular H-bonds that results in the formation of the chains (sheets). (c) The proton transfer coordinates $\delta_1$ and $\delta_2$ at a junction of two TPA molecules. In (a) and (b) the topmost layer atoms are shown with solid spheres and the bottom layer atoms are shown as points. In this and the subsequent figures green, red and white spheres represent carbon, oxygen and hydrogen atoms respectively.
lying DPT process. Therefore, in order to understand the temperature dependence of NQEs, we have plotted the effective free energy ($F_{eff}$) corresponding to the joint probability distribution function (JPDF) between the $\delta_1$ and $\delta_2$ (Figure 2) at 70 and 300 K for the BOMD and PIGLET simulations. The free energy ($F$) corresponding to a discrete and normalized JPDF ($p$) between two quantities $X$ and $Y$ at $(X_i, Y_j)$ can be written as:

$$F(X_i, Y_j) = -k_B T \ln [p(X_i, Y_j) \, dX \, dY] \quad (1)$$

where $k_B$ and $T$ are the Boltzmann constant and the simulation temperature, respectively. $p(X_i, Y_i)$ is the normalized JPDF of $X$ and $Y$ at $X_i$ and $Y_j$ respectively. $dX$ and $dY$ are the binning widths used to discretize the $X$ and $Y$ variables respectively. The minima of the discrete free energy surface correspond to the maxima of the joint probability. The effective free energy ($F_{eff}(X_i, Y_j)$) is computed by shifting all $F(X_i, Y_j)$ with the $F_{min}(X_{min}, Y_{min})$ as shown in the equation below:

$$F_{eff}(X_i, Y_j) = F(X_i, Y_j) - F_{min}(X_{min}, Y_{min}) \quad (2)$$

Events in the third (first) quadrant of the FES correspond to the L (R) tautomer where both the protons are covalently bonded to the donor (acceptor) oxygen atoms. Therefore, in these two quadrants, the DPT junction is neutral as the participating carboxylate groups have one hydrogen atom each. On the other hand, events in the second and fourth quadrants correspond to the state of charged DPT junction where both the hydrogen atoms are near to one of the carboxylate groups. At 70 K, for the classical nuclei, since there are no proton transfer events, we observe a single local minima in the third quadrant (Figure 2(a)) corresponding to the state where the two hydrogen atoms are covalently bonded to the donor oxygen atoms ($O_D$). Upon increasing the temperature to 300 K, we find minima in both the first and third quadrants (Figure 2(b)) showing that room temperature induces proton transfer events which create the R tautomers.
When the NQEs are turned on, local minima in FES are observed in the first and third quadrant even at 70 K (Figure 2(c)). This implies that the proton is significantly more delocalized along the hydrogen bonds, fully consistent with previous studies reporting this effect in numerous other organic molecular systems.\textsuperscript{37,38,40,68–76} Furthermore, the free energy profile extends to the second and fourth quadrant forming an \textit{elbow} suggesting presence of charged DPT junctions where both the transferring protons are close to the same molecule. However, since these are less probable (higher in energy), their occurrences are rare. All in all, these results suggest that at 70 K DPT in the TPA crystal primarily results in formation of \(L\) and \(R\) tautomers with the system transiently accessing “rare” configurations where there exists pairs of positively and negatively charged TPA molecules along the chain.

Figure 2: The effective free energy \((F_{\text{eff}})\) as a function of the proton transfer coordinates \(\delta_1\) and \(\delta_2\) at 70 (left column) and 300 K (right column). The top and bottom row are from BOMD and PIGLET simulations respectively.
Upon increasing the temperature to 300 K, we find an enhanced proportion of events in the first quadrant corresponding to the R tautomer suggesting an increase in proton transfer activities. This symmetrizes the shape of the FES in the first and the third quadrant indicating that at this temperature the disorder in the hydrogen bond network is almost complete. Additionally, the spread of the free energy profile decreases (the *elbow* observed at 70 K softens) along the $\delta_1 = -\delta_2$ direction. This implies that at higher temperatures the probability of finding the configurations where both the protons are on the same molecule is diminished.

