

Polarisation switching mechanism of a proton transfer ferroelectric

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Statement of originality

I declare that the work presented in this thesis was carried out by myself under the supervision of Dr. Laura Ratcliff and Prof. Aron Walsh.

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Abstract

Ferroelectricity is a phenomenon which scientists have investigated since its discovery – for its own sake, as well as the practical applications which have been later revealed. Although most research has historically focused on inorganic ferroelectrics such as the perovskites lead zirconate titanate and barium titanate, organic ferroelectrics often possess different characteristics which may inspire novel applications in the future.

An important aspect of a ferroelectric’s behaviour is the mechanism by which its polarisation switches in an external field. This thesis describes the development of an effective Hamiltonian to simulate polarisation switching in the organic, proton transfer ferroelectric, croconic acid (CRCA). CRCA is a single-component, room temperature ferroelectric with a large spontaneous polarisation ($30 \mu\text{Ccm}^{-2}$). Density functional theory (DFT) was used to map out the potential energy surface (PES) of CRCA from first principles, and to generate the data which was used to train the effective Hamiltonian.

The effective Hamiltonian was developed to satisfy translational invariance in a way which allows the molecular degrees of freedom to be coarse-grained. This improves the efficiency with which the effective Hamiltonian can be trained and used relative to previous versions of the method from which our model was adapted. The accuracy of the effective Hamiltonian was verified by calculating the minimum energy path (MEP) of a single unit cell between its two domain states and comparing it to the results of DFT calculations of the MEP. Polarisation switching in the non-activated regime of CRCA was then simulated using the kinetic Monte Carlo method with the effective Hamiltonian. These simulations suggest that the domain wall velocity and the electric field strength follow a linear relationship with a negative intercept. The similarities and differences between this result and the results of previous theoretical studies are considered and discussed.

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Chapter 1

Introduction

In simple terms, ferroelectricity is the presence of a spontaneous, switchable, electric polarisation within a material. The phenomenon was first discovered in Rochelle salt by Valasek in 1920 [1]. In spite of their name, ferroelectrics do not necessarily involve iron. Instead, their name was inspired by the analogy drawn between the behaviour first observed in Rochelle salt and the phenomenon of ferromagnetism which had been known to scientists for centuries. Indeed, Valasek remarked that the ‘dielectric displacement D , electric intensity E , and the polarization P are analogous to B , H , and I in the case of magnetism’ [1]. By this, he referred to the hysteretic, i.e. history-dependent, relationship between P and E .

Since its initial discovery, ferroelectricity has been observed in a range of materials apart from Rochelle salt. However, ferroelectrics did not achieve widespread practical application until the discovery of the perovskite ferroelectrics lead zirconate titanate (PZT) and barium titanate. The perovskites possess better stability, relative to their predecessors such as Rochelle salt, under everyday temperatures and humidity levels. Subsequently, perovskite ferroelectrics as well as similarly stable ferroelectrics with other crystal structures, have been incorporated into actuators, memory devices, and infrared sensors, to name specific examples.

Accompanied by this success, however, is the recognition of the environmental impact of these devices’ production. PZT contains lead which is chemically toxic, and the methods commonly used to produce perovskite ferroelectrics are energetically intensive, since they involve melting and mixing solid precursors at high temperatures ($\sim 1000^\circ\text{C}$). Environmentally friendly alternatives are therefore sought. Organic ferroelectrics may eventually satisfy this need, as they are generally produced using more energetically efficient methods. In order to assess their suitability for certain practical applications, however, it is necessary to understand their polarisation switching behaviour. Due to the historically greater level of practical application of perovskite ferroelectrics, the study of polarisation switching has focused on this class. Less is known about polarisation switching mechanisms in organic and, in particular, proton transfer ferroelectrics.

This thesis describes our theoretical study of polarisation switching in a recently discovered organic, proton transfer ferroelectric, croconic acid (CRCA) [2]. *Ab initio* calculations according to density functional theory (DFT) were performed, and subsequently used to construct an effective Hamiltonian of the interatomic potential energy surface. This latter model was used to perform Monte Carlo simulations in order to study supercells of CRCA beyond the practical reach of DFT in terms of length- and time-scales. These Monte Carlo simulations modelled

the process of polarisation switching in CRCA, so that the atomistic mechanism of this process could be studied.

The thesis is organised as follows. In Chapter 2, a more extensive background is given surrounding the phenomenon of ferroelectricity. Chapter 3 explores the particular class of proton transfer ferroelectrics of which croconic acid is a member. Chapter 4 explains DFT, the *ab initio* method we used to study CRCA, in more detail. Chapter 5 discusses the DFT calculations we performed on CRCA. Chapter 6 discusses various types of effective Hamiltonians which have been used to study ferroelectric materials in the past, including the method we adapted in order to model CRCA, which is explained in Section 6.3. Chapters 7 and 8 discuss the results of nudged elastic band and kinetic Monte Carlo calculations which we performed to study the minimum energy polarisation switching path, and polarisation switching kinetics respectively, of CRCA according to the aforementioned model. Finally, Chapter 9 ends the thesis with our conclusions.

Chapter 2

Ferroelectric materials

2.1 The meaning of ferroelectricity

When an external electric field is applied to an insulator, the electrons and positive ions it comprises will be displaced electrostatically in opposite directions. These displacements produce microscopic dipoles, which aggregate into a macroscopic polarisation, quantified as the dipole moment per unit volume, within the material. The tendency for a material to develop a polarisation in the presence of a field is quantified by its dielectric susceptibility tensor χ , which has elements

$$\chi_{ij} = \frac{\partial P_i}{\partial \mathcal{E}_j}, \quad (2.1)$$

where $\mathcal{E}$ is the external field and $\mathbf{P}$ is the polarisation. For some materials, the polarisation exists before an external field is applied. These materials are known as *ferroelectrics*. Ferroelectricity exists within a broader family of *ferroic* phenomena, which also includes ferroelasticity and ferromagnetism. In general, a ferroic possesses a high-symmetry phase G and a low-symmetry phase F . The point groups of their microscopic structures satisfy

$$F \subset G. \quad (2.2)$$

Rigorously defined, a ferroelectric is a ferroic which, as a result of a structural phase transition from a high-symmetry parent phase G to low-symmetry daughter phase F , acquires non-zero components of its spontaneous polarisation which were originally zero due to the symmetry of phase G [3]. This can be compared to a ferroelastic which acquires non-zero strain components, and a ferromagnet which acquires non-zero components of the internal magnetisation.

A sufficient condition for the presence of ferroelectricity in a material is the existence of a finite number of phases whose structures are related by symmetry elements of the point group G . These phases are known as *domain states*. Experimentally, in most cases the material can be switched between domain states by applying an external electric field in the same direction as the polarisation of the target domain, and with a magnitude greater than the material's *coercive field*, $\mathcal{E}_c$. This condition is often used to experimentally confirm a material's ferroelectricity.

Experimentalists apply an oscillating voltage across a plate of a suspected ferroelectric, and measure the polarisation as a function of applied field. Electrodes are attached to a plate of

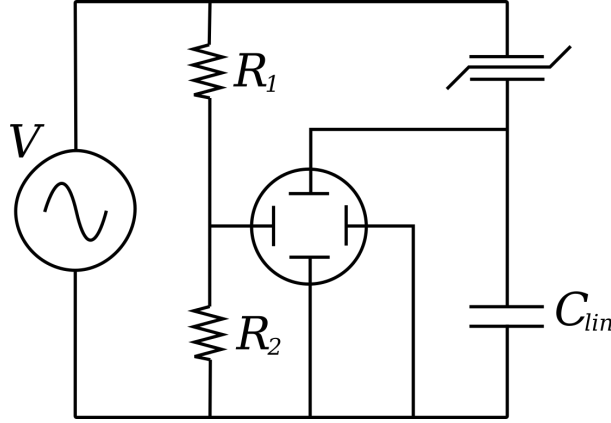


Figure 2.1: A schematic of the Sawyer-Tower circuit used to determine the relationship between polarisation and electric field for an alleged ferroelectric. Each symbol is defined in the text.

a ferroelectric which has been cut perpendicular to its polar axis. This can be achieved by painting these surfaces with silver or gold paste [4, 5], evaporating gold onto these surfaces [6], or creating a channel of LiCl solution between the surfaces and the rest of the circuit [7], for example. In this way, they create a ferroelectric capacitor [6–9]. An electric field parallel to the polar axis in either direction can then be easily applied to the plate, and the polarisation measured by assembling a Sawyer-Tower circuit [8]. The ferroelectric capacitor is connected in series with a linear capacitor of a known capacitance C_{lin} and a voltage source V . The potential difference (p.d.) across the linear capacitor is measured on the y-axis of an oscilloscope, from which the charge stored by both capacitors (due to their being in series) can be deduced. The p.d. across a resistor R_2 , which is itself in series with a resistor R_1 , is measured on the x-axis of the oscilloscope. This p.d. divides the source voltage. If $\frac{Q}{VC_{lin}} \ll 1$ where Q is the charge stored by the capacitors, then the p.d. across the ferroelectric $V_{FE} \approx V$ from which the electric field strength within the ferroelectric can be deduced. The oscilloscope plots a quantity proportional to the electric displacement,

$$\mathbf{D} = \epsilon_0 \mathbf{E} + \mathbf{P},$$

which is approximately equal to the polarisation for most ferroelectrics [3]. The Sawyer-Tower circuit is illustrated in Figure 2.1.

Switchable ferroelectrics exhibit hysteresis in the relationship between $\mathbf{P}$ and $\mathbf{E}$. A schematic hysteresis loop is represented in Figure 2.2. The figure illustrates the difference between the spontaneous and remanent polarisations, the latter of which is defined as the polarisation of the sample at zero field. In an ideal ferroelectric, when the external field is removed, no switching of the polarisation occurs anywhere within the crystal, and $P_s = P_{rem}$. However, in practice, defects which are present in real ferroelectric crystals mean that some nucleation of reverse domains occurs upon removal of the field, and $P_s \neq P_{rem}$. P_s is calculated by extrapolating the top part of the $P(\mathcal{E})$ loop to the P -axis, in order to eliminate the contribution of the (linear) lattice dielectric permittivity to the polarisation.

Although the hysteresis of $\mathbf{P}$ with respect to $\mathbf{E}$ can be used to demonstrate ferroelectricity, failure to observe it does not preclude the latter, since there are examples of ferroelectrics such as lithium niobate [3] [10, p.9], for which switching between domain states is difficult to achieve

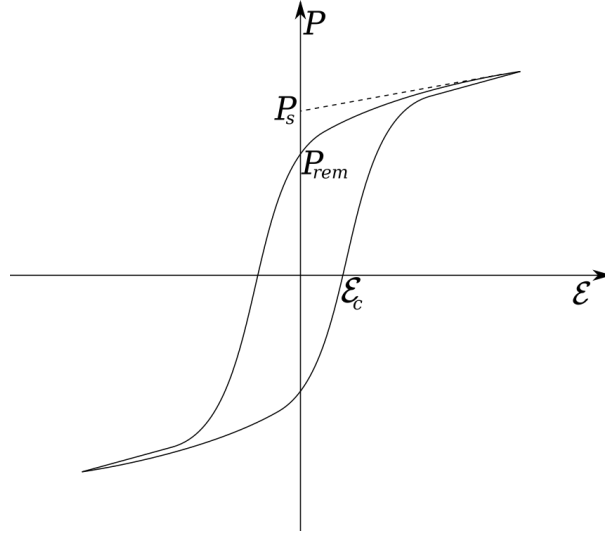


Figure 2.2: A schematic ferroelectric hysteresis loop. The coercive field $\mathcal{E}_c$, remanent polarisation P_{rem} and spontaneous polarisation P_s are labelled.

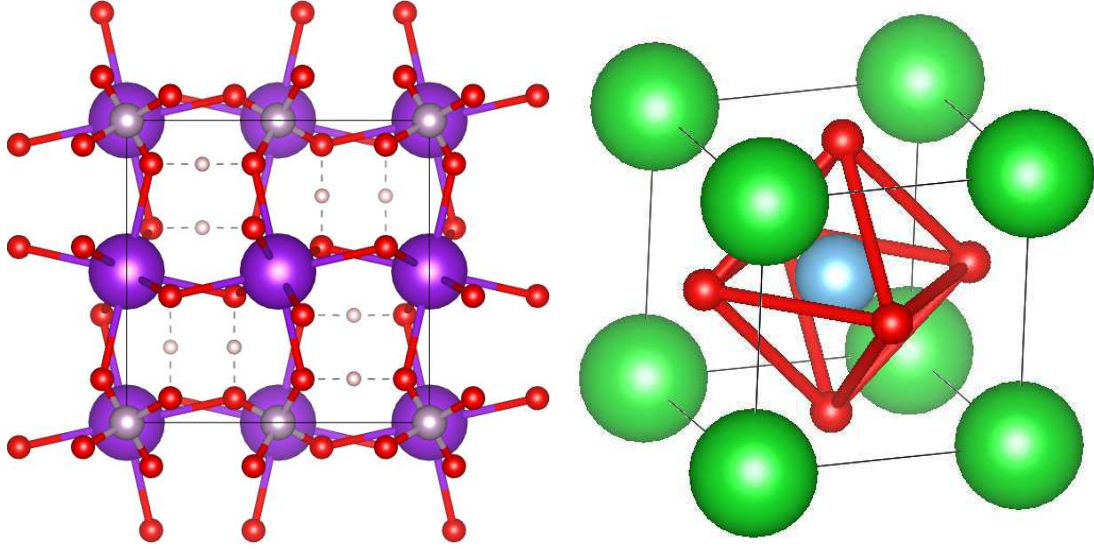
experimentally, despite the multiple domain states which are much easier to observe coexisting in a single sample of the material.

2.1.1 Order-disorder and displacive phase transitions

A ferroelectric exists in phase G at high temperature and in phase F at low temperature. The temperature that divides the two phases is known as the Curie temperature, T_C . The structural phase transition that occurs at T_C can be described as having *order-disorder* or *displacive* character [10]. For order-disorder transitions, the microscopic dipoles which aggregate to produce the macroscopic polarisation of phase F are randomly disordered in a real sample of the material in phase G . The ions associated with these dipoles make thermally activated jumps between local minima of their potential energy surface. It is only the average positions of the ions within each unit cell that are associated with the point group G . This disorder is lost in phase F , the dipoles align, and $\mathbf{P} \neq 0$.

An example of an order-disorder ferroelectric is potassium dihydrogen phosphate KH_2PO_4 (KDP) [10, p.304]. Apart from the K-atoms, the structure of KDP involves PO_4 tetrahedra to which protons are covalently bonded and hydrogen bonded (H-bonded). This structure is illustrated in Figure 2.3a. Although the average atomic positions in KDP's parent phase satisfy the point group $\bar{4}2m$, the protons frequently jump between two potential wells located $\sim 0.04\text{nm}$ apart [10, p.305].

On the other hand, the atoms in the parent phase of a material which undergoes a displacive phase transition oscillate about a single minimum of the potential energy surface which truly does satisfy the point group G . During the phase transition, the location of this minimum is displaced, hence the name. An example of a ferroelectric that undergoes a displacive transition is lead titanate PbTiO_3 (LTO) [10, p.248]. In its parent phase, LTO possesses the perovskite crystal structure, which has the cubic point group $m\bar{3}m$. This is illustrated in Figure 2.3b.



(a) A c -axis view of the structure of potassium dihydrogen phosphate where H-atoms are white, P-atoms grey, K-atoms purple, and O-atoms red. (b) The crystal structure of a perovskite material with chemical formula ABX_3 , where A-atoms are coloured green, B-atoms are coloured blue-grey, and X-atoms coloured red.

Figure 2.3: Illustrations of two ferroelectric crystals in their non-ferroic phases.

2.2 Theoretical approaches

2.2.1 Landau theory

Since ferroelectricity was discovered, a number of theories have been developed in order to understand the phenomenon. Naturally, the first attempts to understand ferroelectricity focused on explaining the macroscopic behaviour, since this was the easiest to measure. Landau theory was such an attempt, and was originally developed to understand ferromagnetic phase transitions. However, as noted in Section 2.1, ferromagnetic and ferroelectric phase transitions both involve the loss of structural symmetry. Therefore, it is perhaps understandable that the same macroscopic theory can be used to understand them both. Mueller [11] and Devonshire [12, 13] were the first to apply Landau theory to understand ferroelectric transitions (Rochelle salt and barium titanate, respectively) in a phenomenological way.

The theory assumes that near T_C , an appropriate free energy F can be Taylor expanded in the system's *order parameter*, which quantifies the system's loss of symmetry from phase G to F [14]. For a *proper ferroelectric*, this is the polarisation. (This contrasts with an *improper ferroelectric* for which distinct pairs of domain states may have the same polarisation, and so the polarisation does not fully characterise the loss of symmetry.) Other thermodynamic variables such as temperature T and pressure p are parameters for the expansion coefficients. Landau theory exploits the fact that the free energy must be invariant to the symmetry transformations of G to eliminate polynomial terms which do not satisfy this condition. For a uniaxial ferroelectric, this means that the free energy density, expanded to sixth order, has the form

$$F(P; T, p) = \frac{1}{2}a(T, p)P^2 + \frac{1}{4}b(T, p)P^4 + \frac{1}{6}c(T, p)P^6 - P\mathcal{E}. \quad (2.3)$$

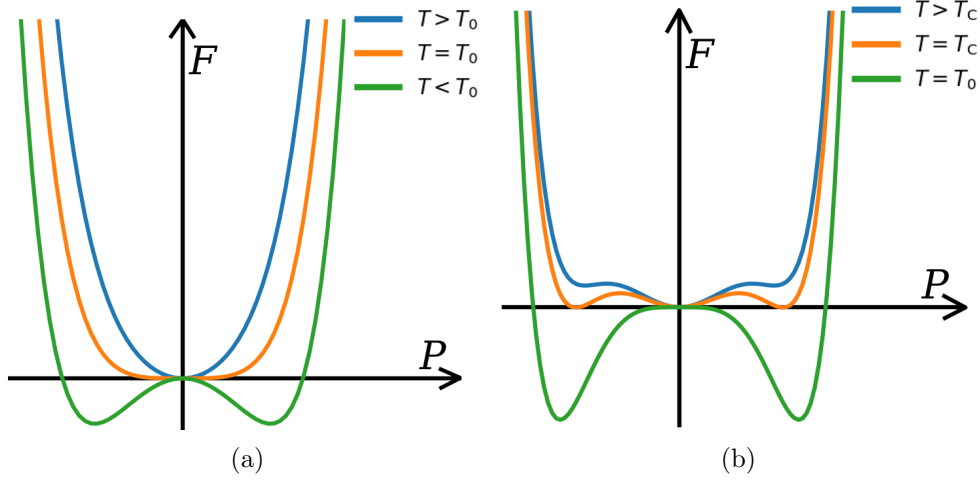


Figure 2.4: Schematic plots of the Landau free energy for ferroelectrics which undergo (2.4a) second and (2.4b) first order transitions.

The P value that is realised at a given T and p at thermodynamic equilibrium is the one which minimises F , that is

$$\left. \frac{\partial F}{\partial P} \right|_{P_0} = 0 \text{ and } \left. \frac{\partial^2 F}{\partial P^2} \right|_{P_0} > 0, \quad (2.4)$$

where P_0 is the equilibrium polarisation. Let us first consider the situation with $\mathcal{E} = 0$. As explained in Section 2.1, a ferroelectric transitions into one of a finite set of energetically equivalent domain states (2 in the uniaxial case). To recover this behaviour, we may assume that $b > 0$ for all T while a has the form

$$a = a'(T - T_0), \quad (2.5)$$

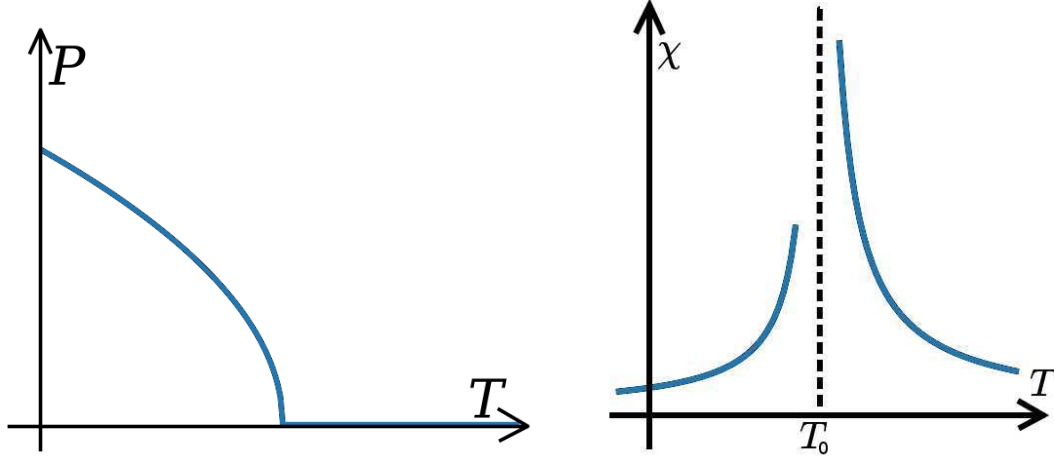
and so changes sign at $T = T_0$, where T_0 is a constant of the model. The shape of F for the cases of $T > T_0, T = T_0, T < T_0$ under this assumption is illustrated in Figure 2.4a.

For $T > T_0$ we find that F is minimised for $P_0 = 0$, whereas for $T < T_0$, F is minimised for

$$P_0 = \pm \sqrt{\frac{a'}{b}(T_0 - T)}. \quad (2.6)$$

Also, we see that as T is decreased to T_0 and beyond, P_0 varies continuously. This relationship is illustrated in Figure 2.5a. We see that the parameter T_0 of the quadratic coefficient a coincides with T_C .

When $\mathcal{E} \neq 0$, the inversion symmetry of $F(P)$ is broken and the domain state with P parallel to $\mathcal{E}$ falls in energy while the energy of the domain state with P anti-parallel to $\mathcal{E}$ rises in energy. However, if the system is initially in its domain state with $P > 0$ and the field is switched on to a small, negative amplitude, the thermodynamically favourable transition into the negative domain state will not spontaneously occur due to the energy barrier between the two states. The transition will spontaneously occur only if $\mathcal{E}$ exceeds the *thermodynamic coercive field*, $\mathcal{E}_{\text{crit}}$. The cases of $|\mathcal{E}| < \mathcal{E}_{\text{crit}}$ and $|\mathcal{E}| = \mathcal{E}_{\text{crit}}$ are illustrated in Figure 2.6. Based on Equation 2.4, the



(a) A schematic plot of the remanent polarisation vs temperature according to Landau-Devonshire theory for a ferroelectric which undergoes a second order phase transition. (b) A schematic plot of the dielectric susceptibility vs temperature according to Landau-Devonshire theory for a ferroelectric which undergoes a second order phase transition.

Figure 2.5: Illustrations of the T -dependent behaviour at a second order ferroelectric phase transition according to Landau theory.

polarisation of each domain state satisfies

$$\mathcal{E} = aP + bP^3. \quad (2.7)$$

When $|\mathcal{E}| < \mathcal{E}_{\text{crit}}$ this equation has three solutions for P , two of which have

$$\frac{\partial^2 F}{\partial P^2} > 0.$$

These correspond to the physically observable arms of the hysteresis loop. $\mathcal{E}_{\text{crit}}$ is the value of $\mathcal{E}$ for which there is a P satisfying

$$\frac{\partial^2 F}{\partial P^2} = 0.$$

This ultimately gives

$$\mathcal{E}_{\text{crit}} = \frac{2}{3\sqrt{3}} \sqrt{\frac{-a^3}{b}}. \quad (2.8)$$

For small $\mathcal{E}$, we can calculate the dielectric susceptibility. We find that

$$\chi = \begin{cases} \frac{1}{2a'(T_0-T)} & T < T_0 \\ \frac{1}{a'(T-T_0)} & T > T_0, \end{cases} \quad (2.9)$$

and diverges at $T = T_0$. This behaviour is illustrated in Figure 2.5b. The significant peak in χ that is experimentally observed in real ferroelectrics as $T \rightarrow T_0$ justifies the assumptions of Equation 2.5 and of $b > 0$. While P , the first order derivative of the free energy with respect to $\mathcal{E}$ is continuous in the neighbourhood of T_0 , χ the second derivative of the free energy with respect to $\mathcal{E}$ is not. Hence, transitions of this type are called *second order* transitions.

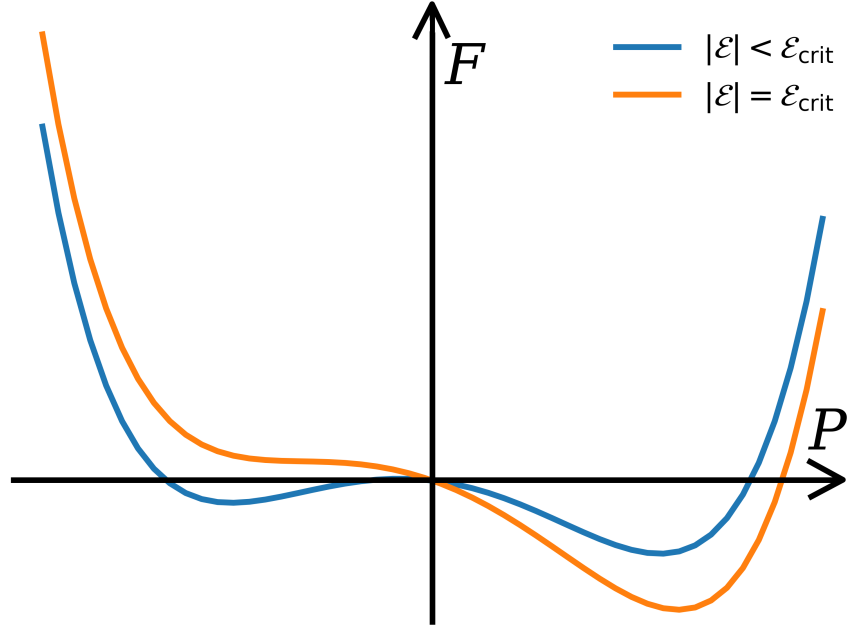


Figure 2.6: A schematic plot of the dielectric susceptibility vs temperature according to Landau-Devonshire theory for a ferroelectric which undergoes a second order phase transition.

On the other hand, if $b < 0$ for all T , the dependence of F and P on T is more complicated. We see from Figure 2.4b that for some T values there are two local minima in F with $P \neq 0$. As T is decreased, these minima decrease in energy, until they subceed the minimum at $P = 0$, at $T = T_C$. In this case, we clearly see that $T_C > T_0$, and that P jumps discontinuously at the transition. Hence, transitions of this type are called *first order*.

2.2.2 Statistical models: the first effective Hamiltonians

An important shortcoming of Landau-Devonshire theory is that it does not capture the spatial variation of P . An alternative approach to the theoretical understanding of ferroelectric phase transitions attempted to approximate the atomic Hamiltonian

$$H(\{\mathbf{r}_a\}) = \sum_a \frac{1}{2} m_a \dot{\mathbf{r}}_a^2 + V(\{\mathbf{r}_a\}), \quad (2.10)$$

where $\mathbf{r}_a$ is the position of atom a , and V is an interatomic potential. This was simplified by assuming that only one degree of freedom per unit cell (represented by a displacement coordinate ξ_l and conjugate momentum π_l of unit cell l) was significant to the transition, and that long range interactions could be approximated by bilinear couplings. This yielded an effective Hamiltonian [10, p. 18]

$$H = \sum_l \frac{1}{2} \pi_l^2 + V_{\text{loc}}(\xi_l) - \sum_{ll'} v_{ll'} \xi_l \xi_{l'}, \quad (2.11)$$

where V_{loc} is a local potential and $v_{ll'}$ is a coupling coefficient for unit cells l, l' . This approximation is invalid if multiple degrees of freedom per unit cell are relevant to the transition. This is shown in Chapter 5 to be the case for the material which is the focus of this thesis: croconic

acid. On the other hand, its simplicity makes it easier to analyse mathematically. If fluctuations of ξ_l from its mean are small, then a mean field approximation can be applied to the intercell interaction terms of Equation 2.11. The Hamiltonian is approximated as

$$H_{\text{mf}} = \sum_l \frac{1}{2} \pi_l^2 + V_{\text{loc}}(\xi_l) - v_l(0) \xi_l \langle \xi \rangle, \quad (2.12)$$

where

$$v_l(0) = \sum_{l'} v_{ll'}, \quad (2.13)$$

and $\langle \dots \rangle$ denotes a statistical average. This allows the problem to be separated into N_{cell} independent non-interacting cells [10, p.25]. The simplicity of H_{mf} also allows it to be physically interpreted more easily. For example, if the local potential V_{loc} is assumed to have a quartic form, then we find in a classical statistical mechanical analysis that [10]

$$k_{\text{B}} T_{\text{C}} = v_l(0) \langle \xi^2 \rangle, \quad (2.14)$$

where k_{B} is Boltzmann's constant. On the other hand, if V_{loc} is a deep double-well potential, then a quantum mechanical analysis is feasible. Experimental evidence suggested that the protons in KDP (introduced in Section 2.1.1) experience such a potential [15] between adjacent PO_4 tetrahedra. Such a system can be well approximated by considering only its lowest 2 states [16, p. 126], one of which is symmetric and the other anti-symmetric. Their sum and difference are states where the proton is localised in the 'left' and 'right' wells respectively. This allows the *pseudospin* formalism to be applied. The effective Hamiltonian is expanded in a basis of the 'left' and 'right' states for each proton in order to obtain an Ising model-like expression [16, p. 130]. The 'left' and 'right' states are partially delocalised and so allow the possibility of tunnelling between the potential wells.

It is well known that T_{C} increases from 123 K to 213 K upon deuteration of KDP (*i.e.* the protons are replaced by deuterons). Deuteration is captured in the pseudospin model by the assumed lower tunneling frequency of the deuterons due to their greater mass and spatial localisation. This enhances the order of their associated dipoles and raises the Curie temperatures of deuterated ferroelectric compounds [17].

The accuracy of the proton-tunneling model has been challenged more recently. The above-mentioned pseudospin models assume that the double-welled proton potentials are not affected by the state of other nearby protons. Secondly, they do not explicitly account for the distortion of the PO_4 tetrahedra and K ions. A first principles study [18] has fostered doubt over this simple picture of protons and deuterons tunnelling independently of the other ions. Therein, it is argued that a picture of a cluster of atoms (e.g. a H_2PO_4 unit) collectively tunnelling through its Born-Oppenheimer potential barrier is more accurate. Upon deuteration, H-bond lengths increase and the potential energy surface (PES) of the entire cluster changes. It is clear that any future effective Hamiltonian for KDP must involve local coordinates that capture correlated motion of the heavier and lighter ions.

2.2.3 Atomistic models

More recently, especially with the advent of first principles methods such as density functional theory (explained in more detail in Chapter 4) microscopic models have become easier to construct and parameterise, and therefore more popular. They benefit from requiring fewer assumptions of the degrees of freedom that are important for the description of ferroelectricity, and can therefore provide more credible insights into polarisation switching mechanisms, which is the subject of this thesis. Effective Hamiltonians and interatomic potentials fall under this category. Examples of these models are described in Chapter 6.

2.3 Ferroelectric domains

2.3.1 Why do domains form?

As explained in Section 2.1, ferroelectric domain states are distinct but energetically equivalent phases with the point group F , whose microscopic structures are related by operations in the point group G . Distinct domains often coexist within a single sample of a real ferroelectric because it is energetically favourable to do so. This follows from a standard result of classical electrostatics, which is that the electric potential within a polarised dielectric can be interpreted as being due to bound charge within the bulk, of density

$$\rho_{\text{bound}} = -\nabla \cdot \mathbf{P}, \quad (2.15)$$

and on the surface, of density

$$\sigma_{\text{bound}} = \mathbf{P} \cdot \hat{\mathbf{n}}, \quad (2.16)$$

where $\hat{\mathbf{n}}$ is the surface normal. The boundary between two coexisting domains is called a *domain wall*. According to Equation 2.16, the net bound charge at a wall between domains with polarisation $\mathbf{P}_1$ and $\mathbf{P}_2$ is given by

$$\sigma_{\text{dw}} = (\mathbf{P}_1 - \mathbf{P}_2) \cdot \hat{\mathbf{n}}, \quad (2.17)$$

where $\hat{\mathbf{n}}$ points from domain 1 to 2. If we consider an ideal single-domain sample of a ferroelectric crystal, charge will accumulate at the surfaces which are normal to $\mathbf{P}$, according to Equation 2.16. The surface charge creates an electric field, called the *depolarising field*, which opposes the internal polarisation, raising the energy.

In extreme cases, especially in thin films, the depolarising field may be strong enough to prevent ferroelectricity altogether. However, the depolarising field can be screened if mobile charge carriers are available at the surface. This is possible if the ferroelectric is attached to a metallic electrode, or if the ferroelectric itself contains charged defects. A striking demonstration [19] of this was implemented on a heterostructure consisting of a SrTiO_3 substrate, on which a (metallic) SrRuO_3 layer was grown, which in turn was covered in a terminating PbTiO_3 layer. When the partial pressure of oxygen in the atmosphere in contact with the PbTiO_3 layer was high, the polarisation pointed upwards. Whereas when the oxygen partial pressure p_{O_2} was reduced, the polarisation pointed downwards. The negative charge at the free surface due to

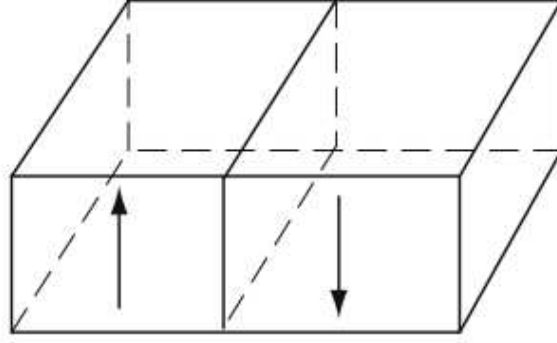


Figure 2.7: A 180 degree domain wall of a uniaxial ferroelectric. Taken from Figure 2.2.1a of Ref 3. Reproduced under a limited use license.

the downward facing polarisation was compensated by the positively charged oxygen vacancies which emerged due to the low $p\text{O}_2$ value.

Forming an inhomogeneous domain structure can also reduce the strength of the depolarisation field. This is especially the case when the domain walls, are *electrically compatible* [3], that is $\sigma_{\text{dw}} = 0$. For example, if the ferroelectric is uniaxial, meaning that the polarisation directions of its domain states are antiparallel, then the total surface charge can be minimised by the material adopting a structure of alternating domains separated by *180 degree domain walls*. One such domain wall is illustrated in Figure 2.7. This domain structure causes the depolarising field to alternate in direction, which significantly reduces its associated energy penalty. On the other hand, the domain wall itself also incurs a penalty because it breaks the symmetry of the domain states. Therefore, the ultimate domain structure of a ferroelectric sample is the result of an energy balance between the surface charge, the domain wall, and any available compensating charges [3, p.209].

2.3.2 Imaging domains

The ability of a ferroelectric to switch its polarisation is both scientifically and practically important. In order to understand the mechanism by which this occurs it is clearly necessary for researchers to be able to observe the spatially resolved polarisation state of a ferroelectric crystal. More recently new applications for ferroelectrics which depend on the precise domain structure have been developed. For example, periodically poled lithium niobate (PPLN) relies on a regular pattern of narrow ($\sim 10\mu\text{m}$) antiparallel domains to produce second harmonic generation of incident laser radiation [20]. For applications such as this, domain imaging methods are important for the precision of the domain pattern to be verified [21]. A number of methods have been developed over the years. They vary in their achievable spatial resolution and speed. Below, we briefly describe the principles that underpin some commonly used methods.

Piezoresponse force microscopy

Piezoresponse force microscopy (PFM) is a member of the family of scanning force microscopy-based methods. A scanning force microscope (SFM) includes a nanoscopic conductive tip connected to a flexible cantilever. As the tip is dragged across a surface, the microscopic peaks

and troughs cause the cantilever to be deflected. PFM additionally involves applying an oscillating voltage from the tip to each point on the surface of a ferroelectric sample. This induces a piezoelectric deformation which oscillates at the same frequency as the applied voltage and with a particular phase difference relative to the applied field. This phase difference is zero if the electric field induced by the tip within the sample is parallel to the polarisation in the initial part of the cycle, and 180 degrees if the electric field and polarisation are antiparallel [21, p.7].

The deflection of the cantilever is detected by reflecting a laser beam off the head of the cantilever onto a position sensitive detector, and measuring the position of the spot on its surface. The phase difference between the applied voltage and the output of the position sensitive detector is calculated using a lock-in amplifier. This device extracts the magnitude and phase difference of the component of a carrier wave within an input signal, relative to the carrier wave. Since it reflects the local domain state, a phase difference map can be used to create an image of the domain structure.

PFM is relatively slow and cumbersome since it requires the raster scanning of the sample multiple times in order to obtain a full image of its topography [21, p.4]. However, it can achieve lateral resolution of about 10 nm [21, p.5]. This significantly improves upon optical methods, whose resolution is limited by the wavelength of the (visible) light they use ($\sim 100\text{nm}$) [3, p.162].

Polarised light microscopy through birefringence

When an electromagnetic wave propagates through a linear dielectric medium, there are two directions of optical polarisation (which should be distinguished from dielectric polarisation $\mathbf{P}$) with which the wave can travel through the medium without this polarisation changing direction. These two directions can be found by using the indicatrix construction [22, p.308] [3, p.163]. The indicatrix is the representation quadric of the dielectric impermeability tensor $B_{ij} = \frac{d\epsilon_i}{dD_j}$, where $\mathbf{D} = \epsilon \mathbf{E} + \mathbf{P}$ is the electric displacement. It is an ellipsoid expressed as

$$\sum_{ij} B_{ij} x_i x_j = 1. \quad (2.18)$$

We denote the principle coordinate system of the indicatrix, i.e. the coordinate system in which B_{ij} is diagonal, by $\{\hat{\mathbf{e}}_j\}$, $j = 1, 2, 3$. In this system, the indicatrix is expressed as

$$B_1 x_1^2 + B_2 x_2^2 + B_3 x_3^2 = 1. \quad (2.19)$$

Consider a section of the indicatrix passing through the origin and whose normal is the wave direction $\hat{\mathbf{k}}$. It can be shown that this section is elliptical and that its semi-major and semi-minor axes are the abovementioned two special directions of optical polarisation [22, p.308]. The lengths of these axes are the inverse squares of the refractive indices experienced by waves polarised in the corresponding directions. For example, for a wave propagating with $\hat{\mathbf{k}} = \hat{\mathbf{e}}_1$ the appropriate ellipsoid would be

$$B_2 x_2^2 + B_3 x_3^2 = 1. \quad (2.20)$$

Furthermore, such a wave is generally not polarised parallel to either $\hat{\mathbf{e}}_2$ or $\hat{\mathbf{e}}_3$. It has components in both directions which will experience different refractive indices $n_2 \neq n_3$, in the absence of

the appropriate symmetry. This is referred to as birefringence. The presence of birefringence can be detected by placing a plate of a medium cut perpendicular to a principal axis between crossed polarisers [3, p. 164]. Without birefringence, light which is polarised by the first polariser and which is normally incident on and transmitted by the plate will be blocked by the second polariser. With birefringence, polarised light will have its polarisation state changed by the plate and some light will be transmitted by the second polariser.

B_{ij} is a second rank tensor which transforms like strain. Therefore, this technique can only be used to detect pairs of regions with different strain. For example, BaTiO₃ is an improper ferroelastic as well as being a proper ferroelectric. Therefore, 90 degree domain walls between *a*- (polar axis parallel to the plate's surface) and *c*-domains (polar axis perpendicular to the plate's surface) in the material can be imaged in this way [9].

A more subtle example is the imaging of 180 degree domain walls between antiparallel *c*-domains in BaTiO₃ [6]. In theory, since the strains of these domains are identical, so are their indicatrices. Therefore, 180 degree domain walls should not be visible using birefringence. However, it turns out that immediately after being switched, a region that is newly added to a *c*-domain does not have perfectly tetragonal symmetry [23] [3, p.175]. The wave normal no longer aligns with any of the principal axes of the indicatrix of such a region. Therefore, the newly switched region is visible in the birefringence image.

Before Miller and Savage demonstrated that 180 degree domain walls could be imaged in this way [6], Merz used a DC field parallel to the plate surface to strain the crystal and its associated indicatrices so that antiparallel domains could be imaged during polarisation reversal according to the mechanism first described above [9].

2.3.3 Neutron scattering

Neutron scattering is a method which is generally useful for probing the structure of condensed matter. By bombarding a sample with a neutron beam and measuring the scattered intensity as a function of the angle between the incoming and outgoing beams it is possible to deduce the crystal structure of a material. Neutrons interact mainly through the short-ranged strong nuclear force with atomic nuclei whose radii ($\sim 10^{-15}$ m) are very small compared to typical atomic separations ($\sim 10^{-10}$ m). Therefore, neutrons penetrate far into a sample ($\sim 10^{-2}$ m) before interacting [24]. This contrasts with x-rays, which typically penetrate between 10^{-7} and 10^{-4} m, since they interact through the long-range electromagnetic force with the more ubiquitous electrons in a material. This makes neutron scattering a more effective probe of a material's bulk structure.

As well as probing a crystal's static structure, it can also probe its dynamic structure in the form of the dispersion relationship between the frequency ω_μ and wavevector $\mathbf{q}$ of each of its phonon branches, indexed by μ . (The formalism of lattice dynamics which defines the function $\omega_\mu(\mathbf{q})$ is explained in Section 4.4.) In a neutron scattering experiment, the sum of a neutron's momentum and the crystal momentum is conserved to within a reciprocal lattice vector. Further, the combined energy of the neutron and crystal is also conserved. For neutron scattering processes which involve the emission or absorption of a single phonon by the neutron, these two conservation laws are enough to deduce $\omega_\mu(\mathbf{q})$ by measuring the initial and final

values of the neutron energy and momentum corresponding to peaks in the scattered intensity spectrum [25, p. 474].

Neutron scattering measurements have been historically vital to the study of ferroelectrics. They were used to confirm the theory that the ferroelectric phase transition in SrTiO_3 , and many other ferroelectrics, is due to the temperature dependence of the frequency of its lowest transverse optic (TO) phonon mode [26, 27]. Phonon frequencies are strictly temperature-independent in the harmonic approximation. Therefore, this behaviour is indicative of the significant anharmonicity of the crystal potential energy surface. Specifically, it was shown that

$$\omega_{\text{T}}^2 \propto T - T_{\text{C}},$$

where ω_{T} is the frequency of the temperature-dependent TO mode. This result means that as T is decreased from above T_{C} a ferroelectric becomes softer to deformations along the mode. At $T = T_{\text{C}}$ the crystal becomes unstable to such a deformation and relaxes by freezing in the soft mode distortion [28, p.109].

The method has also been used to deduce the structure of ferroelectric domain walls [29, 30]. In general, the loss of translational symmetry in an initially periodic crystal leads to diffuse scattering [24, p.46]. The peaks of the scattered neutron intensity in reciprocal space become less sharp. The presence of a domain wall can be interpreted as such a loss of translational symmetry in the direction normal to the wall. Ref 30 develops and applies a model of a ferroelectric domain wall which shows that in the direction normal to a single domain wall, the Bragg peaks in the scattered intensity spectrum are split, and are each surrounded by broad wings to form a continuous ridge instead of being discretely isolated. Further, the scattering intensity is modulated by an oscillatory term whose frequency can be used to deduce the domain wall width. The model was used to estimate the width of domain walls in KDP to be two unit cells.

2.4 Polarisation switching mechanisms

2.4.1 Experimental observations of polarisation switching

The most theoretically simple example of switching involves an ideal monocrystalline uniaxial ferroelectric, because the polar axis is constant throughout the material. This contrasts with a polycrystalline material whose polar axis varies in orientation for different grains in the material. The simplicity of the former means that experiments are often designed for ferroelectric single crystals so that their results can be compared to the theoretical predictions of polarisation switching in order to test these theories.

If we assume an initial single domain state, and that the external electric field is antiparallel to $\mathbf{P}$, the polarisation switching process can be basically described in two main steps [3, p.351].

Firstly, new domains are nucleated whose polarisation is parallel to $\mathcal{E}$. These nuclei rapidly extend along the polar axis due to the large surface charge – according to Equation 2.17 – associated with head-to-head domain walls for which one of $\mathbf{P}_1$ and $\mathbf{P}_2$ is parallel to $\hat{\mathbf{n}}$ while the other is anti-parallel. This is followed by the sideways motion of domain walls such that

the nucleated domains grow and coalesce.

Merz made the first measurements of polarisation switching in barium titanate BaTiO_3 [9]. He specifically measured the switching current through a BaTiO_3 -filled ferroelectric capacitor upon the application of square voltage pulses. He repeated this for a number of pulse amplitudes such that the electric field varied up to a magnitude of ~ 14 kV/cm and found that the peak switching current i_{max} was related to the electric field $\mathcal{E}$ according to

$$i_{\text{max}} \sim \exp\left(-\frac{\alpha}{\mathcal{E}}\right), \quad (2.21)$$

where α is a constant. He also noted that for his crystal, there was very little sideways motion of domain walls. Instead, the polarisation was switched mostly by the nucleation of narrow ($\sim 1\mu\text{m}$) domains, which rapidly grew between the two electrodes.

Miller and Savage made the first measurements of domain growth velocity in BaTiO_3 [6, 7]. Specifically, they used birefringence imaging to measure the velocity of the walls surrounding square domains in barium titanate plates with thicknesses between 2×10^{-3} cm and 3×10^{-2} cm. They did observe sideways domain wall motion and attributed the difference between their results and Merz's to the large DC field parallel to the plate surface that Merz used to strain his crystal, as described in Section 2.3.2. Miller and Savage used a similar range of electric field values to Merz, and found that the domain wall velocity v and $\mathcal{E}$ obeyed a similar relationship to Merz's law

$$v = v_{\infty} \exp\left(-\frac{\delta}{\mathcal{E}}\right), \quad (2.22)$$

where v_{∞} and δ are constants.

They also found that the values of these constants depended on a number of extrinsic properties of the system. For example, they initially used liquid electrodes (LiCl solution) to apply the field, which they later replaced with Au films evaporated onto the surfaces of the BaTiO_3 plate in order to compare their results to other literature which used solid electrodes such as this. They found that with all other conditions held equal, the domain wall velocity was greater with liquid electrodes than with solid electrodes [6]. Like Merz, they found that the domain wall velocity in thinner plates is generally lesser than in thicker plates. Specifically, they both found that δ of Equation 2.22 (and α of Equation 2.21) was related to the plate thickness d according to

$$\delta = \delta_{\infty}\left(1 + \frac{d_0}{d}\right), \quad (2.23)$$

where d_0 and δ_{∞} are constants [6, 31].

Stadler and Zachmanidis carried out polarisation switching experiments on BaTiO_3 with $\mathcal{E}$ between 2 and 450 kV/cm [32]. In contrast to the exponential Merz's law, this experiment found that for such large field strengths, $v(\mathcal{E})$ satisfies a power law

$$v = v_0 \mathcal{E}^{1.4}, \quad (2.24)$$

where v_0 is a constant. The departure of $v(\mathcal{E})$ from Merz's law suggests that polarisation switching in BaTiO_3 proceeds by a different mechanism under high ($\gg 1$ kV/cm) fields to the mechanism under low fields. The best explanation of the difference between these two regimes

was provided by Burtsev and Chervonobrodov [33, p.98] and is recounted in Section 2.4.2.

