Quantum proton transfer and interconversion in the benzoic acid crystal: vibrational spectra, mechanism and theory

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Abstract

The infrared and Raman spectra of powdered crystals at various temperatures from liquid helium to 300 K of fully hydrogenated benzoic acid (BA-h$_6$), ring deuterated (BA-d$_5$h) and OD (BA-h$_5$d) analogues are presented. In the frequency range corresponding to internal modes there is no evidence for thermal equilibrium due to tautomerisation. Noticeable temperature effects are observed in Raman for a band at ~80 cm$^{-1}$. As the temperature increases, the band intensity decreases according to an Arrhenius law with activation energy of (54 ± 6) cm$^{-1}$. It is concluded that interconversion of protons occurs upon specific excitation of the lattice mode observed at $\nu_{\text{R}} = 55$ cm$^{-1}$. In the ground state all dimers have the same configuration throughout the crystal, whilst the excited phonon state is a coherent superposition of the two tautomers. An isotopic mixture containing 5% of OH and 95% of OD residues demonstrates the absence of dynamical correlation between protons. The OH (OD) stretching band profiles in the infrared are decomposed into two broad components whose shapes are rationalised with the strong coupling scheme for the $\nu$ OH and $\nu$ O $\cdots$ O coordinates. The splitting is attributed to proton tunnelling in the $n = 2$ and 3 states of a quasi-symmetric double minimum potential. This assignment is confirmed with the $0 \rightarrow 1$ transition (the splitting of the ground state) observed with the inelastic neutron scattering technique at $\nu_{\text{QNS}} = 172$ cm$^{-1}$ for BA-d$_5$h. The potential governing the quantum transfer dynamics of a single proton is thus totally determined from experimental data. The potential barrier is ~5000 cm$^{-1}$ and semiclassical jumping over the top is negligible. We propose a theory based on uncorrelated transfer of protons via thermally activated tunnelling to account for the interconversion dynamics. The analytical function for the interconversion rate versus temperature accounts for NMR T$_1$ and quasi-elastic neutron scattering (QENS) measurements. Both the potential function for protons and the coherent superposition of tautomers survive at room temperature. © 2002 Elsevier Science B.V. All rights reserved.

1. Introduction

Proton transfer along hydrogen bonds is of fundamental importance to many physical, chemical and biochemical processes [1–10]. There is a general agreement that proton transfer dynamics
have properties characteristic of a light particle in a heavy framework that can be represented with an effective potential along a local reaction coordinate coupled to the motions of heavy atoms [11–40]. In simple linear systems such as XH⋯Y the potential energy for the hydrogen atom along the hydrogen bond may have two inequivalent minima corresponding to the schematic structures XH⋯Y and X⋯H−Y, respectively. The top of the potential barrier corresponds to the transition state. Only in symmetric systems AH⋯A can the two wells be equivalent and proton transfer mediated by tunnelling may take place, even at very low temperature. Indeed, there is a manifold of intermediate cases between perfectly symmetric and highly asymmetric systems. In all cases, the key parameters for proton transfer dynamics are the distance between the two wells (r), the barrier height (Ea), the potential asymmetry (ΔU) and the tunnelling matrix element (υ0). In addition, proton transfer occurs in a complex multidimensional environment and strong coupling with the surrounding degrees of freedom is also regarded as a major factor determining the transfer rate. According to the great complexity of the microscopic mechanism for proton transfer an accurate determination of these parameters from experimental and theoretical studies is not easy.

From the theoretical viewpoint, there is no unique way to partition the binding energy resulting from simultaneous changes of the electronic and vibrational wave functions upon hydrogen bond formation (see for example [8]). Modelling of proton transfer dynamics with quantum chemistry is further hampered by the complexity of treating thermal and quantum fluctuations in complex systems with high accuracy [9,41–43]. On the other hand, the characterisation of hydrogen bonds and proton transfer with experimental means is often ambiguous as each particular approach highlights a different view. Structural studies emphasise bond lengths and angles [44,45]. NMR and quasi-elastic neutron scattering (QENS) are mainly concerned with dynamics at a rather long time scale (typically longer than ~10−10 s) [11–31,46] whilst quantum effects are observed with vibrational spectroscopy [47,48]. Consequently, quite different views of the proton transfer mechanism have emerged from previous works.

A typical example of conflicting views arising from experiments carried out with different techniques is the tautomerisation mechanism in centrosymmetric cyclic dimers of carboxylic acids and related systems such as hydrogen carbonate salts (MHCO3 with M = K, Rb or Cs):

For an isolated dimer I and II are equivalent and a symmetric double well potential is anticipated for simultaneous transfer of the two protons. In the crystalline state intermolecular interaction may

![Fig. 1. Schematic view of the effective potential for concerted proton transfer in benzoic acid after [18]. The dimensionless reaction coordinate ξ is arbitrarily normalised.](image-url)
destroy the potential symmetry (Fig. 1). Two prototypical systems have been thoroughly investigated: potassium hydrogen carbonate (KHCO₃) [15,49–58] and benzoic acid (C₆H₅COOH) [11–14,16–32,59–82]. Quite different pictures have emerged for interconversion dynamics in these apparently similar systems and it is not yet clear whether the difference is real or due to imperfection of the theoretical framework, or to the lack of experimental information.