*Nuclear quantum tunnelling.* Our simulations also allow for selectively understanding the role of nuclear tunnelling in DPT. The effect of nuclear tunnelling can be quantified by an increase in the radius of gyration of the ring polymer representing the quantum nucleus.\(^{77}\) The radius of gyration probes the quantum uncertainty in position of the nucleus and is proportional to the thermal de Broglie wavelength of that nucleus. Hence, it is expected that a proton transfer event due to tunnelling is to be accompanied with an enhancement of the radius of gyration of the proton. This enhancement in the delocalization of the hydrogen ring polymer during the course of tunnelling is known to occur in the low temperature region of paraelectric squaric acid\(^{38}\) and hexagonal ice.\(^{78}\) Therefore, to examine the extent of this effect in our study, we have computed the radius of gyration, $r_G = \sqrt{\frac{1}{P} \sum_{i=1}^{P} (r_{i}^{H} - r_{c}^{H})^2}$, where H is the hydrogen atom, $P$ is the number of beads in the ring polymer, $r_{i}^{H}$ is the position of the H-atom in the $i^{th}$ bead of the proton ring polymer and $r_{c}^{H}$ is the position of the centroid of the proton ring polymer ($r_{c}^{H} = \frac{1}{P} \sum_{i=1}^{P} (r_{i}^{H})$).

Figure 3(a) and (b) show two random proton transfer coordinates of the centroid of the ring polymers ($\delta_{1,2}^{c}$; blue graph) and their radius of gyration ($r_G$; red graph) as a function of the simulation time at 70 and 300 K respectively. We note that at 70 K, whenever $\delta_{1,2}^{c}$ changes sign there is a peak/enhancement of $r_G$ (Figure 3(a)) suggesting that the quantum fluctuations is delocalizing the proton that is being transferred thereby resulting in an enhancement of its de Broglie’s wavelength, a consequence of which is that the proton is
tunnelled from one potential well to another through a barrier. In contrast, at T=300 K (Figure 3(b)), we do not observe any enhancement of $r_G$ when a proton transfer event is occurring.

![Figure 3](image)

**Figure 3:** Plots of $\delta_{i,2}$ and $r_G$ as a function of sampling time at (a) 70 and (b) 300 K.

To get a statistical idea regarding the effect of temperature on tunneling, we constructed the joint probability distributions of $r_G$ and $\delta_{i,2}$ (Figure 4(a) and (d) at 70 and 300 K respectively). If the proton transfers are dominated by tunnelling, we expect a large spread in $r_G$ at around $\delta_{i,2} = 0.00$. Additionally, this delocalization should be along the direction of the H-bond for the tunnelling to occur from one well to the other. To check whether this is indeed the case for our system, we have also computed the projection of $r_G$ on the parallel ($r_G^\parallel$, Figure 4(b) and (e) at 70 and 300 K respectively) and perpendicular directions ($r_G^\perp$, Figure 4(c) and (f) at 70 and 300 K respectively) of the hydrogen bond. Consistent with our previous observation for a single proton transfer coordinate, here also we find
Figure 4: The JPDF plots of $\delta_{1,2}^c$ and radius of gyration at 70 K (left panel) and 300 K (right panel). (a) and (d) correspond to the radius of gyration ($r_G$), (b) and (e) correspond to the component of $r_G$ parallel to the O-H bond ($r_G^\parallel$), and (c) and (f) correspond to the component of $r_G$ perpendicular to the O-H bond ($r_G^\perp$).
that at T=70 K, there is a large spread of $r_G$ at around $\delta_{1,2}^c=0.00$ (Figure 4(a)) while the spread is uniform for T=300 K (Figure 4(d)). Analysing the contributions from the parallel and perpendicular components of $r_G$, we note that these enhancements at 70 K are due to enhancements observed in $r_G^\parallel$ (Figures 4(b) and (e)), thereby further verifying that at 70 K, it is more likely that the proton transfer occurs through tunnelling while at 300 K the thermal activation seems more important. However, we would like to note that since these proton transfers are rare events making quantitative statements of the relative role of activated hopping versus tunneling cannot be currently made.

**Correlation between proton transfer and H-bond fluctuations**

The manifestation of NQEs in these type of systems are not restricted to the distribution of the transferring protons but also affect the vibrations of the heavy atoms connected to the proton transfer coordinate. The vibronic coupling of the heavy atoms with the protons is prominent in most hydrogen bonded systems such as protonated water,\textsuperscript{79–81} protein analogues,\textsuperscript{82} crystal hydrates\textsuperscript{83–85} and even other molecular crystals.\textsuperscript{38} Using PI simulations on a single Zundel ion, Benoit et al.\textsuperscript{81} reported the dependence of the proton transfer on the distance between the oxygen atoms. A large separation leads to the proton being localized on one water separated by a large barrier. On reducing the separation to ultra small values, the two peaks merge into one broad peak corresponding to a single potential well. Similar effects have also been observed in molecular dynamics simulations of various crystal hydrates.\textsuperscript{83–85}

This dependence in TPA is illustrated by computing the joint probability distribution as a function of the proton transfer coordinates ($\delta_{1,2}$) and its heavy atom separation ($d_{O-O}$), resulting in banana-shaped free energy profiles (Figure 5). Careful inspection of the free energy profiles obtained from the BOMD simulations at 300 K (Figure 5 (b)) shows that the proton transfer is coupled to a reduction of 0.13 Å in the $d_{O-O}$. At both the temperatures (70 and 300 K) we obtain a linear correlation with Pearson correlation coefficient between $\delta_{1,2}$ and $d_{O-O}$ of ±0.83 for positive and negative values of $\delta_{1,2}$.