2.4.2 Theories of polarisation switching

Miller and Weinreich were the first to propose an explanation for the relationship between domain wall velocity and the applied field in BaTiO₃ expressed in Merz's law [34]. The energy associated with displacing an ideally flat, 180 degree wall parallel to its normal in its entirety is a lattice-periodic function of the displacement in this direction. This is often referred to as the Peierls potential [3] to draw an analogy with the energy associated with displacing a dislocation in an elastic medium [35, p.213].

An applied field distorts the periodic Peierls potential. Below a critical field strength $\mathcal{E}^*$, the distorted potential still has local minima and maxima which prevent the domain wall from spontaneously moving across lattice planes. Thermally activated 'jumps' are required for domain wall motion to occur. Hence, the situation where $\mathcal{E} < \mathcal{E}^*$ is known as the activated regime. Conversely, the situation where $\mathcal{E} > \mathcal{E}^*$ is known as the non-activated regime. Qualitatively different behaviours in the two regimes are found.

The rate of thermally activated 'jumps' of the entire domain wall is $\sim \exp\left(-\frac{U_P}{kT}\right)$ where U_P is the size of the Peierls barrier. It can be shown that when calculated for a macroscopically sized domain wall at room temperature, $\frac{U_P}{kT} \gg 1$. Therefore, the observed domain wall velocity cannot be attributed to jumps of the entire wall.

Miller and Weinreich proposed a more energetically favourable domain wall motion mechanism. Instead of the entire wall being displaced simultaneously, a small region within the antiparallel domain at the surface of the domain wall aligns itself with the applied field. The energy associated with this nucleus is a sum of three contributions [34]

$$\Delta U = -2P_s \mathcal{E} V_{\text{nuc}} + \sigma_w A + U_d, \quad (2.25)$$

where P_s is spontaneous polarisation, V_{nuc} is the nuclear volume, A is the extra domain wall area created by the nucleus, σ_w is the surface energy density of the wall, and U_d is the depolarisation energy, since there are faces of the nucleus which are not electrically compatible (see Section 2.3.1). The first term on the right hand side represents the change in the bulk energy, while the second term represents the increase in surface energy of the domain wall. Miller and Weinreich assumed that the nucleus is triangular, that it nucleates with its base in contact with an electrode, has height l , half-width a and thickness c , and is narrow ($l \gg a$). Assuming this geometry simplified the subsequent calculations which involved optimising ΔU with respect to l and a . This gave the dimensions and energy of the energetically optimal or *critical nucleus* [34]. The critical nucleus, denoted by ΔU^* , was found to satisfy

$$\Delta U^* \propto \frac{\sigma_w^{\frac{3}{2}}}{\mathcal{E}}. \quad (2.26)$$

Miller and Weinreich also assumed that the domain wall velocity was proportional to the nu-

cleation rate R_{nuc} . Therefore,

$$v \propto R_{\text{nuc}} \propto \exp\left(-\frac{\Delta U^*}{kT}\right) \propto \exp\left(-\frac{\delta(T)}{\mathcal{E}}\right), \quad (2.27)$$

as described by Merz's law.

Although Miller and Weinreich's theory explained the qualitative behaviour of $v(\mathcal{E})$, it is not quantitatively consistent with experimental observations. For example, based on experimental measurements of δ , whose σ_w -dependence is given by the theory, a value of σ_w which is an order of magnitude smaller than its experimentally observed value was predicted [3, p.397]. Furthermore, subsequent experimental measurements of δ for variable T showed that δ does not have the $\frac{1}{T}$ dependence predicted by the theory [36]. Finally, by design Miller and Weinreich's theory only explains the activated regime defined above. Experiments have shown that, for BaTiO₃ at least, $v(\mathcal{E})$ departs from Merz's law, transforming to a power law at large field (> 10 kV/cm) values.

Subsequent improvements upon Miller and Weinreich's theory attempted to reduce these shortcomings. For example, although the assumption of triangular nuclei with side faces which are perpendicular to the domain wall made the theory mathematically simple, this assumption was also arbitrary. Chervonobrodov and Burtsev constructed a functional for $\Delta U[z]$ in terms of the local displacement $z = z(x, y)$ of the nucleus relative to the unperturbed wall, where (x, y) refers to a position on the domain wall [33]. They optimised this functional with respect to z to obtain ΔU^* and found that the critical nucleus is elliptical, and has slanted faces. This contrasts starkly with the Miller and Weinreich assumption. Moreover, Chervonobrodov and Burtsev's theory predicted a σ_w value which agrees with experimental values to within an order of magnitude.

As described in Section 2.4.1, $v(\mathcal{E})$ transforms to a power law (Equation 2.24) for large ($\mathcal{E} \gg 1$ kV/cm) fields. Chervonobrodov and Burtsev also explained why $v(\mathcal{E})$ transforms by noting that the Miller and Weinreich theory is only valid when the motion of the entire domain wall in unison is kinetically prohibited due to the Peierl's potential barrier (which necessitates the nucleation of critical nuclei) i.e. in the activated regime, $\mathcal{E} < \mathcal{E}^*$ [33, p.98]. In the non-activated regime $\mathcal{E} > \mathcal{E}^*$, the entire wall can move in unison, and is only hindered by a frictional interaction with the lattice.

The dynamics of a domain wall, which is limited only by its interaction with the lattice, was studied theoretically by Collins et al [37]. They parametrised the state of a general uniaxial ferroelectric crystal with the local amplitude of a single soft mode associated with the ferroelectric distortion, and constructed its equation of motion:

$$\zeta \frac{\partial^2 u}{\partial t^2} + \eta \frac{\partial u}{\partial t} + \alpha u + \beta u^3 - \delta \frac{\partial^2 u}{\partial x^2} = R(x, t) + e^* \mathcal{E}, \quad (2.28)$$

where e^* is an effective charge of the plane of atoms displaced by the soft mode at position x along an axis which is perpendicular to the polar axis, and $\zeta, \eta, \alpha, \beta$ and δ are all constants. On the left hand side, the first term captures the inertia of these mobile atoms; the third and fourth terms capture the conservative interaction between the soft mode and the crystal; the fifth term is the force due to the gradient energy, which penalises a deviation from the homogeneous,

monodomain state. As well as this conservative force on u , lattice vibrations apart from the soft mode are coupled to the latter in a non-conservative way. The second term on the left hand side represents the dissipative, frictional interaction between u and these lattice vibrations, while the first term on the right hand side is a random, fluctuating force which models the set of vibrations that non-conservatively couple to the soft mode as a thermal bath. This is characteristic of Langevin dynamics. Finally, the second term on the right hand side is the force on u due to an external field.

They find an exact solution for the thermal average $\langle u(x, t) \rangle$. This solution moves with a velocity v which satisfies

$$v = \frac{3(P_+ + P_-)v_0^2}{P_S \lambda t_{\text{th}}} \left[1 - \frac{v^2}{v_0^2} \right]^{\frac{1}{2}}, \quad (2.29)$$

where $\lambda = \eta/\zeta$, $P_{\pm}$ is the polarisation of the positive (negative) domain state (which depends on $\mathcal{E}$) according to Landau theory, $v_0 = \sqrt{\frac{6}{\zeta}}$ is a critical velocity defined by the gradient energy term of Equation 2.28, and t_{th} is the theoretical thickness of a static domain wall. The solution in Ref 37 shows that

$$-\frac{P_+ P_- (P_+ + P_-)}{P_S^3} = \frac{2}{3\sqrt{3}e^*} \frac{\mathcal{E}}{\mathcal{E}_{\text{crit}}},$$

which, when combined with Equation 2.29, gives [3]

$$v = \mu e^* \mathcal{E}, \quad (2.30)$$

where

$$\mu = \frac{3t_{\text{th}}}{2\eta P_S}, \frac{P_S^2}{|P_+ P_-|} \left[1 - \frac{v^2}{v_0^2} \right]^{\frac{1}{2}}. \quad (2.31)$$

In the low field ($\mathcal{E} \ll \mathcal{E}_{\text{crit}}$) regime, μ is practically constant, predicting a linear relationship between v and $\mathcal{E}$ in this regime. However, when $\mathcal{E} \sim \mathcal{E}_{\text{crit}}$ we can identify two different behaviours, which depend on whether v_0 is reached before $\mathcal{E}_{\text{crit}}$ or beyond [3]. Let v_m denote the velocity where $\mathcal{E}_{\text{crit}}$ is reached. If $v_m \ll v_0$, then $\left[1 - \frac{v^2}{v_0^2} \right]^{\frac{1}{2}} \approx 1$ at all field strengths below $\mathcal{E}_{\text{crit}}$, and

$$\mu = \frac{P_S^2}{|P_+ P_-|} \mu_0, \quad (2.32)$$

where μ_0 is a $\mathcal{E}$ -independent constant. In the range $0 < \mathcal{E} < \mathcal{E}_{\text{crit}}$, $\frac{P_S^2}{|P_+ P_-|}$ increases from 1 to $\frac{3}{2}$. This effectively means that Equation 2.30 could be observed as a power law relationship with an exponent slightly greater than 1.

On the other hand, if $v_m \gg v_0$, then at high field values which are still below $\mathcal{E}_{\text{crit}}$, v is comparable to v_0 and the factor $\left[1 - \frac{v^2}{v_0^2} \right]^{\frac{1}{2}} < 1$. It, rather than $\frac{P_S^2}{|P_+ P_-|}$, determines this high field behaviour. In this case, Equation 2.30 could be observed as a power law relationship with an exponent slightly less than 1. Hence, the theory of Ref 37 explains the power law relationship between v and $\mathcal{E}$ which has been previously observed, as described in Section 2.4.1.

In spite of the plausibility of this explanation, Ref 37 is somewhat unsatisfactory since the theory uses the continuum approximation, which implicitly assumes that the soft mode amplitude varies on a length scale much greater than the lattice parameter parallel to the x -axis

[30]. For many ferroelectrics, however, experimental measurements and theoretical calculations suggest that this assumption is invalid [30]. As a result, the observed power law of ferroelectric domain wall velocity in the non-activated regime of switching is yet to be satisfactorily explained.

Chapter 3

Proton transfer ferroelectrics: the case of croconic acid

The subject of this thesis is polarisation switching in croconic acid, a proton transfer ferroelectric. In this chapter, we will firstly describe the family of proton transfer ferroelectrics, and the broader family of organic ferroelectrics with which it substantially overlaps. This will provide the context in which croconic acid may be considered.

3.1 Proton transfer ferroelectrics

A proton transfer ferroelectric is a ferroelectric in which polarisation switching is achieved by the transfer of protons between donor-acceptor atom pairs. The structures of these materials typically comprise networks of covalently bonded molecules, which are themselves connected with hydrogen bonds (H-bonds) via the protons which are transferred during switching. During polarisation switching, a covalent bond is broken and an adjacent one is formed for each proton as it is transferred.

Most proton transfer ferroelectrics are also organic, although there are notable exceptions such as potassium dihydrogen phosphate (KDP) which was introduced in Chapter 2. Although the original ferroelectric, Rochelle salt, is organic, inorganic ferroelectrics like lead zirconate titanate (PZT) and barium titanate (BTO) dominate practical applications. Such inorganic crystals are typically grown using methods, such as the flux method [38, 39] for single crystals and calcination for polycrystalline ceramics [40], which involve heating solid precursors to rather high temperatures (~ 1000 C). In spite of this energy intensity, the implementation of these methods has improved in efficiency and scale to the extent that PZT – the most popular, commercially utilised ferroelectric – can be produced easily and cheaply.

On the other hand, organic ferroelectric single crystals can be grown from solution at comparatively low temperatures. Further, they do not contain the toxic lead which makes the production of PZT environmentally unfriendly. This suggests the possibility for their competition with PZT and other inorganic ferroelectrics for use in some applications as an energy-efficient, environmentally-friendly alternative. They are often also mechanically flexible, which suggests the potential for them to be incorporated into wearable, biocompatible devices [41].

About one third of all organic ferroelectrics exhibit the proton transfer mechanism [42]. Apart from proton transfer, organic ferroelectrics exhibit a variety of different mechanisms. Polyvinylidene fluoride is a polymer ferroelectric whose structure comprises long chains of vinylidene fluoride ($\text{CH}_2\text{-CF}_2$) molecules. The C-F bond is polar, and so each molecule possesses a dipole which, in the material's β -phase, contributes towards a macroscopic spontaneous polarisation of $13 \mu\text{Ccm}^{-2}$ [43]. The polar polymer chains are rotated during polarisation switching. This rotation is sterically hindered, which leads to the high coercive field ($\sim 50 \text{ MV/m}$) of this material [43, p.151]. On the other hand, the substantial molecular motion associated with changes in its polarisation state also makes PVDF and its copolymers strong piezoelectrics [41]. Its Curie temperature $T_C = 70^\circ\text{C}$ is above room temperature. Consequently, active research into incorporating PVDF and its copolymers into devices, especially energy-harvesting transducers and nonvolatile memories is currently being pursued.

On the other hand, triglycine sulphate (TGS) is a proton transfer ferroelectric whose investigation has allowed us to test fundamental theories of ferroelectricity. After its ferroelectricity was first reported in 1956 [44], subsequent measurements of its dielectric constant at varying temperature implied a second order phase transition into its paraelectric state at 48°C [45]. Landau theory predicts that both the square of the spontaneous polarisation and the inverse dielectric susceptibility vary linearly with temperature near T_C of a second order transition [46, p.76]. In TGS, P_s satisfies this relationship. However, $1/\chi$ does not.

This disagreement was explained by the effect of 'domain clamping' on χ . This behaviour was originally proposed to explain measurements of the dielectric constant of BaTiO_3 as a function of an applied static biasing field which was set well above $\mathcal{E}_c$ [47, p.1562]. In a depolarised single crystal plate of BaTiO_3 – or, as the authors of Ref 45 argue, TGS – cut normal to the polar axis, the domain structure involves antiparallel domains with equal and opposite contributions from each opposed domain state. The electric displacement D and axial strain X obey

$$\begin{aligned} D &= dT + \epsilon \mathcal{E} \\ X &= ST + d\mathcal{E}, \end{aligned} \tag{3.1}$$

where T is axial stress, d is the piezoelectric constant, S is the elastic compliance and ϵ is the dielectric constant of the unstressed crystal. The antiparallel domains are clamped together and there is no strain relative to the static bias-deformed crystal. d has opposite values in antiparallel domains. Therefore, an additional perturbing field induces oppositely directed axial stresses to antiparallel domains:

$$T = -\frac{d}{S}\mathcal{E}. \tag{3.2}$$

Therefore,

$$\frac{D}{\mathcal{E}} = \epsilon_{\text{eff}} = \epsilon \left(1 - \frac{d^2}{\epsilon S} \right), \tag{3.3}$$

where ϵ_{eff} is an effective dielectric constant. The stresses effectively diminish the dielectric constant relative to its free, unclamped value. Domain clamping effects explain why measurements of the dielectric constant in the ferroelectric phase of TGS were smaller than predicted by Landau theory of second order phase transitions.

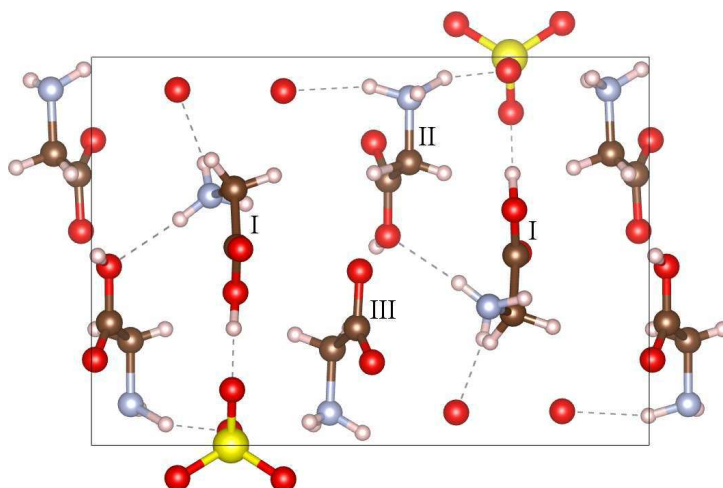


Figure 3.1: A *c*-axis view of the unit cell of triglycine sulphate. The three glycine molecules of the unit cell are given their conventional labels. S-atoms are yellow, C-atoms are brown, O-atoms are red, H-atoms are white, N-atoms are blue-grey. The structure was extracted from Ref 48.

As well as being a useful example of a ferroelectric with a second order transition, TGS and its doped variants have been effectively applied to the creation of radiation sensors for infrared spectrometers [49]. This application utilises the pyroelectric effect, which generates a current through a pyroelectric like TGS as a result of a temperature change caused by incident radiation. The finite polarisation retention time of TGS means that it gradually depolarises over time. This can be avoided by doping TGS with l-alanine such that around 0.1% of the glycine molecules are replaced [10, p.114]. Polarisation reversal in TGS involves the rotation of glycine I (as labelled in Figure 3.1) into its mirror image as well as the transfer of protons between glycines II and III. This is possible because the two H-atoms on the NH_2 group can swap their roles in H-bonding with neighbouring molecules. However, if glycine I is replaced by an l-alanine molecule, the H-atom connected to the α -C-atom is replaced with a CH_3 group. Due to its chirality, l-alanine cannot be changed into its mirror image (d-alanine) by rigid rotation [49, p.252-253] and so this rotation does not occur. The l-alanine molecules are, however, still dipolar and their presence creates an internal, irreversible electric field which subsequently prevents polarisation reversal [49]. L-alanine doped TGS has made pyroelectric radiation detectors more sensitive and reliable [49, p.257].

3.2 Croconic acid

3.2.1 Structure

As stated previously, croconic acid (CRCA) is a proton transfer ferroelectric. Its structure consists of a hydrogen bonded (H-bonded) network of $\text{C}_5\text{O}_5\text{H}_2$ molecules, one of which is illustrated in Figure 3.3. This structure has the symmetry of the $Pca2_1$ space group. Its primitive unit cell is orthorhombic and contains four molecules, which are arranged in folded, stacked sheets; the angle of this fold is 69.90 degrees [50]. The views down the three crystallographic axes are illustrated in Figure 3.2. The structure has two crystallographically unique protons. ‘Hinge’

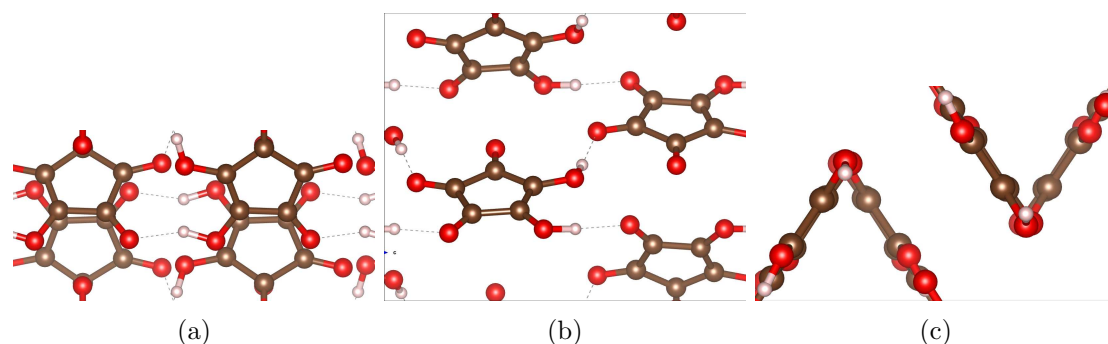


Figure 3.2: Views down the (3.2a) a -axis, (3.2b) b -axis, and (3.2c) c -axis of the primitive unit cell of croconic acid.

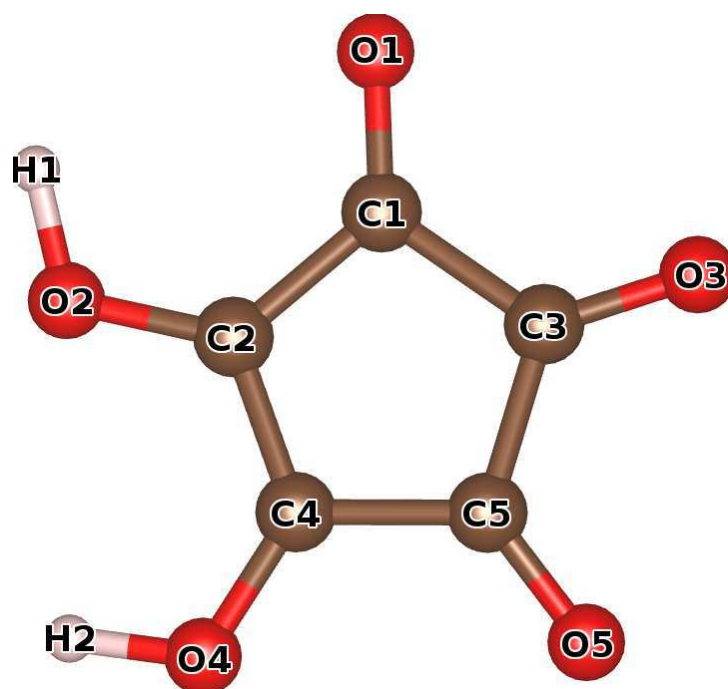


Figure 3.3: A single molecule of croconic acid. C-atoms are brown, O-atoms are red, H-atoms/protons are white. The hinge proton is labelled H2, while the terrace proton is labelled H1.

protons (defined in Ref 51) are surrounded by O-atoms O4 and O5 in adjacent CRCA molecules, as illustrated in Figure 3.3, while ‘terrace’ protons (also defined in Ref 51) are surrounded by O-atoms O2 and O3 in adjacent molecules, as illustrated in Figure 3.3. The pair of protons associated with each molecule is two covalent bonds away from a pair of C-atoms (C2 and C4 in Figure 3.3) which are connected through a π -bond. The three other C-atoms (C1, C3, and C5 in Figure 3.3) are each part of a keto group.

In the late 1980s and early 1990s, Gilli et al developed a theory to explain the empirical observation that for molecules containing the β -diketone fragment, the strength of intramolecular hydrogen bonds formed during the enolisation of these molecules was strongly correlated with the amount of electron delocalisation within the conjugated bonding system connecting the donor and acceptor atoms [52]. Their theory of *resonance-assisted hydrogen bonding* proposes that one of the resonance forms, of which the conjugated bonding system of a fragment

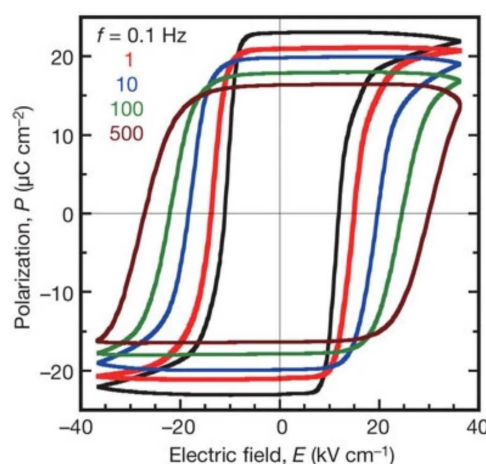


Figure 3.4: The measurements of $P(E)$ reported in Ref 2 at various applied field frequencies. The data demonstrate a hysteretic relationship between P and E that implies ferroelectricity. Reproduced under a limited use license.

such as β -diketone is a hybrid, possesses positive and negative partial charges on the donor and acceptor O-atoms respectively. The H-atom is additionally attracted to the acceptor and repelled from the donor, strengthening the H-bond [52, p.1026].

3.2.2 Ferroelectricity in bulk croconic acid

Ferroelectricity in croconic acid was discovered by Horiuchi et al [2], eight years after it had first been crystallised from a solution of HCl 1 M by Braga et al [50]. It was the first single-component proton transfer ferroelectric, and possesses a remanant polarisation ($30 \mu\text{Ccm}^{-2}$) which is the largest of all known organic ferroelectrics, comparable to that of BaTiO_3 [53]. Its coercive field of 14 kVcm^{-1} is small in comparison to organic ferroelectrics with more energetically prohibitive polarisation switching mechanisms such as TGS and PVDF described in Section 3.1. The measurements of P - E hysteresis in CRCA that are included in Ref 2 have been reproduced in Figure 3.4.

The large remanent polarisation of CRCA can be understood by comparing the structures of its two domain states. As the polarisation is reversed from one domain state to the other, each H-atom is displaced across the gap between its corresponding donor-acceptor pair, and the π -bond between the C-atoms which are two covalent bonds away from the covalently bonded H-atoms is redistributed to the opposite side of the molecule. The combination of these two transfers of charge in the crystal contributes to the large remanent polarisation [54, p.32223].

The identification of this mechanism as the source of CRCA's large remanent polarisation inspired the search for ferroelectricity in other organic crystals which also comprise molecules with conjugated π -bond systems which are connected through H-bonds [53]. At least seven, including CRCA, have been found. The ferroelectric phase of each of these materials is stabilised by the resonance assisted hydrogen bonds explained in Section 3.2.1. Accordingly, the Curie point of each of these materials is above room temperature. Since the proton transfer mechanism is not as sterically hindered as the molecular rotation exhibited by PVDF, the coercive fields of the seven PTFs are two orders of magnitude smaller than that of PVDF.

By calculating the electrostatic contribution to the remanent polarisation and comparing it to the remainder of the total for seven proton transfer ferroelectrics which have been discovered since CRCA, it has been shown that the redistribution of charge in π -orbitals provides the majority of the remanent polarisation in the known ferroelectrics with this mechanism [53].

As well as being important for the large remanent polarisation of CRCA, its π -orbitals also strongly influence its optical behaviour. Sawada et al [55] measured the polarised light reflectivity and second harmonic generation (SHG) spectra of CRCA plates which were cut normal to the b -axis. They derived a formula for the dielectric function from a Lorentz model which included transitions between the ground state and first two excited states. This model accurately fit the measured spectra of reflectivity, extinction coefficient, refractive index, and imaginary part of the dielectric constant. Concurrently, they performed DFT calculations on a 5-molecule cluster of CRCA. They identified the highest occupied (HOMO) and lowest unoccupied (LUMO) molecular orbitals which were localised to the central molecule, and calculated the transition frequency between the two orbitals using time-dependent density functional theory. The discrepancy between the experimental (3.63 eV) and theoretical (3.08 eV) transition energy values was attributed to the small size of the cluster which was meant to simulate a macroscopically-sized (~ 1 mm) crystal. Finally, they also fit the SHG spectrum to a two-level model which allowed them to deduce the difference in dipole moments of the HOMO and LUMO. Its large value was supported by a qualitative inspection of the DFT-calculated states. Transitioning between the two states flips the dipole of the central molecule. Hence, a large peak in the SHG response is found at the energy of this transition.

The importance of the π -orbitals to the polarisation mechanism of CRCA was demonstrated by Miyamoto et al [56]. They were able to modulate the intensity of second harmonic generation (SHG) of visible, red light from near-infrared input and the reflectivity of visible input by ‘pumping’ the crystal with a terahertz pulse. Notably, the displacement of protons induced by the pulse was negligible. Instead, the time-varying reflectivity behaviour was explained by the adiabatic perturbation of the highest occupied and lowest unoccupied π -orbitals by the terahertz field; the electrons transition between these states when the material is optically excited. The possibility of modulating the optical activity of CRCA on a ps timescale suggests that H-bonded systems containing non-centrosymmetric π -electron molecular orbitals could be applied to ultrafast optical modulation devices in the future.

The nonlinear optical activity of CRCA can also be used to image the domain structure of a CRCA crystal. In a study a laser, emitting pulses with a ~ 10 THz spectral width, was focused on a CRCA crystal [57]. Due to the difference frequency generation property of CRCA, a transmitted field in the terahertz frequency range was detected. The amplitude, direction and phase of the terahertz field was sufficient to deduce the direction and magnitude of the polarisation within a localised region of the crystal in the ab -plane. By raster scanning the plane with the laser and measuring the terahertz field at each point on the plane, an image of the domain structure could be obtained. This was repeated while varying an external DC field applied parallel to the crystallographic b -axis. After poling the virgin crystal once with a 30 kVcm^{-1} field, polarisation switching occurred in both directions successively by the motion of 180 degree domain walls [57, p.041101-4].

The principal feature of the domain structure of the virgin crystal was a tail-to-tail domain wall. The observation of such a domain wall implies the presence of mobile charges or immobile charged defects which are able to neutralise the bound charge created by this domain wall configuration (see Equation 2.17). Charged domain walls become pinned at the sites of these charges. The presence of such localised charge sources in CRCA single crystals is also the cause of the initial discrepancy between the measured spontaneous polarisation of CRCA and its theoretical value calculated using the modern theory of polarisation [58,59], according to a more recent study [53]. For ferroelectrics with an accessible Curie point, domain wall pinning sites can be removed by heating the crystal above T_C . However, it is also possible to remove pinning sites electrically by applying on the order of 10^4 bipolar rectangular electric field pulses with amplitude well over the coercive field ($33\text{--}55\text{ kVcm}^{-1}$) [53, p.4].

In practice, CRCA has no Curie temperature since it thermally decomposes at 450 K before it ever transitions to a paraelectric state. However, in contrast to most ferroelectrics, the spontaneous polarisation of CRCA *increases* as the temperature increases before thermal decomposition [2, p.791]. This unusual effect was explained by Mukhopadhyay et al [54,60]. They found that as temperature is increased, the hinge H-bonds lengthen and the hinge hydroxyl bonds shorten. Furthermore, the increase with increasing temperature of hinge proton displacements due to thermal fluctuations occurs mostly perpendicular to the polar c -axis. Therefore, the time-averaged dipole across each hinge H-bond increases, which increases the spontaneous polarisation as a result.

Although CRCA never transitions to a paraelectric phase, it is possible to deduce the symmetry of this phase by finding the minimal centrosymmetric supergroup of $Pca2_1$ from which the $Pca2_1$ structure can be obtained through the smallest atomic displacements (corresponding to point group F in Equation 2.2). This happens to be $Pbcm$. The calculation of the atomic positions of $Pbcm$ -CRCA is explained in Section 5.2.

In summary, CRCA is a proton transfer ferroelectric whose mechanism of polarisation also includes a large electronic component. The relative ease with which single crystals can be grown and its high, albeit hypothetical, Curie temperature makes it a useful testbed for investigations of this relatively rare form of ferroelectricity. These investigations suggest that in the future, ferroelectrics like CRCA could find practical applications, especially in nonlinear optics.

Chapter 4

Density functional theory

Density functional theory (DFT) is a formulation of quantum mechanics that uses the electron density of a many-electron system as its central quantity, instead of the wavefunction that is central to Schrödinger's wave mechanics. Its development has reduced the computational cost of quantum mechanical calculations by such an extent that some calculations which are otherwise unfeasible are made feasible. For example, it has enabled the computational study from first principles of systems, such as materials, whose properties are the result of their electronic structure. In this chapter we outline the theoretical foundations of DFT; its practical implementation in a number of software projects; and its application to the study of proton transfer ferroelectrics.

4.1 The Hohenberg-Kohn theorems

A material is a system consisting of positively charged nuclei and negatively charged electrons. In the Born-Oppenheimer approximation, these two systems are treated separately. The approximation is justified because nuclei are at least three orders of magnitude more massive than the electrons. Therefore, the nuclei move slowly and the electrons respond adiabatically to changes in the nuclei positions. The Hamiltonian of the subsystem of electrons in a potential due to a group of fixed nuclei can be expressed as

$$\begin{aligned} H &= T + V_{ee} + V_{\text{ext}} \\ &= \sum_{i=1}^N -\frac{\hbar^2}{2m_e} \nabla_i^2 + \sum_{i=1}^N \sum_{j<i}^N \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_{i=1}^N V_{\text{ext}}(\mathbf{r}_i), \end{aligned} \quad (4.1)$$

where T denotes the kinetic energy operator, V_{ee} denotes the electron-electron interaction operator, V_{ext} denotes the potential due to the fixed nuclei. N denotes the number of electrons of mass m_e and charge e in the system, whose positions are denoted by $\{\mathbf{r}_i\}$; The straightforward way to tackle this system would be to solve the time independent Schrödinger equation (TISE)

$$H\Psi(\{\mathbf{r}_i\}) = E\Psi(\{\mathbf{r}_i\}), \quad (4.2)$$

for its spectrum of eigenstates and eigenvalues. However, the TISE cannot be solved exactly for the vast majority of systems, and usually must be solved numerically. In order to do so, a computer must manipulate the $3N$ -dimensional many-electron wavefunction $\Psi(\{\mathbf{r}_i\})$. The memory requirements of storing such a highly multi-dimensional object are far beyond the potential capability of classical computers, except for very simple systems.

However, the possibility of an alternative approach, which formulates quantum mechanics in terms of the density – which, having only 3 dimensions, is more convenient to store and manipulate with a computer – is demonstrated by two theorems attributed to Hohenberg and Kohn [61]:

1. The external potential $V_{\text{ext}}(\mathbf{r})$ is determined to within a constant by the ground state density $n_0(\mathbf{r})$.
2. There exists a functional of the density $E[n]$ which is minimised by $n_0(\mathbf{r})$ and whose minimum is the ground state energy E_0 .

Theorem 1 can be proved simply by considering two systems with distinct external potentials $V_{\text{ext}}^{(1)}, V_{\text{ext}}^{(2)}$, but with the same ground state density n_0 . Assuming that the two ground states are non-degenerate,

$$\begin{aligned}
 E_0^{(1)} &= \langle \psi_0^{(1)} | T + V_{\text{ee}} + V_{\text{ext}}^{(1)} | \psi_0^{(1)} \rangle \\
 &< \langle \psi_0^{(2)} | T + V_{\text{ee}} + V_{\text{ext}}^{(1)} | \psi_0^{(2)} \rangle \\
 &= \langle \psi_0^{(2)} | T | \psi_0^{(2)} \rangle + \langle \psi_0^{(2)} | V_{\text{ee}} | \psi_0^{(2)} \rangle + \int d^3r n_0(\mathbf{r}) V_{\text{ext}}^{(1)}(\mathbf{r}) \\
 &= E_0^{(2)} + \int d^3r n_0(\mathbf{r}) [V_{\text{ext}}^{(1)}(\mathbf{r}) - V_{\text{ext}}^{(2)}(\mathbf{r})] \\
 E_0^{(1)} &< E_0^{(2)} + \int d^3r n_0(\mathbf{r}) [V_{\text{ext}}^{(1)}(\mathbf{r}) - V_{\text{ext}}^{(2)}(\mathbf{r})].
 \end{aligned} \tag{4.3}$$

Similarly,

$$E_0^{(2)} < E_0^{(1)} + \int d^3r n_0(\mathbf{r}) [V_{\text{ext}}^{(2)}(\mathbf{r}) - V_{\text{ext}}^{(1)}(\mathbf{r})]. \tag{4.4}$$

However, Equations 4.3 and 4.4 imply

$$E_0^{(1)} + E_0^{(2)} < E_0^{(1)} + E_0^{(2)},$$

an impossibility.

To prove Theorem 2, it must be clarified that $E[n]$ is a functional on the space of v -representable densities, *i.e.* those which are each the ground state density of a system with some V_{ext} . In this case, $E[n]$ is well-defined because, according to Theorem 1, n determines V_{ext} , which determines Ψ which determines E . The variational principle states that E is minimised by Ψ_0 which is only generated by n_0 . This argument also allows us to define density functionals from other quantities such as $T[n]$ and $V[n]$, which are calculated as expectation values with

Ψ . Theorem 2 implies that when $n = n_0$,

$$\begin{aligned} \delta \left[E[n] - \mu \left(\int d^3r n(\mathbf{r}) - N \right) \right] &= 0 \\ \Rightarrow \frac{\delta F[n]}{\delta n(\mathbf{r})} + v_{\text{ext}}(\mathbf{r}) &= \mu, \end{aligned} \quad (4.5)$$

where μ is a Lagrange multiplier, and the *universal functional* is

$$F[n] = T[n] + V_{\text{ee}}[n]. \quad (4.6)$$

4.2 The Kohn-Sham formalism

The exact form of $F[n]$ is unknown. However, DFT is practically useful thanks to a formalism that treats an auxiliary, non-interacting system that is related to the original interacting system described by Equation 4.1. This formalism was devised by Kohn and Sham shortly after the discovery of the Hohenberg-Kohn theorems [62]. It assumes that the ground state density of the interacting system is also non-interacting v -representable, *i.e.* it is the ground state density of a separate system with $V_{\text{ee}} = 0$. In this case, we may define a functional $T_{\text{s}}[n]$ as the kinetic energy of a non-interacting system of electrons whose ground state density is n . Non-interacting v -representability of n implies that

$$\begin{aligned} \delta \left[T_{\text{s}}[n] + \int d^3r v_{\text{s}}(\mathbf{r})n(\mathbf{r}) - \mu \left(\int d^3r n(\mathbf{r}) - N \right) \right] &= 0 \\ \frac{\delta T_{\text{s}}[n]}{\delta n(\mathbf{r})} + v_{\text{s}}(\mathbf{r}) &= \mu, \end{aligned} \quad (4.7)$$

for some potential v_{s} . If we define the exchange-correlation (xc) energy functional

$$E_{\text{xc}}[n] = F[n] - (T_{\text{s}}[n] + U[n]), \quad (4.8)$$

then Equations 4.7 and 4.5 are satisfied for the same n if and only if

$$v_{\text{s}}[n](\mathbf{r}) = v_{\text{ext}}(\mathbf{r}) + \frac{\delta E_{\text{H}}[n]}{\delta n(\mathbf{r})} + \frac{\delta E_{\text{xc}}[n]}{\delta n(\mathbf{r})}. \quad (4.9)$$

Like $F[n]$, the form of $E_{\text{xc}}[n]$ as a functional of n is unknown. However, the benefit of the manipulation described above is that the non-interacting system can be tackled by expressing n in terms of orbitals:

$$n(\mathbf{r}) = \sum_i |\psi_i(\mathbf{r})|^2, \quad (4.10)$$

which we demand to be orthonormal. Minimising the energy functional of the non-interacting system with respect to the orbitals under the orthonormality constraint gives:

$$\delta \left(T_{\text{s}}[n] + \int d^3r v_{\text{s}}(\mathbf{r})n(\mathbf{r}) - \sum_{ij} \lambda_{ij} \left(\int d^3r \psi_i^*(\mathbf{r})\psi_j(\mathbf{r}) - \delta_{ij} \right) \right) = 0, \quad (4.11)$$

which eventually leads to the Kohn-Sham equations:

$$\left(-\frac{\hbar^2}{2m} \nabla^2 + v_s[n](\mathbf{r}) \right) \psi_i(\mathbf{r}) = \epsilon_i \psi_i(\mathbf{r}). \quad (4.12)$$

$v_{xc}[n](\mathbf{r}) = \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})}$ represents the part of the electronic interaction that is not captured by its mean field treatment in the Kohn-Sham formalism. In practice, it must be approximated. However the ingenuity of the Kohn-Sham formalism is that relatively simple approximations of $v_{xc}[n](\mathbf{r})$ are applicable to many systems of interest. Some specific examples of these approximations are described in Section 4.3. The orbitals ψ_i depend on the potential $v_s[n](\mathbf{r})$, which has a functional dependence on the density, which depends on the orbitals through Equation 4.10. Therefore, the Kohn-Sham equations must be solved self-consistently. This means repeatedly solving the equations, updating the density based on the most recently solved orbitals each time. Convergence criteria for self-consistency vary among different DFT implementations. However, they typically involve computing a quantity from the orbitals such as the density, total energy or even the orbitals themselves, and demanding that the change in its value between successive iterations falls below some threshold.

4.3 Practical implementation

4.3.1 Periodic boundary conditions and Bloch's theorem

In the solid state, periodic boundary conditions are usually imposed on the simulation cell so that an infinite crystal of the system of interest can be simulated with a finite number of atoms. Bloch's theorem states that an eigenfunction of a Hamiltonian with a periodic potential can be expressed as

$$\psi_{n,\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} u_{n,\mathbf{k}}(\mathbf{r}), \quad (4.13)$$

where $u_{n,\mathbf{k}}(\mathbf{r})$ is a function, with the same periodicity as the periodic potential, corresponding to the eigenstate with band index n and wavevector $\mathbf{k}$ which belongs to the first Brillouin zone.

4.3.2 Basis sets

To solve the Kohn-Sham equations efficiently for a particular system, it is beneficial to express the orbitals in terms of a set of basis functions that are suited to the problem. In the following, we describe two commonly used examples from the large range of basis sets which are used in DFT simulations currently.

Plane waves

Plane waves with the same periodicity as the cell are often used as the basis set since wavefunctions expressed in this basis automatically satisfy these periodic boundary conditions. This means expanding $u_{n,\mathbf{k}}(\mathbf{r})$ like [63, p.238]

$$u_{n,\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{\Omega_{\text{cell}}}} \sum_m c_{n,m}(\mathbf{k}) \exp(i\mathbf{G}_m \cdot \mathbf{r}), \quad (4.14)$$

where the $\mathbf{G}_m$ are reciprocal lattice vectors, and Ω_{cell} is the volume of the primitive unit cell. Plane waves are eigenstates of the free electron gas. Therefore, beyond the range of the ionic potentials in a condensed matter system, eigenstates of the system are well approximated by the sum of a small number of plane waves [63, p.201,240]. The smoothness of the wavefunction far from ionic potentials is formalised in the pseudopotential approximation, which is outlined in Section 4.3.5. In principle, the sum in Equation 4.14 is infinite. However, in practical calculations the basis set must be truncated. When expressed in terms of the coefficients $c_{n,m}(\mathbf{k})$, the kinetic energy term of the Kohn-Sham equations becomes

$$\frac{\hbar^2}{2m_e} |\mathbf{k} + \mathbf{G}_m|^2.$$

The truncation of the basis set is usually achieved by defining a plane wave cutoff energy E_{cut} such that the $\mathbf{G}_m$ with $\frac{\hbar^2}{2m_e} |\mathbf{k} + \mathbf{G}_m|^2 > E_{\text{cut}}$ are left out of the basis set. The deeper the ionic potential, the larger plane wave cutoff energy is required to achieve accurate calculations.

Atom-centred basis functions

For molecular systems, basis sets of atom-centred functions are more suitable. Since molecules are small sets of bonded atoms, it is intuitive that electronic eigenstates of molecular systems have atomic-like structure. In contrast to plane waves, there is a wide variety of atom-centred basis sets.

The simplest type of atom-centred basis set, from which more sophisticated basis sets were developed, consists of Slater-type orbitals (STOs) whose radial parts have the form [64]

$$R^{(\text{STO})}(r) = Nr^{n-1}e^{-\zeta r}, \quad (4.15)$$

where n denotes an effective principal quantum number, N is a normalisation constant and ζ parametrises the width of the function. Slater type orbitals behave like the 1s eigenfunction of a hydrogenic atom ($\sim e^{-\zeta r}$) at large distances, which is the approximately correct behaviour.

Gaussian-type orbitals (GTOs), on the other hand, have radial functions of the form

$$R^{(\text{GTO})}(r) = Nr^l e^{-\zeta r^2}, \quad (4.16)$$

where l parametrises the angular momentum, ζ sets the width and N is a normalization constant. They are often preferred over STOs because overlap integrals of these functions centred on different atomic sites can be evaluated analytically. GTOs are often contracted into a sum in order to approximate STOs, in order to benefit from both the physically motivated behaviour of STOs and the computational simplicity of GTOs. Such *contracted Gaussian type-orbitals* have radial functions with the form

$$R^{(\text{CGTO})}(r) = Nr^l \sum_j c_j e^{-\zeta_j r^2}, \quad (4.17)$$

with contraction coefficients c_j which are chosen to suit the problem of interest. For example, they may be chosen by minimising the least squares fitting error relative to a chosen STO [65],

or by minimising the energy of the appropriate atomic ground state expressed in the basis [66]. Spherical harmonics are used as the angular parts of STOs and GTOs.

A *minimal* basis set includes one basis function per atomic orbital. For example, a minimal basis set for carbon, whose electrons occupy orbitals with

$$(n, l, m) \in \{(1, 0, 0), (2, 0, 0), (2, 1, -1), (2, 1, 0), (2, 1, 1)\},$$

would include 5 basis functions. However, minimal basis sets are not flexible enough to accurately calculate total energies and forces on molecular crystals such as croconic acid. Additional flexibility is achieved by adding multiple basis functions per atomic orbital. These are referred to as the multiple- ζ or nZ basis sets, where n denotes the number of basis functions per atomic orbital and ζ refers to widths of the STOs which the basis functions (typically CGTOs) are constructed to approximate. An nZ basis set for carbon, therefore, would have n radial functions for each of the aforementioned atomic orbitals (n, l, m) .

In atom-centred basis sets used to describe covalent bonding within molecules, additional basis functions with greater angular momentum than that of the occupied states in the corresponding isolated atom are also included, *e.g.* a basis function approximating a d state may be added to the basis set of a carbon atom in a molecular system. These additional basis functions are known as *polarisation functions* since they provide greater flexibility for the charge polarization of atoms within a molecular system to be described [67, p.189]. The inclusion of a polarization function in a basis set is represented by a “P” in its abbreviated name, *e.g.* “DZP” would imply a double- ζ basis set with polarization functions.

Finally, *diffuse* functions with small ζ values may also be included in atom-centred basis sets in order to capture electron density far away from the nuclei. This is important when calculating relative energies of configurations of a molecular system where bonds are not broken [68]. The inclusion of diffuse functions in a basis set is often represented by a “X”.

An important difference between plane waves and atom-centered basis sets is the fact that calculations with the former can be systematically improved by simply increasing the cutoff energy E_{cut} mentioned previously. In contrast, the variety of approaches to constructing a Gaussian basis set means that these basis sets cannot be systematically improved in the same way [69, p.245]. Instead, the suitability of an atom-centred basis set to a particular system must be depends on the chemistry of the system, and the property of the system which is to be calculated. For example, a popular choice for use with the Gaussian and plane waves method [70] described in Section 4.3.6 is the MOLOPT basis set [71] whose contraction coefficients and exponents were chosen to minimise an objective function which involved the total energy of a set of small molecules, as well as a term which penalised the creation of a basis set which would produce poorly conditioned overlap matrices during total energy calculations.

4.3.3 Brillouin zone sampling

In order to evaluate quantities such as the total energy and density for periodic systems, the appropriate functions must be integrated over the Brillouin zone, the primitive cell centred on

the origin of reciprocal space

$$\langle Q \rangle = \int_{\text{BZ}} \frac{d^3k}{\Omega_{\text{BZ}}} Q(\mathbf{k}). \quad (4.18)$$

The form of $Q(\mathbf{k})$ can usually only be known on a discrete set of points. Therefore, an integral like Equation 4.18 is approximated as a weighted sum of the integrand over a set of points, for which a number of selection methods have been devised. Perhaps the most popular of these methods is attributed to Monkhorst and Pack [72], which defines a grid of points indexed by $\mathbf{n} = (n_1, n_2, n_3)$, with arbitrary dimensions (N_1, N_2, N_3)

$$\mathbf{k}_{\mathbf{n}} = \sum_{i=1}^3 \frac{2n_i - N_i - 1}{2N_i} \mathbf{G}_i, \quad (4.19)$$

where the reciprocal lattice vectors are denoted by $\mathbf{G}_i$. In order to achieve accurate calculations of quantities using DFT, these calculations must be converged with respect to the density of the sampling grid.

4.3.4 Exchange-correlation functionals

As outlined in Section 4.2 the true xc potential is unknown and must be approximated in DFT calculations. Since the Kohn-Sham formalism was introduced, hundreds of different xc potential approximations have been designed [73]. They can be categorised based on the complexity of their dependence on the density, and their explicit dependence on the Kohn-Sham orbitals themselves. These categories were famously arranged in a hierarchy, imagined as a version of Jacob's ladder from the biblical story [74]. Several rungs of the ladder relevant to our investigation are described in the following subsection. These rungs only include factors of n and ∇n . However, above them one finds meta-generalised gradient approximations, which include factors of $\nabla^2 n$; and hybrid functionals, which include a fraction of the exact exchange energy density expressed in terms of the Kohn-Sham orbitals explicitly, in order to correct the spurious self-interaction from which the Hartree potential suffers [63, p.166].