1.1. KHCO₃

In the KHCO₃ crystal the carbonate entities form centrosymmetric dimers linked by moderately strong hydrogen bonds with distance O···O = 2.587 or 2.607 Å for KDCO₃. From diffraction measurements at 298 K protons are distributed among two sites located at \( \sim \pm 0.3 \) Å off-centre of the hydrogen bond, with population ratio of \( \sim 1:4 \) [57,58]. The proton dynamics have been thoroughly investigated with vibrational spectroscopy techniques [49–53]. The stretching vibration gives broad bands in the infrared and Raman with several submaxima between 1800 and 3500 cm\(^{-1}\) compatible with a quasi-symmetric double minimum potential and a potential barrier of \( \sim 5000 \) cm\(^{-1}\) [52]. The \( v_{01} \) transition corresponding to the splitting of the ground state was observed as a rather sharp band (half width at half maximum \( \sim 10 \) cm\(^{-1}\)) at 216 cm\(^{-1}\) with the INS technique [53]. This is representative of the potential asymmetry \( \Delta U \). Measurements performed on oriented single crystals confirmed that this band is polarised along the OH stretching direction [54]. Moreover, INS demonstrates that the effective mass for all proton modes is equal to 1 amu [55]. The proton displacements are almost totally independent of the crystal lattice dynamics. To our knowledge, this is a unique case where the double minimum potential for the transfer of a single proton along the hydrogen bond was entirely determined from experimental data. Similar tunnelling transitions have been observed in various hydrogen bonds [83–85].

The effective potential revealed by vibrational spectroscopy is a snapshot of the proton dynamics on the time scale of the OH stretching mode (\( \sim 10^{-14} \) s). The tunnelling matrix element (\( v_{0k} \)) is proportional to the overlap integral of the proton wave functions localised in each well and characterises the mean-residence time in a well. It is largely independent of the potential asymmetry. The estimated value \( v_{0k} \sim 18 \) cm\(^{-1}\) for KHCO₃ is about 1 order of magnitude smaller than the potential asymmetry. As the delocalisation degree in the ground state depends on the ratio \( v_{0k}/v_{01} \), the wave functions are largely localised in each well. Nevertheless, the INS intensity of the \( v_{01} \) transition demonstrates that the delocalisation of the proton wave function over the two wells is observable.

There is thus a list of experimental evidences that proton dynamics are decoupled from the lattice and proton transfer occurs via coherent tunnelling. Thermally activated jumps over the barrier are negligible even at room temperature. Unfortunately, the thermodynamics of interconversion is not precisely known. Systematic neutron diffraction measurements at various temperatures are not available and we are not aware of any published QENS study. NMR measurements on KDCO₃ analysed within the phonon-assisted tunnelling framework (see below) [18] give an activation energy of \( \sim 480 \) cm\(^{-1}\) for the simultaneous classical jumps of two protons [15]. This is almost one order of magnitude smaller than the potential barrier of 3500 cm\(^{-1}\) for the transfer of a single deuteron derived from vibrational spectroscopy [52]. It transpires that different techniques give different activation energies because modelling is not appropriate. To our best knowledge, there is no report of quantum mechanical calculation of proton transfer in KHCO₃ performed with advanced techniques of quantum chemistry.

1.2. Benzoic acid

In the benzoic acid crystal dimerisation takes place through hydrogen bonds across a centre of symmetry. The O···O distance of 2.608 Å at 20 K is slightly longer than in KHCO₃. The interconversion of hydrogen atoms has been thoroughly investigated with NMR [13,14,16–30], QENS [14,21,31,32], vibrational spectroscopy [59–70], optical spectroscopy [71–78] and diffraction techniques [79–82].
Temperature effects observed for the C=O stretching and OH bending bands in the infrared spectra of oriented crystals [59,61,62,66,70] were regarded as first evidences for the coexistence of tautomers I and II (Fig. 2) at thermal equilibrium. One component (at 1688 cm⁻¹) of the ν C=O band whose intensity decreases at low temperature and almost disappears at ~7 K was attributed to the less stable isomer II in Fig. 2. A much weaker component at 1710 cm⁻¹ that survives at low temperature was supposed to correspond to the most stable isomer I. The estimated energy difference was of ~0.4 kJ mol⁻¹ or ~32 cm⁻¹. For the OH bending modes, relative intensities are reversed. Strong bands at 1298, 1328 cm⁻¹ (δ OH) and 948 cm⁻¹ (γ OH) were attributed to the most stable configuration and much weaker bands at 1334 cm⁻¹ (δ OH) and 959 cm⁻¹ (γ OH) to the less stable isomer. Surprisingly, the OH stretching band profiles were ignored as if they were unaffected by tautomerisation. This is in marked contrast to the rather large frequency shifts reported for the CO stretching and OH bending modes.

Single-crystal neutron diffraction measurements provide unquestionable evidences that the bridging protons are distributed over two sites separated by 0.70 Å at 20 K or 0.78 Å at 175 K [81,82]. Simultaneously, the O···O distance increases from 2.608 to 2.629 Å and the relative population of the most stable form decreases from 0.87 (20 K) to 0.62 (175 K). The estimated energy difference between the two isomers is of 0.12 ± 0.01 kcal mol⁻¹ or 40 ± 3 cm⁻¹.

The tautomerisation rate derived from NMR T₁ relaxation [12,63–65] and QENS [14,21,31,32] measurements ranges from ~10⁸ to 10¹¹ s⁻¹ as the temperature increases from liquid helium to room temperature. This is widely recognised as a prototypical case of transition from the quantum regime at low temperature (tunnelling) to the semiclassical regime compatible with an Arrhenius law at room temperature. These dynamics are represented with the Hamiltonian [12–15,17–22, 27,32–35]:

\[
H = H_\xi + H_{Q\xi} + H_Q.
\] (1)

The zero-order term \( H_\xi \) describes a pseudo-particle in a double well potential along the collective dimensionless coordinate \( \xi \) representing the simultaneous transfer of two protons (Fig. 1). The temperature dependence of the transfer rate is represented with coupling to a heat bath \( H_Q \) via \( H_{Q\xi} \). In the phonon-assisted tunnelling model the coupling is normally limited to the bilinear term \( a_\xi Q \) and the stochastic bath is represented with a set of harmonic oscillators [18].