Upon turning on the NQE, we observe an asymmetric banana-shaped free energy profile
Figure 5: The effective free energy ($F_{\text{eff}}$) as a function of the proton transfer coordinate ($\delta_{1,2}$) and the heavy atom distance ($d_{O-O}$) at 70 (left column) and 300 K (right column). The top and bottom row are from BOMD and PIGLET simulations respectively.
at 70 K (Figure 5(c)), with two minima, one at $\delta_{1,2} = -0.54 \text{ Å}$, $d_{O-O} = 2.61 \text{ Å}$ and the other at $\delta_{1,2} = 0.5 \text{ Å}$, $d_{O-O} = 2.58 \text{ Å}$, in accordance with the proton transfer events observed at this temperature. Moreover, for both the negative and positive values of $\delta_{1,2}$ we observe a larger spread along the $d_{O-O}$ axis suggesting a weakening of the coupling between the shrinkage of the O-O distance and proton transfer compared to that observed when NQEs are ignored. Indeed the Pearson correlation coefficient is reduced to -0.39 for $\delta_{1,2} < 0$ and 0.38 for $\delta_{1,2} > 0$ at 70 K. Increasing the temperature to 300 K, we observe that the spread of the free energy profile increases (Figure 5(d)). However, the Pearson correlation coefficients are improved (-0.53 for $\delta_{1,2} < 0$ and 0.54 for $\delta_{1,2} > 0$) compared to that observed at 70 K from PIGLET simulations. These results suggest that while NQE weakens the coupling between proton transfer and the shrinkage of the O-O distance whereas the increase in temperature strengthens the coupling.

We further note that occurrence of proton transfer events at 70 K is in accordance with the experimental observations where the order disorder transition sets in at around 80 K.$^{52,53}$ The free energy difference between the two minima is about 13 meV. The asymmetric nature of the FES, as discussed earlier, can be attributed to the crystal field effect where the L and R tautomers are not degenerate. At 300 K the difference between these two minima increases marginally to 15 meV. Moreover, a comparison of the heavy atom distances, $d_{O-O}$ between BOMD (2.63 Å at 70 K and 2.65 Å at 300 K) and PIGLET (2.60 Å at 70 K and 2.62 Å at 300 K) shows that the NQEs strengthen the strong H-bonds. We note that similar strengthening has been observed in pentamers and hexamers of HF,$^{69}$ charged clusters of $\text{N}_2\text{H}_5^-$,$^{69}$ dimers of formic acid,$^{69}$ a molecular chain of 2,5-diamino-1,4-benzoquinonediimine$^{39}$ on Au(111) and solid HF and squaric acid.$^{38,69}$

### 3.3 Charge state of the transferring H atom

The shuttling of the H atom involves simultaneous cleavage and formation of covalent O-H bonds. Intuitively, one might expect that during the proton transfer event the H atom
is transferred as $H^+$, particularly when it is equally shared between a donor (O$_D$) and an acceptor (O$_A$) oxygen atoms. To verify this and to understand the effect of the proton transfer fluctuations on the electronic density, we have computed the maximally localized Wannier functions (MLWF). A single Wannier center can be associated with an electron pair. Each O atom of the -COOH group of TPA is associated with four Wannier centres. At 0 K, the Wannier centre ($X_D$) corresponding to the covalent O$_D$-H bond is 0.55 Å away from the H atom. On the other hand the acceptor O atom that forms the C=O bond has a pair of Wannier centres corresponding to the lone pairs at about 1.26 and 1.80 Å from the hydrogen atom. The nearest Wannier center ($X_A$) from the H lies along the O-H···O H-bond. As the proton moves from the donor O to the acceptor O, we monitored the change in the distance of the H atom from the Wannier center corresponding to (i) the covalent O$_D$-H bond (labelled as $d_{X_D-H}$ in Figure 6(a)) and (ii) the nearest lone pair of the O$_A$ atom (forming C=O bond) (labelled as $d_{X_A-H}$ in Figure 6(a)).