Local density approximation

Since DFT was first discovered, many different approximations to the exchange-correlation energy functional have been invented. The first, local density approximation (LDA) was suggested by Kohn and Sham [62], and is defined by

$$E_{\text{xc}}^{\text{LDA}}[n](\mathbf{r}) = \int d^3r \epsilon_{\text{xc}}^{(\text{LDA})}(n(\mathbf{r})), \quad (4.20)$$

where $\epsilon_{\text{xc}}^{(\text{LDA})}(n)$ is the exchange-correlation energy per electron for a uniform electron gas of density n . The LDA is often still used today, especially for systems for which the density varies only weakly in space. A significant reason for its accuracy is that it corresponds to a real physical system, namely the homogeneous electron gas. Consequently, the LDA satisfies a number of constraints which the exact exchange-correlation functional can be shown to also

satisfy [69]. For example, the exchange energy is defined as

$$E_x[n] = \langle \Phi_n^{\min} | V_{ee} | \Phi_n^{\min} \rangle - U[n], \quad (4.21)$$

where $\Phi_n^{\min}$ appears in an alternative definition of $T_s[n]$ [69, p.13]

$$T_s[n] = \min_{\Phi \rightarrow n} \langle \Phi | V_{ee} | \Phi \rangle = \langle \Phi_n^{\min} | V_{ee} | \Phi_n^{\min} \rangle. \quad (4.22)$$

The correlation energy may then be defined as

$$E_c[n] = E_{xc}[n] - E_x[n].$$

It can be shown that $E_x[n] < 0$ and $E_c[n] < 0$ in both the LDA and exact forms of the corresponding quantities.

Generalised gradient approximation

For many systems, the LDA's assumption of a slowly varying density is invalid and the LDA is not accurate enough. The generalised gradient approximation (GGA) was developed to overcome this shortcoming. GGAs express the xc energy per particle as

$$\epsilon_{xc}^{(\text{GGA})} = \epsilon_{xc}^{(\text{GGA})}(n, s) = \epsilon_{xc}^{(\text{LDA})} F_{xc}(n, s), \quad (4.23)$$

where

$$s = \frac{|\nabla n|}{2k_F n}. \quad (4.24)$$

Different types of GGA use different forms for the enhancement factor F_{xc} . However, in general all GGAs correct the overbinding of atoms which is a well-known weakness of the LDA by producing exchange energies which are lower for isolated atoms than for condensed systems [63].

Van der Waals density functionals

Van der Waals interactions occur between atoms and molecules due to mutually induced dipoles. If two neutral molecules are separated by a large distance, electrons from the first will slightly repel electrons from the second. In a classical picture, each molecule induces a fluctuating dipole in the other which results in an attractive force between the molecules. In a quantum mechanical picture, the van der Waals interaction is an intrinsically nonlocal component of electronic correlation. The LDA and GGAs are local and semi-local approximations to the exchange and correlation energies, and so are not able to accurately capture the effects of van der Waals interactions which exist in supramolecular crystals like CRCA.

To overcome this, different schemes have been developed to capture van der Waals interactions such as semi-empirical pairwise potentials which depend on the separation of atoms [75, 76]. Recently, a range of nonlocal density functionals [77, 78] have also been developed. These functionals express the correlation energy as the sum of local and nonlocal parts

$$E_c^{(\text{vdW-DF})}[n] = E_c^{(\text{vdW-DF,loc})}[n] + E_c^{(\text{vdW-DF,nl})}[n], \quad (4.25)$$

with the nonlocal part $E_c^{(\text{vdW-DF,nl})}$ being expressed in terms of a kernel Φ like [77]

$$E_c^{(\text{vdW-DF,nl})} = \int n(\mathbf{r}_1) \Phi(q(n(\mathbf{r}_1), |\nabla n(\mathbf{r}_1)|), q(n(\mathbf{r}_2), |\nabla n(\mathbf{r}_2)|), r_{12}) n(\mathbf{r}_2) d^3r_1 d^3r_2, \quad (4.26)$$

where $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$. The evaluation of $E_c^{(\text{vdW-DF,nl})}$ involves a double spatial integral, whose computational cost scales as $\mathcal{O}(N^2)$, where N is the size of the numerical integration grid. A more efficient method for its approximation of $E_c^{(\text{vdW-DF,nl})}$ has also been developed [79]. It interpolates the kernel

$$\Phi(q_1, q_2, r_{12}) \simeq \sum_{\alpha\beta} \Phi(q_\alpha, q_\beta, r_{12}) p_\alpha(q_1) p_\beta(q_2),$$

on a logarithmic grid of q values, where $p_\alpha(q)$ are a set of interpolating functions. This approximated form for $E_c^{(\text{vdW-DF,nl})}$ can be evaluated in $\mathcal{O}(N \log N)$ time using the Fast Fourier Transform [80].

For proton transfer ferroics like CRCA and its sibling squaric acid, the revised version [81] of the Vydrov-Van Voorhis density functional [82] and the vdW-DF2 density functional [78] have been shown to give lattice parameters and bond lengths which are in significantly better agreement than LDA and the PBE GGA functionals [83–85]. The implementations of both of these functionals use the method described in Ref 79 to optimise their efficiency.

4.3.5 The pseudopotential approximation

Electronic structure calculations can be made more efficient by exploiting the fact that for many problems, only the variation in the valence electronic states is relevant. In a material, for example, only valence electrons take part in bonding. As atoms are displaced relative to each other, the core electronic states are not significantly affected. This idea is formalised by replacing the Coulomb potential of an atomic nucleus and its corresponding core electrons with a pseudopotential, which is the effective potential experienced by the valence electrons.

The valence eigenfunctions associated with pseudopotentials are often constructed to be identical to their corresponding all-electron valence eigenfunctions beyond a certain cutoff radius, depending on the pseudopotential construction scheme. Within the cutoff radius a *pseudowavefunction*, *i.e.* eigenfunction of the pseudopotential, does not possess the nodes which its corresponding all-electron wavefunction possesses due to its orthogonality to the core states. The pseudopotential itself is also generally softer than its all-electron counterpart. The lack of nodes in the pseudowavefunction and the softness of the pseudopotential mean that fewer basis functions are needed for electronic structure calculations. Without the pseudopotential approximation, the majority of useful plane wave-DFT calculations would be computationally unfeasible.

Norm-conservation

Pseudopotentials are not unique and many schemes have been developed for their construction. One of the more significant early milestones in the history of their development was the in-

vention of norm-conserving pseudopotentials. Hamann, Schlüter and Chiang (HSC) designed a method to construct pseudopotentials which satisfy particular properties that improve their transferability to different chemical environments. One of these is that each pseudowavefunction must match its all-electron counterpart beyond a cutoff radius which the user selects. To achieve this, HSC pseudopotentials are expressed as a sum of semi-local terms which each act on a different angular momentum component of the function being operated on [63, p.211]:

$$\hat{V} = \sum_{lm} |Y_{lm}\rangle V_l(r) \langle Y_{lm}|, \quad (4.27)$$

Each $V_l(r)$ is calculated by considering the corresponding all-electron valence orbital with angular momentum l . For HSC pseudopotentials the logarithmic derivative of each radial pseudowavefunction $\phi_l^{\text{PP}}(r)$ and its derivative with respect to energy must match their corresponding values for the all-electron wavefunction $\phi_l^{\text{AE}}(r)$. The matching of the first energy derivative means that the scattering phase shifts $\eta_l(E)$ for the l -components of plane waves with energy E are reproduced by the pseudopotential.

HSC also explain that the matching of the first energy derivative implies that the integral of the norm of the all-electron wavefunction is conserved in the pseudowavefunction. This norm conservation is important since it means that the electrostatic potential, due to the nucleus and the electronic charge enclosed within the cutoff radius, experienced by the all-electron wavefunction is the same for the pseudowavefunction. The transferability of a HSC pseudopotential can be optimised by reducing the cutoff radii. However, small cutoff radii also produce harder potentials, *i.e.* those having greater Fourier components with high frequency.

Separability

Subsequently, Kleinman and Bylander (KB) [86] found that they could construct separable, non-local pseudopotentials, which were ‘efficacious’ and more efficient to use than the HSC form. Firstly, they reformulate Equation 4.27 as

$$\hat{V} = V_{\text{local}}(r) + \sum_{lm} |Y_{lm}\rangle \delta V_l(r) \langle Y_{lm}|, \quad (4.28)$$

where $V_{\text{local}}(r)$ is a local, l -independent term, which tends to $\frac{Z_{\text{ion}}}{r}$ as $r \rightarrow \infty$ and $\delta V_l(r)$ is the remaining semilocal l -dependent part. KB found that the second term could be replaced by

$$\hat{V}_{\text{NL}} = \sum_{lm} \frac{|\delta V_l \psi_{lm}^{\text{PS}}\rangle \langle \psi_{lm}^{\text{PS}} \delta V_l|}{\langle \psi_{lm}^{\text{PS}} | \delta V_l | \psi_{lm}^{\text{PS}} \rangle}, \quad (4.29)$$

whose effect on each pseudowavefunction $\psi_{lm}^{\text{PP}}(r)$ was the same as that of the HSC equivalent.

If an electronic structure calculation is carried out using HSC pseudopotentials in a plane wave basis set of size n with the BZ sampled with a mesh of size m , matrix elements of the pseudopotential are evaluated as radial integrals of the form

$$\int dr j_l(|\mathbf{k} + \mathbf{G}|r) V_l(r) j_l(|\mathbf{k} + \mathbf{G}'|r) r^2,$$

where $\mathbf{k}$ is a vector in the BZ, $\mathbf{G}$ and $\mathbf{G}'$ are reciprocal lattice vectors and j_l is a spherical Bessel function. The number of such integrals at each l value which must be calculated is $\frac{mn(n+1)}{2}$. This can be prohibitive for certain systems like thin films as KB explain. However, if the non-local term of Equation 4.29 is used instead, the matrix elements are evaluated as products of pairs of radial integrals which separate the Bessel functions like

$$\int dr j_l(|\mathbf{k} + \mathbf{G}|r) \phi_l^{\text{PS}}(r) \int dr' j_l(|\mathbf{k} + \mathbf{G}'|r') \phi_l^{\text{PS}}(r'),$$

where ϕ_l^{PS} is the radial part of the pseudowavefunction ψ_{lm}^{PS} . The number of distinct radial integrals required for each l in this case is mn , which scales more favourably than the HSC case.

More recently, the PK pseudopotential was adapted by Goedecker, Teter and Hutter (GTH) [87]. They replaced the radial part of the projectors ψ_{lm}^{PS} in Equation 4.29 with Gaussian functions with adjustable parameters. In contrast to Equation 4.29, the nonlocal parts of GTH pseudopotentials are localised in both real and Fourier space. This makes their use more efficient for DFT implementations which use Gaussian basis sets, such as CP2K described in Section 4.3.6. However, they are also efficient to use with plane wave basis sets. Furthermore, GTH pseudopotentials are encoded by a small number of parameters, which contrasts with common implementations of KB pseudopotentials, which require the storage of large files containing the projector functions evaluated on a dense radial grid.

4.3.6 The Gaussian and plane waves method: Quickstep

As explained in Section 4.3, a large number of DFT packages that have been used to study materials use plane waves as their basis set. The computational cost of solving the Kohn-Sham equations with these packages scales like $\mathcal{O}(N^3)$, which makes the study of systems comprising $\sim 10^3$ electrons prohibitively expensive. To overcome this, alternative approaches have been developed to reduce the scaling of the computational expense.

The Quickstep [70] Gaussian and plane wave (GPW) algorithm implemented in CP2K is one such approach. The density is concurrently represented by both atom-centred Gaussian and plane wave basis sets. The plane wave representation is used to calculate the Hartree energy using the Fast Fourier Transform in $\mathcal{O}(N \log N)$ time, while the Gaussian representation is used to calculate the remaining parts of the Kohn-Sham energy functional. Representing the density with Gaussians means that these contributions to the Kohn-Sham matrix are sparse, since the overlap of atom-centred Gaussian functions becomes negligible once the distance between the centres is large enough.

Ultimately, the computational cost of calculating the Kohn-Sham – as well as the overlap and density – matrices scales linearly with system size. Although the original GPW method uses traditional, cubic-scaling methods to diagonalise the Kohn-Sham matrix, existing parallel implementations of these methods are efficient enough that for moderately sized systems, the majority of the computing time is spent constructing the Kohn-Sham matrix which, as just explained, is rather efficient.

In order to Fourier transform the density to calculate the Hartree energy, and to numerically compute some parts of the Kohn-Sham matrix elements (*e.g.* those involving the selected

pseudopotential), the Gaussians are sampled on a set of discrete, real-space grids with a range of resolutions. While physical quantities are converged with respect to cutoff energy and BZ sampling density when plane wave basis sets are used, for the GPW method physical quantities are converged with respect to the resolution of the grids. The resolution of the grid used to sample each Gaussian is parametrised by two input parameters. The first is the cutoff energy for a grid in reciprocal space whose real-space counterpart is the finest grid in the multi-grid. The second is a relative cutoff that determines which grid a particular Gaussian is mapped to. Each Gaussian is mapped to the coarsest grid for which the number of samples underneath that Gaussian is greater than or equal to the number of samples that the grid defined by this relative cutoff would have underneath a Gaussian of unit standard deviation [70].

4.4 Lattice dynamics

Interatomic interactions affect how a crystal lattice vibrates. The collective motions that emerge from these interactions also characterise the macroscopic behaviour of materials like ferroelectrics. DFT can be used to calculate these collective motions.

The Born-Oppenheimer approximation states that the dynamics of electrons in a material can be separated from the dynamics of the atomic nuclei. The electronic energy is parametrised by the atomic positions. From the perspective of the system of nuclei, this is a potential energy, whose function is often referred to as the potential energy surface (PES). We consider a supercell with dimensions (N_0, N_1, N_2) in terms of primitive unit cells. The primitive lattice vectors are denoted by $\mathbf{a}_j$ and the unit cell with its origin at $\sum_{j=1}^3 n_j \mathbf{a}_j$ in the supercell is denoted by $\mathbf{n}$. We assume periodic boundary conditions on the displacements within the supercell. We can approximate the energy near a reference state with atomic positions $\mathbf{R}^{(0)}$ by a Taylor expansion

$$E = E(\mathbf{R}^{(0)}) + \frac{\partial E}{\partial R_{\mathbf{n}ai}} X_{\mathbf{n}ai} + \frac{1}{2} \frac{\partial^2 E}{\partial R_{\mathbf{n}ai} \partial R_{\mathbf{m}bj}} X_{\mathbf{n}ai} X_{\mathbf{m}bj} + \dots \quad (4.30)$$

where $R_{\mathbf{n}ai}$ is position coordinate i of atom a in unit cell $\mathbf{n}$ and $X_{\mathbf{n}ai} = R_{\mathbf{n}ai} - R_{\mathbf{n}ai}^{(0)}$. For ferroelectrics, we are interested in reference states where the atomic forces vanish, *i.e.* $\frac{\partial E}{\partial X_{\mathbf{n}ai}} = 0$. If we neglect $\mathcal{O}(X^3)$ terms in the expansion, the equations of motion for the atoms becomes

$$M_a \frac{\partial^2 X_{\mathbf{n}ai}(t)}{\partial t^2} = - \sum_{\mathbf{m}bj} \Phi_{\mathbf{n}ai \mathbf{m}bj} X_{\mathbf{m}bj}(t), \quad (4.31)$$

where $\Phi_{\mathbf{n}ai \mathbf{m}bj} = \frac{\partial^2 E}{\partial R_{\mathbf{n}ai} \partial R_{\mathbf{m}bj}}$. To solve Equation 4.31, we assume an ansatz

$$X_{\mathbf{n}ai}(t) = \frac{1}{\sqrt{M_a}} U_{\mathbf{n}ai} \exp(-i\omega t), \quad (4.32)$$

and find that

$$\omega^2 U_{\mathbf{n}ai} = \sum_{\mathbf{m}bj} D_{\mathbf{n}ai \mathbf{m}bj} U_{\mathbf{m}bj}, \quad (4.33)$$

where $D_{\mathbf{n}ai \mathbf{m}bj} = \frac{\Phi_{\mathbf{n}ai \mathbf{m}bj}}{\sqrt{M_a M_b}}$. This is an eigenvalue equation with $3N_{\text{atom}}N_{\text{cell}}$ solutions, where

N_{atom} = number of atoms in the unit cell. Periodic boundary conditions can be satisfied if

$$U_{\mathbf{n}ai} = c_{ai}(\mathbf{q}) \exp(i\mathbf{q} \cdot \mathbf{R}_{\mathbf{n}}), \quad (4.34)$$

where $\mathbf{R}_{\mathbf{n}} = \sum_k n_k \mathbf{a}_k$ is the origin of the unit cell $\mathbf{n}$, which implies that

$$\omega^2 c_{ai}(\mathbf{q}) = D_{\mathbf{n}ai \mathbf{m}bj} \exp(i\mathbf{q} \cdot (\mathbf{R}_{\mathbf{m}} - \mathbf{R}_{\mathbf{n}})) c_{bj}(\mathbf{q}). \quad (4.35)$$

Translational invariance of $\mathbf{D}$ means that $D_{\mathbf{n}ai \mathbf{m}bj} = D_{\mathbf{0}ai \mathbf{m}-\mathbf{n}bj}$ so

$$\omega^2 c_{ai}(\mathbf{q}) = D_{\mathbf{0}ai \mathbf{m}-\mathbf{n}bj} \exp(i\mathbf{q} \cdot (\mathbf{R}_{\mathbf{m}} - \mathbf{R}_{\mathbf{n}})) c_{bj}(\mathbf{q}). \quad (4.36)$$

Now summing over $\mathbf{m}$ is the same as summing over $\mathbf{m}' = \mathbf{m} - \mathbf{n}$ so we have

$$\begin{aligned} \omega^2 c_{ai}(\mathbf{q}) &= \sum_{bj} \left[\sum_{\mathbf{m}'} D_{\mathbf{0}ai \mathbf{m}'bj} \exp(i\mathbf{q} \cdot \mathbf{R}_{\mathbf{m}'0}) \right] c_{bj}(\mathbf{q}) \\ \omega^2 c_{ai}(\mathbf{q}) &= \sum_{bj} D_{ai bj}(\mathbf{q}) c_{bj}(\mathbf{q}), \end{aligned} \quad (4.37)$$

where the expression in the square brackets is the dynamical matrix $D_{ai bj}(\mathbf{q})$. Equation 4.37 is another eigenvalue equation with $3N_{\text{atom}}$ solutions, each with a real eigenvalue ω^2 and which each depend on $\mathbf{q}$. For each of the N_{cell} $\mathbf{q}$ values that are compatible with the periodic boundary conditions, there are $3N_{\text{atom}}$ orthonormal solutions $\hat{\mathbf{e}}_{\mu}(\mathbf{q})$ which we index with $\mu = 0, \dots, 3N_{\text{atom}} - 1$ and which satisfy

$$\omega_{\mu}^2(\mathbf{q}) \hat{e}_{\mu ai} = \sum_{bj} D_{ai bj}(\mathbf{q}) \hat{e}_{\mu bj}(\mathbf{q}). \quad (4.38)$$

The general solution of Equation 4.31 is a superposition of these special solutions:

$$X_{\mathbf{n}ai}(t) = \frac{1}{\sqrt{N_{\text{cell}} M_a}} \sum_{\mathbf{q}\mu} Q_{\mu}(\mathbf{q}) \hat{e}_{\mu ai} \exp(i(\mathbf{q} \cdot \mathbf{R}_{\mathbf{n}} - \omega_{\mu}(\mathbf{q})t)). \quad (4.39)$$

For ferroelectrics, if the reference state is the structure of the high-symmetry phase, at least one of the modes at Γ *i.e.* $\mathbf{q} = \mathbf{0}$ has $\omega_{\mu}^2(\mathbf{0}) < 0$. The system is dynamically unstable to distortions in the corresponding directions $\hat{\mathbf{e}}_{\mu}(\mathbf{0})$.

The results of calculations of the Γ -point modes of *Pbcm*-CRCA are explained in Section 5.2. They were calculated using the finite differences method, which approximates

$$\Phi_{\mathbf{n}ai \mathbf{m}bj} \approx \frac{F_{\mathbf{m}bj}(X_{\mathbf{n}ai} = -h) - F_{\mathbf{m}bj}(X_{\mathbf{n}ai} = h)}{h}, \quad (4.40)$$

where $F_{\mathbf{m}bj}$ is the force in the j direction on atom b in unit cell $\mathbf{m}$. The method is implemented in the Phonopy software package [88], which provides the appropriate structures whose atomic forces should be calculated with a DFT package to utilise the method, and post-processes the output of these calculations in order to evaluate Equation 4.40.

An alternative method for the calculation of $D_{ai bj}(\mathbf{q})$ is density functional perturbation

theory (DFPT) [89–92]. In general, DFPT demonstrates ways to calculate the response of the ground state energy to perturbations such as atomic displacements and electric fields. It proceeds from conventional perturbation theory in quantum mechanics, and assumes that a perturbation, parametrised by a variable λ , is applied to a Hamiltonian. Quantities such as the wavefunction and energy are then expanded in powers of λ like

$$Q(\lambda) = \sum_{j=0}^{\infty} \lambda^j Q^{(j)},$$

where Q denotes an arbitrary quantity.

Central to the formalism is a pair of theorems, one which states that there exists a functional $\hat{E}^{(2n)}$ of the n th order wavefunction $\psi^{(n)}$

$$E^{(2n)} = \min_{\psi^{(n)}} \hat{E}^{(2n)} \left[\psi^{(n)}; \sum_{j=0}^{n-1} \lambda^j \psi^{(j)} \right],$$

which is minimised at the $2n$ th order energy $E^{(2n)}$, if the wavefunction up to order $n - 1$ is provided. The second theorem states that only the wavefunction up to order n is needed to determine the $(2n + 1)$ th order energy,

$$E^{(2n+1)} = E^{(2n+1)} \left[\sum_{j=0}^n \lambda^j \psi^{(j)} \right]. \quad (4.41)$$

The formalism does require specialisation to the case of Kohn-Sham DFT [92], however the principles still apply to this case. Explicit expressions have been found for the second order energy in response to mixed atomic displacements, *i.e.* $\Phi_{\mathbf{n}ai\mathbf{m}bj}$, in terms of the first order Kohn-Sham orbitals. The Born effective charge tensor

$$Z_{in}^a = V \frac{\partial P_i}{\partial X_{an}} = - \frac{\partial^2 E}{X_{an} \partial \mathcal{E}_i}, \quad (4.42)$$

where V is the simulation cell volume, P is the polarisation, X_{an} is the displacement of atom a in the n direction, and $\mathcal{E}_i$ is the amplitude of the electric field in the i direction can be cast as a second derivative of the energy with respect to mixed perturbations. Therefore, it can also be calculated using DFPT. Our results of these calculations for CRCA are described in Section 5.3.3.

4.5 The nudged elastic band method

The nudged elastic band method [93] is a popular way of numerically determining the MEP between two states of a system of interacting atoms, and is commonly used to investigate the mechanisms of processes like diffusion and molecular conformation. DFT can be used to calculate the interatomic forces required for these calculations. The MEP is defined as the path

with the lowest maximum energy which satisfies

$$\nabla V_{\perp}(\mathbf{R}) = (\mathbf{1} - \hat{\boldsymbol{\tau}}(\mathbf{R}) \otimes \hat{\boldsymbol{\tau}}(\mathbf{R})) \cdot \nabla V(\mathbf{R}) = 0, \quad (4.43)$$

for all atomic positions $\mathbf{R}$ along the path, where $\perp$ denotes the component of the vector that is perpendicular to the tangent $\hat{\boldsymbol{\tau}}(\mathbf{R})$ to the curve at that point.

The method works by discretising the path into a finite number of images or replicas. Each pair of adjacent images in the path is connected by a spring of zero unstretched length. In order to evolve the discretised path towards the MEP, the atomic positions of image j is incremented in the direction of the sum of two ‘nudged’ (*i.e.* projected) force contributions:

1. The component of the spring force that is parallel to the tangent to the path at that image. This force acts to evenly distribute the images along the path, while avoiding the generation of paths which ‘cut the corners’ of path segments along troughs in the potential energy surface (PES), which would otherwise be a source of error in the method’s MEP result.
2. The component of the Hamiltonian force that is perpendicular to the tangent at the image. This force propagates each image towards lower energy regions, without causing the images to become bunched up or spaced out, which would happen if the component parallel to the tangent was included.

This means that the positions are incremented by

$$\Delta \mathbf{R}_j = \alpha(-\nabla_{\perp} V(\mathbf{R}_j) + (\hat{\boldsymbol{\tau}}(\mathbf{R}_j) \otimes \hat{\boldsymbol{\tau}}(\mathbf{R}_j)) \cdot \mathbf{F}_j^{\text{spring}}), \quad (4.44)$$

where $\mathbf{F}_j^{\text{spring}}$ is the spring force on image j and α is a step size coefficient that can be adjusted.

4.6 Modern theory of polarisation

The spontaneous polarisation is the fundamental phenomenological quantity associated with a ferroelectric. It is defined as the dipole moment per unit volume, and this definition motivated the Clausius-Mossotti model for its theoretical calculation, which assumed that the polarisation was the sum of dipole contributions from discrete, polarisable units. However, quantum mechanics has revealed that in a real material, the electron density is distributed throughout each unit cell with the spatial periodicity of the primitive lattice. Therefore, it is impossible to unambiguously draw boundaries around discrete polarisation centres, as the Clausius-Mossotti model assumes.

Having accepted the delocalised nature of the electron density, one might also attempt to define the polarisation as the

$$\mathbf{P} = \frac{1}{\Omega} \int_{\Omega} d\mathbf{r} n(\mathbf{r}) \mathbf{r}, \quad (4.45)$$

where Ω is some chosen volume. This attempt also fails, however, precisely because our choice of volume would be arbitrary. Each choice from a continuum of possibilities would result in a different value of $\mathbf{P}$.

The solution to the problem of defining spontaneous polarisation in crystals was developed in the 1990s by Resta, King-Smith and Vanderbilt [58, 94]. The basic idea is that the absolute polarisation cannot be defined. Instead, one may only define quantities related to changes in polarisation, *i.e.* finite differences between discrete states and derivatives of polarisation with respect to variable fields. As well as being theoretically sound, it is also consistent with the experience of experimentalists who have only ever measured these types of quantities. Changes in polarisation between the two sides of a hysteresis loop gives twice the spontaneous polarisation value which is usually quoted. Derivatives of polarisation with respect to time, strain, and temperature give polarisation current, piezoelectric coefficient, and pyroelectric coefficient respectively.

Formally, the modern theory of polarisation expresses the change in polarisation between two states as the integral of the derivative of polarisation with respect to a parameter which interpolates between the two states. The parameter is defined to be 0 in the initial state and 1 in the final state. Therefore,

$$\Delta \mathbf{P} = \int_0^1 d\lambda \frac{\partial \mathbf{P}}{\partial \lambda}, \quad (4.46)$$

where λ is the aforementioned parameter. The approach to the calculation of $\frac{\partial \mathbf{P}}{\partial \lambda}$ then explicitly uses the Kohn-Sham formalism, which provides a set of occupied orbitals in the Bloch form of Equation 4.13. Ref 58 shows that

$$\frac{\partial \mathbf{P}}{\partial \lambda} = -\frac{ife}{8\pi^3} \sum_{n=1}^M \int_{\text{BZ}} d^3k \left\{ \left\langle \frac{\partial u_{n\mathbf{k}}^{(\lambda)}}{\partial \mathbf{k}} \left| \frac{\partial u_{n\mathbf{k}}^{(\lambda)}}{\partial \lambda} \right\rangle - \left\langle \frac{\partial u_{n\mathbf{k}}^{(\lambda)}}{\partial \lambda} \left| \frac{\partial u_{n\mathbf{k}}^{(\lambda)}}{\partial \mathbf{k}} \right\rangle \right\}. \quad (4.47)$$

where M is the number of occupied bands, f is the band occupancy. The reciprocal lattice-periodicity of a Bloch function implies that its direct lattice-periodic part must satisfy

$$u_{n\mathbf{k}+\mathbf{G}}(\mathbf{r}) = e^{-i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}} u_{n\mathbf{k}}(\mathbf{r}). \quad (4.48)$$

Integrating Equation 4.47 by parts, and making use of Equation 4.48 eventually gives

$$\Delta \mathbf{P} = \mathbf{P}^{(1)} - \mathbf{P}^{(0)}, \quad (4.49)$$

where

$$\mathbf{P}^{(\lambda)} = \frac{ife}{8\pi^3} \sum_{n=1}^M \int_{\text{BZ}} d^3k \left\langle u_{n\mathbf{k}}^{(\lambda)} \left| \frac{\partial u_{n\mathbf{k}}^{(\lambda)}}{\partial \mathbf{k}} \right\rangle. \quad (4.50)$$

The constraint of Equation 4.48 still allows gauge freedom; the physics derived from the ground state must be invariant under a gauge transformation

$$u_{n\mathbf{k}} \rightarrow e^{i\theta_{\mathbf{k}n}} u_{n\mathbf{k}}, \quad (4.51)$$

for a specific set of functions $\theta_{\mathbf{k}n}$. The general form of $\theta_{\mathbf{k}n}$ is

$$\theta_{\mathbf{k}n} = \alpha(\mathbf{k}) + \mathbf{k} \cdot \mathbf{R}, \quad (4.52)$$

where $\alpha(\mathbf{k})$ is a reciprocal lattice-periodic function and $\mathbf{R}$ is a direct lattice vector. The effect of such a gauge transformation on $\Delta\mathbf{P}$ is to shift it by a polarisation quantum $\frac{fe}{\Omega}\mathbf{R}$. If a calculation of $\Delta\mathbf{P}$ according to Equation 4.49 were attempted, the $u_{n\mathbf{k}}^{(\lambda)}$ may not be in the same gauge. They might be related by a transformation like Equation 4.51, shifting the result by a value in the infinite lattice of polarisation quanta. To overcome this, $\mathbf{P}^{(\lambda)}$ can be calculated at multiple intervening points on the path between $\lambda = 0, 1$, so any shifts in the gauge can be detected.

The modern theory of polarisation has become invaluable for the theoretical study of ferroelectricity. A pertinent example of this is found in Ref 53, which used the theory to calculate the spontaneous polarisation of a number of proton transfer ferroelectrics. The theoretical value for croconic acid ($29.4 \mu\text{Ccm}^{-2}$) exceeded the highest value that had previously been observed experimentally ($21 \mu\text{Ccm}^{-2}$). This discrepancy perhaps motivated the development of a practical technique for optimising the polarisation of an actual single crystal of the material, which resulted in a new record ($30 \mu\text{Ccm}^{-2}$) for the highest experimental value which agreed more favourably with the theoretical value.

It was also used to calculate the contributions of different types of molecular distortion towards the total spontaneous polarisation in 1-cyclobutene-1, 2-dicarboxylic acid (CBDC) and 2-phenylmalondialdehyde (PhMDA) [95]. The authors of this study used symmetry analysis software to decompose the ferroelectric distortion, the displacement from the paraelectric state to one of the domain states, of each material into orthogonal modes which each displaced atoms belonging to the same Wyckoff position. For both materials, they found that the ferroelectric distortion modes (FDMs) which produced intermolecular proton transfer gave the largest contributions to the respective spontaneous polarisation totals. They attributed this to the electronic redistribution associated with the switching of π -bonds surrounding the transferring protons, which reveals a similarity with croconic acid, as described in Section 3.2.2.

4.7 Isotope effects in proton transfer ferroelectrics

For many decades it has been known that proton transfer (anti-)ferroelectrics like KDP and squaric acid undergo significant changes in their transition temperatures upon deuteration, *i.e.* the replacement of their H-atoms with deuterium atoms. Due to their lightness, the quantum mechanical nature of the proton/deuteron dynamics has been implicated in this phenomenon. Density functional theory (DFT) has been used to study it from a theoretical point of view.

4.7.1 Potassium dihydrogen phosphate

For example, Koval et al [18] used it to investigate the cause of the giant isotope effect on T_C and lattice parameters experienced by potassium dihydrogen phosphate (KDP), and whether quantum tunnelling is responsible for the double site occupancy of the protons in the paraelectric phases of KDP and deuterated KDP (DKDP), which contemporary Compton scattering experiments suggested.

They considered a range of atomic clusters containing 1, 4, 7, and 10 H- or D-atoms, both with and without the intervening K- and O-atoms, with the lattice parameters of both KDP and

DKDP. They calculated the effective potential energy curves (PECs) of paths along the FDMs of the clusters and treated them quantum mechanically by solving the Schrödinger equation for each cluster. They found no instability in the PECs of single protons or deuterons, suggesting that single particles do not coherently tunnel in the paraelectric phases. However, the PECs for clusters containing > 4 deuterons in the DKDP unit cell do possess instabilities and double wells. Moreover, their ground state energies are below the barrier energy, implying that tunnelling of these clusters in DKDP is possible. Although double well PECs were found for the clusters in the KDP unit cell, the ground state energies of these clusters were above the barrier energy, implying that only clusters containing > 10 H-atoms coherently tunnel in KDP. Nevertheless, the results of the quantum mechanical treatment of the atomic clusters demonstrated that tunnelling of sufficiently large clusters explains the double H-atom site occupancy in the paraelectric phases of (D)KDP.

As explained in Section 2.2.2, previous models of (D)KDP which were used to explain the isotope effect on T_C assumed that the change in the proton/deuteron wavefunctions due to the increase in mass upon deuteration was sufficient to explain the effect. However, the analysis of the atomic cluster PECs described above refutes this picture. Instead, the isotope effect is explained by considering the effect of ‘un-deuterating’ DKDP on the wavefunction of a cluster containing 7 H-atoms. The two peaks in the wavefunction come closer together, causing the H-atom to become more delocalised. This in turn increases the covalency of the bonding between the O-atoms and each proton in each OHO unit, which draws the O-atoms towards each other, shrinking the lattice dimensions. This lowers the barrier of the effective potential, which causes more delocalisation, and so on. This feedback effect eventually results in a singly peaked 7-H-atom cluster wavefunction, meaning that clusters of that size are no longer unstable. Therefore the loss of ferroelectricity arrives at a lower temperature. This explains the giant isotope effect on T_C .

4.7.2 Squaric acid

Squaric acid is a proton transfer antiferroelectric. Structurally, it comprises sheets of square $C_4O_4H_2$ molecules units which are held together by hydrogen bonds. Like CRCA, during ferroic switching protons are transferred from one molecule to another, breaking and creating a OH bond in the process. Figure 4.1 shows a b -axis view of the crystal. *Ab initio* path integral molecular dynamics (AI-PIMD) has been used [85] to study the effect of deuteration (*i.e.* the replacement of H-atoms with deuterium atoms) on T_C and H-bond lengths.

The investigators found that for both deuterated (D_2SQ) and non-deuterated (H_2SQ) squaric acid, as the simulation temperature was increased, the probability distribution of the H- and D-atoms across the range of the δ parameter, which quantifies the proton transfer extent, changed from unimodal to bimodal, with peaks located at the two sites corresponding to the two ferroic domain states. This indicates a loss of the long-range order, which characterises its antiferroelectric phase, with increasing temperature *i.e.* the phase transition. The disorder emerged at a higher temperature for D_2SQ than for H_2SQ which agrees with the experimental observation that T_C is 150 K higher for D_2SQ than for H_2SQ .

The investigators also observed that above T_C , protons transfer between their associated

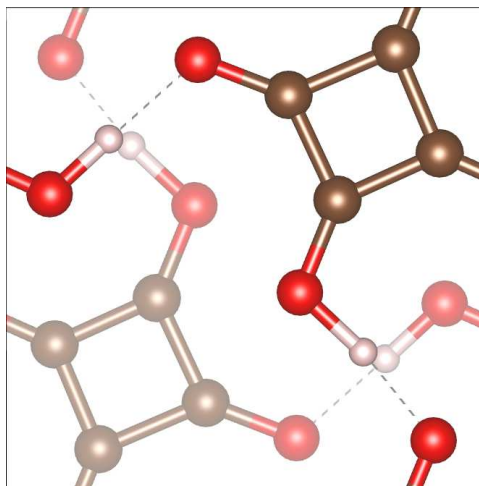


Figure 4.1: A b -axis view of squaric acid, rendered from a structure attached to Ref 96.

surrounding O-O pairs in a collective fashion. The simulation supercell was elongated by 3 primitive unit cells along the c -axis. Collective transfer events where 3 protons within a chain parallel to the c -axis occurred. Some of these events coincided with a peak in the component of the *radius of gyration* parallel to the H-bonding axis, $R_g^{\parallel}$. This implies that these transfer events were assisted by quantum tunnelling, while others, which did not coincide with $R_g^{\parallel}$ peaks were assisted only by thermal fluctuations. The proportion of classical transfer events was observed to increase with increasing temperature. The addition of quantum effects did not appear to alter the H- or D-atom transfer mechanism.

Chapter 5

Density functional theory of croconic acid

This chapter describes the approach taken to simulate croconic acid (CRCA) in the framework of density functional theory (DFT), as well as the results of these calculations.

5.1 Total energy calculations on CRCA

Three DFT software packages were used to perform calculations for CRCA. These were Quantum Espresso [97, 98], Abinit [99] and CP2K [70].

5.1.1 Computational details

Abinit

Abinit is a software package which, among other features, enables DFT calculations using pseudopotentials and a plane wave basis set. It was used to calculate the Born effective charge tensor of *Pbcm*-CRCA, according to density functional perturbation theory [100] (DFPT) which was described in Section 4.4. At the time of our investigation, van der Waals density functionals had not been implemented within Abinit, therefore the Perdew-Berke-Erzenhof generalised gradient approximation (PBE-GGA) [101] xc functional was chosen instead. Norm-conserving pseudopotentials created using the Troullier-Martins procedure [102] were also used. The total energy and atomic forces were converged with respect to the plane wave energy cutoff and Monkhorst-Pack [72] mesh dimensions. A cutoff value of 90 ha and (4,4,3) Monkhorst-Pack mesh were sufficient to converge the total energy to within an error of 2×10^{-6} ha/ion, and atomic forces to within an error of 2×10^{-5} ha/bohr. The convergence criteria for the DFPT calculations of the Born effective charge tensor of *Pbcm*-CRCA are given at the end of Section 5.3.4.

The results of the Born effective charge tensor calculation are given in Appendix C. We found that the spontaneous polarisation was linear in the atomic displacements to a good approximation by comparing the experimental value of the spontaneous polarisation to its

theoretical linear approximation

$$P_i^{(\text{lin})} = \sum_{aj} Z_{ij}^a X_{aj}^{(-)}, \quad (5.1)$$

where Z_{ij}^a is defined in Equation 4.42. We define the ferroelectric distortion

$$\mathbf{X}^{(\pm)} = \mathbf{R}^{(\pm)} - \mathbf{R}^{(0)}, \quad (5.2)$$

where $\mathbf{R}^{(\pm)}$ is the matrix of atomic positions in the $Pca2_1$ -CRCA domain state where the z -component of the hinge proton displacement is $\pm$, and $\mathbf{R}^{(0)}$ is the matrix of atomic positions of $Pbcm$ -CRCA. The domain states were found by optimising the atomic positions of CRCA under the constraints of $Pca2_1$ symmetry elements, with the unit cell dimensions fixed to their $Pbcm$ -CRCA values, in order to carry out the analysis of Section 5.3.3.

We found that $\mathbf{P}^{(\text{lin})} = (1.57 \times 10^{-7}, -1.22 \times 10^{-7}, -3.11 \times 10^1) \mu\text{C}/\text{cm}^2$ which agrees well with the experimental value of $30 \mu\text{C}/\text{cm}^2$ [53]. The linearity of the spontaneous polarisation has also been found in the perovskite ferroelectrics KNbO_3 [103] and BaTiO_3 [104], therefore this agreement was expected.

Quantum Espresso

Quantum Espresso also utilises a plane wave basis set. It was used to calculate phonon modes of $Pbcm$ -CRCA, and to decompose the minimum energy path between its domain states (which possess $Pca2_1$ symmetry) into these modes. A plane wave cutoff value of 100 ha and a (3,3,2) Monkhorst-Pack mesh were sufficient to converge atomic forces to within a tolerance of 2×10^{-5} ha/bohr and total energy to within a tolerance of 1×10^{-6} ha/ion. The vdW-DF2 xc functional [78] was used with ultrasoft pseudopotentials [105]. The dispersion-corrected density functional was preferred over the empirical pairwise potentials [75] designed to correct for van der Waals interactions since it has been shown that, for $Pca2_1$ -CRCA, the PBE+D form of the latter underestimates H-bond lengths by $\sim 7\%$ and overestimates OH covalent bond lengths by $\sim 3\%$ [51, 97]. This was confirmed by the data in Table 5.1, which compares the bond lengths and angles predicted by vdW-DF2 and PBE+D3.

CP2K

CP2K was used to generate the atomic forces data which were required to train our effective Hamiltonian of CRCA. The computational details of these calculations are reported in Section 6.3.2.

5.2 Phonon modes of $Pbcm$ -CRCA

The existence of a phonon mode at Γ with an imaginary frequency implies a dynamic instability which leads to a structural phase transition. The soft mode model of ferroic phase transitions explains these transitions by showing that phonon-phonon interactions effectively lead to a temperature dependent phonon frequency for the imaginary mode [28]. Above the transition

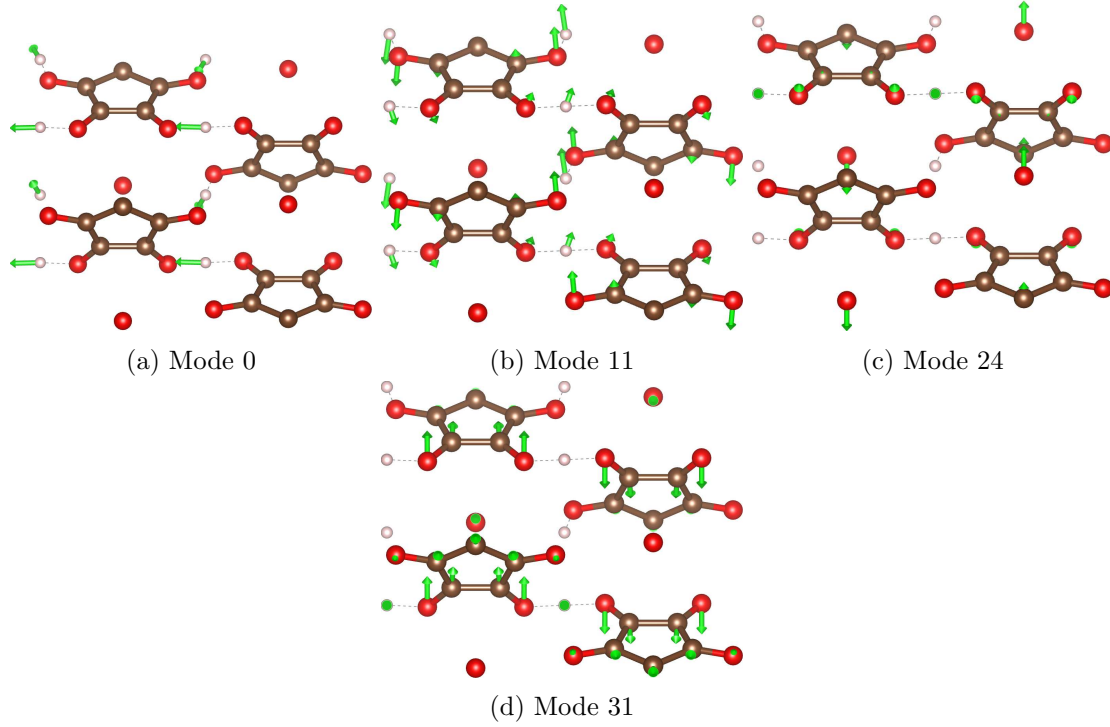


Figure 5.1: An illustration of the Γ -point phonon modes of *Pbcm*-CRCA with the largest amplitude in the ferroelectric distortion. C-atoms are brown, O-atoms are red, and H-atoms are white.

temperature, the frequency is real, while below the transition temperature it becomes imaginary. The mode *softens* before becoming unstable.

Unstable modes correspond to the distortion of the ferroelectric phase relative to the paraelectric phase. Therefore, they have been traditionally theorised to be the degrees of freedom which drive the ferroelectric behaviour. Therefore, in order to understand the polarisation switching mechanism of CRCA, our first step was to calculate the phonon modes at Γ of its high-symmetry phase, *Pbcm*-CRCA. The structure of *Pbcm*-CRCA was obtained by optimising the crystal structure under the constraints of *Pbcm* symmetry elements with Quantum Espresso. Figure A.1 contains a diagram of *Pbcm*-CRCA where the atoms are labelled according to the scheme used throughout this thesis. Then, the Phonopy software package [88] was used to calculate a finite difference approximation of the dynamical matrix at Γ , which was subsequently diagonalised.

The eigenfrequencies and associated irreducible representations of the *Pbcm* space group for the phonon modes at Γ are listed in Appendix B. CRCA has 48 atoms in its unit cell, therefore there are $3 \times 48 = 144$ phonon mode branches. It is convenient to list these modes in order of ascending squared eigenfrequency, and refer to them by their index in this list. In this way, the unstable modes with imaginary eigenfrequencies have indexes 0-6, the acoustic modes are 7-9, while the remaining modes have real, positive frequencies.

Mode 0 is illustrated in Figure 5.1a. It transforms according to the irreducible representation Γ_2^- , exhibiting odd parity under point inversion. It displaces each proton in the unit cell across its respective gap neighbouring O-atom pairs, while leaving the C- and O-atoms fixed. It also

induces the largest polarisation parallel to the polar z -axis of CRCA out of all of the modes. This is illustrated in the upper part of Figure 5.2, which plots the dynamical effective charge, which we define as

$$P_i^j \equiv \sum_{an} Z_{in}^a \frac{\hat{e}_{jan}}{\sqrt{m_a}}, \quad (5.3)$$

where Z_{in}^a is the Born effective charge component corresponding to a dipole moment in the i direction produced by a displacement of atom a of mass m_a in the n direction, and $\hat{e}_j$ is the orthonormalised phonon mode j *i.e.* including the $\sqrt{m_a}$ weighting. Displacing along mode 0 from the paraelectric phase with either positive or negative amplitude pushes CRCA towards its ‘positive’ or ‘negative’ domain state, depending on the sign of the initial perturbation. Optimising the H-atom positions while keeping the other atoms fixed does indeed result in a configuration, similar to a $Pca2_1$ -CRCA domain state, except without tilted C_5O_5 molecules. (We found that in the true domain state, each molecule is tilted by 3.3 degrees relative to its orientation in the fixed-molecule ‘domain state’.) This demonstrates that proton transfer drives the ferroelectric relaxation, rather than the distortion of the C_5O_5 molecules. Similar behaviour has been observed in potassium dihydrogen phosphate (KDP), in which the proton transfer between PO_4 molecular units drives the ferroelectric relaxation, even though the protons are transferred in a direction roughly perpendicular to the polar axis in the material [18].