In the usual representation of the tautomerism process not only the protons migrate simultaneously, as a rigid entity preserving the centre of symmetry, but also the skeleton is rearranged, as the electrons follow adiabatically the protons. Consequently, \( \xi \) is complex. Potential surfaces calculated with quantum chemistry methods [9,12,15,27,30,32,33,41,43] and sophisticated analytical tools have been proposed to treat isolated non-rigid molecules [34–40,42]. However, calcula-

![Fig. 2. Schematic view of the benzoic acid structure showing the alignment of configurations I and II in the crystallographic unit-cell after [63].](image-url)
tions performed on isolated dimer entities are not appropriate for \( H_D \) and \( H_{\infty} \). Moreover, it is difficult to model complex reaction paths in the crystalline state as long as combining advanced techniques of quantum chemistry with sophisticated analytical tools is not yet at the stage of being applied at the level of accuracy corresponding to vibrational spectroscopy.

For practical purpose and data analysis the coordinate \( \xi \) is usually normalised in such a way that minima occur at arbitrarily chosen values \( (\xi = \pm 1, \text{Fig. 1}) \) and contributions from all atoms are included in the effective mass as a “mobility factor”. Estimated values of the mobility factor for benzoic acid between \( \sim 14 \) and \( 80 \text{ cm}^{-1} \) [17,21,27] correspond to effective masses in the range from \( \sim 1 \) to 5 amu. With these approximations the detailed contribution of atom displacements to \( \xi \) is partially lost and it is not possible to distinguish reaction paths with the same effective mass. However, the Hamiltonian is simpler and the tautomerisation rate can be estimated analytically [18]:

\[
\tau^{-1} = \frac{3\pi}{2\hbar} a^2 \Delta U \left( \frac{v_{\infty}}{v_D} \right)^2 \coth \left( \Delta U / 2kT \right) + \tau_0^{-1} \left\{ \exp \left( -E_a / kT \right) + \exp \left[ - \left( E_a - \Delta U \right) / kT \right] \right\},
\]

(2)

At low temperature the quantum mechanism with negligible activation energy, referred to as “incoherent tunnelling”, determines the tautomerisation rate. The tunnelling matrix element \( v_{\infty} \), the Debye frequency \( v_D \) and the coupling strength \( a \) do not correspond to any observable for NMR and QENS techniques. They have to be adjusted or, eventually, they can be transferred from other experimental or theoretical works [18]. The “coth” term accounts for one-phonon emission/absorption due to coupling with the thermal bath. The second term represents the Arrhenius form for thermally activated barrier crossing. Eq. (2) has proven to be useful to interpreting NMR and QENS data [11–15,17,19–33,86,87]. For benzoic acid the estimated energy difference between I and \( \Pi \) is \( \Delta U = (58 \pm 1) \text{ cm}^{-1} \) [31] and the activation energy ranges from 400 to 500 cm\(^{-1}\) (1.2–1.5 kcal/mol) [12,21,30,32]. However, this equation does not fit well intermediate temperature range from liquid Helium to room temperature and the best data analysis with an increased number of adjustable parameters suggests three different dynamical regimes [31]. Qualitative explanation based on further tunnelling in excited vibrational states [29] and multiphonon relaxation [88] has been proposed but this required an increasing number of unknown parameters. Quite recently, even the concept of smooth transition between quantum mechanical and classical dynamics has been revisited [89].

1.3. Outstanding problems

Vibrational spectroscopy gives clear evidences that single proton transfer is a coherent quantum process along the quasi-linear stretching coordinate. The proton is virtually uncoupled to phonons and its effective oscillator mass is 1 amu. However, it is not yet demonstrated that these quantum dynamics can account for the interconversion rate up to room temperature on the much longer time scales relevant to NMR and QENS.

The phonon-assisted tunnelling mechanism, eventually including additional terms that were ignored in the original theory, is successful to account for the tautomerisation rate at various temperatures. However, the resulting potential function is not appropriate for the quantum regime and largely inconsistent with vibrational spectroscopy. The conflicting views arise from imperfection in modelling due to the lack of relevant information. In order to bridge the gap between dynamical models it is necessary to collect information with all experimental techniques. The benzoic acid crystal is the best candidate for this purpose. It has been thoroughly investigated with almost all techniques of interest for proton transfer studies, except temperature effects with Raman. However, the previous interpretation of the infrared spectra in terms of thermal equilibrium between two isomers [61,62] is not satisfactory. For example, diffraction measurements or quantum chemistry calculation [70] reveal that the two isomers are identical and cannot be distinguished. Therefore, to attribute the C=O stretching modes at 1688 and 1710 cm\(^{-1}\) to different isomers with different absorption coefficients [61,62,66,70] is questionable. Furthermore, detailed analyses of
the spectral profiles of the broad $\nu$ OH bands between 2500 and 3000 cm$^{-1}$, analogous to those previously performed on KHCO$_3$ [52], should provide information on the potential function for single proton transfer. So far these bands were totally ignored [61]. Therefore, we have undertaken systematic studies of the infrared and Raman spectra of various isotopic derivatives of the benzoic acid crystal.

Experimental information is given in Section 2. The infrared and Raman spectra of powdered samples at various temperatures are presented in Section 3 for the three analogues of benzoic acid: C$_6$H$_5$COOH (BA-h$_6$); C$_6$D$_5$COOH (BA-d$_5$h) and C$_6$H$_5$COOD (BA-h$_5$d). The observed temperature effects are very much less marked than those previously reported for an oriented crystal [61]. In fact, we cannot distinguish the two isomers. However, unforeseen temperature effects observed in Raman for a lattice mode at $\approx$80 cm$^{-1}$ demonstrate that the interconversion of protons is determined by collective excitation of a lattice mode at $(54 \pm 6)$ cm$^{-1}$. This is tentatively related to specific molecular interactions (see Section 4).

In Section 5 the double minimum potential for single proton transfer dynamics in the quantum regime is determined from the $\nu$ OH profile in the infrared and from the splitting of the ground state observed with INS. The potential barrier is so high ($\approx$5000 cm$^{-1}$) that thermally activated jumps over this barrier are negligible, even at room temperature. Proton transfer in dimers occurs via coherent tunnelling and the quantum theory presented in Section 6 accounts for the interconversion rate with a temperature dependent superposition of states. It is shown that the existence of three distinct dynamical regimes for the proton transfer rate [31] is a consequence of the stepwise transfer mechanism of the two protons. The analytical function for the tautomerisation rate as a function of temperature is in accordance with the best fit to the experimental data.