![Figure 6](image_url)

Figure 6: (a) The positions of the O Wannier centres denoted by blue spheres. The distance, $d_{X_D-H}$, between O (donor)-H Wannier center from the H and $d_{X_A-H}$, between the H and the nearest Wannier center corresponding to one of the two lone pairs at the acceptor O are also marked. (b)-(d): The joint probability distribution between the two distances ($d_{X_D-H}$ and $d_{X_A-H}$) and proton transfer coordinate obtained from BOMD (top panel) and PIGLET (bottom panel) simulations at 70 K (left column) and 300 K (right column).
Figure 6(b) and (c) (Figure 6(d) and (e)) show the joint probability distribution plots of $d_{X_D-H}$ and $d_{X_A-H}$ with $\delta_{1,2}$ for the BOMD (PIGLET) simulations at 70 and 300 K, respectively. For the BOMD simulations at 70 K where no proton transfer event was observed, the position of the Wannier centres ($X_D$ and $X_A$) from the hydrogen atoms fluctuate about their mean positions and are localized. In this state, the hydrogen atom is bonded to an electronegative oxygen atom and behaves like a proton.

When the temperature is raised to 300 K, the fluctuations of the hydrogen atoms increase and only for those cases where the proton transfers occur the $d_{X_D-H}$ and $d_{X_A-H}$ switch their values suggesting that the Wannier centre corresponding to the O$_D$-H covalent bond ($X_D$) changes to the lone pair Wannier center. Meanwhile, the Wannier centre corresponding to the O$_A$ lone pair ($X_A$) modifies into the Wannier center for the newly formed O$_A$-H covalent bond. Understandably, this illustrates that a successful transfer preserves the proton state of the hydrogen atom. In addition, turning on the NQEs finds a considerable proportion of $d_{X_D-H} = d_{X_A-H}$ events at $\delta_{1,2}^c = 0$. This implies that the hydrogen atom continues to maintain the protonic state all along the transfer.

Further, monitoring the evolution of the two Wannier functions during the proton transfer path, we observe that when the H-atom is covalently bonded to one of the O-atoms (forming L or R-tautomer), the Wannier functions, as expected, are similar to that of an -OH bond and an O-lone pair (Figure 7(a) and (c) for L and R tautomers respectively). However, when the proton is shared equally between the two O atoms, the Wannier functions of the donor and acceptor O atoms are similar to that of an O-lone pair (Figure 7(b)) suggesting that the electron pair involved in forming the covalent -OH bond is localized on the donor O atom. As a consequence, the shuttling H atom shared between the two O atoms behaves as a proton.
Figure 7: Evolution of the Wannier functions of the $O_D$-H bond (green isosurface) and the $O_A$ lone pair (blue isosurface) as the proton transfers from the donor to the acceptor oxygen. (a) H covalently bonded to donor O forming L-tautomer, (b) the H atom is equally shared by the donor and acceptor and (c) the H atom covalently bonded to acceptor O atom, R-tautomer. For clarity, only a pair of TPA molecules where the proton transfer is occurring is shown.
4 Conclusions

In summary, using the state of the art PIGLET simulations, we have studied temperature dependent double proton transfer in molecular crystals of terephthalic acid. In accordance with experiments, we observe occurrence of proton transfers and thereby onset of order-disorder transitions at temperatures as low as 70 K. At around 300 K the H atoms are completely disordered. Our simulations show that, though the neutral L and R tautomers are the dominant species, there is a small but non-negligible amount of charged species present at both low and high temperatures. The simulations suggest that while between 70 and 200 K, the proton transfer happens through tunnelling, at room temperature it most probably occurs through activated hopping. However, we note that in order to conclusively comment on the mechanism through which the transfer events occur, one needs to perform further simulations using enhanced simulation techniques because these are rare events requiring also the identification of the relevant reaction coordinates. Additionally, in accordance with other systems, we observe that NQE reduces the coupling between the proton transfer and reduction of the donor-acceptor heavy atom distances. Further, through the calculations of the Wannier functions, we show that the H atom is transferred in form of a proton from the donor to the acceptor O atom.

Moreover, as mentioned in the introduction, TPA crystals exhibit thermosalient and mechanosalient effects that leads to polymorphic phase transition. Since the stability of TPA crystals are determined by a subtle balance of the intra and interchain H-bonds and the van der Waals interaction between two TPA sheets, we envisage that it would be interesting to explore the role of NQEs on the above mentioned properties exhibited by TPA in particular and similar molecular crystals in general. We believe that our study on form I of TPA has laid the foundation to further explore role of NQEs and DPT on polymorphic phase transitions exhibited by these crystals.
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Supporting Information Available

Supporting Information: 0K structures of the three polymorphs of TPA, results of convergence tests of the PIGLET simulations as a function of number of beads, data related to the NQE and finite temperature effects on DPT at 100K and 200K, and a discussion on the weak improper C-H⋯O hydrogen bonds and its connection to the asymmetry of the double well potential related to proton transfer.
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