The significance of mode 0 was also supported by our calculation of the distortion of the ferroelectric domain states. The ferroelectric distortion defined in Equation 5.2 was projected onto each phonon mode. The amplitudes of the phonon modes in the ferroelectric distortion were calculated according to

$$Q_j(\mathbf{X}) \equiv \sum_{ai} \hat{e}_{jai} X_{ai} \sqrt{m_a}, \quad (5.4)$$

where j indexes the phonon modes $\hat{e}_j$, a indexes atoms of mass m_a and i indexes Cartesian components, and are plotted in Figure 5.2. Since the distortions of the two domain states are related by point inversion, it is enough to consider only the + domain state. Figure 5.2 shows us that, of the unstable phonon modes of $Pbcm$ -CRCA, mode 0 has the greatest amplitude in the ferroelectric distortion. It also shows that a number of other modes also make significant contributions to the ferroelectric distortion, and would therefore couple to mode 0 during the ferroelectric phase transition in the soft mode picture, if CRCA were stable in its paraelectric phase. Modes 11, 24, and 31 are in this group of modes, and involve mainly distortion of the C_5O_5 molecules, rather than proton displacement like mode 0. A qualitative description of Mode 11 would be that it rotates each molecule about an axis which bisects it, running parallel to the C=O bond. Molecules connected along the z -axis in the same H-bond chain rotate in opposite directions, while molecules in adjacent chains, displaced in the y -axis rotate in the same direction. Mode 24 can be qualitatively described as involving swinging of the molecules on the terrace C=O bonds. Molecules connected along the z -axis swing in opposite directions, as do molecules separated in the y axis. Finally, mode 31 involves sliding of the molecules roughly parallel to the C=O bond. Modes 11, 24, and 31 are also illustrated in Figure 5.1.

The ability of the phonon modes at Γ to capture the polarisation switching process of CRCA was the subject of our publication in Reference 106, an adapted version of which is inserted below.

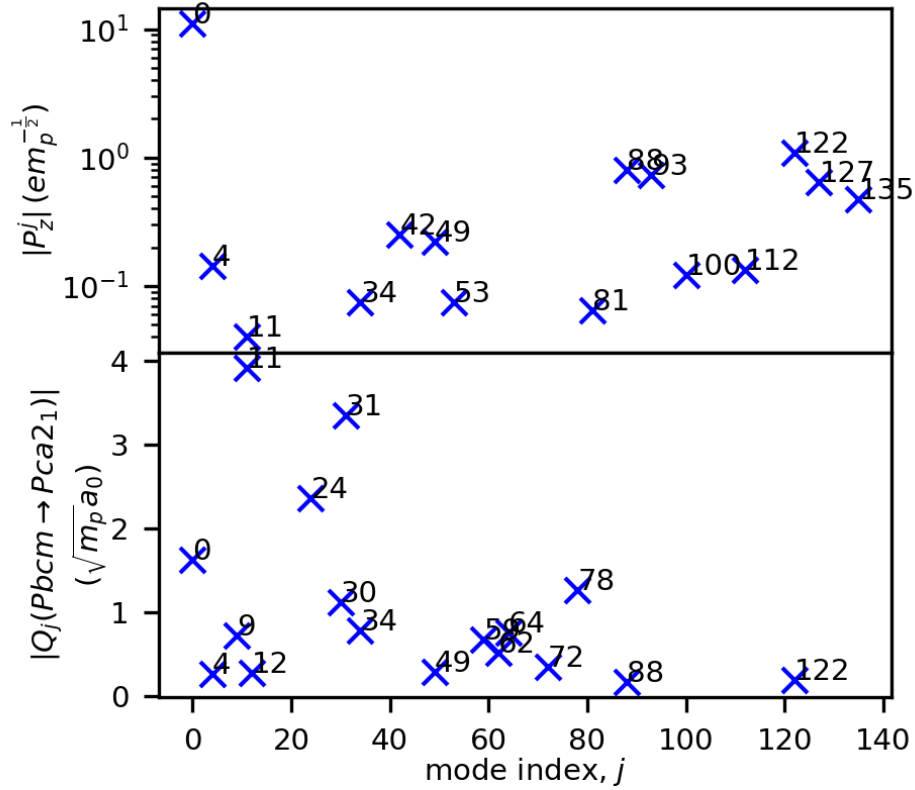


Figure 5.2: **Upper:** the dynamical effective charge (defined in Equation 5.3) of normal modes in the polar direction of *Pbcm*-optimized croconic acid. Only modes j that satisfy $|P_z^j| > 4 \times 10^{-2} em_p^{-1/2}$ have been plotted. Mode 0, the primary polar mode, has the greatest magnitude for this quantity. **Lower:** decomposition of the pathway between the centrosymmetric and non-centrosymmetric structures onto normal modes, as defined in Equation 5.4. Only modes j which satisfy $|Q_j| > 0.1\sqrt{m_p}a_0$ have been plotted.

5.3 Multi-phonon proton transfer pathway in a molecular organic ferroelectric crystal

While the majority of ferroelectrics research has been focused on inorganic ceramics, molecular ferroelectrics can also combine large spontaneous polarization with high Curie temperatures. However, the microscopic mechanism of their ferroelectric switching is not fully understood. We explore proton tautomerism in the prototypical case of croconic acid, $C_5O_5H_2$. In order to determine how efficiently ferroelectricity in croconic acid is described in terms of its Γ -point phonon modes, the minimum energy path between its structural ground states is approximated by projection onto reduced basis sets formed from subsets of these modes. The potential energy curve along the minimum energy path was found to be sensitive to the order of proton transfer, which requires a large subset ($\gtrsim 8$) of the modes to be approximated accurately. Our findings suggest rules for the construction of effective Hamiltonians to describe proton transfer ferroelectrics.

5.3.1 Introduction

A ferroelectric is a material that exhibits a spontaneous, switchable electric polarization. Since polarization switching is the crucial function, the microscopic mechanism by which this switching occurs holds important scientific interest. This topic has been researched both experimentally [107–110] and theoretically [9, 111, 112] over the course of many decades for many systems.

Different theoretical approaches have been used to provide insights into ferroelectrics. Before the development of *ab initio* methods like density functional theory (DFT) [61, 62], polarization reversal processes were modelled using continuum methods such as the Landau-Ginzburg theory [113], from which models for domain nucleation and growth could be derived [9, 34]. More recently, DFT has been used to model the atomic structure of defect-free ferroelectric crystals [114]; and the atomic structure and properties of domain walls [115], which is outside the realm of applicability of continuum models. It has also been used to calculate the parameter values of effective Hamiltonian models [116] constructed in order to simulate large systems beyond the reach of first-principles methods [117, 118].

The microscopic switching mechanism of organic ferroelectrics such as potassium dihydrogen phosphate and triglycine sulphate is characterised by proton transfer between molecular units. Croconic acid (CRCA) is another member of this category [2, 53]. The motion of protons parallel and perpendicular to the polar axis, and consequent electronic rearrangement are understood to induce the observed polarization in CRCA [53]. Like many proton transfer ferroelectrics, however, it is less thermally stable than inorganic ferroelectrics such as lead zirconate titanate and polymer ferroelectrics such as polyvinylidene fluoride. The relative ease of practical experimentation and potential application to future devices might explain why, upon surveying the literature, more progress has been made toward explaining switching mechanisms in the latter types of ferroelectrics [95, 119] than in proton transfer ferroelectrics.

In previous work, the degrees of freedom for an effective Hamiltonian for barium titanate were constructed by projecting the unstable phonon modes of the crystal onto individual unit cells [120]. This effective Hamiltonian successfully described the phase transition sequence of the

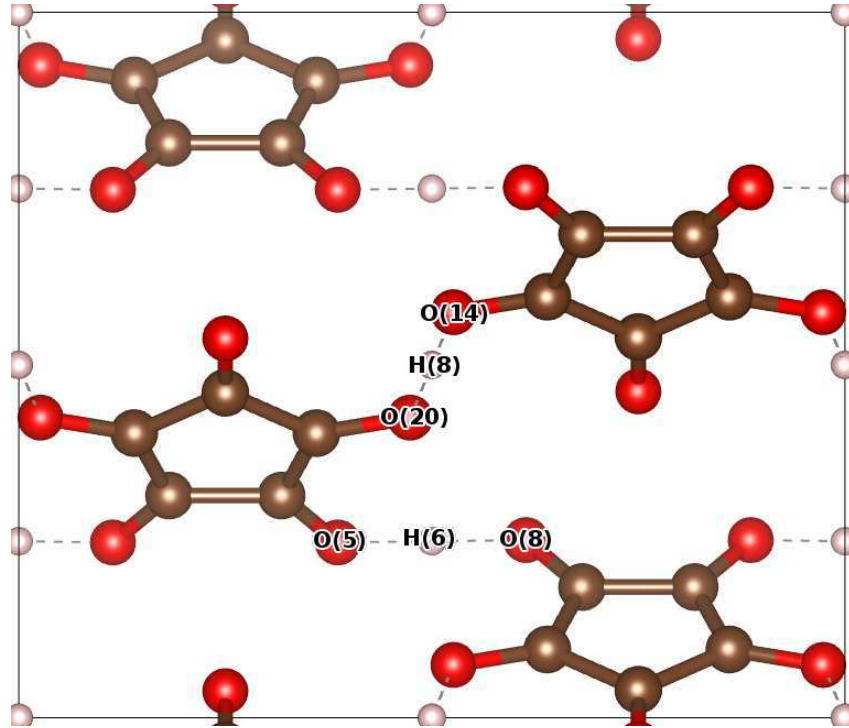


Figure 5.3: A view down the a -axis of croconic acid, after $Pbcm$ -constrained relaxation of the atomic positions and cell dimensions. Carbon, oxygen and hydrogen atoms are coloured brown, red and white respectively. The atoms that comprise the terrace (O(20), H(8), O(14)) and hinge (O(5), H(6), O(8)) OH $\cdots$ O triples are labelled.

material. On the other hand, a similar effective Hamiltonian for the proton transfer ferroelectric potassium dihydrogen phosphate (KDP) used its unstable gamma point mode to derive the degrees of freedom [121] but significantly overestimated KDP's phase transition temperature and predicted a second order phase transition, rather than the weakly first order transition that is experimentally observed [121].

In this study, the possibility of describing the ferroelectricity of the proton transfer ferroelectric croconic acid (CRCA) by selecting the correct subset of its phonon modes was considered. The minimum energy path (MEP) for polarization switching in CRCA has been calculated with the nudged elastic band (NEB) method [93] in previous work [54], and found to involve pairwise transfer of protons. Any reduced basis of atomic displacements that can be used to describe ferroelectricity in CRCA must at least be able to express the MEP. Therefore, the ability of the phonon modes of CRCA to efficiently describe ferroelectricity in CRCA was assessed by using these modes as a basis in which to approximate the MEP.

The following analysis bears similarities with previous work [95] which decomposed polar distortions of two other proton transfer ferroelectrics 1-cyclobutene-1,2-dicarboxylic acid and 2-phenylmalondialdehyde. Both analyses seek to conceptualise the collective atomic distortions that give rise to ferroelectricity in proton transfer ferroelectrics. On the other hand, the authors of Ref 95 decompose the polar distortions of these materials into three different types of atomic distortion instead of the spectra of the materials' Γ -point phonon modes.

5.3.2 Methods

The ground-state crystal structure of CRCA has the $Pca2_1$ space group, which is polar. The initial crystal structure of CRCA was taken from entry 147324 of the Cambridge Crystallographic Data Centre and was obtained from X-ray diffraction [50]. As a starting point, we linearly interpolate a path between the two orientation states, where the direction of polarization is reversed. The mid-point is a non-polar structure that has the space group $Pbcm$. Equivalently, it is the minimal supergroup from which the $Pca2_1$ structure is obtained through the smallest atomic displacements, i.e. $Pbcm$ -CRCA would be its *prototype phase*, as defined by Aizu [122]. We take the $Pbcm$ structure to approximate the hypothetical paraelectric phase, which CRCA would reach if it did not thermally decompose at $T \approx 450\text{ K}$ [2].

Firstly, we optimise the crystal structures separately under the constraints of the $Pca2_1$ and $Pbcm$ symmetry elements. The total energy and forces were calculated from plane-wave DFT as implemented in the *Quantum Espresso* [97,98] and *Abinit* [99] software packages. To determine whether dispersion corrections to the exchange-correlation energy functional would give a more accurate description of the potential energy surface, geometry optimizations were performed with two different dispersion-corrected functionals: DFT-D3 [123] (*Abinit*'s implementation) and vdW-DF2 [78] (*Quantum Espresso*'s implementation). The normal modes were calculated at the Γ point by finite differences with the Phonopy package [88]. Further computational details are given in the Section 5.3.5.

5.3.3 Results

Crystal structure

The optimised structure of the $Pca2_1$ phase can be compared to the results of neutron scattering experiments [51]. The unit cell dimensions, OH/O $\cdots$ H bond lengths and angles are presented in Table 5.1. We distinguish between ‘hinge’ protons and ‘terrace’ protons whose associated OH $\cdots$ O triplets are oriented parallel to the [001] and $\bar{1}10$ directions, respectively. The hinge and terrace triplets are indicated in Figure 5.3 as O(5)-H(6)-O(8) and O(20)-H(8)-O(14), respectively.

The vdW-DF2 functional gave lattice parameters of a similar overall accuracy to DFT-D3, while uncorrected PBE gave much larger errors for the a and b parameters but a smaller error for the c parameter. This is consistent with earlier results [51]; dispersion interactions between pleated layers of CRCA binds these layers together.

vdW-DF2 also gave the most accurate bond lengths and angles; however these parameters were also well reproduced by the uncorrected functional. This may be explained by the fact that strong hydrogen bonds (*i.e.* those possessing donor-hydrogen-acceptor angles ($\angle\text{DHA}$) $\sim 180^\circ$) exist between the $\text{C}_5\text{O}_5\text{H}_2$ molecules in CRCA. Such bonds are understood to contain a smaller dispersive element than that of weak hydrogen bonds, which generally have $\angle\text{DHA}$ substantially smaller than 180° [124].

As vdW-DF2 gave the most accurately optimized structure overall, it was used for the subsequent calculations of the dynamical matrix at Γ and the minimum energy path. For the calculation of the Born effective charge (BEC) tensor, a structure found by $Pbcm$ symmetry-

Table 5.1: Comparison between calculated parameters of the crystal structure of croconic acid relaxed with dispersion corrections (DFT-D3, vdW-DF2) and without. The Hermann–Mauguin symbols refer to the space groups to which the crystal was constrained during unit cell optimisation. The error is given with respect to the result calculated from low temperature neutron diffraction measurements¹. The convention adopted in the literature¹, which refers to protons of OH $\cdots$ O triples oriented parallel to [001] as ‘hinge’ protons and those of triples oriented parallel to $[\bar{1}10]$ as ‘terrace’ protons is used. θ_{hinge} and θ_{terrace} refer to angles of the corresponding triples.

	<i>Pca2₁</i>						<i>Pbcm</i>	
	GGA-PBE + DFT-D3		GGA-PBE		vdW-DF2		Expt. ¹	vdW-DF2
	result	error	result	error	result	error		
<i>a</i> (bohr, %)	16.44	0.94	17.20	5.60	16.63	2.13	16.29	16.62
<i>b</i> (bohr, %)	10.00	3.82	10.87	12.88	9.81	1.89	9.632	9.70
<i>c</i> (bohr, %)	20.44	0.89	20.62	0.03	20.98	1.71	20.63	20.32
<i>l</i> (OH) _{hinge} (bohr, %)	1.96	2.91	1.95	2.16	1.92	0.98	1.90	2.33
<i>l</i> (O $\cdots$ H) _{hinge} (bohr, %)	2.87	5.39	2.95	2.72	3.12	2.82	3.03	2.33
<i>l</i> (OH) _{terrace} (bohr, %)	1.95	2.83	1.94	1.93	1.92	1.02	1.90	2.31
<i>l</i> (O $\cdots$ H) _{terrace} (bohr, %)	2.87	5.74	2.97	2.46	3.09	1.34	3.04	2.31
θ_{hinge} (deg., deg.)	167.2	0.9	167.2	0.9	167.4	0.7	168.1	169.4
θ_{terrace} (deg., deg.)	174.1	1.9	172.9	0.7	172.0	0.2	172.2	180.0

¹ S. Mukhopadhyay *et al.*, *Chemical Physics*, 2013, **427**, 95-100

constrained relaxation of CRCA with the uncorrected PBE functional was used. The accurate bond lengths and angles predicted by this functional implied that the electronic rearrangement induced by atomic displacement that contributes to the BEC tensor would also be accurately predicted. Further details are given in the Section 5.3.5.

Vibrational structure

A complete listing of the normal modes of *Pbcm*-CRCA, including irreducible representations, is given in the Supplementary Information. As there are $N = 48$ atoms in the unit cell, there are 144 ($3N$) phonon branches. Referring to these modes by their associated *Pbcm* symmetry labels would be ambiguous; therefore, in the following we refer to each mode by its index when the modes are arranged in order of ascending frequency. Modes 0–6 are imaginary, while modes 7–9 are acoustic (zero frequency) translations. The remaining modes are stable with positive frequencies.

The minimum energy path

The minimum energy path for ferroelectric switching in CRCA has been calculated according to the nudged elastic band algorithm in previous work [54] which used the same vdW-DF2 [78] exchange-correlation functional that was used in the present work. This calculation was reproduced in the present work in order to determine how efficiently the Γ -point phonon modes approximate this path. The PEC of the calculated MEP is illustrated in Figure 5.4a, while the proton transfer extent (PTE) trajectory is illustrated in Figure 5.4b. In this chapter’s figures λ denotes a coordinate, normalised between -1 and +1, which quantifies the location of an atomic configuration projected onto a line in $3N_{\text{atom}}$ -dimensional configuration space between the two

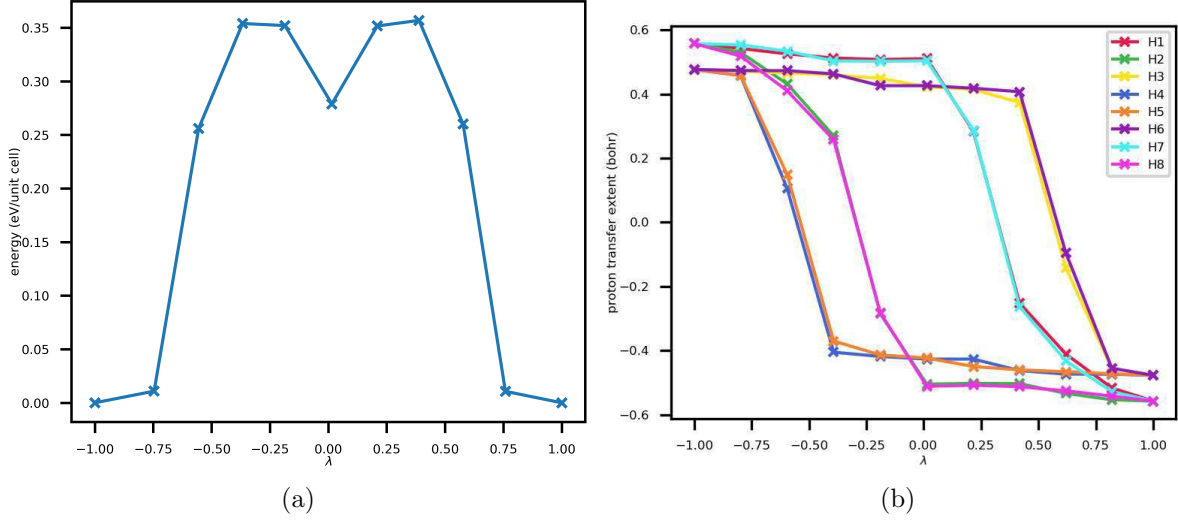


Figure 5.4: (a) A plot of the potential energy against the normalised reaction coordinate along the MEP between the domain states of CRCA with *Pbcm*-CRCA unit cell dimensions. (b) A plot of the transfer extent of each proton against the normalised reaction coordinate along the MEP between the domain states of CRCA with *Pbcm*-CRCA unit cell dimensions.

domain states. Precisely, λ is defined as

$$\lambda \equiv 2 \left(\mathbf{X} - \mathbf{X}^{(-)} \right) \cdot \frac{\Delta \mathbf{X}}{|\Delta \mathbf{X}|} - 1, \quad (5.5)$$

for an atomic configuration $\mathbf{X}$ where X_{ai} is the coordinate i of atom a 's position, and $\Delta \mathbf{X} \equiv \mathbf{X}^{(+)} - \mathbf{X}^{(-)}$ is the atomic displacement between the 'positive' and 'negative' orientation states.

The MEPs calculated in both Ref 54 and the present work involve the transfer of the 8 protons in the CRCA unit cell in 4 successive pairs. In Ref 54 the NEB calculation was carried out with the unit cell dimensions fixed to their experimental *Pca2*₁-CRCA values, and revealed an MEP with an energy barrier of 51 meV/proton. Along the MEP the proton pairs transfer in the order: terrace, hinge, hinge, terrace (THHT). In contrast, our initial NEB calculation was carried out with the unit cell dimensions fixed to their calculated *Pbcm*-CRCA values, and revealed an MEP with an energy barrier of 45 meV/proton. Along this MEP, the proton pairs transfer in the order hinge, terrace, terrace, hinge (HTTH).

In order to verify that the HTTH MEP was still present in the PES with *Pca2*₁-CRCA unit cell dimensions, we performed another NEB calculation with our calculated *Pca2*₁-CRCA unit cell dimensions. The middle images of the path were initialised according to the HTTH path that we initially found, rescaled to the new unit cell dimensions. This calculation did converge to a HTTH MEP, with an energy barrier of 53 meV/proton, which is slightly higher than the barrier of the THHT MEP found in Ref 54. The PEC and PTE trajectories are shown in Figure 5.5.

Apart from the increased energy barrier, the PEC of the second HTTH path shows other significant differences from the first HTTH path (HTTH1). The energy increases (decreases) more strongly during the first (last) hinge proton transfer in the second HTTH path (HTTH2) than in HTTH1. This is a consequence of the difference in the c parameters for the *Pbcm*-CRCA

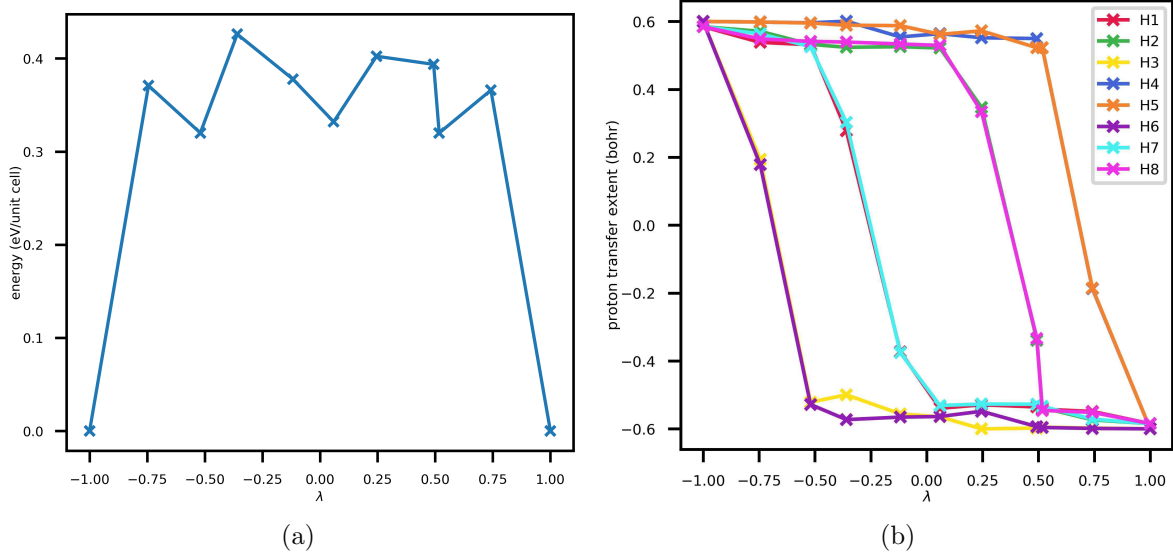


Figure 5.5: (a) A plot of the potential energy against the normalised reaction coordinate along the MEP between the domain states of CRCA with $Pca2_1$ -CRCA unit cell dimensions. (b) A plot of the proton transfer extent trajectory against the normalised reaction coordinate along the MEP between the domain states of CRCA with $Pca2_1$ -CRCA unit cell dimensions.

(20.32 bohr) and $Pca2_1$ -CRCA (20.98 bohr) unit cells. The corresponding $l(\text{O} \cdots \text{H}_{\text{hinge}})$ values for $Pca2_1$ -CRCA in the $Pbcm$ -CRCA and $Pca2_1$ -CRCA unit cells are 2.89 bohr and 3.12 bohr respectively. Increasing $l(\text{O} \cdots \text{H}_{\text{hinge}})$ weakens the hinge H-bond and increases the proton transfer barrier [125], which is why the energy increases more strongly during the first hinge proton transfer in the HTTH2 PEC ($\frac{dE}{d\lambda} = 83$ meV/proton) than in the HTTH1 PEC ($\frac{dE}{d\lambda} = 70$ meV/proton).

Secondly, although the nudged force did fall below our threshold of 3×10^{-4} Ry/bohr the HTTH2 PEC is somewhat asymmetric, in contrast to the more precise symmetries of the HTTH1 and Ref 54 PECs. We were unable to converge the MEP with a smaller threshold. However, based on these previous calculations we believe that it is likely that the true HTTH MEP does have a symmetric PEC. The failure of our NEB calculation with $Pca2_1$ -CRCA unit cell dimensions to find one can be explained by the weaker hinge H-bonds described above. As well as increasing the proton transfer barrier, the maximum gradient of the PEC for hinge proton transfer is also increased. On the other hand, the forces on the hinge protons perpendicular to their axis of transfer remain comparatively small. This combination of a large force parallel to the MEP and a small force perpendicular to the MEP is known to cause instability and slow convergence of the NEB method [126], which explains why our calculated HTTH2 MEP has an asymmetric PEC. Although the symmetry of our calculated HTTH2 PEC likely differs from that of the true HTTH MEP PEC, it is also likely that our calculated energy barrier is a quantitatively accurate approximation. Notwithstanding the asymmetry of our calculated HTTH2 PEC, its calculation does show that in CRCA's PES, there are two 'local' MEPs satisfying Equation 4.43 with the HTTH and THHT pairwise proton transfer orders. Due to their similar energy barrier values, both would be expected to contribute to polarisation switching in CRCA.

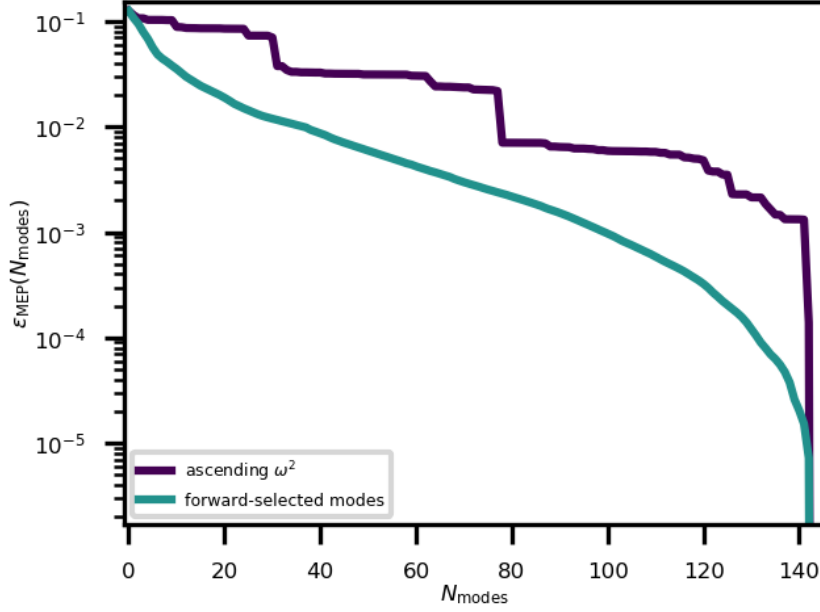


Figure 5.6: The error in approximating the minimum energy path for ferroelectric switching with Γ -point phonon modes added in an order determined by a forward selection procedure described in Section 5.3.3. The corresponding error found by adding the modes in order of ascending ω^2 is added for comparison.

Approximating the minimum energy path

Approximations to the minimum energy switching path were made by repeatedly projecting it onto a reduced basis comprised of a varying number (N_{modes}) of Γ -point phonon modes. The order in which modes were added to the basis was found by forward-selection so that the most important modes were added first. Specifically, the algorithm involved the following steps. For $N_{\text{modes}} = 1, \dots, 3N_{\text{atom}}$:

1. Calculate the error in approximating the MEP according to

$$\epsilon_{\text{MEP}}(N_{\text{modes}}) \equiv \sqrt{\frac{1}{3N_{\text{image}}N_{\text{atom}}} \sum_{an} (\mathbf{x}_{an}(N_{\text{modes}}) - \mathbf{x}_{an}(\text{MEP}))^2}, \quad (5.6)$$

where $\mathbf{x}_{an}$ is the position of atom a in NEB image n after separately adding each of the remaining modes to the basis.

2. Add the mode which gives the smallest ϵ_{MEP} value, and remove it from the set of remaining modes.
3. If $N_{\text{modes}} < 3N_{\text{atom}}$, increment N_{modes} by 1 and return to step 1, else terminate.

The energy along approximations to the MEP found by adding modes to the basis in the order described above was evaluated. The results of these calculations are illustrated in Figure 5.7 which plots the potential energy against λ . It can be seen that after 8 modes were added to the basis, the qualitative shape of the MEP potential energy curve (PEC) was reproduced. Modes that were added subsequently led to a downward shift of the entire PEC as the basis

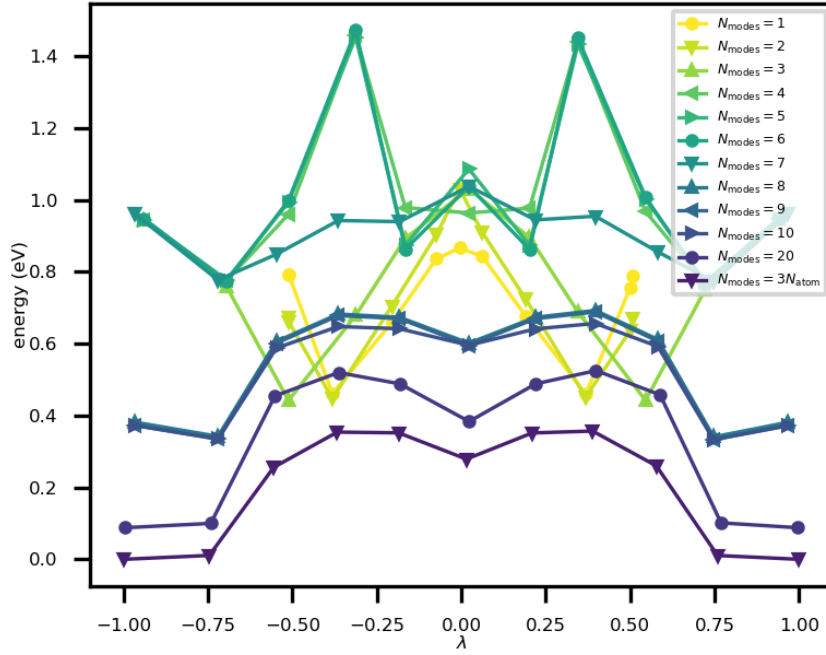


Figure 5.7: The potential energy curve along approximations to the minimum energy switching path between states with opposite polarization ($\lambda \pm 1$). These vary in the number of phonon modes (N_{modes}) in the approximation basis of the structural transformation.

for approximating the MEP became more complete. Adding modes in order of ascending ω^2 , for example, instead of determining the order of mode inclusion using the method described above would have led to PECs that do not approach the MEP PEC in a continuous way for $N_{\text{modes}} \lesssim 120$. This contrast is illustrated in Figure 5.6.

Proton transfer extent and the minimum energy path

An explanation of how the PECs of approximations to the MEP improved for $N_{\text{modes}} \leq 8$ was sought. As described in previous work [54] and reproduced here, the MEP of ferroelectric switching in CRCA involves successive pairwise transfer of protons. Crucially, the protons of CRCA transfer in a well-defined order which is only accurately reproduced with 8 modes in the basis. This is illustrated in Figure 5.8 which plots the mean absolute error in proton transfer extent (PTE) defined as

$$\epsilon_{\text{PTE}}(N_{\text{modes}}) \equiv \frac{1}{N_{\text{protons}} N_{\text{image}}} \sum_{pn} \left| \delta l_p^{(n)}(N_{\text{modes}}) - \delta l_p^{(n)}(\text{MEP}) \right|, \quad (5.7)$$

where

$$\delta l_p^{(n)}(N_{\text{modes}}) \equiv \frac{l_{(O_{\text{donor}} H^{(p)})}^{(n)}(N_{\text{modes}}) - l_{(O_{\text{acceptor}} H^{(p)})}^{(n)}(N_{\text{modes}})}{2}, \quad (5.8)$$

is the extent of transfer of proton p in image n of the MEP when approximated by N_{modes} modes.

It can be seen in the figure that between $N_{\text{modes}} = 1$ and 8, ϵ_{PTE} drops significantly by 88% to a small plateau, at which point the qualitative shape of the MEP PEC is recaptured. The

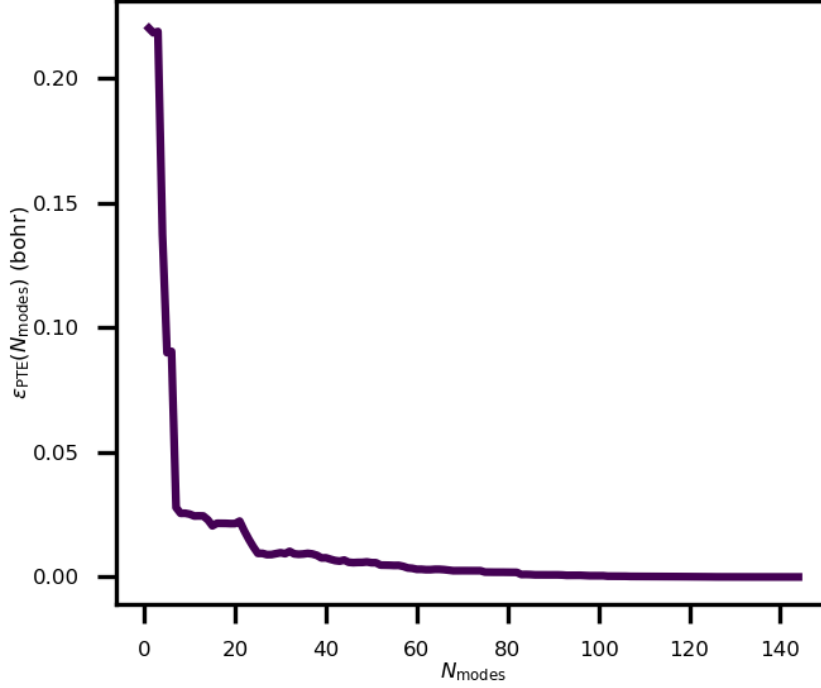


Figure 5.8: The mean absolute error in proton transfer extent, as defined in Equation 5.7, incurred by approximating the minimum energy path for ferroelectric switching in croconic acid by a finite number of phonon modes, N_{modes} .

configuration of hydroxyl bond lengths appears to be a critical determinant of the potential energy of the crystal.

Figure 5.7 shows that the MEP PEC features a local minimum at its centre; the structure at $\lambda = 0$ is metastable. An analysis of the contributions to the potential energy for each image in the MEP suggests that this state is stabilised by electrostatic interactions in the system. This analysis is illustrated in Figure 5.9 which plots the electrostatic (Hartree plus ionic) and non-electrostatic contributions to total energy for each MEP image. The Figure shows a drop in electrostatic energy at the centre of the MEP which is evidently greater than the increase in non-electrostatic contribution to the total energy for that image.

The Born effective charge (BEC) tensors of each H ion in CRCA has a large *anomalous* component i.e. the proportion of its value beyond the formal charge of the ion. This is shown in Table 5.2, that reports the norms of the BEC tensor associated with H ion displacements along the three coordinate axes i.e. $\sqrt{\sum_i (Z_{im}^a)^2}$ for ion a , displacement direction m . The configuration of hydroxyl bond lengths in CRCA, therefore, has a significant effect on the electrostatic energy, stabilising the $\lambda = 0$ structure, as well as affecting the coordination of valence electrons in the ions surrounding the hydroxyl bonds.

5.3.4 Conclusion

The analysis of the phonon modes of a crystal structure can often be used to describe mechanisms of the structural phase transitions for a given material. While this is well established to the specific cases of inorganic perovskite ferroelectrics, this study has demonstrated that the

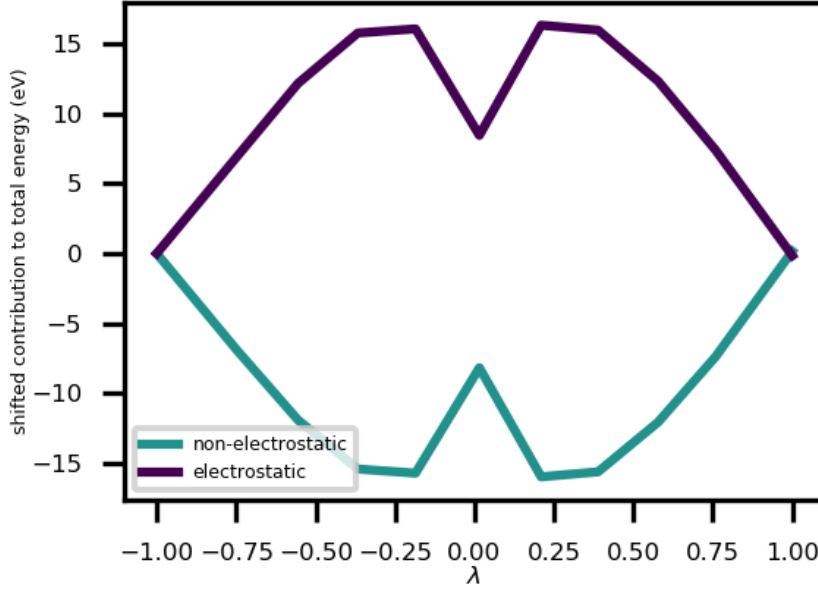


Figure 5.9: A plot of the ‘electrostatic’ (*i.e.* Hartree energy plus ionic interaction energy) and ‘non-electrostatic’ (*i.e.* total energy minus electrostatic contribution) contributions to the total energy at each point on the minimum energy path, relative to their values at $\lambda = -1$.

Table 5.2: A representative sample of the Born effective charge tensor of the H ions in croconic acid. Due to the $Pbcm$ symmetry of the hypothetical paraelectric phase of CRCA, these values apply to all hinge and terrace protons in the unit cell.

Ion	Norm of Born effective charge tensor in direction (e)		
	x	y	z
H (terrace)	3.10	2.15	1.58
H (hinge)	0.28	0.40	4.02

mechanism of field-induced polarization switching in croconic acid - and, likely, in other proton transfer ferroelectrics - is not efficiently expressed in terms of its phonon modes.

As described in Section 5.3.1, the successful effective Hamiltonian for barium titanate [117] constructed its degrees of freedom by projecting the three unstable modes of the crystal onto individual unit cells, and also including strain. We have shown, however, that the shape of the potential energy curve along the minimum energy switching path of CRCA is sensitive to the precise order of proton transfer, and that the proton transfer mechanism requires at least 8 modes to be approximated accurately enough for the resulting potential energy curve to be qualitatively similar in shape to that of the ideal path. If the construction of an effective Hamiltonian similar to Ref. 117 were attempted, at least this many modes would need to be projected onto individual unit cells to construct the degrees of freedom, leading to an impractical number of polynomial terms to fit. A basis for atomic displacements that allows individual atoms to move independently, instead of collectively within a unit cell, would be more suitable for the description of ferroelectricity in a proton transfer ferroelectric.

5.3.5 Computational details

For the ground state DFT calculations, an SCF convergence tolerance of 10^{-10} Ry/ion on the total energy was used. A cutoff of 200 Ry and Monkhorst-Pack mesh of (3,3,2) was sufficient to converge the ground state energy within a tolerance of 8.0×10^{-4} Ry/ion, and atomic forces to within a tolerance of 4.0×10^{-5} Ry/bohr. Ultrasoft pseudopotentials [105,127] were used to approximate the core electrons. Dispersion-corrected functionals [78,128] were used as described in Section 5.3.3.

In order to compute the non-analytical term correction [100] to the dynamical matrix at Γ the Born effective charge tensor was calculated according to density functional perturbation theory [100] as implemented in *Abinit*. Following the structure optimisation, the Kohn-Sham wavefunctions from the *Pbcm* structure were recalculated with an SCF convergence condition of the absolute difference between the squared residual of the Kohn-Sham potential at successive SCF iterations falling below a threshold of 10^{-18} Ha². The first order wavefunctions with respect to perturbations of atomic positions were calculated with an SCF convergence tolerance on the squared (effective) potential residual of 10^{-8} Ha². The potential energy surface calculations were supported by custom scripts to generate distorted atomic configurations and post-process the resulting *Quantum Espresso* output files.

Chapter 6

Effective Hamiltonians for ferroelectrics

Over the past several decades density functional theory (DFT) has been used to study interatomic interactions in various systems. When combined with appropriate algorithms, it is possible to calculate the structures of structural ground states, phonon spectra, and transition pathways, for example. In order to explain the behaviour of materials, however, it is often necessary to study the effect of these interactions on length- and time-scales beyond the practical reach of DFT. Effective Hamiltonians and interatomic potentials are models which approximate the potential energy of a system as a function of the atomic positions, without the expensive quantum mechanical calculation of the electronic structure.

In this chapter, we outline several studies on effective Hamiltonians and interatomic potentials for ferroelectrics, before describing in more detail the approach which we chose in order to model croconic acid (CRCA).

6.1 Effective Hamiltonians for ferroelectrics

6.1.1 Local mode expansion

The transition of a crystal from a paraelectric to ferroelectric state can be attributed to a limited number of the paraelectric state's normal phonon modes. At the transition temperature, the initially paraelectric crystal becomes dynamically unstable to at least one of these distortions, indicated by vanishing dynamical matrix eigenvalues corresponding to the unstable modes. These modes are said to *soften* [28].

Zhong, Vanderbilt and Rabe constructed an effective Hamiltonian of barium titanate (BTO) by assuming that the low energy distortions relative to its cubic phase can be expressed in terms of the transverse optic, and acoustic phonon modes which soften upon its cubic-tetragonal phase transition [117, 120]. They chose a set of *local modes* which can express these modes at any $\mathbf{k}$ in the Brillouin zone (BZ). An illustration of their local modes is provided in Figure 1 of Ref 120.

They also assume that the energy relative to the cubic phase can be written as a fourth-order Taylor expansion in the atomic distortions, which can be separated into a number of

contributions: (i) long-range, electrostatic interactions between separate local modes; (ii) short-range, quadratic covalent interactions between neighbouring local modes; (iii) local anharmonic self energy of each local mode (third and fourth order terms); (iv) elastic interaction between strain components; and (v) interaction between strain and local modes. Each contribution is associated with a number of parameters whose values were determined from a series of DFT total energy calculations of different distorted supercells of BTO. The local modes were chosen to be highly symmetric in order to reduce the number of independent parameters in the model, and the number of required calculations as a result.

After calculating the parameters of the model, they used it to carry out Metropolis Monte Carlo (MMC) simulations of the variation of BTO’s structure with temperature. Analysis of the average values of the local mode amplitudes revealed transitions between phases in a sequence (cubic-tetragonal-orthorhombic-rhombohedral) which agrees with experiment. This analysis also implied that the cubic-tetragonal transition of BTO has both displacive and order-disorder characteristics.

Given this success, Colizzi used the method to construct an effective Hamiltonian for potassium dihydrogen phosphate (KDP) [121]. In Colizzi’s MMC simulations, all strain contributions were neglected, apparently for the sake of computational simplicity [121, p.160]. His model calculated T_C estimates of 420 K and 630 K, depending on how dipole-dipole interactions were calculated, and indicated a second order phase transition (i.e. no finite jump in the order parameter $\langle Q_l \rangle$).

Colizzi acknowledges [121, p.164], however, that his model substantially overestimates KDP’s true Curie temperature of 123 K [25] and differs from experimental characterizations of its weakly first order transition [129]. He suggests that the omission of the strain degrees of freedom and higher energy (i.e. hard) local modes which strongly couple to the included modes and strain contributed to the errors he found. The significance of strain and hard modes to ferroelectric transitions is echoed by Tinte *et al* [130], who isolated their contribution to the MMC-estimated values of BTO’s transition temperatures.

6.1.2 Bond valence model

Simulations with the local mode expansion model of BTO were able to successfully reproduce many features of its phase transitions. However, alternative models, which make fewer assumptions about the significant atomic distortions, have typically been preferred for the purpose of simulating polarisation switching in ferroelectric perovskite oxides. A bond-valence model for PbTiO_3 was developed in order to study the polarisation switching mechanism of the material [118]. This interatomic potential allows the atoms to move independently of one another in contrast to the local mode expansion model, and expresses the potential energy as a sum of four terms, the first of which uses bond valence theory to express the potential energy of the system as a function of each atom’s deviation from its ‘desired’ bond-valence value [116].

The potential also accounts for the Coulomb interaction between atoms. Therefore, it is able to simulate the mixed ionic and covalent bonding which is responsible for ferroelectricity in PbTiO_3 . The potential’s error relative to a database of *ab initio* molecular dynamics (AIMD) energies and forces was optimised with respect to its ten parameters by simulated annealing.

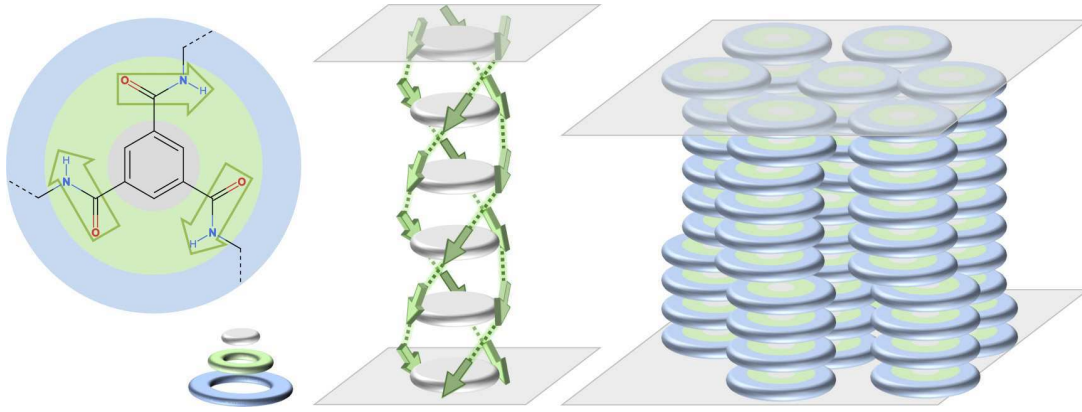


Figure 6.1: An illustration of structural hierarchy of ferroelectric trialkylbenzene-1,3,5-tricarboxamide (BTA), reproduced from Figure 1 of Ref 131 under the Creative Commons Attribution 4.0 International licence. On the left, an isolated BTA molecule showing the dipole of the amide groups. In the center, a vertical stack of BTA molecules, showing the alignment of the amide dipoles. On the right, an assembly of hexagonally packed stacks.

This use of first principles calculations on PbTiO_3 in order to calibrate the potential gave credibility to the conclusions drawn from the subsequent simulations.

Using molecular dynamics (MD), Shin *et al* were able to observe the nucleation and growth of critical nuclei at the simulated domain wall, and quantify the dependences of the nucleation and growth rates on temperature and external field strength. The classical nucleation theory of Miller and Weinreich [34] suggests that critical nuclei in PbTiO_3 are triangular and atomically thin. However, the more recent molecular dynamics simulations revealed square nuclei which, once nucleated, grow in two dimensions across the domain wall. The MD was also able to show that the switching rate of a unit cell on an edge of the nucleus depends on the polarisation states of the four horizontal and vertical neighbours.