2. Experimental

The fully hydrogenated (BA-h$_6$) and ring deuterated (BA-d$_5$h) benzoic acids were commercial products. They were sublimated. The BA-h$_5$d derivative was obtained after three exchanges with commercial methanol CH$_3$OD.

2.1. Crystal structure and symmetry

At room temperature, the benzoic acid crystal is monoclinic, P$2_1$/c ($C_{2h}$) with four molecules in the unit cell [79–82]. There are 177 vibrational modes that can be decomposed into 156 internal and 21 external vibrations. In the present work the benzene vibrations are largely ignored, in as much as they do not interfere with the bridging protons [60]. The external modes can be represented as 12 hydrogen bond vibrations (3$A_g$ + 3$B_u$ + 3$A_u$ + 3$B_g$), six Raman active lattice vibrations corresponding to vibrations of dimers around the three axes of inertia (3$A_g$ + 3$B_g$) and three infrared active translational vibrations of one dimer with respect to the other (2$A_u$ + $B_u$). In the $(a, b)$ plane, the $A_u$ or $B_u$ modes are extinguished for electrical field vectors parallel to the $a$ or $b$ crystal axes, respectively [69].

2.2. Spectra

Infrared spectra were recorded with a FTIR Perkin Elmer$^{\text{®}}$ 983 with a mean resolution of $\approx$2 cm$^{-1}$. Powdered samples in Nujol$^{\text{®}}$ or Fluorolube$^{\text{®}}$ mulls between KBr plates were loaded into a closed cycle refrigerator. It is difficult to estimate the effective temperature of the sample from that measured with a thermometer on the plates. Fortunately, the intensity at maximum of the very sharp band at 1787 cm$^{-1}$ (BA-h$_6$) is very sensitive to temperature (see below) and visual comparison with the spectra presented in [61] confirms that effective temperatures of the samples were similar in all experiments. Spectra are free of saturation effects.

The Raman spectra were obtained with a RTI-DILOR$^{\text{®}}$ triple monochromator equipped with an Ar$^+$ laser. Powdered samples were sealed in capillary glass tubes and then loaded into a liquid helium cryostat. The temperature was measured with a thermometer just above the sample.

The INS spectrum of BA-d$_5$h is the same as that presented in [90]. The original file (TRSL3033.ana)
was downloaded from the TFXA database at the ISIS pulsed neutron source (Rutherford Appleton Laboratory, Chilton, Didcot, Oxon, UK).

2.3. Calculations

Energy levels and wave functions were calculated with the variational method [91–94] utilising a basis sets of 40 harmonic wave functions with fundamental frequency $\hbar \omega_0$. For each potential function the parameter $\omega_0$ is optimised so as to obtain the lowest energy for the ground state. The transition moment of order $n$ for transition $i \rightarrow j$ is calculated according to $M_{ij}^n = \int \Psi_i^* x^n \Psi_j \, dx$.

3. Results

A full analysis of the vibrational spectra of benzoic acid and partially deuterated analogues is beyond the scope of this paper. The discussion is focussed on the frequency ranges most appropriate to observing the thermal equilibrium of the two isomers [61]. In addition, the OH/OD stretching band profiles in the infrared and the Raman spectra at low frequency are analysed.

3.1. CO stretching

For BA-h$_6$ the Raman active $\nu$ C=O (1616 and 1631 cm$^{-1}$ at 7 K) and the ring vibration at 1600 cm$^{-1}$ are very close to each other (Fig. 3(a)) and some mixing of these modes is likely. For the BA-d$_5$h analogue these modes are better separated (1618–1625 and 1570, respectively, Fig. 3(b)) and can be analysed with more confidence. The $\nu$ C=O bands are almost unchanged between 7 and 140 K, whilst the population ratio for the two isomers is supposed to vary from ~0 to ~0.65. The splitting is thus attributed to interdimer interaction (A$_g$–B$_g$). At room temperature the bands are broad and the frequency at the maximum is 1630 cm$^{-1}$. This is consistent with the increase of the O⋯O distance [81,82]. The ring mode at 1570 cm$^{-1}$ is sharp and almost temperature independent.

In the infrared the $\nu$ C=O and the ring modes are well separated (Figs. 3(c) and (d)). The spectra are almost temperature independent. There is no significant change of the total intensity and this is in marked contrast to Fig. 2 in [61]. We attribute the two $\nu$ C=O components partially resolved at 1685 and 1710 cm$^{-1}$ for BA-h$_6$ or 1680 and 1710 cm$^{-1}$ for BA-d$_5$h to the A$_g$–B$_g$ splitting due to interdimer interaction. Intradimer coupling terms give a rather large splitting of ~70 cm$^{-1}$ between the infrared and Raman active components.

Temperature effects previously observed for oriented crystals with the $(a, b)$ plane perpendicular to the beam [61] were tentatively attributed to the different orientations of the C=O bonds for the two isomers, as represented in Fig. 2. The C=O bond of II that is almost parallel to $a$ was supposed to have a much weaker intensity than the C=O bond of I. The spectrum at low temperature was thus attributed to II. At high temperature the spectrum of the mixture of I and II was supposed to be dominated by the most intense $\nu$ C=O band of I. However, this was based on the wrong assumption that the $\nu$ C=O bands of I and II are at different frequencies. In fact, the two isomers have the same electronic structure and crystal environment. Consequently, the $\nu$ C=O frequencies for isomers I and II are identical and cannot be distinguished. The observed splitting corresponds to dynamical correlation A$_u$–B$_u$ and temperature effects were probably due to thermal expansion of the crystal.

3.2. OH bending modes

Band assignments for the OH in-plane bending mode is complicated by strong interaction of the $\delta$ OH mode (intense in the infrared) with other modes (for example $\nu$ C=O, $\delta$ C–H,...) clearly visible in Raman (Fig. 4). Similarly, strong interaction between the $\gamma$ OH mode and vibrations involving CH or CD bonds are observed in the infrared between 900 and 1000 cm$^{-1}$ (Fig. 5). We did not observe any Raman band in this frequency range. For all spectra, there is no visible change with temperature that could be due to thermal equilibrium between the two isomers.

3.3. The OH and OD stretching modes

The $\nu$ OH and $\nu$ OD bands are very weak in Raman. They are largely hidden by the extremely
intense $\nu$ CH or $\nu$ CD bands at ~3000 and 2300 cm$^{-1}$, respectively, and cannot be distinguished from overtones and combinations in the same spectral range. These bands are not discussed any further.

In the infrared the $\nu$ OH and $\nu$ OD profiles are complex (Fig. 6). The $\nu$ OH mean frequency is little affected by ring deuteration and temperature effects below $\sim$150 K. At room temperature, the band intensity around 3000 cm$^{-1}$ increases and the mean frequency is shifted upwards by $\sim$100 cm$^{-1}$. This is a consequence of the expansion of the O ⋯ O distance at high temperature [81,82]. As for the other modes, the two isomers cannot be distinguished.

The doublets at 1787–1906 cm$^{-1}$ (BA-h$_6$) and 1788–1902 cm$^{-1}$ (BA-d$_5$h) show spectacular temperature effects (Figs. 6(a) and (b)). These bands are ill defined at room temperature. They become sharp and intense at low temperature without any
significant frequency shift. Frequencies are close to those anticipated for the $\gamma$ OH or $\gamma$ CH overtones but the corresponding intensities should be very weak and temperature effects are not those anticipated for Fermi resonance with the main $\nu$ OH band. These sharp doublets are attributed to “zero-phonon” transitions (see below) [95–98].

Several band-shaping mechanisms associated to hydrogen bond formation contribute to the spectral profiles [95–112]: mechanical and electrical anharmonicity, strong coupling with hydrogen bond modes, Fermi resonance, interaction of the broad $\nu$ OH profile with sharp overtones or combinations of skeleton modes (Evans transmission windows [113]), dynamical correlation (Davydov coupling), tunnel splitting, etc. It is not easy to unravel these contributions.

Davydov coupling can be eliminated safely because dynamical correlation between OH oscillators are cancelled in an isotopic mixture containing
The sample contains ~90% of fully deuterated dimers, less than 1% of totally hydrogenated dimers and ~9% of mixed dimers. The residual ν OH profile is thus largely due to mixed dimers free of H ⋯ H dynamical coupling. Apart from intensity, the ν
OH profile is very similar to that observed for the fully hydrogenated crystal. The main maxima of intensity at 2570 and 2840 cm\(^{-1}\) remain at the same frequency. Therefore, Davydov coupling between protons is negligible. This is in marked contrast to the large intradimer coupling of the \(\nu\) C=O modes.

The \(\nu\) OD profile is composed of two well-resolved components at 2050 and 2205 cm\(^{-1}\). The full widths at half maximum (FWHM) are 44 and 58 cm\(^{-1}\), respectively, and the intensity ratio \(I_{2050}/I_{2205}\) is of \(\sim 1.4 \pm 0.1\). This ratio is not compatible with a Fermi resonance between the overtone of the \(\delta\) OD mode at \(\sim 1000\) cm\(^{-1}\) and the \(\nu\) OD mode. (The intensity of the overtone should be weaker than or similar to that of the fundamental.) Temperature effects on intensities and frequencies are tiny.

As dynamical coupling is eliminated it is possible to correlate the \(\nu\) OH profile with the \(\nu\) OD bands. For BA-h\(_6\) at 16 K the maxima of intensity at 2570 and 2840 cm\(^{-1}\) can be regarded as the analogues of the \(\nu\) OD bands at 2050 and 2205 cm\(^{-1}\), respectively. Then, the \(\nu\) OH profile can be decomposed into two virtually identical broad components (Fig. 7(a)) with an intensity ratio \(I_{2560}/I_{2820} \sim 2.0 \pm 0.1\). The splitting is \(\sim 270\) cm\(^{-1}\) and the FWHM of each component is \(\sim 250\) cm\(^{-1}\). To each component we associate one of the sharp bands at 1786 and 1906 cm\(^{-1}\), respectively. The two profiles are very similar but the splitting is not rigorously a constant over the whole spectral range. It increases from \(\sim 120\) cm\(^{-1}\) below 2000 cm\(^{-1}\) to \(\sim 270\) cm\(^{-1}\) at \(\sim 3000\) cm\(^{-1}\). The frequency ratio \(\nu\) OH/\(\nu\) OD for the main components (2570/2050 \(\sim 1.25\) and 2840/2205 \(\sim 1.29\)) and the spectacular narrowing of the profiles upon deuteration confirm strong anharmonicity. Similar band decomposition is presented for BA-d\(_3\)h in Fig. 7(b).

The decomposition of the \(\nu\) OH profiles into two similar broad profiles cannot be explained with Fermi resonance. For example, Fermi resonance with overtones of the \(\delta\) OH containing modes between 1250 and 1350 cm\(^{-1}\) (Fig. 4) should occur in a limited spectral range, roughly between 2500 and 2700 cm\(^{-1}\). Such a local effect cannot account for the band splitting extending itself from 1700 to 3000 cm\(^{-1}\).