As well as revealing insights which are not yet accessible using experimental techniques, the simulations also predicted the values of experimentally determined quantities. The nucleation and growth rates which were extracted from the MD simulations were used to parametrise a Monte Carlo simulation where the five-atom unit cell of PbTiO_3 was coarse-grained into a single unit, so that a supercell large enough to accurately measure the domain wall velocity ($\simeq 10^{-6}$ m) could be simulated. Like the nucleation and growth rate, the domain wall velocity was found to obey Merz's law. The activation field of the latter was found to agree with experimental measurements, which contrasts significantly with the Miller and Weinreich theory, which underestimates the domain wall velocity activation field by several orders of magnitude.

6.1.3 Electrostatic model for molecular dipoles

Trialkylbenzene-1,3,5-tricarboxamide (BTA) is a ferroelectric organic liquid crystal. Its structure comprises vertically stacked columns of benzene rings, each of which is attached to three dipolar groups. This hierarchy is illustrated in Figure 6.1. Ferroelectric switching is achieved by the rotation of these dipoles. The structure of the ferroelectric phase of BTA involves the orientation of dipoles in the same columnar stack into three helical chains, whose total polarisations point in the same direction.

Cornelissen *et al* [131] constructed an electrostatic Hamiltonian of BTA to simulate the switching kinetics of the material with the kinetic Monte Carlo (KMC) method. This Hamiltonian captured only the electrostatic interactions between the dipolar groups. The value of each dipole was expressed as the sum of a permanent component, whose orientation was restricted to two values which only differed in their z -components (i.e. parallel to the columns), and a component induced by the local electric field.

Similar to the simulations of PbTiO_3 [118] described in Section 6.1.2, BTA showed a clear nucleation and growth mechanism during polarisation switching. The dependence of this mechanism on temperature and the nucleation energy barrier has previously been explained by the theory of thermally activated nucleation-limited switching (TA-NLS) [132]. The values of the simulated coercive field for various temperature and external field sweep frequency values was fit to the formula for the coercive field provided by TA-NLS. This procedure resulted in a nucleation volume that corresponded to the space between the defects in the columns that were added to approximate the disorder in real BTA.

This restriction of the permanent dipole orientations to two values initially meant that during the KMC simulations, polarisation switching could only occur by changing only the z -component of all dipole orientations (a so-called z -flip) which changes the handedness of the triple helices of each column. However, in real BTA it is also possible for the dipoles to flip 180 degrees (a so-called full flip), switching the polarisation of a stack without changing the handedness of its triple helix. Switching via the full flip mode was found to have a coercive field 4 times greater than via the z -flip mode, which suggests the energetic favourability of the latter. The higher energy barrier of the full flip mode was explained by the head-to-head interaction that occurs upon the nucleation of a new domain through this mechanism.

This study demonstrates the applicability of KMC to the problem of field-induced switching mechanisms in organic ferroelectrics.

6.1.4 ReaxFF

At the time of the development of the ReaxFF force field [133], the majority of current interatomic potentials for molecular systems did not allow the breaking and formation of covalent bonds. The few which did, such as the Brenner potential [134] could not accurately describe the potential energy curves of bond dissociation, which is necessary for the study of the reactivity of hydrocarbons. ReaxFF was designed to fulfil this need, by defining many of the terms of a system's potential energy in terms of bond orders, which the developers assumed can be calculated from only interatomic separations. Moreover, bond orders as well as van der Waals and Coulomb interactions are calculated between all pairs of atoms in ReaxFF, so that bonds dissociate in a smooth manner.

With the goal of simulating hydrocarbon reactivity in mind, the parameters of ReaxFF were optimised to closely approximate a dataset which comprised dissociation energy curves of small molecules calculated with hybrid DFT, as well as optimised structures and heats of formation of a range of small and larger molecules. The resulting model was able to outperform PM3 [135], a significantly more expensive interatomic potential, in the accuracy of its prediction for the dependence of the potential energy of different molecules on selected bond lengths, valence bond

angles, torsion angles etc, with respect to DFT reference data.

A later version of ReaxFF [136] was developed to simulate the combustion of hydrocarbons by augmenting the dataset of the original version with DFT-calculated energies of transition states involved in hydrocarbon oxidation reaction mechanisms. This version of ReaxFF also achieved impressive accuracy in its predicted potential energy curves with respect to DFT reference data. Molecular dynamics simulations of the combustion of a range of different hydrocarbon molecules revealed the mechanisms of these reactions with atomistic detail, which current kinetic models had not been able to achieve.

Even more recently, a ReaxFF version was trained to simulate the effects of several extrinsic factors on ferroelectricity in barium titanate (BTO) [137]. These factors include the presence of oxygen vacancies, film thickness, and immersion in an aqueous medium. This investigation was focused on the behaviour of BTO in its cubic and tetragonal phases. Therefore the training dataset included DFT data which captured the equations of state for these two phases. So that the potential could accurately model the behaviour of oxygen vacancies, the dataset also included their formation energies and migration barriers.

NPT-molecular dynamics simulations with the model exhibited the expected ferroelectric phase transition at 240 K, which is closer to the experimental value (393 K) than the predictions of previous effective Hamiltonians and interatomic potentials. Subsequent simulations also emulated the experimentally observed dependence of polarisation in BTO on film thickness and oxygen vacancy concentration.

Before adopting and adapting the method described in Section 6.2, the combustion version of ReaxFF [136] was tested to see how well it could describe CRCA by attempting to find the ferroelectric ground state according to the implementation of ReaxFF in the LAMMPS software package [138], having initialised the atomic positions and unit cell dimensions to their values measured with x-ray diffraction [50]. However, a ground state with the appropriate Pca_2 symmetry could not be found.

6.1.5 Machine learning potentials

In the last two decades, machine learning techniques have become increasingly ubiquitous in material science. DFT and computational material science more generally have complemented practical experiments by giving researchers access to the electronic structure of materials from first principles. This has enabled a deeper understanding into the relationship between this structure and the properties of materials.

A material’s properties are often functionally useful; they may make the material suited to the solution of a particular problem. For example, an ideal photoconverter material for a photovoltaic solar cell has a band gap in a region of the solar spectrum where the irradiance is at its highest, so that plenty of photons are absorbed [139]. Researchers understandably believe that materials to solve problems such as this should be found somewhere in the vast chemical space of possible compounds. However, it is practically infeasible to conduct experiments to test even just the stability of all four-component compounds, for example, as this space has $\sim 10^{12}$ possible combinations [140]. Moreover, studying a set of systems as large as this is also beyond the reach of DFT. Therefore, researchers have used machine learning methods

to create computationally inexpensive models which utilise knowledge of existing materials to predict the properties of new ones, initially without the need to perform electronic structure calculations or practical experiments. These models shrink the set of compounds which are most likely to reward the investment of more expensive methods of computation and practical experimentation.

This is an example of supervised learning, whereby the developed algorithm is intended to approximate a function which accurately maps a material, represented by a vector in so-called feature space, to the space of some target variable (e.g. $\mathbb{R}$ in the case of the band gap). Mathematically, the potential energy surface of a crystal is a function $E : \mathbb{R}^{3N} \rightarrow \mathbb{R}$. Therefore, machine learning methods have also been applied to the creation of interatomic potentials.

Constructing an ML potential of a system involves designing a set of *descriptors*, which mathematically represent the atomic positions [141]. These descriptors are defined such that the potential satisfies the appropriate translational, rotational, and permutation symmetries. For example, the ANI neural network (NN) potential uses *atomic environment vectors* (AEVs) to represent the local environment surrounding each atom [142, 143]. The AEVs satisfy translational and rotational symmetries. The ANI potential energy is invariant under permutation of atoms of the same species since it is defined as the sum of the outputs of neural networks corresponding to each atom, and the neural networks of atoms of the same species are defined to be identical.

ANI was developed to calculate the energy of organic molecules. It is a deep NN potential, which effectively means that its adjustable parameters grant it great flexibility to approximate the shape of a complicated function. Due to this flexibility, deep NN potentials require large datasets to train accurately. The dataset used to train ANI-1, the first version of ANI, included DFT-calculated data from over 57 000 molecules [142, p. 3199]. With such a rich dataset, ANI-1 was able to achieve an impressive root mean squared energy error (RMSE) evaluated on a set of random, unseen conformations of the molecules in its training set equal to 1.8 kcal/mol [142].

TorchANI, the PyTorch implementation of ANI [143], was tested to see if this accuracy transferred to CRCA, an organic system containing C-, H-, and O-atoms like the molecules in the test set of ANI-1. The geometry of CRCA was optimised according to the model, similar to the ReaxFF test described in Section 6.1.4. Although a ground state with the correct $Pca2_1$ symmetry was found, the errors in the structure fostered doubt that TorchANI could describe ferroelectricity in CRCA in a physically valid way. The lengths and angles of the bonds which involve hinge and terrace protons from the relaxed structure are compared to their values obtained from neutron diffraction [51] in Table 6.1.

6.2 The second principles approach

The second principles approach [144, 145] to constructing an effective Hamiltonian for the perovskites strontium titanate and lead titanate has recently been developed. In the current section, we explain the method, as well as the adaptations we made to it to make it more suitable for modelling CRCA. The modified method was implemented as a package of related tools which the author has named Cronic.

This approach assumes that the potential energy of the system relative to a reference state

Variable	TorchANI	Neutron diffraction [51]
$l(\text{OH})_{\text{hinge}} (\text{\AA})$	0.96	1.01
$l(\text{O} \cdots \text{H})_{\text{hinge}} (\text{\AA})$	1.81	1.60
$l(\text{OH})_{\text{terrace}} (\text{\AA})$	0.96	1.01
$l(\text{O} \cdots \text{H})_{\text{terrace}} (\text{\AA})$	1.65	1.61
$\theta_{\text{hinge}} (\text{deg.})$	122.4	168.1
$\theta_{\text{terrace}} (\text{deg.})$	144.4	172.2

Table 6.1: A comparison of the values of bond lengths and valence angles associated with H-atoms in $Pca2_1$ -CRCA calculated using the TorchANI neural network potential to their corresponding values measured by neutron diffraction.

can be written as a Taylor expansion in the atomic positions and strain. For a ferroelectric, this reference state is usually the structure of the high-symmetry, parent phase. The expansion can be split into sums which couple only atomic displacement components ($E_p(\mathbf{X})$), only strain components ($E_s(\boldsymbol{\eta})$), and those which mix atomic displacement and strain components together ($E_{sp}(\mathbf{X}, \boldsymbol{\eta})$),

$$E(\mathbf{X}, \boldsymbol{\eta}) = E_p(\mathbf{X}) + E_s(\boldsymbol{\eta}) + E_{sp}(\mathbf{X}, \boldsymbol{\eta}). \quad (6.1)$$

Experimental measurements of CRCA suggest that its polarisation switching mechanism does not strongly depend on mechanical deformation. Its direct piezoelectric coefficient is two orders of magnitude smaller than those of commercially utilised lead zirconate titanate (PZT) piezoelectric alloys [146], for example. This has been attributed to the proton transfer mechanism of ferroelectricity, which involves significantly less deformation of the crystal structure than the mechanisms of many non-proton transfer ferroelectrics [146]. Moreover, in Section 5.3.3 we reported our calculation of the minimum energy path (MEP) between the two domain states of CRCA using the nudged elastic band (NEB) algorithm with unit cell dimensions fixed to their $Pbcm$ -CRCA values. We found that this path involved the transfer of the 8 protons in the CRCA unit cell in 4 successive pairs. Although the proton transfer order for this path (HTTH) differed from the THHT order of the MEP calculated previously [54], we showed that a HTTH MEP does also exist when the unit cell dimensions are changed to their calculated $Pca2_1$ -CRCA values. The occurrence of the HTTH MEP with both sets of unit cell dimensions suggests that the straining of the crystal during its hypothetical transition between the paraelectric and ferroelectric phases does not effect the polarisation switching mechanism. Therefore, it is physically valid to make the approximation that relative to $Pbcm$ -CRCA, $\boldsymbol{\eta} = \mathbf{0}$ during polarisation switching between its domain states, and to adopt the simplified case of $E(\mathbf{X}) = E_p(\mathbf{X})$.

6.2.1 Satisfying translational invariance

The energy of a crystal does not change if all of its atoms are translated by the same amount in the same direction. Therefore, an effective Hamiltonian describing a crystal in terms of its atomic positions must be translationally invariant. In the original expansion described in Refs 144 and 145 translational invariance was satisfied by expanding E in terms of products of displacement differences. In our modified version of the second principles approach, however,

translational invariance is satisfied by firstly defining a projection matrix $\mathbf{P}$ whose elements are

$$\begin{aligned} P_{ai\,bj} &= \mathbf{1}_{ai\,bj} - \sum_k [\mathbf{D}^{(k)} \otimes \mathbf{D}^{(k)}]_{ai\,bj} \\ &= \delta_{ij}(\delta_{ab} - \frac{1}{N}), \end{aligned} \quad (6.2)$$

where

$$D_{ai}^{(j)} = \frac{1}{\sqrt{N}} \delta_{ij}, \quad (6.3)$$

is a normalised vector which displaces the entire system in Cartesian direction j and N is the number of atoms in the crystal. Note that in the following presentation, the Einstein summation convention is used unless the summation symbol is explicitly included. We find that

$$\begin{aligned} [\mathbf{P} \cdot \mathbf{D}^{(k)}]_{ai} &= P_{ai\,bj} D_{bj}^{(k)} \\ &= \sum_{bj} \delta_{ij}(\delta_{ab} - \frac{1}{N}) \frac{1}{\sqrt{N}} \delta_{jk} \\ &= \sum_b (\delta_{ab} - \frac{1}{N}) \frac{1}{\sqrt{N}} \delta_{ik} \\ &= \left(\sum_b \delta_{ab} - \frac{1}{N} \right) \frac{1}{\sqrt{N}} \delta_{ik} \\ &= \left(1 - \frac{N}{N} \right) \frac{1}{\sqrt{N}} \delta_{ik} = 0, \end{aligned} \quad (6.4)$$

so $\mathbf{P} \cdot (\mathbf{X} + w^j \mathbf{D}^{(j)}) = \mathbf{P} \cdot \mathbf{X}$. Therefore translational invariance is satisfied if $E(\mathbf{X})$ is expressed as

$$E(\mathbf{X}) = E'(\mathbf{P} \cdot \mathbf{X}), \quad (6.5)$$

for some function E' .

6.2.2 Satisfying space group symmetry

The energy of a distorted crystal does not change if the crystal is transformed according to one of the space group symmetry operations of the undistorted crystal. We therefore demand that E satisfies this symmetry. A space group operation transforms a set of atomic displacements by mapping each atom a according to a permutation σ and rotating its displacement under a matrix $\boldsymbol{\rho}$, *i.e.*

$$X_{ai} \rightarrow X'_{ai} = \rho_{ij} X_{\sigma^{-1}(a)j} \equiv [\mathbf{G}(\mathbf{X})]_{ai}. \quad (6.6)$$

Space group symmetry of a function $f = f(\mathbf{X})$ is expressed as

$$f(\mathbf{G}(\mathbf{X})) = f(\mathbf{X}). \quad (6.7)$$

We find that if E' satisfies the space group symmetry of the system, then $E(\mathbf{X}) = E'(\mathbf{P} \cdot \mathbf{X})$ does too. To prove this, we first show that $\mathbf{G}(\mathbf{P} \cdot \mathbf{X}) = \mathbf{P} \cdot \mathbf{G}(\mathbf{X})$.

$$\begin{aligned}
[\mathbf{P} \cdot \mathbf{G}(\mathbf{X})]_{ai} &= P_{ai} b_j [\mathbf{G}(\mathbf{X})]_{bj} \\
&= P_{ai} b_j \rho_{jk} X_{\sigma^{-1}(b)k} \\
&= P_{ai} \sigma(b)_j \rho_{jk} X_{bk} \\
&= \delta_{ij} \left(\delta_{a\sigma(b)} - \frac{1}{N} \right) \rho_{jk} X_{bk} \\
&= \delta_{ij} \left(\delta_{\sigma^{-1}(a)b} - \frac{1}{N} \right) \rho_{jk} X_{bk} \\
&= \rho_{ik} \left(\delta_{\sigma^{-1}(a)b} - \frac{1}{N} \right) X_{bk} \\
&= \rho_{ij} \delta_{jk} \left(\delta_{\sigma^{-1}(a)b} - \frac{1}{N} \right) X_{bk} \\
&= \rho_{ij} P_{\sigma^{-1}(a)j} X_{bk} \\
&= [\mathbf{G}(\mathbf{P} \cdot \mathbf{X})]_{ai}.
\end{aligned} \tag{6.8}$$

Therefore,

$$E(\mathbf{G}(\mathbf{X})) = E'(\mathbf{P} \cdot \mathbf{G}(\mathbf{X})) = E'(\mathbf{G}(\mathbf{P} \cdot \mathbf{X})) = E'(\mathbf{P} \cdot \mathbf{X}) = E(\mathbf{X}),$$

as claimed.

6.2.3 Generalised displacement couplings

Satisfying translational invariance in the way described in Section 6.2.1 allows us to use couplings apart from displacement differences. In our implementation, an expansion term is a product of amplitudes of a set of displacement basis modes, each of which can displace an arbitrary number of atoms. In the case of croconic acid, this allowed the distortion of each C_5O_5 molecule to be coarse-grained with its ferroelectric distortion modes, instead of the 30 degrees of freedom associated with each molecule. That is, we assumed that the region of configuration space most relevant to polarisation switching could be expressed as

$$X_{ai} = Q^{(n)} V_{ai}^{(n)}, \tag{6.9}$$

for basis modes $\mathbf{V}^{(n)}$ and amplitudes $Q^{(n)}$. The $Q^{(n)}$ can be calculated according to

$$Q^{(n)}(\mathbf{X}) = \bar{\mathbf{A}}^{nm} V_{ai}^{(m)} X'_{ai}. \tag{6.10}$$

where $\bar{\mathbf{A}}$ is the inverse of the Gram matrix $\mathbf{A}$ of the basis which has elements

$$A^{nm} = \mathbf{V}^{(n)} \cdot \mathbf{V}^{(m)}. \tag{6.11}$$

E' is therefore expressed as

$$E'(\mathbf{X}) = \sum_p \theta_p u_p(\mathbf{X}) = \sum_p \theta_p \prod_s Q^{ps}(\mathbf{X}), \tag{6.12}$$

where the Q have now been labelled by their term p and their index s in the term.

6.2.4 Generating the symmetry-adapted terms

Two terms p and r are symmetry equivalent if there exists a $\mathbf{G}$ which satisfies $u_p(\mathbf{G}(\mathbf{X})) = u_r(\mathbf{X})$. Space group symmetry of E' is satisfied if for all pairs of symmetry equivalent terms p and r , $\theta_p = \theta_r$. The terms u_p and u_r are symmetry equivalent if their couplings can be ordered such that each pair of couplings $(Q^{ps}(\mathbf{X}), Q^{rs}(\mathbf{X}))$ is also equivalent. To generate classes of symmetry equivalent couplings, we assume that the atoms are partitioned into sets S_α and the basis modes into sets $W_\alpha = \{\mathbf{V} | V_{ai} \neq 0 \Rightarrow a \in S_\alpha\}$. In this case the Gram matrix $\mathbf{A}$ for the basis set $\mathbf{V}^{(n)}$ is block diagonal, *i.e.*

$$A^{\alpha\mu, \beta\nu} = \delta^{\alpha\beta} A^{\alpha\mu, \beta\nu}. \quad (6.13)$$

In the following, it is convenient to now label the $\mathbf{V}^{\alpha\mu}$ and corresponding $Q^{\alpha\mu}$ by their class of atoms S_α and their index μ within the set W_α . We also define the set

$$f(\mathbf{G}; W_\alpha) \equiv \{\mathbf{G}(\mathbf{V}) \forall \mathbf{V} \in W_\alpha\},$$

i.e. the action [14] of the space group operation $G \in \mathcal{G}$ on the set W_α , where $\mathcal{G}$ is the space group. We demand that the set $\{W_\alpha\}$ is closed under each of the operations $f(\mathbf{G}, \cdot)$. This is satisfied by the basis set which was used for our effective Hamiltonian of CRCA described in Section 6.3.1. In this case, for sets α, β which satisfy $W_\alpha = f(\mathbf{G}; W_\beta)$, we have $\mathbf{V}^{(\alpha\mu)} = \mathbf{G}(\mathbf{V}^{(\beta\mu)}) \forall \mu \in \{1, \dots, |W_\alpha|\}$. If we denote $\mathbf{X}' = \mathbf{G}(\mathbf{X})$, this implies that

$$\begin{aligned} Q^{\alpha\mu}(\mathbf{X}') &= \sum_{\gamma\nu ai} \delta^{\alpha\gamma} \bar{A}^{\alpha\mu\gamma\nu} V_{ai}^{\gamma\nu} X'_{ai} \\ &= \sum_{\nu ai} \bar{A}^{\alpha\mu\alpha\nu} V_{ai}^{\alpha\nu} X'_{ai} \\ &= \sum_{\nu a j k i} \bar{A}^{\alpha\mu\alpha\nu} (\rho_{ik} V_{\sigma^{-1}(a)k}^{\beta\nu}) (\rho_{ij} X_{\sigma^{-1}(a)j}) \\ &= \sum_{\nu a j k} \bar{A}^{\alpha\mu\alpha\nu} \delta_{jk} V_{\sigma^{-1}(a)k}^{\beta\nu} X_{\sigma^{-1}(a)j} \\ &= \sum_{\nu a j} \bar{A}^{\alpha\mu\alpha\nu} V_{\sigma^{-1}(a)j}^{\beta\nu} X_{\sigma^{-1}(a)j} \\ &= \sum_{\nu a j} \bar{A}^{\alpha\mu\alpha\nu} V_{aj}^{\beta\nu} X_{aj}, \end{aligned} \quad (6.14)$$

Now, Equation 6.13 implies that

$$\begin{aligned}
A^{\alpha\mu,\alpha\nu} &= V_{ai}^{\alpha\mu} V_{ai}^{\alpha\nu} \\
&= \rho_{ij} V_{\sigma^{-1}(a)j}^{\beta\mu} \rho_{ik} V_{\sigma^{-1}(a)k}^{\beta\nu} \\
&= \delta_{jk} V_{\sigma^{-1}(a)j}^{\beta\mu} V_{\sigma^{-1}(a)k}^{\beta\nu} \\
&= V_{\sigma^{-1}(a)j}^{\beta\mu} V_{\sigma^{-1}(a)j}^{\beta\nu} \\
&= V_{aj}^{\beta\mu} V_{aj}^{\beta\nu} \\
&= A^{\beta\mu,\beta\nu} \\
\rightarrow \bar{A}^{\alpha\mu,\alpha\nu} &= \bar{A}^{\beta\mu,\beta\nu}.
\end{aligned} \tag{6.15}$$

Therefore,

$$\begin{aligned}
Q^{\alpha\mu}(\mathbf{X}') &= \sum_{taj} \bar{A}^{\alpha\mu\alpha t} V_{aj}^{\beta t} X_{aj} \\
&= \sum_{atj} \bar{A}^{\beta\mu\beta t} V_{aj}^{\beta t} X_{aj} \\
Q^{\alpha\mu}(\mathbf{X}') &= Q^{\beta\mu}(\mathbf{X}).
\end{aligned} \tag{6.16}$$

Reverting to the original index scheme, where p indexes terms and s indexes couplings owned by the term, we find that we can generate classes c_λ of terms equivalent to u_p by repeated application of the symmetry operations on the basis modes V^{ps} owned by its couplings Q^{ps} . Symmetry-adapted terms,

$$t_\lambda(\mathbf{X}) = \sum_{p \in c_\lambda} u_p(\mathbf{X}), \tag{6.17}$$

are sums of these classes, so E' can be expressed as

$$E'(\mathbf{X}) = \sum_{\lambda} \theta_{\lambda} t_{\lambda}(\mathbf{X}). \tag{6.18}$$

The infinite pool of possible symmetry-adapted terms that exist in Equation 6.18 must be truncated to practically train a model. As described in Ref 145 a term is included if the separation of the atoms it couples, the number of atoms that it couples, and its polynomial order are all lower than upper limits that are adjusted appropriately to train an accurate model. Large limits tend to produce a large pool of terms, small limits tend to produce a smaller pool of terms. Training a model from a larger pool can potentially be more accurate since it permits the model to have greater flexibility. However, it can also be more computationally expensive. As ever, one must balance the desire for accuracy against the computational cost.

6.2.5 The iterative training scheme

To be practically computed, E' must also be truncated. We seek a series of models of increasing size p with successively improving accuracy. In statistical model fitting, the accuracy of a model is often quantified by a *goal function* (GF). Therefore, for each p we seek a set of terms $\mathcal{T}_p \equiv \{t_1, \dots, t_p\}$ and corresponding coefficients $\Theta_p \equiv \{\theta_1, \dots, \theta_p\}$ that minimise the

goal function.

Training a model involves minimising the GF with respect to the model's parameters. Reference 145 defines a goal function which is quadratic in the model parameters θ_λ . We found it useful to generalise this definition to include arbitrary weights for the averaging since it allowed us to experiment with constructing initial rough models with fixed C_5O_5 rings, and free H-atoms. It was also appropriate to use forces in the basis introduced in Equation 6.9, as this was consistent with our acceptance of the limitation of the effective Hamiltonian's region of applicability to the space spanned by this basis. Analogously to [145] we denote forces in the basis of the $\{\mathbf{V}^{(j)}\}$ by

$$f_n = -\frac{\partial E}{\partial Q_n}, \quad (6.19)$$

so that G is defined as

$$G(\Theta_p, \text{TS}) = \sum_{sn} (f_n^{\text{TS}}(s) - f_n[\Theta_p](s))^2 w_n, \quad (6.20)$$

where the training set ($f_n^{\text{TS}}(s)$) and model ($f_n[\Theta_p](s)$) forces correspond to configurations in the training set, indexed by s , and the w_n are the averaging weights described above. As a result, the definitions of Δ and Γ from [145] are changed to

$$\Delta_{\mu\lambda} = \sum_{sn} \bar{f}(s)_{\lambda n} \bar{f}(s)_{\mu n} w_n, \quad (6.21)$$

and

$$\Gamma_\mu = \sum_{ns} (f_n^{\text{TS}}(s) - f_n^{\text{fixed}}(s)) \bar{f}_{\mu n}(s) w_n, \quad (6.22)$$

where

$$\bar{f}_{\lambda n}(s) = -\frac{t_\lambda(\mathbf{X}_s)}{Q_n}, \quad (6.23)$$

and $f_n^{\text{fixed}}(s)$ is the n component of forces due to any part of the Hamiltonian which can be calculated before hand (e.g. harmonic force constants which can be calculated using finite difference approximations or density functional perturbation theory).

Given a set of terms $\mathcal{T}_p$, the corresponding Θ_p are found by solving the set of linear equations [145]

$$\Delta_{\mu\lambda} \theta_\lambda = \Gamma_\mu. \quad (6.24)$$

Although the quadratic dependence of G on θ_λ makes its minimisation with respect to a selected $\{\theta_\lambda\}$ efficient, it is not computationally feasible to calculate Θ_p for all possible models of length p which can be extracted from a typical pool of terms. For example, the pool of terms that was used to train our effective Hamiltonian for CRCA described in Chapter 6.3 contained 19076 terms. If an effective Hamiltonian with a typical number of ~ 20 terms were desired, $\simeq 10^{67}$ candidate models would have to be checked.

Therefore, an iterative *forward selection* scheme is used to train models of length p instead.

1. Calculate $G(\Theta_{p+1})$ for all models $\mathcal{T}_p \cup \{t_i\}$, where $t_i \in \mathcal{T}_P \setminus \mathcal{T}_p$.
2. Add the term t_{i^*} with the smallest $G(\Theta_{p+1})$ value.

3. If G has converged, exit, else increment $p \rightarrow p + 1$ and return to Step 1.

This method generates an ordered set of models with different numbers of fitted terms. Section 6.3.4 explains how we selected the optimal model from the set of models generated to simulated CRCA.

6.3 An effective Hamiltonian for croconic acid

6.3.1 The pool of Hamiltonian terms

The previous iteration of the effective Hamiltonian method [144, 145] used polynomial terms which were products of atomic displacement differences and strain components. If we ignore the strain couplings, in the notation of Section 6.2.3, each term $u_p(\mathbf{X})$ had the form

$$u_p(\mathbf{X}) = \prod_s (\mathbf{v}^{(ps)} \cdot \mathbf{X}), \quad (6.25)$$

where

$$V_{ai}^{(ps)} = \begin{cases} +1 & a = a_{ps}^{(+)}, i = i_{ps} \\ -1 & a = a_{ps}^{(-)}, i = i_{ps} \\ 0 & \text{otherwise,} \end{cases} \quad (6.26)$$

where $a_{ps}^{(\pm)}$ are the atoms and i_{ps} is the Cartesian direction that is coupled by this displacement difference. Using displacement differences as the basis modes of the Hamiltonian is desirable because, in principle, any potential energy surface (PES) can be fitted by adding more terms at higher orders. However, in practice, a larger model requires a larger training set to obtain accurate coefficients (θ_λ in Equation 6.18) which are not overfitted to that dataset. Refs 144 and 145 demonstrate that these terms were appropriate for effective Hamiltonians of the perovskites SrTiO_3 and PbTiO_3 . This suggests that the PESs of these perovskites are efficiently expressed as a sum of a relatively small number of symmetry-adapted terms whose constituents have the form of Equation 6.25. However, the mixed ionic and covalent bonding in the aforementioned perovskites is qualitatively different to the covalent and hydrogen bonding in supramolecular systems like croconic acid (CRCA). The PES of a system like CRCA cannot be efficiently captured by terms in the form of Equation 6.25 alone. Indeed, interatomic potentials for covalent bonds have been historically expressed as products of changes in bond lengths, bond angles, dihedral angles etc.

The purpose of our effective Hamiltonian for CRCA is to simulate the switching of its polarisation. It is most important to accurately capture the low energy regions of the PES between the domain states, because the polarisation switching path is most likely to traverse these regions due to their energetic favourability. Sections 5.3.3 and 7.1 describe the minimum energy path (MEP) between domain states of a unit cell of CRCA calculated with the nudged elastic band algorithm according to DFT. Along this MEP, the protons are transferred in coordinated pairs, while the C_5O_5 molecules tilt as largely rigid units. Therefore, we decided to use generalised displacement couplings (explained in Section 6.2.3) for the C_5O_5 molecules that included all ten atoms within these units, rather than the adjacent pairs included in the displacement differences described in Equation 6.25. A convenient choice for these couplings is the set of 8 *ferroelectric distortion modes* (FDMs), which we can define in the notation of

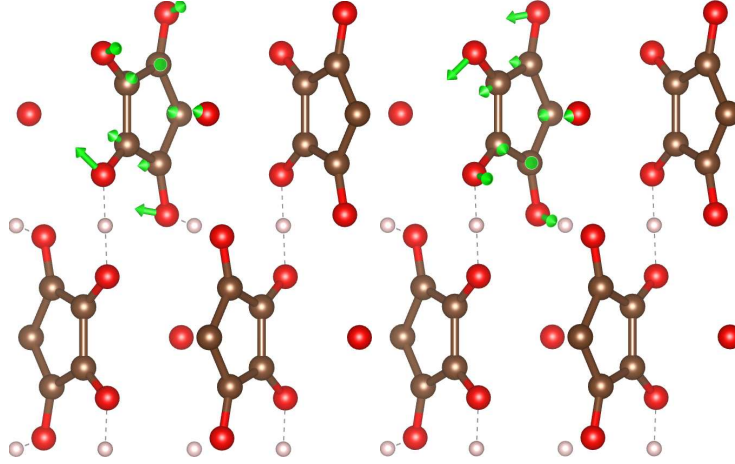


Figure 6.2: Two ferroelectric distortion modes for a single C_5O_5 of croconic acid.

Section 6.2.3 for each C_5O_5 molecule α as

$$V_{ai}^{(\alpha\mu)} = \begin{cases} X_{ai}^{(\mu)} & a \in S_\alpha \\ 0 & \text{otherwise,} \end{cases} \quad (6.27)$$

where $\mu = \pm$ and $\mathbf{X}^{(\pm)}$ are the atomic distortions of the positive and negative domain states, defined by Equation 5.2. The FDMs for a single C_5O_5 molecule are illustrated in Figure 6.2.

The FDMs $\{\mathbf{V}^{(\alpha\mu)}\}$ are a convenient choice due to their symmetry. They comprise a set of objects on which we can define the action [14] of the space group of CRCA, $Pbcm$. We can show that $\{\mathbf{V}^{(\alpha\mu)}\}$ is identical to the $Pbcm$ -orbit of an arbitrary FDM, say $\mathbf{V}^{(\alpha'\mu')} \in \{\mathbf{V}^{(\alpha\mu)}\}$. Firstly, we note that $Pbcm$ can be partitioned into two right cosets of $Pca2_1$:

$$Pbcm = Pca2_1 \cup Pca2_1 i, \quad (6.28)$$

where i is the point inversion operation, and

$$G g_j = \{g_1 g_j, \dots, g_n g_j\}, \quad (6.29)$$

for a finite group G of order n , with elements g_k . The $Pbcm$ -orbit of $\mathbf{V}^{(\alpha'\mu')}$ can be partitioned in an analogous way:

$$Pbcm \mathbf{V}^{(\alpha'\mu')} = Pca2_1 \mathbf{V}^{(\alpha'\mu')} \cup Pca2_1 i \mathbf{V}^{(\alpha'\mu')}. \quad (6.30)$$

$Pca2_1 i \mathbf{V}^{(\alpha'\mu')}$ is the set of FDMs in the opposite domain state (i.e. with $\mu \neq \mu'$). Therefore the orbit $Pbcm \mathbf{V}^{(\alpha'\mu')}$ is partitioned by the sets of FDMs of the two domain states, and the union of these sets of FDMs is equal to the orbit $Pbcm \mathbf{V}^{(\alpha'\mu')}$, as claimed.

This property of the FDMs contrasts with the corresponding property of a general set of C_5O_5 displacement couplings. There are elements in the $Pbcm$ -orbit of an element from a set of general displacement couplings that are not in the set of couplings. In the worst case, each orbit is disjoint, and the set of displacement couplings has $n_{\text{couplings}} |Pbcm|$ elements, where $n_{\text{couplings}}$ is the number of couplings assigned to each molecule, and $|Pbcm| = 8$ is the size of

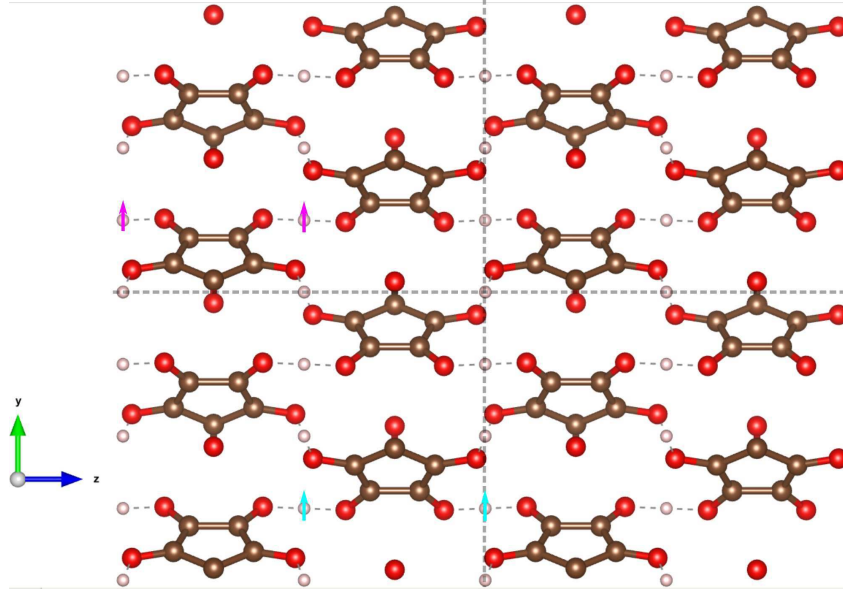


Figure 6.3: An illustration of polynomial terms p_1 (magenta) and p_2 (cyan) given in Equation 6.32.

the space group $Pbcm$. For our effective Hamiltonian, $n_{\text{couplings}} = 2$, so the set of displacement couplings would have equalled $16 > 8$. The pool of polynomial terms is generated by combining the displacement couplings, and the elements of their $Pbcm$ -orbits. The union of $Pbcm$ -orbits of the set of FDMs is smaller than that of a general set of C_5O_5 displacement couplings. This reduces the number of displacement couplings to be combined and vastly reduces the size of the resulting pool of terms. This in turn reduces the time required to train a model by forward selection; the computing time required in Step 1 in the algorithm outlined at the end of Section 6.2.5 scales linearly with the size of the pool.

On the other hand, we chose Cartesian modes, defined as

$$V_{ai}^{(p\mu)} = \begin{cases} 1 & a = a_p, i = \mu \\ 0 & \text{otherwise,} \end{cases} \quad (6.31)$$

where a_p is the index in the unit cell of the p th proton and $\mu \in \{0, 1, 2\}$, rather than FDMs as the basis modes of the H-atoms. In practice, we found that constructing a model from terms which included H-atom FDMs and molecular FDMs gave unacceptably large errors, likely due to the additional bias error introduced to the model relative to that incurred by the use of Cartesian modes.

For our model, the pool comprised all terms which combined molecular FDMs and H-atom Cartesian modes, whose atoms were separated by $< 6.9\text{\AA}$. This effectively meant that each FDM and its four surrounding H-atoms could be coupled together, but distinct FDMs could not be coupled in the same term. Symmetry-adapted terms up to fourth-order were generated since this is the lowest order [144, 145] of an effective Hamiltonian which can capture the structural instability at $\mathbf{X} = \mathbf{0}$ and the minima at $\mathbf{X} = \mathbf{X}^{(\pm)}$.

	CP2K		Quantum Espresso		Expt. ¹
	result	error	result	error	
a (bohr, %)	16.01	1.71	16.63	2.13	16.29
b (bohr, %)	9.78	1.54	9.81	1.89	9.70
c (bohr, %)	20.55	0.40	20.98	1.71	20.32
$l(\text{OH})_{\text{hinge}}$ (bohr, %)	1.97	3.43	1.92	0.98	1.90
$l(\text{O} \cdots \text{H})_{\text{hinge}}$ (bohr, %)	2.90	4.26	3.12	2.82	3.03
$l(\text{OH})_{\text{terrace}}$ (bohr, %)	1.96	3.18	1.92	1.02	1.90
$l(\text{O} \cdots \text{H})_{\text{terrace}}$ (bohr, %)	2.89	5.08	3.09	1.34	3.04
θ_{hinge} (deg., deg.)	167.2	0.9	167.4	0.7	168.1
θ_{terrace} (deg., deg.)	174.2	2.0	172.0	0.2	172.2

¹ S. Mukhopadhyay *et al.*, *Chemical Physics*, 2013, **427**, 95-100

Table 6.2: A comparison of the energies and bond geometries of the $Pca2_1$ -CRCA domain state, calculated by optimising atomic positions and unit cell dimensions using CP2K and Quantum Espresso. Computational details are explained in Sections 5.1.1 and 6.3.2.

6.3.2 Generating training data

Distinguishability of Hamiltonian terms

In order to train an effective Hamiltonian using the method described in Section 6.2 for the simulation of a material’s behaviour, it is necessary to obtain a dataset of atomic force data which captures the relevant regions of the potential energy surface (PES) of the material. The dataset-supercell must be large enough for every term in the pool to be instantiated distinctly. In the case of an orthorhombic supercell, if the cutoff for the separation of atoms coupled by the terms in the model is denoted by l_{cut} , such a distinction between the polynomial terms is possible if $l_{\text{cut}} < a_{\text{min}}/2$ where a_{min} is the smallest dimension of the supercell. An example of the violation of this condition is illustrated in Figure 6.3. This figure represents two terms:

$$p_1(\mathbf{X}) = \theta_1 y_{H5,0,0,0} y_{H4,0,0,0} \text{ and } p_2(\mathbf{X}) = \theta_2 y_{H5,0,0,0} y_{H4,0,0,1}, \quad (6.32)$$

where $w_{a,k,l,m}$ is the w -component of the displacement relative to its position in $Pbcm$ -CRCA of atom a in the unit cell in position (k, l, m) in relative coordinates. The magenta arrows represent the primitive-lattice-translational image of p_1 centred on unit cell $(0,1,0)$, while the cyan arrows represent the primitive-lattice-translational image of p_2 centred on unit cell $(0,0,0)$. These two terms would both be instantiated as $\theta y_{H5,0,0,0} y_{H4,0,0,0}$ (represented by the pair of magenta arrows) in a $(1,1,1)$ cell due to periodic boundary conditions. As explained in Ref 145, from the perspective of the model training algorithm, these two terms are identical. If they were both selected by the algorithm, linear dependencies in the system of equations 6.24 would arise, resulting in infinite solutions. However, if the supercell is expanded to have dimensions of at least $(1,1,2)$, the two terms are instantiated distinctly, and this problem is avoided.

Computational details

Due to this necessity for a large supercell size, we used CP2K [147] to generate the dataset, since the Quickstep algorithm [70] that it implements is more computationally efficient for molecular systems of $\gtrsim 100$ atoms. To simulate CRCA with CP2K, the revised Vydrov-van Voorhis (rVV10) van der Waals density functional [81] was used to capture van der Waals interactions. The inclusion of van der Waals interactions in the Kohn-Sham potential would be expected to significantly impact the effect of stress on the polarisation switching mechanism of CRCA, insofar as the stress effect is significant. As explained in Section 6.2, the stress effect was neglected for the present work, but could be explored in the future using this methodology.

Spin-restricted DFT was used throughout. Although this provided computational savings, including spin polarisation is necessary, in principle, to accurately model bond breaking, such as that which occurs due to the transfer of protons during polarisation switching in CRCA. Its exclusion meant that proton transfer barriers were slightly overestimated, due to the relative lack of variational freedom in the wavefunction, especially at structural transition states. The impact of this exclusion was estimated by calculating the total energy both with and without spin-restriction for the same *Pbcm*-CRCA configuration. The difference between the two values was 6.23×10^{-7} eV/atom, a negligible amount.

The separable, norm-conserving pseudopotentials of Goedecker, Teter, and Hutter [87] were used to capture the effects of core electrons. The TZV2PX-MOLOPT basis set, which was optimised for calculations on small molecules [71], was also selected. It was chosen because it was the largest set from the family, and the only set that included diffuse functions, which are important for the calculation of relative energies of structures where bonds are not broken [68], such as those arising as the C_5O_5 molecules of CRCA tilt during polarisation switching.

Although the Quickstep algorithm allows larger systems to be simulated more efficiently than with plane wave codes, it is more difficult to reach the basis set limit for calculations of the PES of a solid state system using atom-centred basis sets, than it is with a plane wave basis set. The incompleteness error (BSIE) for the TZV2PX-MOLOPT basis set, evaluated on a set of molecules which was separate to the set used to optimize its coefficients and exponents, was estimated to be ~ 1 mHa/atom [71]. The systematic nature of the BSIE means that energy differences (e.g. calculated relative to the *Pbcm*-CRCA total energy) are expected to benefit from some error cancellation. Nonetheless, the BSIE represents a substantial lower bound of the error in the training data of the PES of CRCA relative to the basis set-converged PES at the rVV10 level of theory. So that the actual error in our training data would be as close to this lower bound as possible, the total energy was converged with respect to the coarse grid cutoff, relative cutoff and supercell dimensions such that the estimated error due to the boundedness of these parameters was significantly less than the BSIE.

A coarse grid cutoff of 3500 Ry, relative cutoff of 50 Ry was sufficient to converge the total energy with an accuracy of 41 μ Ha/atom. The supercell size was set to (2,2,2) since this was the smallest size of supercell which allowed the fitting algorithm to distinguish all terms in our pool when instantiated in the supercell, avoiding the problem described earlier in the current section.

The accuracy of the calculations with CP2K was compared to the accuracy of the plane

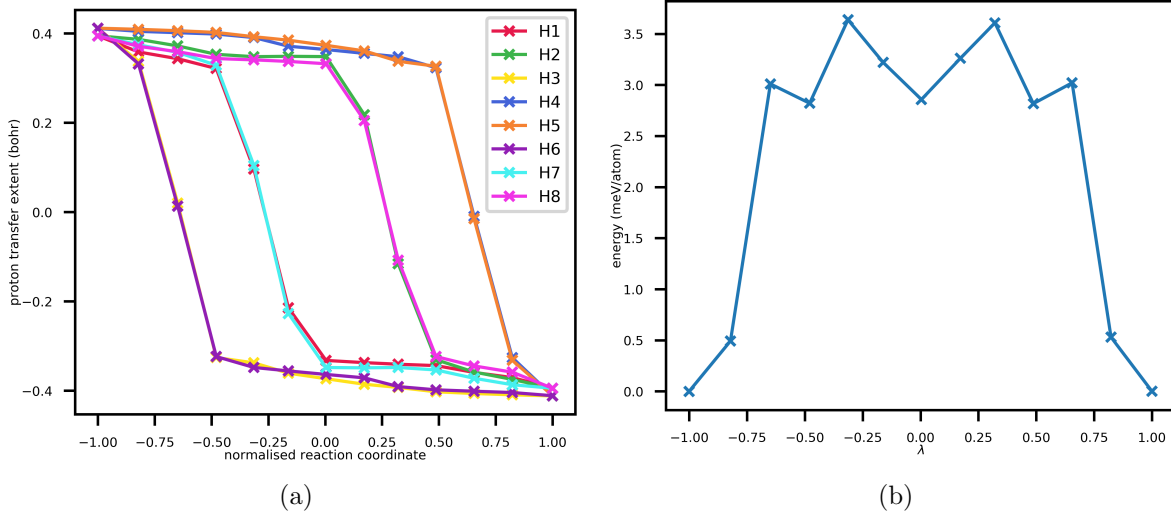


Figure 6.4: (a) A plot of the proton transfer extent trajectories along the minimum energy path between croconic acid’s domain states, calculated using the NEB method and CP2K. (b) A plot of the potential energy curve along the minimum energy path between croconic acid’s domain states, calculated using the NEB method and CP2K.

wave calculations with Quantum Espresso (described in Chapter 5) by comparing the $Pca2_1$ -CRCA crystal structures predicted by the two methods. CP2K gives unit cell dimensions with a similar accuracy to Quantum Espresso. Evidently, the accuracy of the unit cell dimensions is less strongly dependent on basis set completeness than the bond lengths and angles, which CP2K predicts reasonably but somewhat less accurately than Quantum Espresso. The atomic positions of $Pca2_1$ -CRCA calculated by CP2K and Quantum Espresso are given in Table A.3.

The physical validity of the PES of CRCA according to the Quickstep method was also confirmed by calculating the minimum energy path (MEP) between domain states using the nudged elastic band (NEB) method, and comparing it to the MEP which was calculated with Quantum Espresso, and reported in Section 5.3.3. At the time of our study, CP2K did not allow NEB calculations to be performed on a supercell under constraints of primitive lattice translational-symmetry. Therefore, the CP2K NEB calculations were performed on a single unit cell. While we acknowledge that these calculations were not converged with respect to supercell size, it is significant that the MEP involves the pairwise transfer of protons in the order: hinge, terrace, terrace, hinge, which is identical to the proton transfer order of the MEP calculated by Quantum Espresso. Figures 6.4a and 6.4b show the proton transfer extent trajectories and potential energy curve of the MEP calculated with CP2K. The former should be compared to Figure 5.4b to verify the agreement in their proton transfer orders. This agreement implies significant similarity between the PESs of CRCA calculated according to CP2K and Quantum Espresso.

Based on these tests, we judged that the computational method described above was accurate enough for the purpose of generating data to train our effective Hamiltonian of CRCA.