The profiles are similar to those previously reported for various hydrogen bonds with O\(\cdots\)O distances of \(\sim 2.6\) Å [52,53,97,98]. They arise from strong coupling with the O\(\cdots\)O modes due to the fast decrease of the \(\nu\) OH frequency with the length of the hydrogen bond [95,96,98,100,102,103,109–111]. Within the framework of adiabatic separation of the fast \(\nu\) OH and slow O\(\cdots\)O modes the upper adiabatic potential for the \(\nu\) O\(\cdots\)O mode \(V'_\nu(\Delta R)\) can be represented as a Morse-like potential whose minimum is shifted toward short O\(\cdots\)O distances with respect to the equilibrium position in the ground state (Fig. 8) [95,104,114]. Owing to the steep slope of the upper potential, the excited state is largely aperiodic and the dynamics can be treated within the short-time approximation. The spectral density \(I(\nu)\) at \(\nu = V'_\nu(\Delta R)\) is proportional to the probability density for the slow coordinate \(\Delta R\) and to the transition moment: \(I(\nu) = V'_\nu(\Delta R) \propto \Psi_0(\Delta R)M^2(\Delta R)\) [104]. The narrow peaks at low frequency (between 1750 and 2000 cm\(^{-1}\)) are “zero-phonon” transitions from the ground state to the lowest state of the upper potential. This state can have rather long lifetime at low temperature because near the minimum of the upper potential the strong coupling is cancelled \((d\nu/d\Delta R \sim 0)\). As opposed to \(\nu\) OH, the \(\nu\) OD frequency decreases much less rapidly with the length of the hydrogen bond [103]. The anharmonic coupling is weaker and the \(\nu\) OD bands are narrower.

In principle, the shapes of the upper potentials can be adjusted in order to obtain the best fit to the spectral profile [97,98]. However, the model does not account for the fine structure superimposed to the broad profiles. Additional coupling with other modes must be included. For BA-d\(_h\) frequency differences between submaxima of intensity at 2545, 2605, 2630, 2660 cm\(^{-1}\),... (Fig. 7(b)) are reminiscent of the phonon modes at 60, 85, 115, 185 cm\(^{-1}\),... observed in Raman (see Fig. 9, Tables 1–3). For the fully hydrogenated sample, the combination scheme is much less clear. Presumably, it is partially corrupted with \(\nu\) CH bands, overtones and combinations involving the CH bending coordinates, etc.

The observed fine structure suggests combinations arising from complex coupling of phonons to
Fig. 7. Tentative decomposition by hand of the OH stretching profiles of benzoic acid at 16 K (solid line) into two identical profiles (■ and ▲, respectively). The calculated profile (○) is the sum of the two profiles. (a) Fully hydrogenated sample, BA-h. The two profiles with an intensity ratio $I_{2560}/I_{2820} = 2.5 \pm 0.5$ are separated by 270 cm$^{-1}$; (b) ring-deuterated sample, BA-d$_5$. The two profiles with the same intensity ratio of 2.5 are separated by 260 cm$^{-1}$.
be attributed to proton tunnelling in a double minimum potential (see Section 5). Fermi resonance, combination and dynamical correlation are only marginal band-shaping mechanisms.

### 3.4. Lattice modes

At low temperature, at least nine bands are well-resolved in Raman below 220 cm\(^{-1}\) (Fig. 9, Tables 1–3). The COO torsion near 200 cm\(^{-1}\) is shifted by \(~\sim\~10\) cm\(^{-1}\) upon ring deuteration. Five hydrogen bond modes among the six anticipated are observed between 140 and 70 cm\(^{-1}\). The band at \(~100\) cm\(^{-1}\) is asymmetric and two unresolved components are likely. Three lattice modes peak below 60 cm\(^{-1}\). All bands shift toward low frequency and broaden as the temperature increases.

Tentative band decompositions are presented in Fig. 9 and Tables 1–3. At low temperature the bands are extremely narrow and the Gaussian profiles reflect the resolution function of the spectrometer. At higher temperature, the bandwidths are greater than the resolution function and Lorentzian profiles are appropriate. There is no visible anomaly in the temperature effect that could be attributed to a phase transition.

The bands observed at the lowest temperature at 89.0 cm\(^{-1}\) for BA-h\(_6\) or BA-h\(_3\)d (88.5 cm\(^{-1}\) for BA-d\(_3\)h) disappear above 150 K and new bands appear (enhanced in grey in Fig. 9) at 85.5 for BA-h\(_6\), 84.0 cm\(^{-1}\) for BA-d\(_3\)h and 84.5 cm\(^{-1}\) for BA-h\(_3\)d. These bands shift to \(\sim71\) cm\(^{-1}\) at room temperature. Their relative intensities fit the same Arrhenius law (Fig. 10) with an activation energy of \((54 \pm 6)\) cm\(^{-1}\) comparable to the enthalpy differences \(\Delta U\) measured with QENS and NMR [31]. Therefore, we conclude that the bands intense at low temperature are due to the ordered structure with all dimers in the same configuration throughout the crystal. These bands vanish at room temperature. The bands arising upon increasing temperature correspond to the structure with equal probabilities for I and II.

Two Raman bands in the frequency range of \((54 \pm 6)\) cm\(^{-1}\) are observed at any temperature and their frequencies are almost temperature independent below 150 K (Fig. 9 and Tables 1–3). They are both compatible with the activation...
energy for the Arrhenius law. These bands correspond to virtually harmonic collective vibrations with wave vector \( \mathbf{k} \sim 0 \). In principle, the effective activation energy is averaged over the density-of-states for these modes but the frequency dispersion cannot be determined with optical techniques. However, as a rule of thumb, rather modest dispersion is anticipated in a molecular crystal like benzoic acid and the Raman frequency is a pertinent approximation. We conclude that thermal population of particular phonons determines the interconversion process.

Even at room temperature the bands in the range of \((54 \pm 6)\,\text{cm}^{-1}\) are well defined and must...
be regarded as stationary extended states. Consequently, the proton distribution in the phonon-excited state must be regarded as a coherent superposition of the two isomers. As opposed to that, a stochastic distribution of tautomers, as represented in Eqs. (1) and (2), should destroy the translation invariance of the lattice and relax the symmetry-related selection rules. Phonon bands should merge into a very broad density-of-states.

### Table 1
Band decomposition of the Raman spectra of fully hydrogenated benzoic acid (BA-h₆)

<table>
<thead>
<tr>
<th>Temperature (G)</th>
<th>Parameters</th>
<th>1</th>
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<th>3</th>
<th>4</th>
<th>5</th>
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<th>7</th>
<th>8</th>
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<tbody>
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<td>7 K (G) v (cm⁻¹)</td>
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<td>52.0</td>
<td>56.0</td>
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<td>89.0</td>
<td>98.5</td>
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<td>126.0</td>
<td>133.5</td>
<td>199.0</td>
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<td>2.4</td>
<td>–</td>
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<td>–</td>
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<td>56.0</td>
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G: Gaussian profiles; L: Lorentzian profiles.

### Table 2
Band decomposition of the Raman spectra of the ring deuterated benzoic acid (BA-d₅h)

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<th>Temperature (G)</th>
<th>Parameters</th>
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<td>–</td>
<td>88.5</td>
<td>94.5</td>
<td>116.0</td>
<td>122.0</td>
<td>129.5</td>
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<td>3.0</td>
<td>3.0</td>
<td>–</td>
<td>3.0</td>
<td>3.0</td>
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<tr>
<td>Area (%)</td>
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<td>300 K (L) v (cm⁻¹)</td>
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<td>49.0</td>
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<td>88.5</td>
<td>107.5</td>
<td>116.0</td>
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<tr>
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<td>8.6</td>
<td>16.1</td>
<td>–</td>
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<tr>
<td>Area (%)</td>
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<td>11</td>
<td>4</td>
<td>39</td>
<td>12</td>
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<td>13</td>
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<td>2</td>
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</tbody>
</table>

G: Gaussian profiles; L: Lorentzian profiles.
The interplay of phonon excitation and dimer interconversion confirms that the energy difference between the two forms $D_U$ is strongly coupled to a lattice coordinate, say:

$$R_{0j}(k,t) = W_{k,l}(R_0) \exp \left\{ i j k \cdot L - v_F(k)t/\hbar \right\},$$

where $R_{0j}(k,t)$ represents the displacement of molecular entities seen as point mass at crystal site $j$ with lattice parameter $L$ and wave vector $k$.

$\Psi_{k,l}(R')$ is the wave function for harmonic oscillations of the molecular entities at frequency $v_F(k)$. In the ground state the probability density for the centre of mass of the librating entities is a Gaussian function $W_{k,0}(R')$ (see Fig. 11). This distribution with a maximum value at $R' = 0$ corresponds to the ordered structure composed of entities $I_0$. In the first excited state, the density probability $W_{k,1}(R')$ is zero at $R' = 0$ with two symmetrical parts centred at $R'_{k,\text{max}} = \pm \sqrt{R_0^2}$, where $(R_0^2) = \hbar/M\omega_F(k)$ is the mean square amplitude of the harmonic oscillator with effective mass $M$ and frequency $\omega_F(k)$.

For each state, we define the effective energy difference between the two forms as $\langle \Delta U \rangle_k = \langle \Psi_{k,l}(\Delta U(R'))|\Psi_{k,l} \rangle$. This quantity is non-zero for the ordered structure in the ground state (say $\langle \Delta U \rangle_0 = \Delta U_0$) and vanishes in the excited state ($\langle \Delta U \rangle_1 = 0$). Therefore, $\Delta U(R')$ is a symmetrical function of $R'$ and quick examination of Fig. 11 reveals that $\Delta U(R')$ should be a very narrow Dirac-like function centred at $R' = 0$. Therefore, proton ordering in the ground state should be due to a sharp resonance between dimers throughout the crystal.

To summarise, the Raman spectra of the lattice modes reveal that the interconversion of dimers is due to strong coupling to a very limited number of
phonons. In the ground state all dimers have the same configuration. Phonon-excited states are coherent superpositions in 1D of the two isomers. We suspect that the stability of this quantum superposition, compared to the random distribution of isomers I and II, is ensured by the decrease of interdimer interaction.

4. Interconversion and molecular interactions

The role of lattice modes in the interconversion process suggests a delicate balance of weak interactions that can be easily disrupted. Among the intermolecular forces determining the orientation of protons in carboxyl dimers the importance of nearest neighbour interactions is largely acknowledged [115]. Interconversion may occur if the neighbouring contacts of the carboxyl and hydroxyl O atoms are of similar nature and if the hydrogen-bonded pairs of carboxylic acids interact only weakly with one another in the solid [116]. In the benzoic acid crystal the carboxyl groups form interplanar contacts with each other via stacking motifs SI and SII [117]. Crystallographic data suggest that the corresponding interlayer interactions are not sufficient to prevent orientational disorder [115].

Alternatively, the intralayer structure IL suggests weak interactions through CH⋯O contacts of ~3.5 Å with the two O atoms of the carboxyl groups. In principle the lateral symmetric environment of a dimer is compatible with disorder [115].

Electrical charges could induce slight asymmetry for CH⋯O interactions and thus prevent
interconversion at low temperature. As a matter of fact, neutron diffraction measurements suggest that the slightly different CH⋯O distances at 20 K (H⋯O = 2.519(5) and 2.474(5), respectively) become equal and slightly longer at 175 K (2.544(9) and 2.550(11), respectively) [82]. Therefore, it can be supposed that thermal excitation of lattice modes could average out CH⋯O interactions and allow interconversion to appear. Raman bands in the range of (54 ± 6) cm⁻¹ could be translational motions parallel to the dimer axes that monitor the orientational interconversion. The sharp variation of ΔU suggests resonance between mesomeric structures and hydrogen bonds throughout the layer planes. It is not straightforward to propose a microscopic model for this resonance effect.