Initial configuration	Dynamics	Number of configurations
$Pca2_1$ -CRCA + random distortion	Geometry optimisation	29
$Pca2_1$ -CRCA + random distortion	Geometry optimisation	30
Minimum energy path	Geometry optimisation	135
C_5O_5 distorted along ferroelectric distortion modes	Molecular dynamics (fixed C_5O_5 , free H-atoms)	73

Table 6.3: A summary of the set of atomic positions and forces data used to train the effective Hamiltonian.

Choosing configurations

Our aim was to use our effective Hamiltonian to simulate polarisation switching in a ferroelectric like CRCA. It was therefore important for the dataset to include atomic force data corresponding to configurations around the domain states of the system, as well as configurations around low energy switching paths between the domain states. For our model, these configurations were generated by performing geometry optimisations and molecular dynamics simulations from various initial configurations, which are summarised in Table 6.3. The first two rows represent geometry optimisation trajectories whose initial configurations were determined by adding a random value between -0.1 and 0.1 Å to each of the atomic position coordinates of one of the domain states of CRCA. The random distortions in each of the two trajectories were distinct, in order to generate two distinct trajectories. The third row represents a set of 9 geometry optimisation trajectories, initialised with the reduced coordinates of the 9 middle images of the minimum energy path of domain switching that was calculated with the nudged elastic band algorithm, and reported in Section 5.3. Finally the fourth row represents a molecular dynamics trajectory with a Nose-Hoover thermostat at a temperature of 300 K. In this case the C_5O_5 molecules were fixed in distortions within the 2d space spanned by their corresponding ferroelectric distortion modes. These $4 \cdot N_{\text{cell}}$ distortions were defined such that they evenly sampled the range $(-|Q(\mathbf{X}^{(+)})|, +|Q(\mathbf{X}^{(+)})|)$.

Figure 6.5 features a histogram of the mean base 10-logarithm of the atomic force magnitudes in the configurations of the training set. That is,

$$\frac{1}{N_{\text{atom}}} \sum_a \log_{10} \left[\frac{|\mathbf{f}_a(\mathbf{R}^{(n)})|}{\text{Ha/bohr}} \right],$$

where $\mathbf{f}_a(\mathbf{R}^{(n)})$ is the force on atom a in configuration n with atoms in positions $\mathbf{R}^{(n)}$ (using similar notation to Equation 5.2). The plot shows that the training set includes configurations with a range of forces which covers several orders of magnitude. This implies that low energy regions of the PES, and their surrounding wells with steeper gradients are sufficiently represented in the training set.

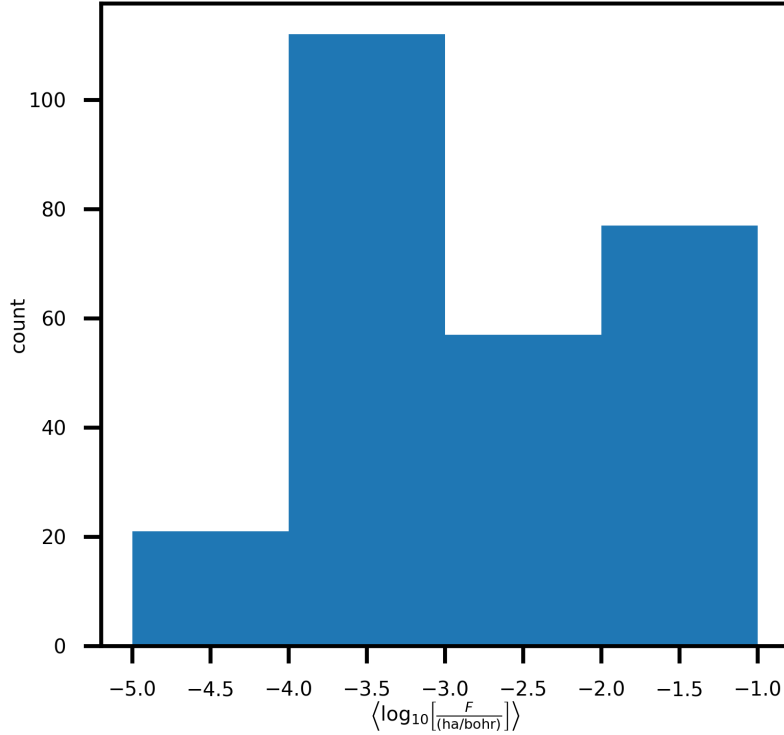


Figure 6.5: A histogram of the distribution of the mean log atomic force magnitude evaluated on configurations in the dataset used to train our effective Hamiltonian of CRCA.

6.3.3 Treatment of the harmonic potential energy surface

As described in Ref 145, if some part of the PES can be calculated independently of the fitting process described in Section 6.2.5, then the number of terms whose coupling parameters require fitting by the algorithm is effectively reduced. In the sense of the classic bias-variance tradeoff, this increases the bias in the model parameters and accordingly reduces the variance in the parameters to be fitted, resulting in a more accurate model. Therefore, we calculated coefficients of harmonic terms of the PES before training the model, so that the fitting method only had to determine the coefficients of the anharmonic terms.

CP2K [147] and Phonopy [88] were used to calculate the dynamical matrix at Γ , $\mathbf{D}(\mathbf{0})$ (see Equation 4.37), by finite differences. Firstly the structure of *Pbcm*-CRCA was determined by optimising the geometry of CRCA under the constraint of *Pbcm* symmetry. CP2K does not natively support symmetry-constrained geometry optimisations like Quantum Espresso and Abinit do, so a Python script was written which used the `minimize` function from the `scipy.optimize` package and the `subprocess` module to optimise the structure through repeated invocation of CP2K. The atomic positions of the optimised structure are reported in Table A.1.

Decomposing the quadratic terms into electrostatic and non-electrostatic components

Let us denote with $\phi_{\mathbf{n}ai,\mathbf{m}bj}$ the coefficient of the term in the harmonic PES which couples the displacements in the i - and j -directions of atoms a and b in the unit cells at positions $\sum_k n_k \mathbf{a}_k$ and $\sum_k m_k \mathbf{a}_k$ in a supercell with dimensions (N_1, N_2, N_3) . $\phi_{\mathbf{n}ai,\mathbf{m}bj}$ can be decomposed into

long- and short-range components. For each interaction between a pair of atoms there is an infinite set of images of that interaction, whose atomic positions are displaced by a supercell lattice vector. We refer to this set as the set of supercell images of the interaction. Consider a pair of atoms with indexes a_1, a_2 within the unit cell and at unit cell positions $\mathbf{n}_1, \mathbf{n}_2$. We define the set of supercell images of this pair as

$$J[(a_1, \mathbf{n}_1), (a_2, \mathbf{n}_2)] \equiv \{((a_1, \mathbf{n}_1 + \Delta\mathbf{n}), (a_2, \mathbf{n}_2)) : \Delta\mathbf{n} \in \mathbb{Z}^3\}. \quad (6.33)$$

Translational invariance of $\phi_{\mathbf{n}ai, \mathbf{m}bj}$ implies that $\phi_{\mathbf{n}_1 a_1 i_1, \mathbf{n}_2 a_2 i_2} = \phi_{(\mathbf{n}_1 - \mathbf{n}_2) a_1 i_1, \mathbf{0} a_2 i_2}$ therefore we can consider only the sets of supercell images of the pairs $(a_1, \mathbf{n}_1 - \mathbf{n}_2), (a_2, \mathbf{0})$ without loss of generality. The long-range component of $\phi_{\mathbf{n}a_1 i, \mathbf{0} a_2 j}$ includes contributions from all supercell images of the interaction between atoms $((a_1, \mathbf{R}), (a_2, \mathbf{0}))$. As stated in Refs 144 and 145, the long-range component is electrostatic, and can be calculated analytically by Ewald summation. Our implementation of the smooth particle mesh Ewald method [148] for the calculation of these terms is described in Section 6.3.3.

On the other hand, only the closest supercell image of each pairwise interaction contributes to its short-range component. An algorithm was created to decompose the quadratic terms derived from ϕ into short- and long-range components. In principle, this means that

$$\phi_{\mathbf{n}ai, \mathbf{m}bj}^{(\text{DFT})} = \phi_{\mathbf{n}ai, \mathbf{m}bj}^{(\text{s.r.})} + \phi_{\mathbf{n}ai, \mathbf{m}bj}^{(\text{l.r.})}, \quad (6.34)$$

where $\phi^{(\text{DFT})}$ denotes ϕ calculated according to DFT, $\phi^{(\text{s.r.})}$ and $\phi^{(\text{l.r.})}$ denote its short- and long-range components. For each pair of atoms, we sort the images in $J[(a_1, \mathbf{n}_1), (a_2, \mathbf{n}_2)]$ in order of ascending separation. If there is one unambiguously closest supercell image, we approximate

$$\phi_{\mathbf{n}ai, \mathbf{m}bj}^{(\text{l.r.})} \approx 0 \Rightarrow \phi_{\mathbf{n}ai, \mathbf{m}bj}^{(\text{DFT})} \approx \phi_{\mathbf{n}ai, \mathbf{m}bj}^{(\text{s.r.})}. \quad (6.35)$$

In our implementation, we defined a pair as having a unique closest image if the estimated ratio of the dipolar interaction strengths of the two closest images in J was smaller than an arbitrary threshold ϵ . Assuming the interaction strengths of different images of the same atom pair scales like $1/r^n$, this means that

$$\begin{aligned} \left(\frac{1/r_2^3}{1/r_1^3} \right) &< \epsilon \\ \left(\frac{r_2}{r_1} \right) &< \epsilon^{-\frac{1}{3}}. \end{aligned} \quad (6.36)$$

We arbitrarily set $\epsilon = 0.05$ for our calculations. For n , we reasoned that dipole-dipole interactions scale $n = 3$, while covalent interactions diminish more rapidly with separation. Therefore, we chose $n = 3.5$ to account for this.

If a pair of atoms does not satisfy this condition, there are multiple supercell images with similar separations, and we cannot unambiguously attribute $\phi^{(\text{DFT})}$ to a particular supercell image. Therefore, we approximate

$$\phi_{\mathbf{n}ai, \mathbf{m}bj}^{(\text{s.r.})} \approx 0 \Rightarrow \phi_{\mathbf{n}ai, \mathbf{m}bj}^{(\text{DFT})} \approx \phi_{\mathbf{n}ai, \mathbf{m}bj}^{(\text{l.r.})}. \quad (6.37)$$

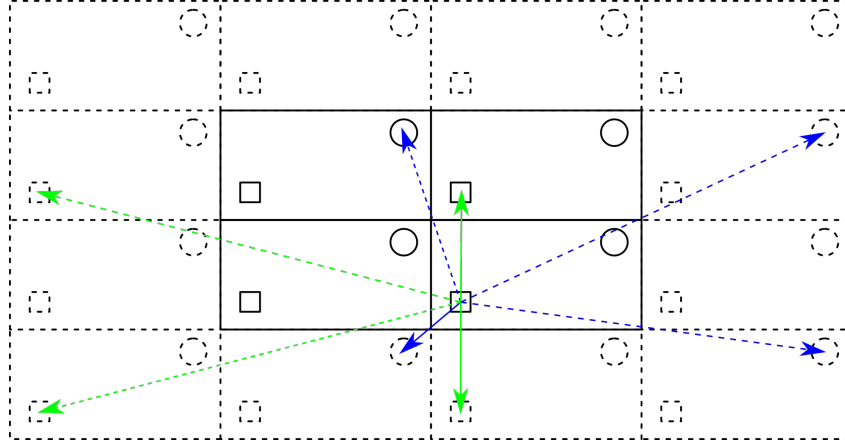


Figure 6.6: A schematic illustration of the problem of decomposing terms from the harmonic PES into long- and short-range components. The green arrows represent a term with multiple equally separated supercell images, while the blue arrows represent a different term with a uniquely closest supercell image.

The supercell used to calculate ϕ must be larger than the maximum length-scale of the short-range interactions for the approximation described above to be valid because if this is not the case, we automatically find that there are multiple supercell images with similar separations and we cannot unambiguously attribute $\phi^{(\text{DFT})}$ to a particular supercell image.

The problem of decomposing components $\phi^{(\text{DFT})}$ into long- and short-range components is illustrated in the schematic diagram of Figure 6.6. It represents a (2,2,2) supercell of an orthorhombic unit cell, along with its periodic images. The green arrows represent supercell images of a harmonic coupling which has two closest images with equal separations, while the blue arrows represent supercell images of a different harmonic coupling for which there is a uniquely closest image. The closest images of both couplings are rendered with solid lines. In Ref 145, this problem is not discussed because the parameters of the short-range harmonic terms (in the displacement differences form of Equation 6.25) are fitted to a training set of data which would typically be used to compute a finite difference approximation of the harmonic force constants. This contrasts with our approach of using this finite difference approximation to set the parameters for the harmonic terms directly.

The error incurred by this approximation was estimated by calculating and comparing the harmonic potential energy values due to the exact and approximated $\phi^{(\text{DFT})}$ values, evaluated on the data set which was used to train the effective Hamiltonian. Figure 6.7 compares these two values for each configuration in the training set. The mean absolute error in the harmonic potential energy was found to be $18.2 \mu\text{Ha/ion}$ (or 0.495 meV/ion).

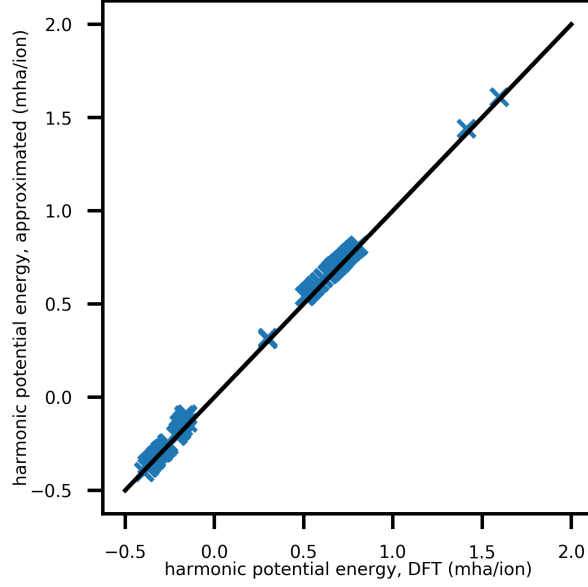


Figure 6.7: A comparison of the harmonic potential energies evaluated on the dataset used to train the effective Hamiltonian by the terms of the harmonic PES calculated using DFT, to their corresponding values evaluated by the approximated harmonic PES terms explained in Section 6.3.3.

Smooth particle mesh Ewald summation method to calculate long-range harmonic interactions

The long-range component of the harmonic interactions described earlier in the current subsection occurs due to the dipoles induced by the atomic displacements $\mathbf{X}$. To first order, the dipole moment p_{ai} of atom a in direction i is given by

$$p_{ai} = \sum_j Z_{ij}^a X_{aj}, \quad (6.38)$$

where

$$Z_{ij}^a = V \frac{\partial P_i}{\partial X_{aj}} \quad (6.39)$$

is the Born effective charge for atom a ; V is the cell volume and $\mathbf{P}$ is the bulk polarisation.

Smith [149] shows how the potential at $\mathbf{r}$ due to a dipole at $\mathbf{r}_a$ can be expressed as the result of the application of an operator $-\mathbf{p}_a \cdot \nabla$ to the Coulomb potential of a unit point charge at $\mathbf{r}_a$. The electric potential due to a set of N unit point charges in an infinite periodic system can be expressed as

$$\phi(\mathbf{r}) = \frac{1}{4\pi\epsilon_\infty} \sum_{\mathbf{n}} \sum_a \frac{1}{|\mathbf{r} - \mathbf{r}_a + \mathbf{T}_{\mathbf{n}}|}, \quad (6.40)$$

where the cell is spanned by the vectors $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$, $\mathbf{T}_{\mathbf{n}} = \sum_l n_l \mathbf{a}_l$ and $\mathbf{r}_a$ is the position of atom a . This sum converges slowly, whereas the Ewald method's approximation to this sum converges rapidly. Smith shows how an Ewald sum expression for the potential energy due to a set of dipoles can be derived by applying the operators $-\mathbf{p}_a \cdot \nabla$ to the Ewald method's result for the electric potential due to a set of unit monopoles.

Ewald's method begins by separating each point charge distribution into two parts

$$\begin{aligned}\rho_i(\mathbf{r}) &= q_i \delta(\mathbf{r} - \mathbf{r}_i) \\ &= q_i (\delta(\mathbf{r} - \mathbf{r}_i) - G_\sigma(\mathbf{r} - \mathbf{r}_i)) + q_i G_\sigma(\mathbf{r} - \mathbf{r}_i) \\ &= \rho_i^{\text{short}}(\mathbf{r}) + \rho_i^{\text{long}}(\mathbf{r}),\end{aligned}\tag{6.41}$$

where $G_\sigma(\mathbf{r}) = \frac{1}{(2\pi\sigma^2)^{3/2}} \exp\left(-\frac{r^2}{2\sigma^2}\right)$. The electric potentials due to $\rho_a^{\text{short}}(\mathbf{r})$ and $\rho_a^{\text{long}}(\mathbf{r})$ are

$$\phi_i^{\text{short}}(\mathbf{r}) = \frac{1}{4\pi\epsilon_\infty} \frac{q_a}{|\mathbf{r} - \mathbf{r}_i|} \text{erfc}\left(\frac{|\mathbf{r} - \mathbf{r}_i|}{\sqrt{2}\sigma}\right)\tag{6.42}$$

and

$$\phi_a^{\text{long}}(\mathbf{r}) = \frac{1}{4\pi\epsilon_\infty} \frac{q_a}{|\mathbf{r} - \mathbf{r}_i|} \text{erf}\left(\frac{|\mathbf{r} - \mathbf{r}_a|}{\sqrt{2}\sigma}\right)\tag{6.43}$$

respectively. The function $\frac{\text{erf}(z)}{z}$ decreases rapidly as $z \rightarrow \infty$ whereas $\frac{\text{erfc}(z)}{z}$ decreases slowly therefore ϕ_a^{long} has a long range while ϕ_a^{short} has a short range. Due to the different spatial ranges of these components of the electric potential due to atom a , the contribution of the long-range components to the total electric potential at $\mathbf{r}$ is evaluated in reciprocal space, while the contribution of the short-range components is evaluated in real space.

The Ewald method expression for $\phi(\mathbf{r})$ is [149]

$$\phi^{\text{Ewald}}(\mathbf{r}) = \frac{1}{V\epsilon_\infty} \sum_{\mathbf{k} \neq \mathbf{0}} A(k) \sum_a \exp(-i\mathbf{k} \cdot (\mathbf{r}_a - \mathbf{r})) + \frac{1}{4\pi\epsilon_\infty} \sum_a \sum_{\mathbf{n}} B_0(\mathbf{r}_a + \mathbf{T}_{\mathbf{n}} - \mathbf{r}),\tag{6.44}$$

where

$$A(k) = \frac{1}{k^2} \exp\left(\frac{-\sigma^2 k^2}{2}\right)\tag{6.45}$$

and

$$B_0(u) = \frac{1}{u} \text{erfc}\left(\frac{u}{\sqrt{2}\sigma}\right).\tag{6.46}$$

The dipole potential operators $-\mathbf{p}_a \cdot \hat{\nabla}$ are applied to $\phi^{\text{Ewald}}(\mathbf{r})$ to obtain the potential of the desired set of dipoles. The interactions between this potential and that of each dipole are then summed. The final result for the potential energy per cell is

$$\begin{aligned}E &= \frac{1}{4\pi\epsilon_\infty} \sum_{ab} \sum_{\mathbf{n}} [(\mathbf{p}_b \cdot \mathbf{p}_a) B_1(|\mathbf{r}_{ba} + \mathbf{T}_{\mathbf{n}}|) - (\mathbf{p}_a \cdot \mathbf{r}_{ba})(\mathbf{p}_b \cdot \mathbf{r}_{ba}) B_2(|\mathbf{r}_{ba} + \mathbf{T}_{\mathbf{n}}|)] + \\ &\quad \frac{2\pi}{V\epsilon_\infty} \sum_{\mathbf{k} \neq \mathbf{0}} \frac{1}{k^2} \exp\left(\frac{-k^2}{4\lambda^2}\right) \sum_{ab} (\mathbf{p}_a \cdot \mathbf{k})(\mathbf{p}_b \cdot \mathbf{k}) \exp(i\mathbf{k} \cdot \mathbf{r}_{ab}) - \sum_b \frac{p_b^2 \lambda^3}{3\epsilon\pi^{3/2}},\end{aligned}\tag{6.47}$$

where

$$B_1(z) = \frac{1}{z^3} \text{erfc}(\lambda z) + \frac{2\lambda}{\sqrt{\pi} z^2} \exp(-\lambda^2 z^2),\tag{6.48}$$

$$B_2(z) = \frac{3}{z^5} \text{erfc}(\lambda z) + \frac{2\lambda}{\sqrt{\pi} z^2} \left(2\lambda^2 + \frac{3}{z^2}\right) \exp(-\lambda^2 z^2),\tag{6.49}$$

$\mathbf{r}_{ab} = \mathbf{r}_a - \mathbf{r}_b$ and $\lambda = \frac{1}{\sigma\sqrt{2}}$. By setting λ to a large enough value, the first sum (over real space)

in Equation 6.47 becomes negligible, leaving the second sum (over reciprocal space, which we denote by E_{rec}) and the last sum (which we denote by E_{self}). The computing time required to numerically evaluate E_{rec} as expressed in Equation 6.47 scales like N^2 [148], where N is the number of multipoles. However, a variety of algorithms exist [148, 150] to calculate E_{rec} more efficiently.

The smooth particle mesh Ewald method [148] is able to calculate E_{rec} in $\mathcal{O}(N \log N)$ time. Therefore, we adapted it for the calculation of $\phi^{(\text{l.r.})}$. We define the structure factor

$$S(\mathbf{k}) = \sum_b (\mathbf{p}_b \cdot \mathbf{k}) \exp(-i\mathbf{k} \cdot \mathbf{r}_b), \quad (6.50)$$

and note that

$$\begin{aligned} E_{\text{rec}} &= \frac{2\pi}{V\epsilon_\infty} \sum_{\mathbf{k} \neq 0} \frac{1}{k^2} \exp\left(\frac{-k^2}{4\lambda^2}\right) \sum_{ab} (\mathbf{p}_a \cdot \mathbf{k})(\mathbf{p}_b \cdot \mathbf{k}) \exp(i\mathbf{k} \cdot \mathbf{r}_{ab}) \\ &= \frac{2\pi}{V\epsilon_\infty} \sum_{\mathbf{k} \neq 0} \frac{1}{k^2} \exp\left(\frac{-k^2}{4\lambda^2}\right) \left[\sum_a (\mathbf{p}_a \cdot \mathbf{k}) \exp(-i\mathbf{k} \cdot \mathbf{r}_a) \right] \left[\sum_b (\mathbf{p}_b \cdot \mathbf{k}) \exp(i\mathbf{k} \cdot \mathbf{r}_b) \right] \\ &= \frac{2\pi}{V\epsilon_\infty} \sum_{\mathbf{k} \neq 0} \frac{1}{k^2} \exp\left(\frac{-k^2}{4\lambda^2}\right) S(\mathbf{k}) S^*(\mathbf{k}). \end{aligned} \quad (6.51)$$

Now let $\mathbf{r}_a = \sum_j x_{ij} \mathbf{a}_j$ and $\mathbf{k} = \sum_j m_j \mathbf{b}_j$ where b_j are the reciprocal lattice basis vectors (*i.e.* $\mathbf{a}_i \cdot \mathbf{b}_j = 2\pi\delta_{ij}$), so

$$S(\mathbf{k}) = \sum_a (\mathbf{p}_a \cdot \mathbf{k}) \exp\left(-2\pi i \sum_j m_j x_{aj}\right). \quad (6.52)$$

We define a mesh

$$\mathbf{y}_\mathbf{q} = \sum_i \frac{q_i}{K_i} \mathbf{a}_i, q_i \in \mathbb{Z}, K_i \in \mathbb{Z}^+, \quad (6.53)$$

define $u_j = x_j K_j$ and approximate $\exp(-2\pi i m_j x_j)$ by Cardinal B-spline interpolation on the mesh. Now

$$\begin{aligned} \exp(-2\pi i \sum_j m_j x_j) &= \prod_j \exp(-2\pi i \frac{m_j u_j}{K_j}) \\ &\approx \prod_j b_j(-m_j) \sum_{q_j \in \mathbb{Z}} M_l(u_j - q_j) \exp\left(-2\pi i \frac{m_j q_j}{K_j}\right), \end{aligned} \quad (6.54)$$

where

$$b_j(m_j) = \frac{\exp\left(\frac{2\pi i(n-1)m_j}{K_j}\right)}{\sum_{q=0}^{n-2} M_n(q+1) \exp\left(\frac{2\pi i m_j q}{K_j}\right)}, \quad (6.55)$$

l is the order of spline interpolation and $M_n(u)$ is defined recursively [148]

$$\begin{aligned} M_n(u) &= \frac{u}{n-1} M_{n-1}(u) + \frac{n-u}{n-1} M_{n-1}(u-1), n > 2 \\ M_2(u) &= \begin{cases} 1 - |u-1| & u \in [0, 2] \\ 0 & \text{otherwise.} \end{cases} \end{aligned} \quad (6.56)$$

In this approximation,

$$\begin{aligned} S(\mathbf{k}) &= \sum_a (\mathbf{p}_a \cdot \mathbf{k}) b_1(-m_1) b_2(-m_2) b_3(-m_3) \sum_{\mathbf{k} \in \mathbb{Z}^3} \prod_{j=1}^3 M_l(u_{aj} - q_j) \exp\left(-2\pi i \frac{m_j q_j}{K_j}\right) \\ &= b_1(-m_1) b_2(-m_2) b_3(-m_3) \mathbf{k} \cdot \left\{ \sum_a \mathbf{p}_a \sum_{\mathbf{q} \in \mathbb{Z}^3} \prod_{j=1}^3 M_l(u_{aj} - q_j) \exp\left(-2\pi i \frac{m_j q_j}{K_j}\right) \right\}. \end{aligned} \quad (6.57)$$

Now for each $q_j \in \mathbb{Z}$, there is a $d_j \in \mathbb{Z}$ and $q'_j \in \{0, \dots, K_j - 1\}$ such that $q_j = d_j K_j + q'_j$. Noting that $\exp\left(-2\pi i \frac{m_j d_j K_j}{K_j}\right) = 1$, we have

$$\begin{aligned} S(\mathbf{k}) &= b_1(-m_1) b_2(-m_2) b_3(-m_3) \mathbf{k} \cdot \left\{ \sum_a \mathbf{p}_a \sum_{\mathbf{d} \in \mathbb{Z}^3} \sum_{\mathbf{q}' \in \text{mesh}} \prod_{j=1}^3 M_l(u_{aj} - d_j K_j - q'_j) \times \right. \\ &\quad \left. \exp\left(-2\pi i \frac{m_j q'_j}{K_j}\right) \right\} \\ &= b_1(-m_1) b_2(-m_2) b_3(-m_3) \sum_{\mu} k_{\mu} \sum_{\mathbf{q} \in \text{mesh}} \sum_a Z_{\mu\nu}^a X_{a\nu} \sum_{\mathbf{d} \in \mathbb{Z}^3} \prod_{j=1}^3 \left[M_l(u_{aj} - d_j K_j - q_j) \times \right. \\ &\quad \left. \exp\left(-2\pi i \frac{m_j q_j}{K_j}\right) \right] \\ &= \sum_{a\nu} X_{a\nu} b_1(-m_1) b_2(-m_2) b_3(-m_3) \sum_{\mu} k_{\mu} \sum_{\mathbf{q} \in \text{mesh}} Z_{\mu\nu}^a \sum_{\mathbf{d} \in \mathbb{Z}^3} \prod_{j=1}^3 \left[M_l(u_{aj} - d_j K_j - q_j) \times \right. \\ &\quad \left. \exp\left(-2\pi i \frac{m_j q_j}{K_j}\right) \right]. \end{aligned} \quad (6.58)$$

Now define

$$\psi_{\mu\nu}^a(q_1, q_2, q_3) = Z_{\mu\nu}^a \sum_{\mathbf{d} \in \mathbb{Z}^3} \prod_{j=1}^3 M_l(u_{aj} - d_j K_j - q_j), \quad (6.59)$$

so

$$\begin{aligned}
S(\mathbf{k}) &= b_1(-m_1)b_2(-m_2)b_3(-m_3) \sum_{\mu} k_{\mu} \sum_{\mathbf{k} \in \text{mesh}} \left[\sum_a \sum_p X_{ap} \psi_{\mu p}^a(q_1, q_2, q_3) \right] \prod_{j=1}^3 \exp \left(-2\pi i \frac{m_j q_j}{K_j} \right) \\
&= b_1(-m_1)b_2(-m_2)b_3(-m_3) \sum_{\mu} k_{\mu} \sum_a \sum_p X_{ap} \left[\sum_{\mathbf{q} \in \text{mesh}} \psi_{\mu p}^a(q_1, q_2, q_3) \prod_{j=1}^3 \exp \left(-2\pi i \frac{m_j q_j}{K_j} \right) \right] \\
&= b_1(-m_1)b_2(-m_2)b_3(-m_3) \sum_{\mu} k_{\mu} \sum_a \sum_p X_{ap} F(\psi_{\mu p}^a)(m_1, m_2, m_3) \\
&= b_1(-m_1)b_2(-m_2)b_3(-m_3) \sum_{ap} X_{ap} \sum_{\mu} k_{\mu} F(\psi_{\mu p}^a)(m_1, m_2, m_3),
\end{aligned} \tag{6.60}$$

where $F(\psi_{\mu p}^a)(m_1, m_2, m_3)$ is the discrete Fourier transform of $\psi_{\mu p}^a(k_1, k_2, k_3)$. From this, we obtain

$$\begin{aligned}
E_{\text{rec}} &= \sum_{a\mu c\nu} X_{a\mu} X_{c\nu} \left\{ \frac{2\pi}{V\epsilon_{\infty}} \sum_{\mathbf{k} \neq \mathbf{0}} \frac{1}{k^2} \exp \left(\frac{-k^2}{4\lambda^2} \right) B(\mathbf{m}) \times \right. \\
&\quad \left[\sum_j k_j F(\psi_{j\mu}^a)(m_1, m_2, m_3) \right] \left[\sum_l k_l F(\psi_{l\nu}^c)(m_1, m_2, m_3) \right] \Big\} \\
&= \sum_{a\mu c\nu} X_{a\mu} X_{c\nu} \phi_{a\mu c\nu}^{(\text{l.r.})},
\end{aligned} \tag{6.61}$$

where

$$B(\mathbf{m}) = |b_1(m_1)|^2 |b_2(m_2)|^2 |b_3(m_3)|^2, \tag{6.62}$$

and $\phi_{a\mu c\nu}^{(\text{l.r.})}$ is the long-range component of $\frac{\partial^2 E}{\partial X_{a\mu} \partial X_{c\nu}}$ introduced in Equation 6.34, with each atom labelled by its index in the supercell, rather than its index in the unit cell, and unit cell position.

We found that a cardinal B-spline order of 12, a λ value of $2.055a_0^{-1}$ and reciprocal space cutoff of $18a_0^{-1}$ was enough to converge $\phi_{a\mu c\nu}^{(\text{l.r.})}$ for a (2,2,2) supercell of *Pbcm*-CRCA.

6.3.4 Generating the model

After we obtained the pool of Hamiltonian terms, the training set, and decomposed the terms of the harmonic PES into short- and long-range components, we proceeded to train our effective Hamiltonian of CRCA.

The training set was divided into training and validation splits which each had the same composition of data with respect to the trajectories that made up the full set. The dataset was stratified in this way to increase the likelihood that the model was evenly trained on data from each trajectory in the full set, so that the model was not overtrained or undertrained on any of the trajectories.

Only the data in the training split was used to directly train the model. However, at each forward-selection iteration the goal function was also evaluated on the data in the validation split, in order to have a more faithful measure of the model's ability to predict the atomic forces

associated with unseen configurations.

As explained in Section 6.3.1, one of our assumptions is that the region of the PES relevant to polarisation switching in CRCA is spanned by the ferroelectric distortion modes of the C_5O_5 molecules and the Cartesian modes of the H-atoms. These modes were adopted as the degrees of freedom of the model. Therefore, we defined the goal function (GF), the measure of the accuracy of a candidate model, in this basis. The weights w_n in the Equation 6.20 were set to $\frac{1}{N_{\text{TS}}N_{\text{supercell}}n_{\text{basis}}}$ where N_{TS} is the training set size, $N_{\text{supercell}} = 8$, is the number of unit cells in the supercell, and $n_{\text{basis}} = 32$ is the number of basis modes per unit cell.

While a GF defined in a completely Cartesian basis has an intuitive physical interpretation as the mean squared error in the atomic forces, it is more difficult to assess whether a model is sufficiently accurate based on the model’s value of the GF defined in the basis described in Section 6.3.1. Therefore, the root mean squared energy error (RMSEE) was also calculated on the training and validation splits at each forward-selection iteration. Calculating the RMSEE for each candidate model also provided us with a better indication of when the model was being overfitted. Since the validation split was extracted from the same training dataset, it is somewhat correlated with the training split, and therefore may not readily reveal the occurrence of overfitting. On the other hand, although a model which produces a small GF value would be expected to produce a small RMSEE, the forward-selection does not specifically minimise RMSEE. Therefore, studying the evolution of RMSEE with increasing forward-selected terms would reveal when the model was being trained on the ‘noise’ in the atomic forces.

As explained in Section 6.3.3, the quadratic terms of the harmonic PES of CRCA were pre-calculated using CP2K and Phonopy, and so quadratic terms were excluded from the pool of Hamiltonian terms described in Section 6.3.1.

The GF and RMSEE as a function of the number of forward-selected terms is presented in Figure 6.8. We see that although the GF monotonically decreases, the RMSEE evaluated on the validation split reaches a minimum of 2.95×10^{-5} Ha/atom after the 23rd term was selected. The increase in RMSEE beyond 23 forward-selected terms indicates that the model became overfitted beyond this point. Therefore, the 23-term model was chosen for our subsequent simulations. Given the accuracy of the DFT calculations used to generate the training data, it is reasonable to expect an RMSEE value of around this size. This RMSEE value is also 1.5% of the range of energies in the training set (1.94×10^{-3} Ha/atom), which implies an acceptable level of accuracy of the model for our purposes.

6.3.5 Evaluating the model

After training the effective Hamiltonian, we further assessed its physical validity by comparing its predicted domain states of CRCA to those calculated according to DFT. Initially we used the basis described in Section 6.3.1 as the degrees of freedom for the optimisation. However, although the model’s RMSEE value suggested an adequate level of accuracy on the low energy regions of the PES which were sampled by the training set, we frequently found that geometry optimisation trajectories moved the system into configuration states with unphysically large and negative energy values. Evidently the Hamiltonian function $E(\mathbf{X})$ was unbounded from below. This boundedness problem associated with effective Hamiltonians of the form described

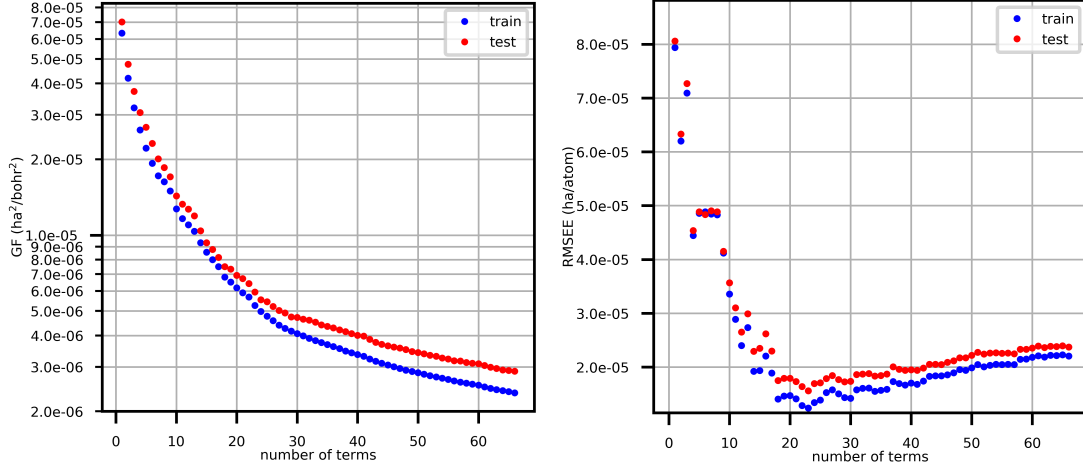


Figure 6.8: The goal function and root mean squared energy error as a function of the number of forward-selected terms.

in this chapter has been previously discussed [151]. In order to avoid this problem, when the effective Hamiltonian was used for simulations which would otherwise evolve the system into energetically unbound regions, an alternative coordinate system was employed. In this system, each C_5O_5 molecule was still constrained to the space spanned by its two ferroelectric distortion modes described in Section 6.3.1. However, the position of each H-atom was constrained to a line parallel to the displacement vector between its neighbouring O-atoms. Consider a H-atom with index a , surrounded by O-atoms $o^{(0)}, o^{(1)}$. We define

$$\mathbf{v} = \mathbf{r}_{o^{(1)}} - \mathbf{r}_{o^{(0)}} \text{ and } \hat{\mathbf{v}} = \frac{\mathbf{v}}{|\mathbf{v}|}, \quad (6.63)$$

where $\mathbf{r}_b$ is the position of atom b in the *Pbcm*-CRCA reference state, i.e. $[\mathbf{r}_b]_i = R_{bi}^{(0)}$ in the notation of Equation 5.2. The line to which H-atom a is constrained is displaced from the O-O axis by a distance

$$h = \left| \mathbf{r}_a - \frac{1}{2} (\mathbf{r}_{o^{(0)}} + \mathbf{r}_{o^{(1)}}) \right|, \quad (6.64)$$

in a direction

$$\hat{\mathbf{z}} = \frac{\mathbf{z}}{|\mathbf{z}|}, \text{ where } \mathbf{z} = \frac{\mathbf{y}^{(0\perp)}}{|\mathbf{y}^{(0\perp)}|} + \frac{\mathbf{y}^{(1\perp)}}{|\mathbf{y}^{(1\perp)}|}, \quad (6.65)$$

and

$$\mathbf{y}^{(j\perp)} = \mathbf{y}^{(j)} - (\mathbf{y}^{(j)} \cdot \hat{\mathbf{v}}) \hat{\mathbf{v}}, \text{ and } \mathbf{y}^{(j)} = \mathbf{r}_{c^{(j)}} - \mathbf{r}_{o^{(j)}}; \quad (6.66)$$

$c^{(j)}$ is the index of the C-atom covalently bonded to the O-atom $o^{(j)}$. These vectors are illustrated in Figure 6.9 which depicts views down and perpendicular to $\hat{\mathbf{v}}$. All of the configurations in the training set had the hinge protons displaced from the O-O axis. Therefore, defining the coordinate system with the proton transfer axis displaced from the O-O axis allowed the hinge protons to access configurations that were closer to the low energy regions of the PES than would otherwise be possible if $h = 0$. By definition, the origin of the axis along which each

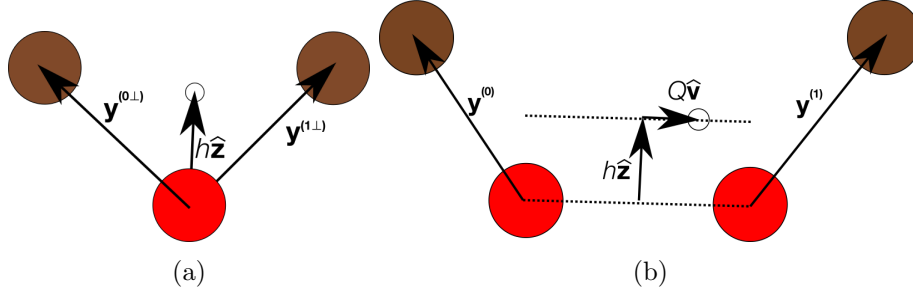


Figure 6.9: A schematic view down (in 6.9a) and perpendicular to (in 6.9b) the proton transfer axis of a particular proton in CRCA, to illustrate the vectors defined in Equations 6.64-6.66 which define the coordinate system that was used during geometry optimisations and nudged elastic band calculations with the effective Hamiltonian.

H-atom is positioned has

$$(\mathbf{r}_a - \mathbf{r}_{o(0)}) \cdot \hat{\mathbf{v}} = (\mathbf{r}_a - \mathbf{r}_{o(1)}) \cdot \hat{\mathbf{v}} \quad (6.67)$$

so that the amplitude Q can be interpreted as a *proton transfer extent*.

In Ref 151, the author explains how the system modelled by an effective Hamiltonian, similar to that described in this Chapter, can be robustly confined to its domain of physical validity without affecting its accuracy within this region by adding confinement terms of the form

$$u_n^{\text{conf}}(Q) = \theta(|Q| - Q_n^{\text{cut}}) k_n^{\text{conf}} \left(\frac{|Q| - Q_n^{\text{cut}}}{Q_n^{\text{cut}}} \right)^{\alpha_n}, \quad (6.68)$$

where θ is the Heaviside step function, Q_n^{cut} is a cutoff amplitude beyond which the confinement term associated with degree of freedom n is activated, α_n is an exponent which should be even and greater than the greatest power in the unbounded function $E'(\mathbf{X})$ (see Equation 6.12) in order to bound it. As well as constraining the atomic degrees of freedom, we also added these terms to ensure that the effective Hamiltonian was bounded from below. For each degree of freedom n , Q_n^{cut} was set to $|Q_n(\mathbf{X}^{(\pm)})|$, the magnitude of its value in either of its domain states (since these magnitudes are equal by symmetry).

Table 6.4 compares the energies relative to the *Pbcm*-CRCA state and the lengths and angles associated with the OHO triples for the *Pca2₁*-CRCA domain states predicted by the model with $h_p = 0$, h_p set according to Equation 6.64, and by DFT. We found that setting h_p according to Equation 6.64 modestly improved the domain state bond lengths, made a more significant improvement to the domain state bond angles, and a very significant (35% reduction in relative error) improvement to the model's predicted domain state energy. This emphasised the importance of defining the proton transfer axis in the way described earlier in this section.

Table 6.4: A comparison of the energies and bond geometries of a domain state predicted by two versions of the effective Hamiltonian and by DFT.

Calculation method	Effective Hamiltonian, $h_p = 0$	Effective Hamiltonian, h_p set according to Equation 6.64	DFT
θ_{hinge} (degrees)	0.0	11.4	10.9
θ_{terrace} (degrees)	0.0	0.0	4.5
$l(\text{OH})_{\text{hinge}}$ (bohr)	2.00	2.00	1.99
$l(\text{O} \cdots \text{H})_{\text{hinge}}$ (bohr)	2.75	2.75	2.76
$l(\text{OH})_{\text{terrace}}$ (bohr)	1.97	1.96	1.97
$l(\text{O} \cdots \text{H})_{\text{terrace}}$ (bohr)	2.84	2.91	2.86
Domain state energy (meV/atom)	-5.09	-8.50	-8.26

Chapter 7

Nudged elastic band calculations

In order to assess the physical validity of the effective Hamiltonian of croconic acid (CRCA) described in Chapter 6.3, the nudged elastic band (NEB) algorithm was used to determine the minimum energy path (MEP) between the two domain states of CRCA according to the model, and compared to the MEPs previously found using density functional theory (DFT) [54] and our study [106].

7.1 NEB calculations with DFT

As reported in Section 5.3.3, we performed DFT NEB calculations of the MEP between the two domain states of CRCA with its unit cell dimensions fixed to their calculated *Pbcm*-CRCA values. The DFT calculations used the vdW-DF2 exchange-correlation functional [78], and the path was optimised using Broyden’s second quasi-Newton method [152]. The MEP has a barrier of 44.6 meV/proton = 7.43 meV/atom, and involves the concerted transfer of protons in four successive pairs. With reference to the naming scheme illustrated in Figure A.1 these pairs, in order of transfer along the MEP, are: (i) H4, H5; (ii) H2, H8; (iii) H1, H7; (iv) H3, H6. Pairs (i) and (iv) are hinge proton pairs (i.e. the four protons that are displaced approximately parallel to the polar axis during polarisation switching) while (ii) and (iii) are terrace proton pairs (i.e. the four protons that are displaced approximately in the $[110]$ and $[\bar{1}\bar{1}0]$ directions during polarisation switching.)

7.2 NEB calculations with the effective Hamiltonian

As explained in Section 6.3.5, the degrees of freedom that we used for our calculations with our effective Hamiltonian of CRCA were not the Cartesian atomic displacement directions which are typically used for systems with the NEB algorithm. Instead, the position of each C_5O_5 molecule was defined by amplitudes of displacement along the two ferroelectric distortion modes, which are defined in Section 6.3.1, while each proton position was defined by the extent of transfer between its neighbouring O-O atom pair. As well as making the model easier to bound, using this restricted set of degrees of freedom made calculations with the model, such as those described in this chapter, more efficient. At the time of our investigation, we were not aware of an existing implementation of the NEB method which would allow us to import our

effective Hamiltonian, and express the potential energy surface in terms of our abovementioned choice of degrees of freedom. Therefore, we implemented the NEB method according to [93,126] in our software package, Cronic.

As explained in Section 6.3.2, a (2,2,2) supercell was used to generate the data used to train our model of CRCA so that all polynomial terms in the training pool would be instantiated distinctly on the training supercell. However, the abovementioned DFT NEB calculations were carried out on a single unit cell of CRCA. Therefore to be able to compare our results to the results of the DFT calculations, it was necessary to be able to constrain the atomic positions in a (2,2,2) supercell such that each unit cell had the same set of atomic displacements, i.e. to impose primitive lattice translational symmetry.

7.2.1 Computational details

As described in Section 6.3.5, we performed geometry optimisations of our model of CRCA to find the $Pca2_1$ -CRCA domain states according to the model. These were used as the end images of the NEB. The nine middle images were initialised in two ways. The first involved a linear interpolation (or lerp) between the two domain states, while the second involved rescaling the NEB MEP calculated in Ref 106 to the $Pbcm$ -CRCA unit cell dimensions calculated with CP2K, and approximating this path in the restricted subspace defined by the degrees of freedom described in Section 6.3.5. In both cases, the NEB was terminated once the norms of the perpendicular components of the Hamiltonian forces on each image fell below 6×10^{-4} ha/bohr. In our implementation, the path was optimised using the steepest descent algorithm. The step size, α from Equation 4.44, was chosen pragmatically such that the path converged in a stable and efficient manner.

7.2.2 Results

When the NEB was initialised with the lerped path, it converged to a path which was qualitatively identical to the initial one, although the barrier height decreased from 16.1 to 8.50 meV/atom. The potential energy curve (PEC) of the final path is shown in Figure 7.1a. λ in the figures of this chapter refer to the normalised reaction coordinate defined by Equation 5.5. The converged path is qualitatively different to the DFT NEB MEP described in Section 7.1. This discrepancy was initially surprising, given the apparent accuracy of the model that was demonstrated in Section 6.3.5. On the other hand, it is well known [93] that the NEB algorithm generally converges to the path satisfying Equation 4.43 which is closest to the initial path. Therefore, we conjectured that the NEB algorithm had converged on an erroneous local minimum in the space of paths between the domain states of the model, whose counterpart may not appear in the DFT PES. Accordingly, the possibility remained that the model’s potential energy surface featured another path between domain states satisfying Equation 4.43 that was more qualitatively similar to the DFT reference MEP. Therefore, another NEB calculation was performed, with the path initialised to the approximated DFT MEP, as described in Section 7.2.1.

In this case, the converged path involves the concerted transfer of protons in the same four successive pairs as the DFT MEP. The qualitative similarities of the MEPs of the DFT and

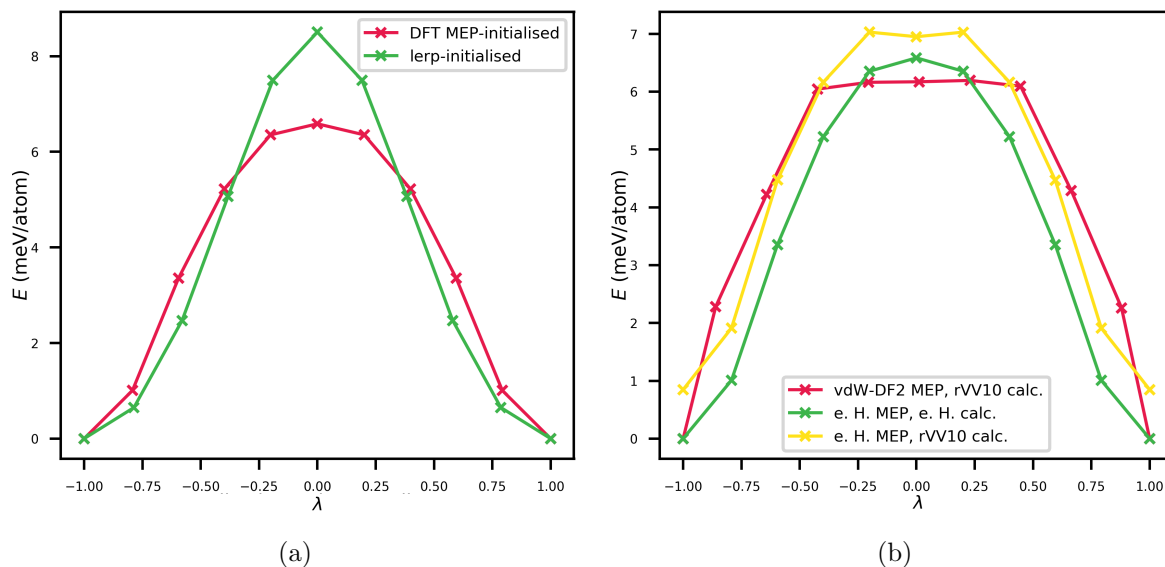


Figure 7.1: (a) A plot of the potential energy curves of the MEPs found by applying the NEB algorithm to the effective Hamiltonian of CRCA, having initialised the path to a linear interpolation (lerp) between the domain states, or an approximation to the DFT MEP. (b) A plot of the potential energy curves of various paths between CRCA’s domain states. (i) the effective Hamiltonian’s (e. H.’s) MEP, calculated with the e. H.; (ii) the e. H.’s MEP, calculated with DFT with rVV10 exchange-correlation; (iii) the MEP according to vdW-DF2 exchange-correlation in QE, calculated with rVV10 exchange-correlation in CP2K.

effective Hamiltonian PESs can be seen by comparing Figures 5.4b and 7.2, which illustrate the trajectories of proton transfer extents (PTEs) along the reaction coordinate for the DFT and effective Hamiltonian NEB MEPs respectively. In both paths, the proton pairs are clearly identifiable. On the other hand, there are also observable quantitative differences between the two paths. In general, the rate of proton transfer varies more strongly in the DFT MEP than in the effective Hamiltonian’s MEP. In the DFT MEP, there is also more variation among the PTE curves than in the effective Hamiltonian’s. The transfer rate of pair (ii) increases more gradually than the other pairs’, which change suddenly upon the occurrence of their respective transfer events. This contrasts with the effective Hamiltonian MEP, in which the transfer rates increase gradually for every pair.

We also find that the DFT MEP is significantly longer (7.11 bohr) than the effective Hamiltonian MEP (3.49 bohr). The path lengths can be interpreted as a measure of how much each path deviates from the shortest (lerped) path between the two domain states, whose length is 2.70 bohr. The fact that the DFT MEP is longer than the effective Hamiltonian MEP can be understood as a consequence of the visibly greater curvature in the former’s proton transfer curves, which are straight for the lerped path. The greater curvature and longer path of the DFT MEP suggest that the effective Hamiltonian captures some but not all of the complex dependence of the strength of each bond involving a particular H-atom on the relative positions of the two C_5O_5 molecules surrounding it, and the transfer extents of the other H-atoms connected to those molecules. In the DFT MEP, the transfer of each proton begins sharply when the surrounding atoms are in the right position, and is completed rapidly in comparison to the corresponding processes in the effective Hamiltonian MEP.

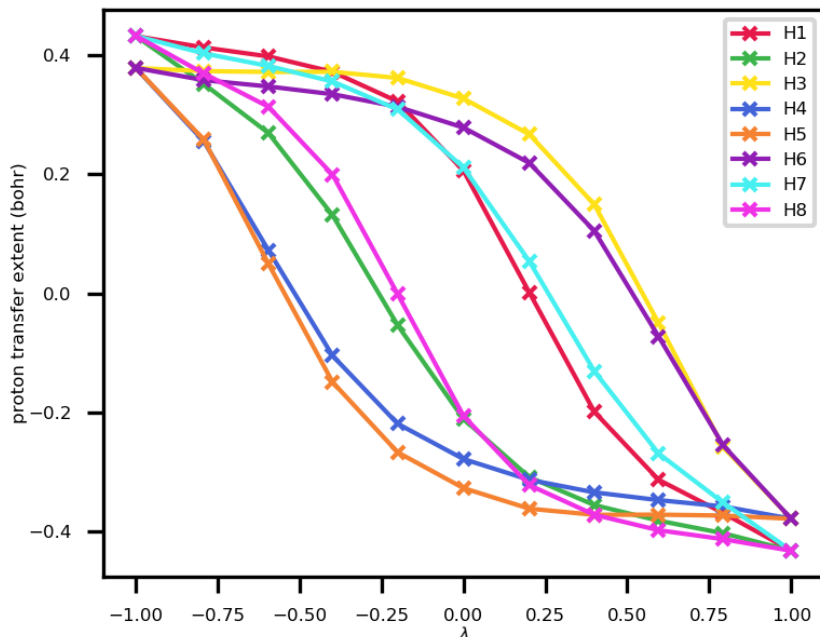


Figure 7.2: A plot of the transfer extent of each proton against the normalised reaction coordinate along the MEP of CRCA’s PES according to the effective Hamiltonian.

The potential energy curve of the converged path is plotted as $\star$ in Figure 7.1b. Its associated energy barrier is 6.49 meV/atom. This ought to be compared to the energy barrier of the MEP calculated at the same level of theory used to generate the data which was used to train the model (i.e. rVV10 exchange-correlation). However, for supercell NEB calculations in CP2K it is not possible to impose the primitive lattice translational symmetry that would be required to meaningfully compare the result of such a calculation to the result of the NEB calculation with the effective Hamiltonian. Instead, we extracted the MEP obtained from the vdW-DF2 calculation with Quantum Espresso reported in Section 5.3.3 and calculated the PEC at the rVV10 level of theory in CP2K. These are plotted as $\star$ in Figure 7.1b.

Figure 5.7 shows that the image at the halfway point of the MEP at the vdW-DF2 theory level is a local minimum in the potential energy curve. However, this feature is absent in the PEC of this path, recalculated with rVV10. This is very likely to be due to our aforementioned inability to optimise the NEB, especially its central images, with CP2K with suitably imposed symmetries. A test NEB calculation with CP2K on a single unit cell instead of a (2,2,2) supercell, illustrated in Figure 6.4, does show a local minimum in the centre of its PEC. The PEC plotted as $\star$ represents an upper bound to that of the true MEP of CRCA at the rVV10 level of theory. Finally, the PEC of the effective Hamiltonian’s MEP calculated at the rVV10 level of theory has been plotted as $\star$ in Figure 7.1b. The difference in barrier heights of this PEC and the first is a way to estimate the error in the effective Hamiltonian’s minimum energy path. This difference is 0.83 meV/atom, which is very similar in size to the expected energy error of the effective Hamiltonian, reported in Section 6.3.5. This suggests that the effective Hamiltonian approximates the true MEP of CRCA about as accurately as one might expect.

In summary, application of the NEB method to the PES of the effective Hamiltonian revealed a spurious polarisation-switching path which satisfies Equation 4.43, but which involves

the simultaneous transfer of all eight protons in the unit cell. However, subsequent calculations also revealed another MEP of the effective Hamiltonian which possesses strong qualitative similarities with the DFT MEP. Although there are also quantitative differences between these two MEPs as we describe above, their qualitative resemblance and the probable close agreement of their energy barriers imply the physical validity of using the effective Hamiltonian to simulate polarisation switching in CRCA. Therefore, we expect that simulations according to the effective Hamiltonian of the kinetics of polarisation switching at room temperature, such as those reported in Chapter 8, should give physically valid results.

Chapter 8

Kinetic Monte Carlo simulations

8.1 The kinetic Monte Carlo method

Monte Carlo methods in general use random numbers to solve problems; the name refers to the famous casinos of the Monégasque region. The kinetic Monte Carlo (KMC) method is a method for the study of non-equilibrium processes of physical systems such as diffusion, radiation damage, defect mobility, and catalysis i.e. it allows one to study the kinetics of a system's evolution towards equilibrium. This contrasts with the famous Metropolis Monte Carlo method which allows one to study a system at equilibrium by generating a sequence of states with frequencies which respect the Boltzmann probability distribution.

When an interatomic potential for a system is known, the most straightforward way to simulate a non-equilibrium process over time would be to use molecular dynamics (MD). The evolution of the positions of the system's particles are determined by numerically solving their classical equations of motion. At each timestep, the state of the system at the next timestep is calculated based on the positions and momenta at the current and previous steps. In order to obtain accurate trajectories, the stepsize must be less than the timescale of the fastest atomic vibrations in the system, which for the OH bond-containing CRCA is $\sim 10^{-15}$ s. However, this timescale is much smaller than the typical timescale of non-equilibrium processes of interest mentioned above. Therefore it is computationally unfeasible to study these processes using MD.

KMC exploits the fact that although atomic vibrations occur on a femtosecond timescale, events which change the thermodynamic state of a system occur much less frequently. Often this is because these events involve the transition of particles beyond energy barriers which otherwise prevent the system from changing its state [153, p.2]. These states form a discrete set which characterise the system.

We imagine a large ensemble of N copies of the system, each transitioning from state to state over time. In the limit of $N \rightarrow \infty$ we define a probability distribution $P_i(t)$ for one of the copies being in state i at time t . The evolution of $P_i(t)$ is defined by the *master equation* [154]

$$\frac{dP_i}{dt} = \sum_j T_{ij}P_j - T_{ji}P_i, \quad (8.1)$$

where T_{ij} is the probability of transitioning from state $j \rightarrow i$. The KMC method can be understood as a way to solve the master equation.

To derive the algorithm, it is helpful to define the matrices

$$\begin{aligned} R_{ij} &= \begin{cases} \sum_k T_{kj} & i = j \\ 0 & i \neq j \end{cases} \\ W_{ij} &= \begin{cases} 0 & i = j \\ T_{ij} & i \neq j, \end{cases} \end{aligned} \quad (8.2)$$

and also

$$\mathbf{Q} = \exp(-\mathbf{R}t). \quad (8.3)$$

This allows Equation 8.1 to be rewritten as [154]

$$\frac{d\mathbf{P}}{dt} = (\mathbf{W} - \mathbf{R}) \cdot \mathbf{P}. \quad (8.4)$$

This is solved by

$$\mathbf{P}(t) = \mathbf{Q}(t) \cdot \mathbf{P}(0) + \int_0^t dt' \mathbf{Q}(t-t') \cdot \mathbf{W} \cdot \mathbf{P}(t'). \quad (8.5)$$

By repeated substitution, we find that

$$\begin{aligned} \mathbf{P}(t) &= [\mathbf{Q}(t) + \int_0^t dt' \mathbf{Q}(t-t') \cdot \mathbf{W} \cdot \mathbf{Q}(t') \\ &\quad + \int_0^t dt' \int_0^{t'} dt'' \mathbf{Q}(t-t') \cdot \mathbf{W} \cdot \mathbf{Q}(t'-t'') \cdot \mathbf{W} \cdot \mathbf{Q}(t'') + \dots] \cdot \mathbf{P}(0). \end{aligned} \quad (8.6)$$

The first term $Q_{ij}(t')P_j(0) = P_i^{(0)}(t')$, is the probability of the system to be in state i after time t' having undergone no transition. The integrand of the second term

$$[dt' \mathbf{Q}(t-t') \cdot \mathbf{W} \cdot \mathbf{Q}(t') \cdot \mathbf{P}(0)]_i,$$

is the sum of probabilities of all the ways for there to be no transition occurring until t' , a transition into state i occurring in the interval $[t', t' + dt']$, then no further transition occurring. The corresponding integral is the probability of the system to be in state i after time t' having undergone one transition. The third term term is the probability of the system to be in state i after time t' having undergone two transitions etc. The KMC algorithm generates a sequence of states with a probability distribution that satisfies Equation 8.6 [155, p.41].

Our simulations of croconic acid (CRCA) were restricted to the subspace of configuration space spanned by the degrees of freedom (DOFs) defined in Section 6.3.1, i.e. molecular ferroelectric distortion modes and H-atom Cartesian modes. The aim of our KMC simulations was to study polarisation switching. Therefore, the discrete set of states was defined as the Cartesian product of discrete sets associated with each DOF n which include their values in the negative and positive domain states, and the value halfway between them. That is, the set of

states S was defined as

$$S = \prod_{n=1}^{N_{\text{DOF}}} s_n, \quad (8.7)$$

where N_{DOF} is the number of DOFs and

$$s_n = \left(Q_n(\mathbf{X}^{(+)}), \frac{Q_n(\mathbf{X}^{(+)}) + Q_n(\mathbf{X}^{(-)})}{2}, Q_n(\mathbf{X}^{(-)}) \right). \quad (8.8)$$

Each KMC simulation involved the following steps:

1. Initialisation.

- Generate an initial configuration α ;
- Set the time $t = 0$;
- Define time t_{max} , when the simulation will be terminated;

2. Calculate the time until the next transition.

- Generate a time interval during which no reaction takes place

$$\Delta t = -\frac{1}{\sum_{\beta} W_{\beta\alpha}} \log r, \quad (8.9)$$

where r is a continuous uniform random variable on the interval $(0, 1]$.

- Increment $t \rightarrow t + \Delta t$

3. Transition.

- Select a transition $\alpha \rightarrow \beta'$ at random with probability

$$P_{\alpha \rightarrow \beta'} = \frac{W_{\beta'\alpha}}{\sum_{\beta} W_{\beta\alpha}} \quad (8.10)$$

- Update configuration to β'

4. Continuation.

- If $t > t_{\text{max}}$, terminate, else return to Step 2.

To calculate the transition probabilities $P_{\alpha \rightarrow \beta'}$, we may consider the steady state where $\frac{dP_i}{dt} = 0$. In this case, Equation 8.1 is satisfied if

$$\frac{T_{ij}}{T_{ji}} = \frac{W_{ij}}{W_{ji}} = \frac{P_{i,\text{steady}}}{P_{j,\text{steady}}} = \exp\left(\frac{E_j - E_i}{k_B T}\right), \quad (8.11)$$

where E_i is the energy of state i . This is satisfied in turn if

$$W_{ij} = \begin{cases} \nu \exp\left(-\frac{E_i - E_j}{k_B T}\right) & E_i > E_j \\ \nu & E_i < E_j, \end{cases} \quad (8.12)$$

where ν is a characteristic frequency of atomic vibrations in the system. For CRCA, ν was set to 1 THz since phonon frequencies have this approximate magnitude.

It is important to recognise that this method does not include the effects of certain factors on the polarisation switching process. Firstly, the model does not include the effects of defects in the CRCA crystal. Defects generally provide sites for the nucleation of new domains [156, p.118], reducing the nucleation energy barrier and the coercive field as a result. This has been experimentally verified by previous studies, including Ref 157 whose authors used a scanning probe microscope to measure hysteresis loops on a fine grid of points at the surface of a lead zirconate titanate (PZT) epitaxial film. The effect of the defects on the nucleation energetics could be derived by the deviation of the locally measured hysteresis loops from the ideal, symmetric version. Regions where the locally measured hysteresis loop revealed smaller *nucleation bias* voltages were the energetically preferred sites of nucleation. This mechanism of inhomogeneous nucleation at defect sites resolves the so-called Landauer paradox [158], the observation that homogeneous nucleation of ferroelectric domains should be impossible under external field and temperature values typically reported in the literature, due to the insurmountable energy barrier associated with this process.

Secondly, the KMC method does not include quantum effects, especially of the H-atoms, on the polarisation switching process. As a consequence, these calculations correspond to the classical limit of thermally activated barrier hopping. Experiments on intermolecular proton transfer in benzoic acid crystals, a somewhat similar system which undergoes correlated proton tautomerism, suggest that this limit is well-approximated at high temperature [159]. Therefore, we consider the results of our KMC calculations below in the context of room temperature polarisation switching in CRCA.

8.2 Simulating polarisation switching in croconic acid

8.2.1 Computational details

The effective Hamiltonian described in Chapter 6.3 was used to simulate polarisation switching with the kinetic Monte Carlo (KMC) method. It consisted of three parts:

$$E = E_{\text{SPME}} + E_{\text{non-SPME}} + E_{\text{anh}} - \sum_a \mathbf{p}_a \cdot \mathcal{E}, \quad (8.13)$$

where E_{SPME} is the sum of electrostatic components of the quadratic terms of the Hamiltonian for the desired supercell, calculated using the smooth particle mesh Ewald method described in Section 6.3.3; $E_{\text{non-SPME}}$ is the sum of non-electrostatic components, extracted using the method described in Section 6.3.3, of the quadratic terms which were calculated by finite differences; E_{anh} is the sum of anharmonic terms described in Section 6.3.4; and the last summation represents the interaction between the external field and the dipoles $\{\mathbf{p}_a\}$ associated with the displacements of atoms indexed by a , calculated according to Equation 6.38.

In the following, we denote positions within the supercell in reduced units with $\mathbf{x} = (x_1, x_2, x_3)$ where $x_j \in [0, 1)$. As explained in Section 2.4.1, the dependence of the domain wall velocity v on the applied field $\mathcal{E}$ provides an indication of whether the switching occurs by

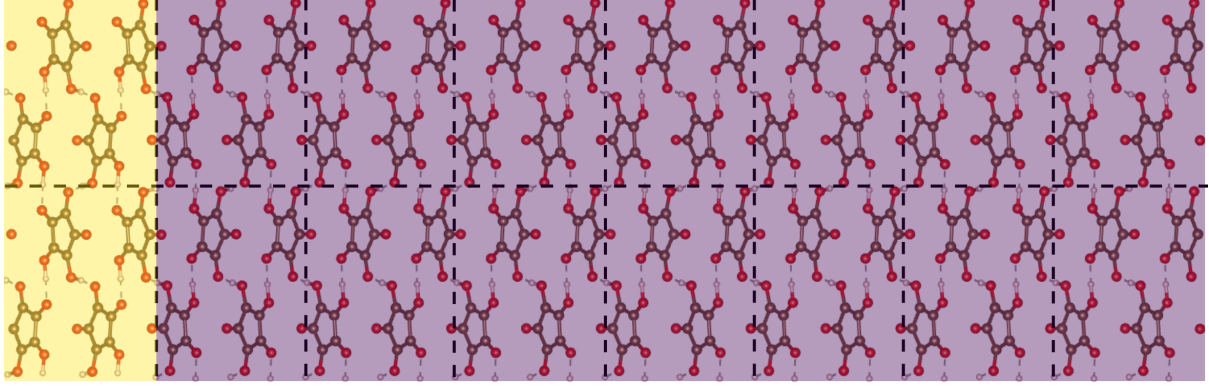


Figure 8.1: An illustration of the initial supercell configuration used in the KMC simulations. The purple region is in the ‘negative’ domain state, while the yellow region is a domain initialised in the ‘positive’ domain state.

the activated or non-activated regime. In order to measure the domain wall velocity v as a function of the applied field $\mathcal{E}$, a $(N_1, N_2, N_3) = (2, 8, 2)$ supercell of CRA was used. This supercell width was deliberately greater than the spatial cutoff of the terms in E_{anh} and $E_{\text{non-SPME}}$ so that the terms in the model would be instantiated distinctly, as explained in Section 6.3.2. The supercell was also elongated in the x_2 direction so that these simulations would be analogous to previous terahertz imaging experiments [57] described in Section 3.2.2. (Note that the x_2 -axis in the $Pbcm$ standard setting is equivalent to the x_1 -axis in the $Pca2_1$ standard setting.) The supercell was long enough in the x_2 direction for an accurate average domain wall velocity to be calculated at each value of $\mathcal{E}$.

8.2.2 Results

The system was initialised in its negative domain state. $\mathcal{E}$ was applied parallel to the polar x_3 -axis and its amplitude was varied between 0 and 2000 kV/cm, at a temperature of 300 K. We found that switching did not occur within a practically accessible timescale ($\lesssim 200$ ps) with this initial configuration and field amplitude. However, when the supercell was initialised such that the unit cells with origins at $x_2 = 0$ were set to the positive domain state while the other cells were still set to the negative domain state (thus nucleating a positive domain), switching did occur promptly. This initial configuration is illustrated in Figure 8.1. As one might have expected, the polarisation of the entire supercell appeared to switch by the mechanism of domain wall motion. This is illustrated in Figure 8.2, a colour map of the local lineal polarisation (electric dipole per unit length along the elongated x_2 -axis) over the course of a single KMC simulation with $\mathcal{E} = 2000$ kV/cm. Each row of the figure represents the polarisation of a ‘slice’ of the supercell cut normal to the x_2 -axis, with a half-unit cell width.

Electric field effect on domain wall velocity

KMC simulations were repeated with electric fields between 2000 and 8000 kV/cm. For each simulation the velocities of the domain walls moving in the positive and negative x_2 directions were calculated. By definition the domain wall passed a given position along the x_2 -axis when the running mean of the lineal polarisation had passed zero at that position. The running mean

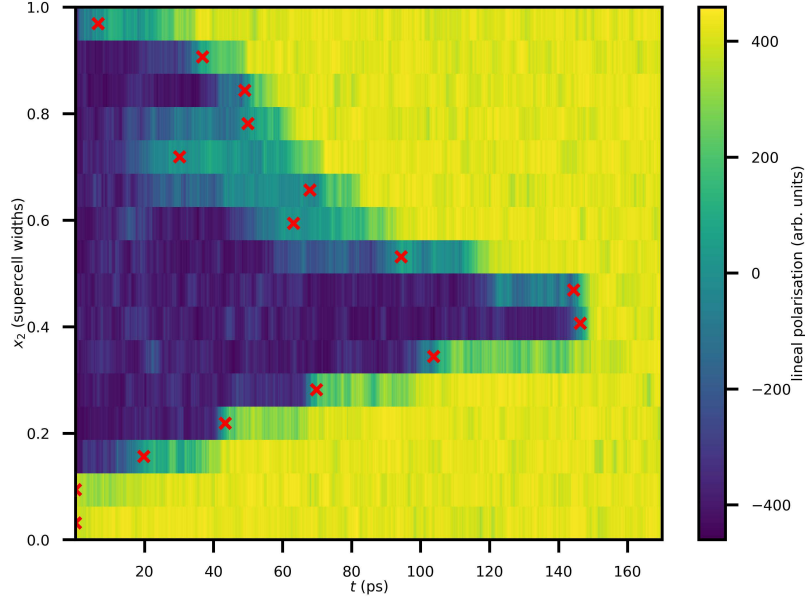
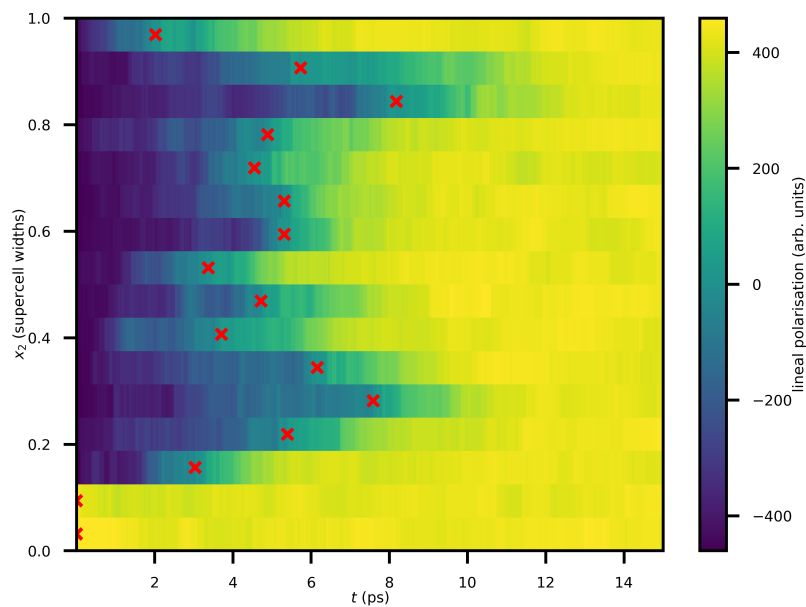


Figure 8.2: A colour map of the lineal polarisation during a kinetic Monte Carlo simulation of our effective Hamiltonian of a (2,8,2) supercell of CRCA, with an external field strength of 2000 kV/cm. The red crosses indicate the times when the running mean of the polarisation in each ‘slice’ with a half-unit cell’s width passes zero.

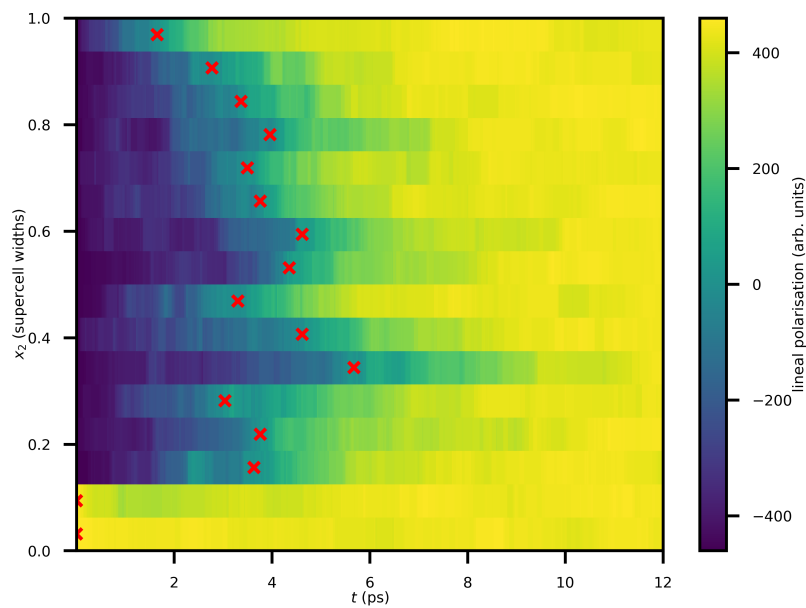
was calculated over a window equal to $1/5$ th of the ‘half-switching’ time, $t_{\frac{1}{2}}$ which we defined as the time when the net polarisation of the entire supercell passed zero. The switching time of each slice is indicated by the red cross in its associated row in the polarisation colour maps. Running means were used because occasionally during the simulations the local polarisation fluctuates temporarily past zero before the domain wall has truly passed that point. Using the running mean of the polarisation prevented these fluctuations from spuriously affecting the domain wall velocity calculation. Subsequently, linear regressions were performed to calculate the domain wall velocities and associated errors.

In the simulations with $\mathcal{E} = 7000, 8000$ kV/cm, the system did not follow a switching mechanism of well-defined domain wall motion. The polarisation over the course of these simulations is illustrated in Figure 8.3. When $\mathcal{E} = 7000$ kV/cm, although the domain walls remained well-defined as they moved along 3 half-unit cells on each side of the original nucleus, the majority of the cell switched polarisation in a disordered manner, with little well-defined domain wall motion. When $\mathcal{E} = 8000$ kV/cm, although the wall on the $-x_2$ side of the pre-nucleated domain moved along the x_2 -axis for around 3 half-cells, there was no perceptible wall on the $+x_2$ side of the pre-nucleated domain at all. As with the 7000 kV/cm simulation, most of the supercell switched polarisation in a nonlocal manner. Since these two simulations did not generally follow a switching mechanism of domain wall motion, they have been omitted when considering the relationship between v and $\mathcal{E}$.

In the simulations with $\mathcal{E} = 2000, 2500, 3000$ kV/cm the supercell switched polarisation by the expansion of the domain which was nucleated in the initial configuration. As explained in Section 2.4.2, domain wall motion due to field-induced switching can be separated into two regimes: the activated regime at low fields, and the non-activated regime at high fields. Since



(a)



(b)

Figure 8.3: Colour maps of the lineal polarisation during kinetic Monte Carlo simulations of our effective Hamiltonian of a (2,8,2) supercell of CRCA, with external field strengths of (8.3a) 7000 and (8.3b) 8000 kV/cm.

the mechanism of domain wall motion broke down for $\mathcal{E} \geq 7000$ kV/cm, it is reasonable to assume that the simulations with $\mathcal{E} \leq 6000$ kV/cm represent the non-activated (i.e. high field) regime of domain wall motion. Under this regime, a linear proportionality relationship between v and $\mathcal{E}$ has been theoretically explained [3, 37], as outlined in Section 2.4.2. In contrast, our results suggest a linear relationship with a non-zero intercept

$$v = a + b\mathcal{E}. \quad (8.14)$$

A least squares fit of this relationship to the $\mathcal{E} = 2000, 2500, 3000$ kV/cm data gives $a = -1.75 \pm 0.69$, $b = (1.08 \pm 0.30) \times 10^{-3}$, if v is measured in bohr/ps and $\mathcal{E}$ is measured in kV/cm. This is illustrated by the blue line in Figure 8.4.

Unfortunately, the relationship between the domain wall velocity and external field strength in CRCA has not been experimentally measured. Therefore, the linear relationship which our simulations suggest cannot currently be compared to experimental results. However, such an experiment could be carried out in the future using well-known methods. Specifically one could use piezoresponse force microscopy, described in Section 2.3.2, to measure the distance travelled by a domain wall in a CRCA plate due to the effect of external field pulses of various durations, from which the velocity could be calculated.

It should also be noted that the first measurements of the velocity of a domain wall in Rochelle salt also gave a $v(\mathcal{E})$ relationship in the form of Equation 8.14, with a negative a value in contrast to Ref 37 [160]. However, this result is not directly comparable with our KMC simulations of CRCA. Rochelle salt is a ferroelastic-ferroelectric. Hence, as the authors of Ref 160 state, the domain walls are subject to a restoring force due to internal stress which impedes their motion. In the experiment, a square alternating voltage was applied across a Rochelle salt plate and v was measured at its greatest value as it passed its equilibrium position during each cycle. In our simulations, however, CRCA is not ferroelastic, the applied field was constant, and v was measured as an average value.

In the simulations at $\mathcal{E} = 3500, 4000, 5000$ kV/cm we find that another domain, apart from that which was nucleated in the initial configuration, nucleates during the simulation. In these cases, we can see that the mean domain wall velocity is significantly smaller than what the linear relationship quantified above would predict. The likely cause of this deviation is the necessary approximation which was implicit in the KMC simulations. Each allowed transition only altered the value of one of the DOFs at a time. With only a single expanding domain, the KMC algorithm effectively has a choice between 2 domain walls from which to select energetically favourable transitions at each iteration. However, in the simulations where another domain nucleates, there are 4 domain walls. One would accordingly expect each wall to advance $\frac{1}{2}$ as fast as it would if transitions were allowed which simultaneously reversed the dipoles located at the edges of separated domain walls. This reduces their velocities by the same factor. If the data are ‘corrected’ by doubling their velocity values, represented by the $\color{red}{\boxplus}$ points in Figure 8.4, the corrected data agree significantly better with the linear fit described above. The red line represents a new linear fit which includes all data with $\mathcal{E} < 7000$ kV/cm, with the aforementioned corrections applied where necessary. This inclusion changes the parameter values to $a = -2.03 \pm 0.27$, $b = (1.19 \pm 0.09) \times 10^{-3}$.

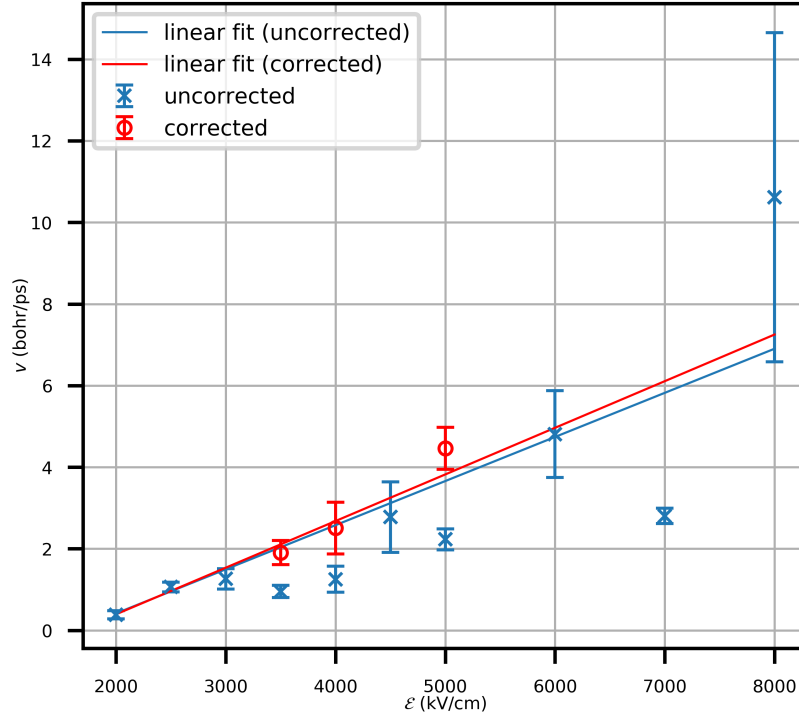
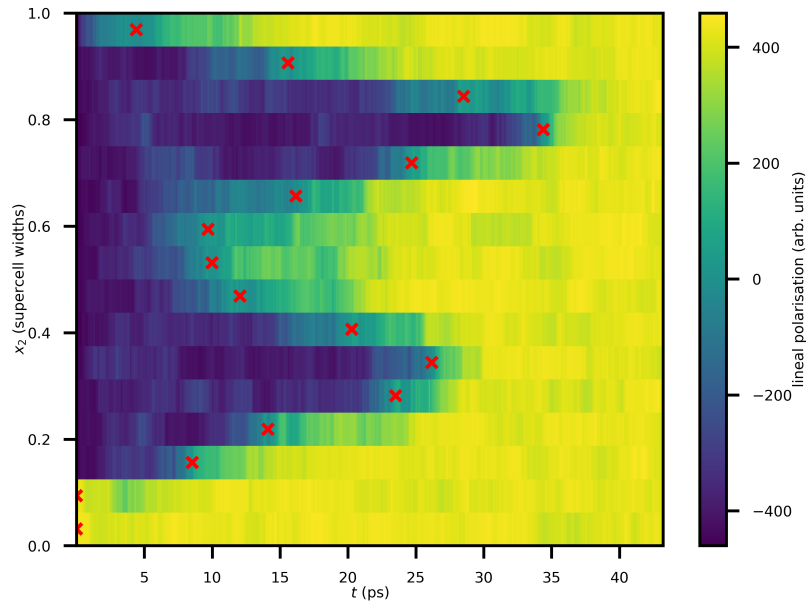
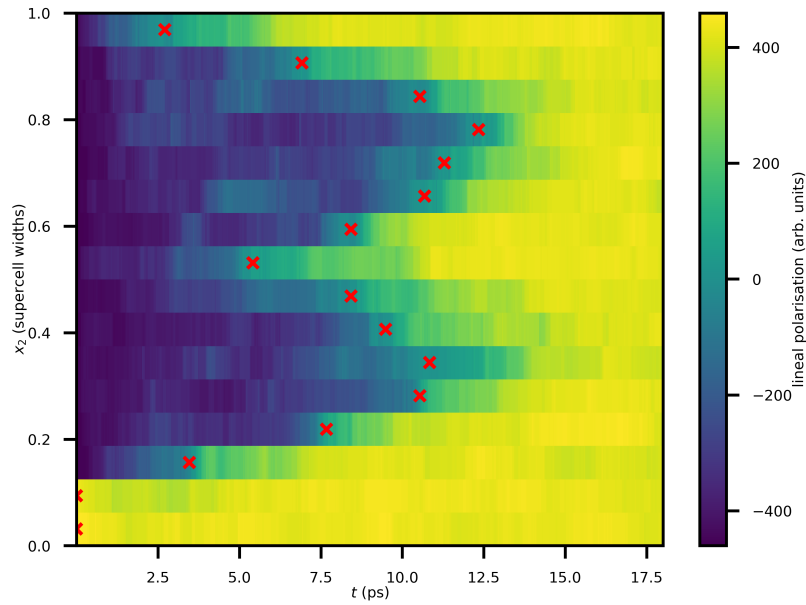


Figure 8.4: A plot of the velocity of domain walls during kinetic Monte Carlo simulations against applied field strength. The blue line represents a linear fit through the data for the simulations which featured a single expanding domain. The red line represents a linear fit through the all data with $\mathcal{E} < 7000$ kV/cm, with the appropriate corrections applied.

We also find that new domains nucleate during the simulations at $\mathcal{E} = 4500$ and 6000 kV/cm, which are illustrated in Figure 8.6. However, their domain velocity values do not appear to have been halved relative to the linear fit's estimate. In the $\mathcal{E} = 4500$ kV/cm case, the two new domains each nucleate closer to the current location of one of the existing domain walls than they do in the 3500 , 4000 , 5000 kV/cm cases. (The first nucleates within 2 half-cell widths of a wall of the pre-nucleated domain, while the second nucleates within 4 half-cell widths of the other wall of the pre-nucleated domain. These distances are significantly smaller than their corresponding values, in the $\mathcal{E} = 3500$, 4000 , 5000 kV/cm cases, where each new domain nucleates within 6 half-cell widths of one of the pre-nucleated domain walls.) The expansion of each new domain in the $\mathcal{E} = 4500$ kV/cm simulation also effectively expands one of the existing domains. This means that during the time interval over which the velocities of the two initial domain walls were calculated, the KMC algorithm could choose a single transition and advance two domain walls simultaneously, instead of choosing one or the other in the way explained above. In the $\mathcal{E} = 6000$ kV/cm case, the second domain nucleates after most of the supercell has already switched by the expansion of the pre-nucleated domain. Perhaps more significantly, the velocities of the pre-nucleated domain walls had to be calculated only over time intervals when the domain wall motion was apparent and well-defined. For the wall on the $+x_2$ side of the pre-nucleated domain, this interval ($t < 5.02$ ps) occurred entirely before the nucleation of the new domain (at 5.58 ps). Whereas for the wall on the $-x_2$ side of the pre-nucleated domain, this interval ($t < 8.09$ ps) occurred mostly before the new domain's nucleation. Therefore, similar

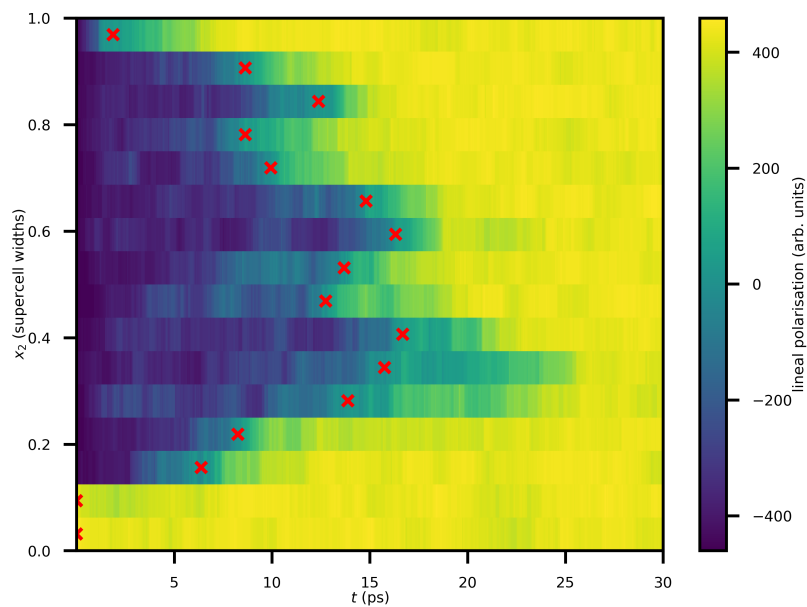


(a)

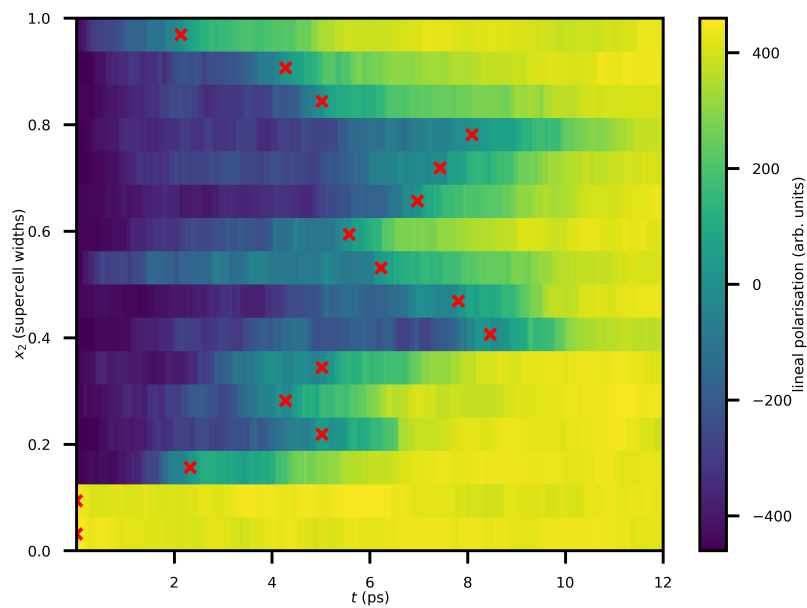


(b)

Figure 8.5: Colour maps of the lineal polarisation during KMC simulations of our effective Hamiltonian of a (2,8,2) supercell of CRCA, with external field strengths of (8.5a) 3500 and (8.5b) 5000 kV/cm.



(a)



(b)

Figure 8.6: Colour maps of the lineal polarisation during KMC simulations of our effective Hamiltonian of a (2,8,2) supercell of CRCA, with external field strengths of (8.6a) 4500 and (8.6b) 6000 kV/cm.

to the $\mathcal{E} = 4500$ kV/cm case, for most of the time interval over which the velocities of the two initial domain walls were calculated, the KMC algorithm did not have to choose between domain walls in the way explained above. For these reasons, the domain wall velocity values calculated in these two simulations agree with the linear fit.

Nevertheless, the approximation of allowing only single-DOF transitions during our KMC simulations may affect the relationship between v and $\mathcal{E}$ that was found. The lack of transitions which move multiple DOFs within the same domain wall could be the source of the disagreement between the result of Ref 37 and the non-zero values we found for both the ‘uncorrected’ and ‘corrected’ linear fits for the intercept a . However, it is likely that transitions which move multiple DOFs within the same domain wall would be attempted less frequently than single-DOF transitions, since they require the coordinated and simultaneous motion of multiple DOFs. Hence their contribution to the velocity of a single domain wall would be smaller than the contribution from single-DOF transitions. Therefore, our adoption of single-DOF transitions functions as a useful approximation. Nevertheless, the effect of allowing multiple-DOF transitions would be an interesting topic for further research.

The thermodynamic coercive field is known to be several orders of magnitude greater than the experimental coercive field for an arbitrary ferroelectric [161, p.118], due to its neglect of spatially heterogeneous switching mechanisms. On the other hand, switching was not demonstrated by our KMC simulations with fields less than 2000 kV/cm, which has the same order of magnitude as the apparent thermodynamic coercive field. The principal reason for this is that, at fields on the order of the experimental coercive field (~ 14 kV/cm), switching occurs [162, p.1113] on a timescale of $\gtrsim 1$ ns which vastly exceeds the ~ 10 ps timescale of our KMC simulations. If computing power were less restricted we would expect switching to eventually occur at experimentally common field magnitudes.

Analysing the proton transfer extent

In order to study the polarisation switching mechanism, the atomic positions during the KMC simulations were also analysed. Specifically, by studying the correlation of proton transfer extents we sought to determine whether or not protons connected to the same CRCA molecule tend to transfer simultaneously more often than more tenuously connected protons, as suggested by the minimum energy paths (MEPs) calculated using the nudged elastic band algorithm with both density functional theory and the effective Hamiltonian. For our simulations, it was not possible to allow transitions which altered multiple DOFs at the same time due to the computational unfeasibility of doing so. We find that there are

$$\begin{aligned} N_{\text{trans},1} &= N_{\text{cell}} \cdot n_{\text{DOF}} \cdot 2 \\ &= 32 \cdot 28 \cdot 2 \\ &= 1792 \end{aligned}$$

potential single-DOF transitions in the (2,8,2) supercell, where N_{cell} is the number of unit cells in the supercell, n_{DOF} is the number of degrees of freedom per unit cell, and 2 equals the number of values each DOF can be transitioned to. There are 2 FDMs per C_5O_5 molecule, 3 Cartesian

DOFs per terrace H-atom, and 2 Cartesian DOFs per hinge H-atom since the displacement in the Cartesian x -direction of each hinge proton has the same value in the two domain states. In the worst case, when all pairwise transitions which alter all pairs of DOFs are allowed, this would mean that

$$N_{\text{trans},2} = {}^{N_{\text{trans},1}}C_2 = 1604736 \gg N_{\text{trans},1} \quad (8.15)$$

potential pairwise transitions would have to be considered in Steps 3 and 2 of the KMC algorithm described above. If a spatial cutoff is applied to the pairs of DOFs which are altered by the allowed transitions, then we can calculate the number of potential transitions as

$$N_{\text{trans},2} = \sum_j B_j^{(1)} B_j^{(2)}, \quad (8.16)$$

where the pairs of DOFs, within the cutoff, are indexed by j and where $B_j^{(1)}$ and $B_j^{(2)}$ are the numbers of values which DOFs 1 and 2 in pair j can transition to. For most DOFS $B = 2$. However, as stated above, the displacement in the Cartesian x -direction of each hinge proton has the same value in the two domain states; in this case $B = 0$. If the spatial cutoff is set to the size of the smallest unit cell dimension, then we find that $N_{\text{trans},2} = 21504 \gg N_{\text{trans},1}$. In either case the computational expense of the KMC simulations increases by at least one order of magnitude. The situation becomes worse still if transitions which move more than 2 DOFs at a time are allowed.

As an alternative to this computationally unfeasible path, we used the data from our simulations which allowed only single-DOF transitions, and calculated the running mean (over a window equal to $t_{\frac{1}{2}}/5$) of the transfer extents of each proton in the (2,8,2) supercell under a 2000 kV/cm external field. We define the transfer time, t_{transfer} of each proton as the time when the running mean of its transfer extent exceeds zero. We may then quantify how correlated the transfer of a pair of protons is by the difference in their t_{transfer} values. In order to quantify how directly connected a pair of protons is in the supercell, we define a graph whose vertices are protons and whose edges connect protons connected to the same molecule in the crystal, and calculate the shortest path n_{path} between each proton pair using the implementation of Dijkstra's algorithm [163] in the NetworkX Python package [164]. A segment of this graph is illustrated in Figure 8.7.

In Figure 8.8, the mean $\Delta t_{\text{transfer}}$ value for proton pairs is plotted against n_{path} . Pairs of protons which are both situated in the pre-nucleated domain at $x_2 = 0$ are excluded. Significantly, we see that the mean $\Delta t_{\text{transfer}}$ for protons connected to the same molecule is about half that of the corresponding value for protons connected via 2 molecules. This suggests that the transfer of protons connected to the same molecule is indeed more correlated than the transfer of proton pairs which are less directly connected. As n_{path} increases, the difference in $\Delta t_{\text{transfer}}$ for adjacent n_{path} values decreases, since at large n_{path} electrostatic interactions between proton pairs, whose strength decreases slowly with distance, dominate the interaction. Accordingly, at large $n_{\text{path}} \gtrsim 10$, increasing the n_{path} by 1 does not significantly affect the difference in transfer times, in contrast to the situation at $n_{\text{path}} \lesssim 4$.

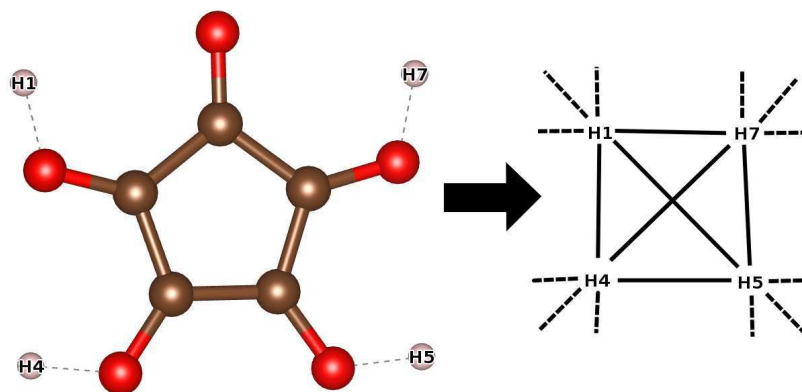


Figure 8.7: A segment of the proton connectivity graph. A CRCA molecule and its four neighbouring H-atoms are interpreted as a portion of a graph whose vertices are the H-atoms, and whose edges connect each H-atom to the others which neighbour the same molecule.

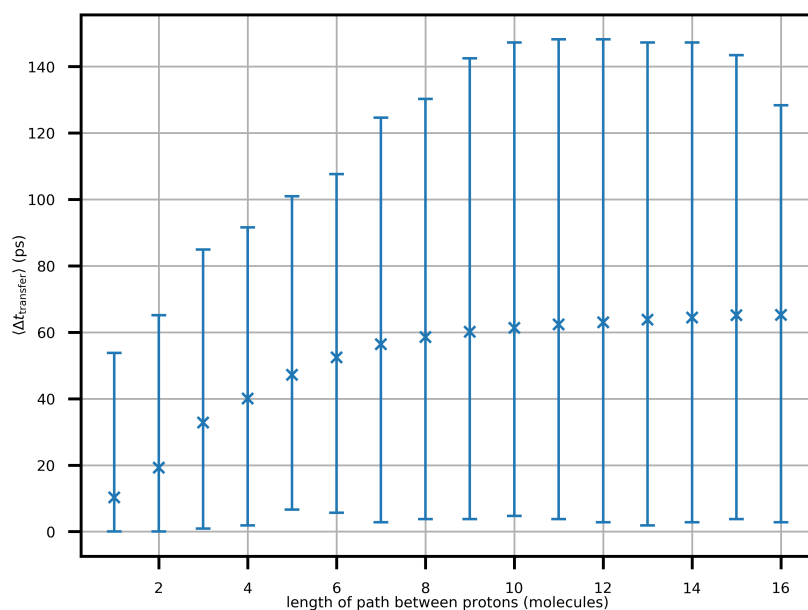


Figure 8.8: A scatter plot of the mean difference in proton transfer times during a KMC simulation of polarisation switching in CRCA in an electric field of 2000 kV/cm against the length of the shortest path between the protons in terms of edges of the proton connectivity graph explained in the text. The error bars represent the range of $\Delta t_{\text{transfer}}$ values between the 2.5th and 97.5th percentile.

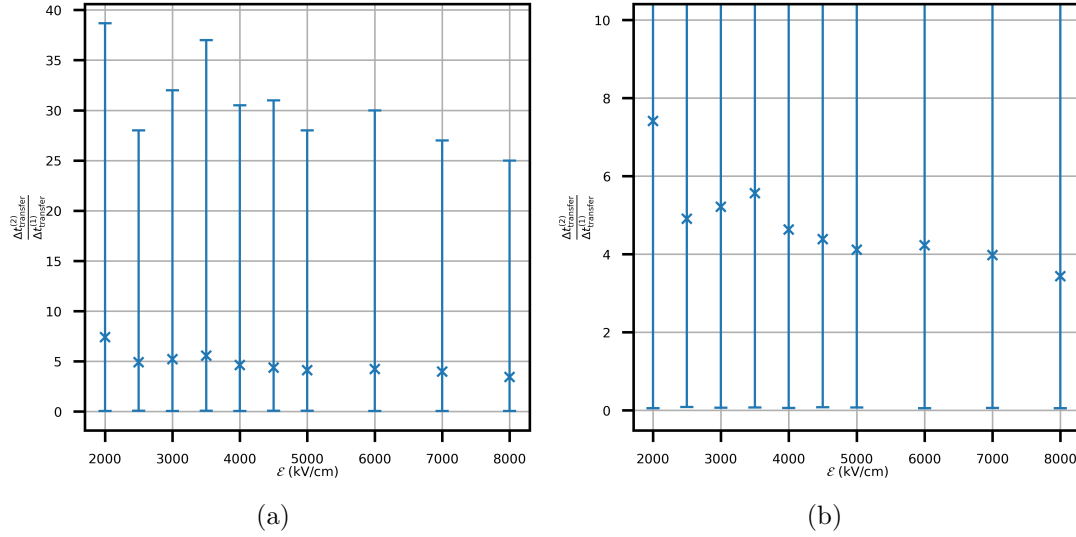


Figure 8.9: A scatter plot of the mean value of $\frac{\Delta t_{\text{transfer}}^{(2)}}{\Delta t_{\text{transfer}}^{(1)}}$, the ratio of the transfer time interval between proton pairs separated by 2 molecules to the transfer time interval between proton pairs separated by 1 molecule, against $\mathcal{E}$. 8.9b is a zoomed-in view of 8.9a. The error bars represent the range of $\frac{\Delta t_{\text{transfer}}^{(2)}}{\Delta t_{\text{transfer}}^{(1)}}$ values between the 2.5th and 97.5th percentile.

The large spread in the time differences at each n_{path} value is due to the difference in how each proton pair is precisely connected. The interaction between two hinge protons connected to the same molecule is different to the interaction between two terrace protons, for example. Hence, their $\Delta t_{\text{transfer}}$ values are expected to differ. The spread in $\Delta t_{\text{transfer}}$ increases as n_{path} increases because the number of ways that two protons in the supercell are connected with a path of length n_{path} also generally increases as n_{path} increases.

The mean of the ratio $\frac{\Delta t_{\text{transfer}}^{(2)}}{\Delta t_{\text{transfer}}^{(1)}}$ is plotted against $\mathcal{E}$ in Figure 8.9, where $\Delta t_{\text{transfer}}^{(n)}$ is the transfer time interval for a proton pair separated by n molecules. We see that it generally decreases as $\mathcal{E}$ increases. This suggests that processes where more widely separated proton pairs are transferred within shorter time intervals become more frequent as $\mathcal{E}$ increases. This is understandable, since increasing $\mathcal{E}$ effectively reduces the energy barrier for these processes.

In summary, kinetic Monte Carlo simulations of polarisation switching in a CRCA supercell were carried out at room temperature and under various external field values. The simulation data suggest a linear relationship between the domain wall velocity and the external field, albeit with a non-zero intercept which differs from previous theoretical predictions. This discrepancy may have been caused by the lack of transitions in the KMC simulations which alter multiple DOFs at the same time. The data also imply that during polarisation switching, the transfer extents of protons connected to the same molecule in the supercell are significantly more correlated than less directly connected protons, which is consistent with the minimum energy path between CRCA's domain states calculated according to the nudged elastic band algorithm discussed in Section 5.3.3.

Chapter 9

Conclusions

One of the quantities which define a ferroelectric is its spontaneous polarisation. Therefore, the mechanism by which the spontaneous polarisation is switched between a ferroelectric’s domain states is one of the latter’s defining behaviours. An understanding of this mechanism is a necessary part of a full understanding of the material as a whole. The study of polarisation switching in ferroelectrics has traditionally been more focused on the inorganic perovskites such as lead zirconate titanate (PZT) due to their more advanced level of practical application and commercialisation. However, organic ferroelectrics have also generated interest more recently due to their lack of toxic lead and comparatively mild synthesis conditions among other favourable characteristics. Studying polarisation switching in an organic ferroelectric like croconic acid (CRCA) is therefore appealing from both the perspectives of fundamental scientific interest and potential future applications.

The aim of the project described in this thesis was to theoretically study polarisation switching in CRCA on a length scale of multiple unit cell widths so that the dynamics of domain walls, which have been experimentally observed in CRCA [57], could be modelled. We achieved this by performing density functional theory (DFT) calculations of the material’s potential energy surface, and by using an effective Hamiltonian which was trained on data obtained in this way.

We calculated the minimum energy path (MEP) between the two domain states of CRCA using the nudged elastic band (NEB) method, and projected the path onto the basis of phonon modes of *Pbcm*-CRCA at Γ . By doing this, we showed that polarisation switching in CRCA is most efficiently described in a basis of atomic displacements which allows atoms to move independently, in contrast to the collective motions of phonon modes.

The construction of the effective Hamiltonian was based on a second principles method which was originally designed to model the perovskites PbTiO_3 [144] and SrTiO_3 [145], and which we modified to make more suitable for the simulation of H-bonded crystals. In our version, translational invariance of the Hamiltonian was imposed by projecting out any rigid shift of the lattice and evaluating the energy as a function of these projected atomic displacements. This approach allowed us the flexibility to define terms for our Hamiltonian which captured the molecular distortions in a coarse-grained way, instead of the displacement differences of the original second principles method. This made the model more efficient to train and use. We hope that these ideas may facilitate the development of similar models for molecular crystals in the future.

We used the method to construct an effective Hamiltonian of CRCA which achieved a root mean squared energy error (RMSEE) of ~ 1 meV/atom, albeit evaluated on the configuration subspace spanned by the ferroelectric distortion modes, rather than the configuration space in its entirety. Nevertheless, this RMSEE value is comparable to those of machine learning potentials which often appear in contemporary research [165].

We calculated the minimum energy path between CRCA’s domain states according to the model using the NEB method. This gave a result which involved proton transfer in four successive pairs, which is qualitatively identical to the MEP which we had previously calculated with the NEB method and DFT. This agreement implied that our effective Hamiltonian is physically valid and suitable for our kinetic Monte Carlo (KMC) simulations of polarisation switching.

We performed KMC simulations of polarisation switching in an elongated supercell of CRCA according to the effective Hamiltonian, and found that the domain wall velocity followed a linear relationship with the applied field in the non-activated regime. A previously reported theoretical result [37] suggests that the domain wall velocity follows a linear relationship with a zero intercept. However, our simulations suggest a linear relationship with a negative intercept.

There are two possible explanations for this discrepancy. As explained in Section 8.2.2 the domain wall velocities calculated from the simulations in which an additional domain nucleated were ‘corrected’ by doubling their values. The crudeness of this approach is a potential source of the discrepancy and could be improved by adopting an alternative simulation approach which allows multiple degrees of freedom (DOFs) to be varied simultaneously in the future. Secondly, while the continuum approximation adopted by Ref 37 implicitly assumes that the local polarisation varies on a length-scale much greater than the lattice parameter, the effective Hamiltonian described in this thesis calculates the local polarisation as a sum over local microscopic dipole moments, and makes no assumption about the continuity of the local polarisation. Indeed, observing the polarisation colour maps which were rendered from the KMC simulations suggests that domain walls in CRCA have a thickness of ~ 1 unit cell, contrary to the continuum assumption. To our knowledge, no experimental measurements of the relationship between the velocity of domain walls in CRCA and the applied field strength have ever been made. Therefore, neither the correctness of our predictions based on the KMC simulations nor those made in Ref 37 can be verified yet.

Finally, by analysing the time intervals between transfers of pairs of protons in the supercell during switching, we found that this time interval was approximately twice as large for proton pairs connected through two molecules than for proton pairs connected to the same molecule. This supports the picture, created by the NEB calculations, of protons being transferred during field-induced switching roughly one molecule at a time.

9.1 Future work

Our effective Hamiltonian modelled an ideal, defect-free crystal of CRCA. Although simulating such a system did allow us to study some features of domain wall motion in CRCA, experimental evidence pertaining to CRCA specifically [57] as well as experience with ferroelectrics generally suggest that the presence of defects influences the position of nucleating domains and the speed

with which their boundaries move under an external field.

Therefore, this research could be progressed by capturing the interaction between defects and domain walls in a subsequent model. Little research concerning the defects present in CRCA has been published. However, the defects of potassium dihydrogen phosphate (KDP), a proton transfer ferroelectric with a greater experimental history, have been studied both theoretically and experimentally. In KDP, possible point defects include H Frenkel pairs, H vacancies and H interstitials [166]. Due to KDP's use as a non-linear optical medium, most research on its defects has focused on these defects' effects on KDP's optical properties. However, density functional theory calculations have [166] demonstrated the strong effect that point defects can have on local bonding geometry. For example, a H vacancy in the positively charged state induces a shortening of the distance between its surrounding O-atoms from 3.13 Å to 2.72 Å. In order to capture a similar effect in CRCA in a future model, if such an effect did exist, a basis of molecular distortion which allows more freedom of independent movement for the O-atoms involved in hydroxyl bonds and H-bonds might be beneficial. The effect of point defects of various charge states on domain wall motion could then be explored.

The effective Hamiltonian also does not include the effect of proton tunnelling on polarisation switching in CRCA. The relative importance of quantum tunnelling- and thermally-assisted proton transfer in CRCA remains unknown. However, this question has been studied for squaric acid, a proton transfer antiferroelectric which has a similar chemical composition to CRCA [85]. During *ab initio* path integral molecular dynamics (PIMD) calculations, both quantum tunnelling- and thermally-assisted proton transfer events were observed. Further, the fraction of thermally-assisted proton transfer events increased at higher temperatures. Based on this result, we would expect that for polarisation switching in CRCA, the importance of tunnelling relative to that of thermally-activated hopping would be minimised at higher temperatures. The authors of Ref 85 also found that regardless of the classical/quantum nature of each proton transfer event, the protons which were connected along the same H-bonded chain transferred collectively. Similarly, we would expect our finding that protons in CRCA transfer in correlated pairs would be unaffected by the inclusion of quantum effects.

Nevertheless the effect of quantum tunnelling on field-induced polarisation switching in CRCA, and its dependence on temperature, remains an open and compelling question. This could be tackled by performing PIMD simulations on CRCA, similar to Ref 85, except with a non-zero external field. This could initially be done from first principles, and then using the effective Hamiltonian described in this thesis. (Empirical force fields have been previously used to perform PIMD simulations on ice to study the nature of the proton dynamics [167, 168].)

In summary, there are many areas of further research to pursue. Both *ab initio* and second principles methods can help us answer our many questions concerning croconic acid and proton transfer ferroelectrics in general. It has been a rewarding experience to independently contribute in a small but significant way towards this effort.

Appendix A

Atomic positions of the croconic acid unit cell

Table A.1: Atomic positions of *Pbcm*-CRCA with optimised unit cell dimensions in reduced coordinates.

atom	CP2K			Quantum Espresso		
	x	y	z	x	y	z
O1	0.8068	0.9224	0.9755	0.8088	0.9228	0.9747
O2	0.1932	0.4224	0.9755	0.1912	0.4228	0.9747
O3	0.6440	0.2557	0.3859	0.6383	0.2558	0.3860
O4	0.3560	0.7443	0.8859	0.3617	0.7442	0.8860
O5	0.3560	0.7557	0.3859	0.3617	0.7558	0.3860
O6	0.6440	0.2443	0.8859	0.6383	0.2442	0.8860
O7	0.6440	0.2557	0.1141	0.6383	0.2558	0.1140
O8	0.3560	0.7443	0.6141	0.3617	0.7442	0.6140
O9	0.3560	0.7557	0.1141	0.3617	0.7558	0.1140
O10	0.6440	0.2443	0.6141	0.6383	0.2442	0.6140
O11	0.1932	0.0776	0.0245	0.1912	0.0772	0.0253
O12	0.8068	0.9224	0.5245	0.8088	0.9228	0.5253
O13	0.8068	0.5776	0.0245	0.8088	0.5772	0.0253
O14	0.1932	0.4224	0.5245	0.1912	0.4228	0.5253
C1	0.0974	0.0421	0.2500	0.0954	0.0431	0.2500
C2	0.9026	0.9579	0.7500	0.9046	0.9569	0.7500
C3	0.9026	0.5421	0.2500	0.9046	0.5431	0.2500
C4	0.0974	0.4579	0.7500	0.0954	0.4569	0.7500
C5	0.2458	0.1000	0.3608	0.2433	0.1002	0.3604
C6	0.7542	0.9000	0.8608	0.7567	0.8998	0.8604
C7	0.7542	0.6000	0.3608	0.7567	0.6002	0.3604
C8	0.2458	0.4000	0.8608	0.2433	0.3998	0.8604
C9	0.4712	0.1890	0.3180	0.4673	0.1892	0.3178
C10	0.5288	0.8110	0.8180	0.5327	0.8108	0.8178

C11	0.5288	0.6890	0.3180	0.5327	0.6892	0.3178
C12	0.4712	0.3110	0.8180	0.4673	0.3108	0.8178
C13	0.4712	0.1890	0.1820	0.4673	0.1892	0.1822
C14	0.5288	0.8110	0.6820	0.5327	0.8108	0.6822
C15	0.5288	0.6890	0.1820	0.5327	0.6892	0.1822
C16	0.4712	0.3110	0.6820	0.4673	0.3108	0.6822
C17	0.2458	0.1000	0.1392	0.2433	0.1002	0.1396
C18	0.7542	0.9000	0.6392	0.7567	0.8998	0.6396
C19	0.7542	0.6000	0.1392	0.7567	0.6002	0.1396
C20	0.2458	0.4000	0.6392	0.2433	0.3998	0.6396
H1	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
H2	0.0000	0.5000	0.0000	0.0000	0.5000	0.0000
H3	0.3797	0.7500	0.0000	0.3840	0.7500	0.0000
H4	0.6203	0.2500	0.0000	0.6160	0.2500	0.0000
H5	0.6203	0.2500	0.5000	0.6160	0.2500	0.5000
H6	0.3797	0.7500	0.5000	0.3840	0.7500	0.5000
O15	0.8957	0.9636	0.2500	0.8942	0.9656	0.2500
O16	0.1043	0.0364	0.7500	0.1058	0.0344	0.7500
O17	0.1043	0.4636	0.2500	0.1058	0.4656	0.2500
O18	0.8957	0.5364	0.7500	0.8942	0.5344	0.7500
O19	0.1932	0.0776	0.4755	0.1912	0.0772	0.4747
O20	0.8068	0.5776	0.4755	0.8088	0.5772	0.4747
H7	0.0000	0.0000	0.5000	0.0000	0.0000	0.5000
H8	0.0000	0.5000	0.5000	0.0000	0.5000	0.5000

Table A.2: Primitive lattice vectors of the optimised *Pbcm*-CRCA unit cell in units of bohr.

lattice vector	CP2K			Quantum Espresso		
	x	y	z	x	y	z
a	9.6938	0.0000	0.0000	9.6968	0.0000	0.0000
b	0.0000	16.0148	0.0000	0.0000	16.6209	0.0000
c	0.0000	0.0000	20.1418	0.0000	0.0000	20.3152

Table A.3: Atomic positions of *Pca*2₁-CRCA with optimised unit cell dimensions in reduced coordinates.

atom	CP2K			Quantum Espresso		
	x	y	z	x	y	z
O1	0.9132	0.8040	0.9709	0.9105	0.8046	0.9670
O2	0.4132	0.1960	0.9709	0.4105	0.1954	0.9670
O3	0.2632	0.6440	0.3795	0.2650	0.6406	0.3764
O4	0.7368	0.3560	0.8795	0.7350	0.3594	0.8764
O5	0.7632	0.3560	0.3795	0.7650	0.3594	0.3764

O6	0.2368	0.6440	0.8795	0.2350	0.6406	0.8764
O7	0.2504	0.6541	0.1146	0.2514	0.6514	0.1149
O8	0.7496	0.3459	0.6146	0.7486	0.3486	0.6149
O9	0.7504	0.3459	0.1146	0.7514	0.3486	0.1149
O10	0.2496	0.6541	0.6146	0.2486	0.6514	0.6149
O11	0.0730	0.2069	0.0274	0.0733	0.2105	0.0295
O12	0.9270	0.7931	0.5274	0.9267	0.7895	0.5295
O13	0.5730	0.7931	0.0274	0.5733	0.7895	0.0295
O14	0.4270	0.2069	0.5274	0.4267	0.2105	0.5295
C1	0.0448	0.1036	0.2502	0.0475	0.1044	0.2494
C2	0.9552	0.8964	0.7502	0.9525	0.8956	0.7494
C3	0.5448	0.8964	0.2502	0.5475	0.8956	0.2494
C4	0.4552	0.1036	0.7502	0.4525	0.1044	0.7494
C5	0.1054	0.2491	0.3609	0.1079	0.2484	0.3593
C6	0.8946	0.7509	0.8609	0.8921	0.7516	0.8593
C7	0.6054	0.7509	0.3609	0.6079	0.7516	0.3593
C8	0.3946	0.2491	0.8609	0.3921	0.2484	0.8593
C9	0.1945	0.4785	0.3153	0.1969	0.4775	0.3136
C10	0.8055	0.5215	0.8153	0.8031	0.5225	0.8136
C11	0.6945	0.5215	0.3153	0.6969	0.5225	0.3136
C12	0.3055	0.4785	0.8153	0.3031	0.4775	0.8136
C13	0.1858	0.4740	0.1821	0.1868	0.4719	0.1823
C14	0.8142	0.5260	0.6821	0.8132	0.5281	0.6823
C15	0.6858	0.5260	0.1821	0.6868	0.5281	0.1823
C16	0.3142	0.4740	0.6821	0.3132	0.4719	0.6823
C17	0.0989	0.2551	0.1429	0.1004	0.2567	0.1442
C18	0.9011	0.7449	0.6429	0.8996	0.7433	0.6442
C19	0.5989	0.7449	0.1429	0.6004	0.7433	0.1442
C20	0.4011	0.2551	0.6429	0.3996	0.2567	0.6442
H1	0.0077	0.0413	0.0102	0.0099	0.0510	0.0132
H2	0.5077	-0.0413	0.0102	0.5099	-0.0510	0.0132
H3	0.7410	0.3759	0.0203	0.7405	0.3780	0.0247
H4	0.2410	0.6241	0.0203	0.2405	0.6220	0.0247
H5	0.2590	0.6241	0.5203	0.2595	0.6220	0.5247
H6	0.7590	0.3759	0.5203	0.7595	0.3780	0.5247
O15	0.9674	0.9027	0.2494	0.9713	0.9047	0.2482
O16	0.0326	0.0973	0.7494	0.0287	0.0953	0.7482
O17	0.4674	0.0973	0.2494	0.4713	0.0953	0.2482
O18	0.5326	0.9027	0.7494	0.5287	0.9047	0.7482
O19	0.0868	0.1960	0.4709	0.0895	0.1954	0.4670
O20	0.5868	0.8040	0.4709	0.5895	0.8046	0.4670
H7	-0.0077	-0.0413	0.5102	-0.0099	-0.0510	0.5132

H8	0.4923	0.0413	0.5102	0.4901	0.0510	0.5132
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Table A.4: Primitive lattice vectors of the optimised $Pca2_1$ -CRCA unit cell in units of bohr.

lattice vector	CP2K			Quantum Espresso		
	x	y	z	x	y	z
a	16.0105	0.0000	0.0000	16.6345	0.0000	0.0000
b	0.0000	9.7804	0.0000	0.0000	9.8142	0.0000
c	0.0000	0.0000	20.5484	0.0000	0.0000	20.9783

Table A.5: Atomic positions of $Pca2_1$ -CRCA in reduced coordinates with unit cell dimensions fixed to their $Pbcm$ -CRCA values given in Table A.2 after being transformed to the $Pca2_1$ standard setting.

atom	CP2K			Quantum Espresso		
	x	y	z	x	y	z
O1	0.9107	0.8021	0.9737	0.9045	0.8030	0.9728
O2	0.4107	0.1979	0.9737	0.4045	0.1970	0.9728
O3	0.2657	0.6535	0.3780	0.2706	0.6525	0.3751
O4	0.7343	0.3465	0.8780	0.7294	0.3475	0.8751
O5	0.7657	0.3465	0.3780	0.7706	0.3475	0.3751
O6	0.2343	0.6535	0.8780	0.2294	0.6525	0.8751
O7	0.2497	0.6652	0.1124	0.2494	0.6679	0.1119
O8	0.7503	0.3348	0.6124	0.7506	0.3321	0.6119
O9	0.7497	0.3348	0.1124	0.7494	0.3321	0.1119
O10	0.2503	0.6652	0.6124	0.2506	0.6679	0.6119
O11	0.0709	0.2109	0.0220	0.0683	0.2179	0.0224
O12	0.9291	0.7891	0.5220	0.9317	0.7821	0.5224
O13	0.5709	0.7891	0.0220	0.5683	0.7821	0.0224
O14	0.4291	0.2109	0.5220	0.4317	0.2179	0.5224
C1	0.0464	0.1067	0.2490	0.0500	0.1087	0.2490
C2	0.9536	0.8933	0.7490	0.9500	0.8913	0.7490
C3	0.5464	0.8933	0.2490	0.5500	0.8913	0.2490
C4	0.4536	0.1067	0.7490	0.4500	0.1087	0.7490
C5	0.1078	0.2530	0.3615	0.1128	0.2533	0.3616
C6	0.8922	0.7470	0.8615	0.8872	0.7467	0.8616
C7	0.6078	0.7470	0.3615	0.6128	0.7467	0.3616
C8	0.3922	0.2530	0.8615	0.3872	0.2533	0.8616
C9	0.1959	0.4836	0.3145	0.2000	0.4844	0.3134
C10	0.8041	0.5164	0.8145	0.8000	0.5156	0.8134
C11	0.6959	0.5164	0.3145	0.7000	0.5156	0.3134
C12	0.3041	0.4836	0.8145	0.3000	0.4844	0.8134
C13	0.1861	0.4809	0.1793	0.1867	0.4820	0.1788
C14	0.8139	0.5191	0.6793	0.8133	0.5180	0.6788

C15	0.6861	0.5191	0.1793	0.6867	0.5180	0.1788
C16	0.3139	0.4809	0.6793	0.3133	0.4820	0.6788
C17	0.0990	0.2601	0.1393	0.0995	0.2644	0.1398
C18	0.9010	0.7399	0.6393	0.9005	0.7356	0.6398
C19	0.5990	0.7399	0.1393	0.5995	0.7356	0.1398
C20	0.4010	0.2601	0.6393	0.4005	0.2644	0.6398
H1	0.0053	0.0422	0.0067	0.0044	0.0546	0.0087
H2	0.5053	-0.0422	0.0067	0.5044	-0.0546	0.0087
H3	0.7399	0.3617	0.0149	0.7371	0.3568	0.0174
H4	0.2399	0.6383	0.0149	0.2371	0.6432	0.0174
H5	0.2601	0.6383	0.5149	0.2629	0.6432	0.5174
H6	0.7601	0.3617	0.5149	0.7629	0.3568	0.5174
O15	0.9690	0.9041	0.2488	0.9741	0.9064	0.2489
O16	0.0310	0.0959	0.7488	0.0259	0.0936	0.7489
O17	0.4690	0.0959	0.2488	0.4741	0.0936	0.2489
O18	0.5310	0.9041	0.7488	0.5259	0.9064	0.7489
O19	0.0893	0.1979	0.4737	0.0955	0.1970	0.4728
O20	0.5893	0.8021	0.4737	0.5955	0.8030	0.4728
H7	-0.0053	-0.0422	0.5067	-0.0044	-0.0546	0.5087
H8	0.4947	0.0422	0.5067	0.4956	0.0546	0.5087

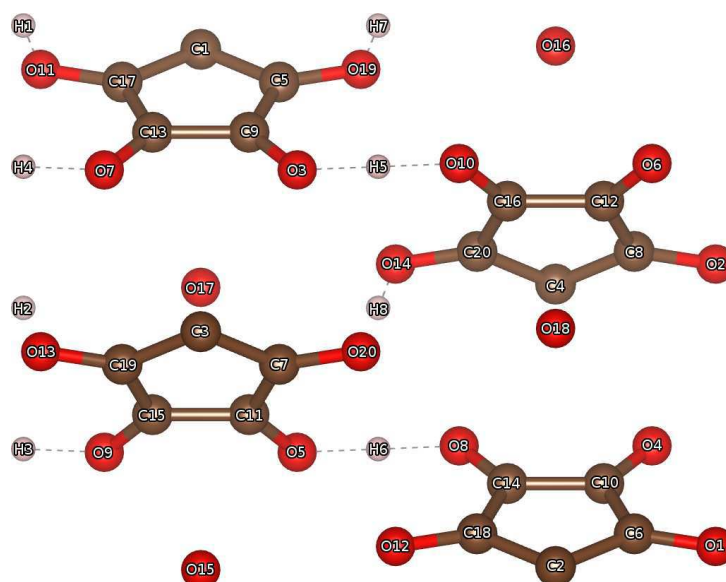


Figure A.1: The crystal structure of croconic acid in its hypothetical paraelectric phase, with atoms labelled using our scheme. C-atoms are brown, O-atoms are red, H-atoms are white.

Appendix B

Phonon modes at Γ of *Pbcm*-CRCA

m	Frequency (Ha)	Irreducible representation [169]	Space group after perturbation of <i>Pbcm</i> -optimized CRCA along mode
0	-4.3454×10^{-3}	Γ_2^-	<i>Pca2</i> ₁
1	-3.6588×10^{-3}	Γ_4^+	<i>P2</i> ₁ / <i>c</i>
2	-3.5984×10^{-3}	Γ_1^-	<i>P2</i> ₁ <i>2</i> ₁ <i>2</i>
3	-3.4783×10^{-3}	Γ_4^-	<i>Pmc2</i> ₁
4	-2.7871×10^{-3}	Γ_2^-	<i>Pca2</i> ₁
5	-3.4363×10^{-7}	Γ_1^+	<i>Pbcm</i>
6	-1.8561×10^{-7}	Γ_1^+	<i>Pbcm</i>
7	8.4146×10^{-8}	Γ_1^+	<i>Pbcm</i>
8	1.7301×10^{-4}	Γ_2^-	<i>Pca2</i> ₁
9	2.0166×10^{-4}	Γ_2^+	<i>P2</i> ₁ / <i>m</i>
10	2.3033×10^{-4}	Γ_1^-	<i>P2</i> ₁ <i>2</i> ₁ <i>2</i>
11	2.4586×10^{-4}	Γ_4^-	<i>Pmc2</i> ₁
12	2.5588×10^{-4}	Γ_1^+	<i>Pbcm</i>
13	2.8593×10^{-4}	Γ_3^-	<i>Pma2</i>
14	3.2781×10^{-4}	Γ_2^+	<i>P2</i> ₁ / <i>m</i>
15	3.6083×10^{-4}	Γ_4^-	<i>Pmc2</i> ₁
16	4.0807×10^{-4}	Γ_1^-	<i>P2</i> ₁ <i>2</i> ₁ <i>2</i>
17	4.0960×10^{-4}	Γ_2^-	<i>Pca2</i> ₁
18	4.2561×10^{-4}	Γ_1^+	<i>Pbcm</i>
19	4.3558×10^{-4}	Γ_3^-	<i>Pma2</i>
20	4.5825×10^{-4}	Γ_4^+	<i>P2</i> ₁ / <i>c</i>
21	5.1199×10^{-4}	Γ_4^-	<i>Pmc2</i> ₁
22	5.1834×10^{-4}	Γ_3^-	<i>Pma2</i>
23	5.3866×10^{-4}	Γ_3^+	<i>P2</i> / <i>c</i>
24	5.6103×10^{-4}	Γ_2^+	<i>P2</i> ₁ / <i>m</i>
25	5.7454×10^{-4}	Γ_4^+	<i>P2</i> ₁ / <i>c</i>
26	6.5081×10^{-4}	Γ_4^+	<i>P2</i> ₁ / <i>c</i>

27	6.6337×10^{-4}	Γ_1^+	<i>Pbcm</i>
28	6.8637×10^{-4}	Γ_3^+	<i>P2/c</i>
29	7.7531×10^{-4}	Γ_1^-	<i>P2₁2₁2</i>
30	7.8574×10^{-4}	Γ_1^+	<i>Pbcm</i>
31	7.8584×10^{-4}	Γ_2^-	<i>Pca2₁</i>
32	8.2151×10^{-4}	Γ_3^+	<i>P2/c</i>
33	8.2296×10^{-4}	Γ_2^+	<i>P2₁/m</i>
34	9.8509×10^{-4}	Γ_4^+	<i>P2₁/c</i>
35	1.0506×10^{-3}	Γ_4^-	<i>Pmc2₁</i>
36	1.0596×10^{-3}	Γ_3^-	<i>Pma2</i>
37	1.0674×10^{-3}	Γ_2^+	<i>P2₁/m</i>
38	1.0836×10^{-3}	Γ_2^+	<i>P2₁/m</i>
39	1.0952×10^{-3}	Γ_1^+	<i>Pbcm</i>
40	1.2060×10^{-3}	Γ_1^-	<i>P2₁2₁2</i>
41	1.2867×10^{-3}	Γ_2^-	<i>Pca2₁</i>
42	1.3876×10^{-3}	Γ_1^-	<i>P2₁2₁2</i>
43	1.4062×10^{-3}	Γ_3^-	<i>Pma2</i>
44	1.4445×10^{-3}	Γ_4^-	<i>Pmc2₁</i>
45	1.4545×10^{-3}	Γ_3^+	<i>P2/c</i>
46	1.6085×10^{-3}	Γ_4^+	<i>P2₁/c</i>
47	1.6541×10^{-3}	Γ_4^-	<i>Pmc2₁</i>
48	1.7837×10^{-3}	Γ_2^-	<i>Pca2₁</i>
49	1.9080×10^{-3}	Γ_1^-	<i>P2₁2₁2</i>
50	1.9120×10^{-3}	Γ_3^+	<i>P2/c</i>
51	2.2641×10^{-3}	Γ_4^+	<i>P2₁/c</i>
52	2.2847×10^{-3}	Γ_2^+	<i>P2₁/m</i>
53	2.3320×10^{-3}	Γ_2^-	<i>Pca2₁</i>
54	2.3379×10^{-3}	Γ_1^-	<i>P2₁2₁2</i>
55	2.3473×10^{-3}	Γ_3^-	<i>Pma2</i>
56	2.3479×10^{-3}	Γ_4^-	<i>Pmc2₁</i>
57	2.3561×10^{-3}	Γ_1^+	<i>Pbcm</i>
58	2.3575×10^{-3}	Γ_3^+	<i>P2/c</i>
59	2.3630×10^{-3}	Γ_4^+	<i>P2₁/c</i>
60	2.3713×10^{-3}	Γ_3^-	<i>Pma2</i>
61	2.3875×10^{-3}	Γ_2^+	<i>P2₁/m</i>
62	2.3908×10^{-3}	Γ_1^+	<i>Pbcm</i>
63	2.4119×10^{-3}	Γ_3^+	<i>P2/c</i>
64	2.4259×10^{-3}	Γ_1^+	<i>Pbcm</i>
65	2.4388×10^{-3}	Γ_3^-	<i>Pma2</i>
66	2.4653×10^{-3}	Γ_4^-	<i>Pmc2₁</i>
67	2.5033×10^{-3}	Γ_2^-	<i>Pca2₁</i>
68	2.6032×10^{-3}	Γ_2^+	<i>P2₁/m</i>

69	2.7947×10^{-3}	Γ_1^+	<i>Pbcm</i>
70	2.8109×10^{-3}	Γ_4^-	<i>Pmc2₁</i>
71	2.8418×10^{-3}	Γ_2^+	<i>P2₁/m</i>
72	2.8956×10^{-3}	Γ_4^+	<i>P2₁/c</i>
73	2.9321×10^{-3}	Γ_1^-	<i>P2₁2₁2</i>
74	3.1087×10^{-3}	Γ_3^-	<i>Pma2</i>
75	3.1289×10^{-3}	Γ_3^+	<i>P2/c</i>
76	3.1636×10^{-3}	Γ_2^+	<i>P2₁/m</i>
77	3.3123×10^{-3}	Γ_1^+	<i>Pbcm</i>
78	3.4880×10^{-3}	Γ_2^-	<i>Pca2₁</i>
79	3.4884×10^{-3}	Γ_3^+	<i>P2/c</i>
80	3.4884×10^{-3}	Γ_4^+	<i>P2₁/c</i>
81	3.4893×10^{-3}	Γ_1^-	<i>P2₁2₁2</i>
82	3.5821×10^{-3}	Γ_3^-	<i>Pma2</i>
83	3.5822×10^{-3}	Γ_4^-	<i>Pmc2₁</i>
84	3.5843×10^{-3}	Γ_2^+	<i>P2₁/m</i>
85	3.5860×10^{-3}	Γ_1^+	<i>Pbcm</i>
86	3.7867×10^{-3}	Γ_3^-	<i>Pma2</i>
87	3.9044×10^{-3}	Γ_1^-	<i>P2₁2₁2</i>
88	3.9231×10^{-3}	Γ_2^-	<i>Pca2₁</i>
89	4.0053×10^{-3}	Γ_3^+	<i>P2/c</i>
90	4.0307×10^{-3}	Γ_4^+	<i>P2₁/c</i>
91	4.9657×10^{-3}	Γ_1^-	<i>P2₁2₁2</i>
92	4.9715×10^{-3}	Γ_4^-	<i>Pmc2₁</i>
93	4.9746×10^{-3}	Γ_2^-	<i>Pca2₁</i>
94	5.0196×10^{-3}	Γ_3^+	<i>P2/c</i>
95	5.0207×10^{-3}	Γ_4^+	<i>P2₁/c</i>
96	5.0575×10^{-3}	Γ_3^-	<i>Pma2</i>
97	5.1033×10^{-3}	Γ_2^+	<i>P2₁/m</i>
98	5.1380×10^{-3}	Γ_1^+	<i>Pbcm</i>
99	5.4494×10^{-3}	Γ_2^-	<i>Pca2₁</i>
100	5.4783×10^{-3}	Γ_1^-	<i>P2₁2₁2</i>
101	5.5300×10^{-3}	Γ_4^+	<i>P2₁/c</i>
102	5.5568×10^{-3}	Γ_3^+	<i>P2/c</i>
103	5.6742×10^{-3}	Γ_4^-	<i>Pmc2₁</i>
104	5.7223×10^{-3}	Γ_4^-	<i>Pmc2₁</i>
105	5.7443×10^{-3}	Γ_3^-	<i>Pma2</i>
106	5.7526×10^{-3}	Γ_2^-	<i>Pca2₁</i>
107	5.7726×10^{-3}	Γ_1^-	<i>P2₁2₁2</i>
108	5.7728×10^{-3}	Γ_3^-	<i>Pma2</i>
109	5.7758×10^{-3}	Γ_2^+	<i>P2₁/m</i>
110	5.7969×10^{-3}	Γ_1^+	<i>Pbcm</i>

111	5.8903×10^{-3}	Γ_4^-	<i>Pmc2₁</i>
112	6.1579×10^{-3}	Γ_2^-	<i>Pca2₁</i>
113	6.1866×10^{-3}	Γ_4^+	<i>P2₁/c</i>
114	6.2547×10^{-3}	Γ_2^+	<i>P2₁/m</i>
115	6.3317×10^{-3}	Γ_4^-	<i>Pmc2₁</i>
116	6.5767×10^{-3}	Γ_1^+	<i>Pbcm</i>
117	6.6082×10^{-3}	Γ_3^+	<i>P2/c</i>
118	6.6132×10^{-3}	Γ_1^-	<i>P2₁2₁2</i>
119	6.6145×10^{-3}	Γ_3^-	<i>Pma2</i>
120	6.8368×10^{-3}	Γ_2^-	<i>Pca2₁</i>
121	6.8412×10^{-3}	Γ_1^-	<i>P2₁2₁2</i>
122	6.8952×10^{-3}	Γ_4^-	<i>Pmc2₁</i>
123	6.9120×10^{-3}	Γ_3^-	<i>Pma2</i>
124	7.0561×10^{-3}	Γ_4^+	<i>P2₁/c</i>
125	7.0640×10^{-3}	Γ_1^+	<i>Pbcm</i>
126	7.1669×10^{-3}	Γ_1^-	<i>P2₁2₁2</i>
127	7.1778×10^{-3}	Γ_2^-	<i>Pca2₁</i>
128	7.1900×10^{-3}	Γ_3^-	<i>Pma2</i>
129	7.2085×10^{-3}	Γ_3^+	<i>P2/c</i>
130	7.2571×10^{-3}	Γ_4^-	<i>Pmc2₁</i>
131	7.2774×10^{-3}	Γ_2^+	<i>P2₁/m</i>
132	7.2899×10^{-3}	Γ_3^+	<i>P2/c</i>
133	7.3382×10^{-3}	Γ_4^+	<i>P2₁/c</i>
134	7.3573×10^{-3}	Γ_1^-	<i>P2₁2₁2</i>
135	7.3800×10^{-3}	Γ_2^-	<i>Pca2₁</i>
136	7.5130×10^{-3}	Γ_2^+	<i>P2₁/m</i>
137	7.5372×10^{-3}	Γ_1^+	<i>Pbcm</i>
138	7.5939×10^{-3}	Γ_4^-	<i>Pmc2₁</i>
139	7.6243×10^{-3}	Γ_3^-	<i>Pma2</i>
140	7.8335×10^{-3}	Γ_4^-	<i>Pmc2₁</i>
141	7.8418×10^{-3}	Γ_2^+	<i>P2₁/m</i>
142	7.8504×10^{-3}	Γ_1^+	<i>Pbcm</i>
143	7.8767×10^{-3}	Γ_3^-	<i>Pma2</i>

Table B.1: The frequencies and space group symmetry properties of the normal modes of *Pbcm*-optimized CRCA.

Appendix C

Born effective charge tensor of *Pbcm*-CRCA

Column ij of row a corresponds to

$$Z_{ij}^{(a)} = \Omega \frac{\partial P^i}{\partial X_{aj}},$$

where P is the polarisation in the i direction of a unit cell with volume Ω due to the displacement of atom a in the j direction. Atom labels are explained by Figure A.1.

atom	xx	xy	xz	yx	yy	yz	zx	zy	zz
O1	-0.991	-0.398	-0.795	-0.680	-0.802	-0.767	-1.642	-1.144	-3.079
O2	-0.991	0.398	0.795	0.680	-0.802	-0.767	1.642	-1.144	-3.079
O3	-1.119	-0.537	-0.767	-0.741	-0.935	-1.280	-1.088	-0.907	-2.873
O4	-1.119	-0.537	0.767	-0.741	-0.935	1.280	1.088	0.907	-2.873
O5	-1.119	0.537	0.767	0.741	-0.935	-1.280	1.088	-0.907	-2.873
O6	-1.119	0.537	-0.767	0.741	-0.935	1.280	-1.088	0.907	-2.873
O7	-1.119	-0.537	0.767	-0.741	-0.935	1.280	1.088	0.907	-2.873
O8	-1.119	-0.537	-0.767	-0.741	-0.935	-1.280	-1.088	-0.907	-2.873
O9	-1.119	0.537	-0.767	0.741	-0.935	1.280	-1.088	0.907	-2.873
O10	-1.119	0.537	0.767	0.741	-0.935	-1.280	1.088	-0.907	-2.873
O11	-0.991	-0.398	-0.795	-0.680	-0.802	-0.767	-1.642	-1.144	-3.079
O12	-0.991	-0.398	0.795	-0.680	-0.802	0.767	1.642	1.144	-3.079
O13	-0.991	0.398	0.795	0.680	-0.802	-0.767	1.642	-1.144	-3.079
O14	-0.991	0.398	-0.795	0.680	-0.802	0.767	-1.642	1.144	-3.079
C1	1.625	0.855	0.000	1.258	1.187	0.000	0.000	0.000	-0.556
C2	1.625	0.855	0.000	1.258	1.187	0.000	0.000	0.000	-0.556
C3	1.625	-0.855	0.000	-1.258	1.187	0.000	0.000	0.000	-0.556
C4	1.625	-0.855	0.000	-1.258	1.187	0.000	0.000	0.000	-0.556
C5	0.005	-0.266	-0.920	-0.250	0.152	-0.895	-1.189	-0.851	3.323
C6	0.005	-0.266	0.920	-0.250	0.152	0.895	1.189	0.851	3.323
C7	0.005	0.266	0.920	0.250	0.152	-0.895	1.189	-0.851	3.323
C8	0.005	0.266	-0.920	0.250	0.152	0.895	-1.189	0.851	3.323

C9	1.046	0.537	1.383	0.814	0.830	1.339	2.182	1.557	0.577
C10	1.046	0.537	-1.383	0.814	0.830	-1.339	-2.182	-1.557	0.577
C11	1.046	-0.537	-1.383	-0.814	0.830	1.339	-2.182	1.557	0.577
C12	1.046	-0.537	1.383	-0.814	0.830	-1.339	2.182	-1.557	0.577
C13	1.046	0.537	-1.383	0.814	0.830	-1.339	-2.182	-1.557	0.577
C14	1.046	0.537	1.383	0.814	0.830	1.339	2.182	1.557	0.577
C15	1.046	-0.537	1.383	-0.814	0.830	-1.339	2.182	-1.557	0.577
C16	1.046	-0.537	-1.383	-0.814	0.830	1.339	-2.182	1.557	0.577
C17	0.005	-0.266	0.920	-0.250	0.152	0.895	1.189	0.851	3.323
C18	0.005	-0.266	-0.920	-0.250	0.152	-0.895	-1.189	-0.851	3.323
C19	0.005	0.266	-0.920	0.250	0.152	0.895	-1.189	0.851	3.323
C20	0.005	0.266	0.920	0.250	0.152	-0.895	1.189	-0.851	3.323
H1	1.582	0.771	0.623	1.134	1.086	0.560	2.413	1.694	1.338
H2	1.582	-0.771	-0.623	-1.134	1.086	0.560	-2.413	1.694	1.338
H3	0.282	0.000	0.000	0.000	0.361	-1.267	0.000	-0.179	3.812
H4	0.282	0.000	0.000	0.000	0.361	-1.267	0.000	-0.179	3.812
H5	0.282	0.000	0.000	0.000	0.361	1.267	0.000	0.179	3.812
H6	0.282	0.000	0.000	0.000	0.361	1.267	0.000	0.179	3.812
O15	-1.371	-0.550	0.000	-0.917	-1.124	0.000	0.000	0.000	-0.490
O16	-1.371	-0.550	0.000	-0.917	-1.124	0.000	0.000	0.000	-0.490
O17	-1.371	0.550	0.000	0.917	-1.124	0.000	0.000	0.000	-0.490
O18	-1.371	0.550	0.000	0.917	-1.124	0.000	0.000	0.000	-0.490
O19	-0.991	-0.398	0.795	-0.680	-0.802	0.767	1.642	1.144	-3.079
O20	-0.991	0.398	-0.795	0.680	-0.802	0.767	-1.642	1.144	-3.079
H7	1.582	0.771	-0.623	1.134	1.086	-0.560	-2.413	-1.694	1.338
H8	1.582	-0.771	0.623	-1.134	1.086	-0.560	2.413	-1.694	1.338

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