5. Proton transfer dynamics

In this section the two components of the ν OH and ν OD bands are attributed to the 0 → 2 and 0 → 3 transitions within asymmetrical double minimum potentials similar to those previously proposed for KHCO₃ and KDCO₃ [52]. This assignment scheme deserves consideration as alternative band-shaping mechanisms (see above dynamical correlation, Fermi resonance, etc.) have been eliminated. The potential function for the proton-stretching mode can be written as

\[ V(x) = ax + bx^2 + c \exp(-dx^2). \] (4)

The coordinate x represents the H or D position along the O⋯O bond. The contribution of the CO coordinates to the effective coordinate for proton transfer is ignored and the effective oscillator mass is that of a bare H or D atom. For each k value, parameters a, b, c and d can be determined from experimental values: v₀₂ and v₀₃ for the 0 → 2 and 0 → 3 transitions, the distance between the two minima r and the intensity ratio I₀₃/I₀₂.

Unfortunately, some ambiguities cannot be avoided. First, v₀₂ and v₀₃ depend on which part of the ν OH profile is considered. For BA-h₆, v₀₂ = 2570 cm⁻¹ and v₀₃ = 2840 cm⁻¹ correspond to a maximum of probability. Second, the intensity ratio depends on the unknown electrical anharmonicity. Third, the distance between the two proton sites of ∼0.70 Å, derived from diffraction data at 20 K [81,82] corresponds to the distance between maxima of the probability density. This is a good approximation to the distance between the potential minima only in the case where x is parallel to the O⋯O direction. Otherwise, if the reaction path were significantly bent the effective distance between potential minima along the curvilinear coordinate could be longer. Finally, the exponent k in (4) is rather arbitrary as long as higher transitions are ignored. This is of little consequences on the overall potential shape and on frequency shifts upon deuteration [52].

The observation of the v₀₁ transition is useful to confirm the double minimum potential and to estimate dynamical parameters. This transition is anticipated in a frequency range below v₀₃ - v₀₂ = 270 cm⁻¹ and most probably around 200 cm⁻¹ [52]. The intensity should be extremely weak in the infrared or Raman and the band should be difficult to distinguish among other contributions in the same frequency range. The INS spectrum of BA-d₅h offers the best opportunity to observing this transition because the scattering cross-section for H atoms is very much greater than for D, C or O atoms and this technique has great sensitivity to proton displacements with large amplitudes.

The INS profile between 150 and 210 cm⁻¹ (Fig. 12) can be decomposed into three bands at 172, 178 and 188 cm⁻¹ and there is no other visible band between 130 and 250 cm⁻¹. The weak band at 178 cm⁻¹ is the antisymmetric τₐ COO mode observed in the infrared (Au + Bu) [69]. The band at 188 cm⁻¹ is the symmetric τₜ COO mode observed at 189 cm⁻¹ in Raman (Au + Bu) (Fig. 9). This assignment scheme is in accordance with the observed intensities, as the mean square amplitudes for proton displacements and the INS intensities are much smaller for the antisymmetric than for the symmetric modes. As we do not anticipate any other mode in this region, the band at 172 cm⁻¹ can be attributed to v₀₁. This band has no visible counterpart in the infrared or Raman. It is rather narrow (FWHM ∼ 10 cm⁻¹) and cannot be confused with the broad density of states for the
lattice modes below 150 cm\(^{-1}\). This is in marked contrast to the broad \(\nu\ OH\) profiles for the \(0 \to 2\) and \(0 \to 3\) transitions (Fig. 6) whose widths are related to the fast variation of \(v_{02}\) and \(v_{03}\) with the \(O \cdots O\) distance (\(\sim 12,000\) cm\(^{-1}\) A\(^{-1}\) [103]). In comparison to that, the variation of \(v_{01}\) with the \(O \cdots O\) distance is determined by the potential asymmetry (\(\frac{dV}{dx}\)\(|_{x=0}=265\) cm\(^{-1}\) A\(^{-1}\)) in Table 4) and band broadening due to this coupling is negligible.

The potential functions given in Table 4 (see also Fig. 13) are best fits to the observed transitions for BA-\(h_6\). As far as higher transitions are ignored all functions are equally acceptable. The calculated intensity ratio for the first-order term of the transition moment (\(\rho=I_{350}/I_{2820}=2.8\)) is compatible with the observed ratio of \(\sim 2.5\).

Table 4

Potential functions and energy levels calculated for the stretching modes: \(V(x)=ax+bx^3+c\exp(-dx^2)\) with \(k=1,2\) and 3, respectively

<table>
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<tr>
<th>(V(x))</th>
<th>(r\ (\text{Å}))</th>
<th>(E_a\ (\text{cm}^{-1}))</th>
<th>(\nu\ OH\ (\text{cm}^{-1}))</th>
<th>(\nu\ OD\ (\text{cm}^{-1}))</th>
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<tr>
<td>(265x+286000x^2+171480\exp(-2.17x^2))</td>
<td>0.70</td>
<td>5000</td>
<td>6.0</td>
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<td>(265x+192330x^4+17219\exp(-4.92x^2))</td>
<td>0.70</td>
<td>5000</td>
<td>6.0</td>
<td>172</td>
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<tr>
<td>(265x+452850x^6+7387.4\exp(-12.4x^2))</td>
<td>0.70</td>
<td>5040</td>
<td>6.0</td>
<td>172</td>
</tr>
</tbody>
</table>

\(V\) and \(x\) are in cm\(^{-1}\) and Å units, respectively. The particle mass is 1 amu for \(\nu\ OH\) and 2 amu for \(\nu\ OD\). \(r\) is the distance between the two minima and \(E_a\) is the barrier height. \(v_{0i}\) is the tunnel splitting calculated for the symmetrised potential (\(a=0\)).

These potentials were obtained with an oscillator mass \(m_H=1\) amu and the distance between the minima \(r_{1H}=0.70\ \text{Å}\) was imposed for the sake of consistency with diffraction data [81,82]. However, these values are not independent: for a given energy level pattern the distance between minima \(r\) is correlated to the mass \(m\) as \(r/r_{1H}=\sqrt{m_H/m}\) [93]. The effective mass can be regarded as an adjustable parameter with relative uncertainty \(\Delta m/m=2\Delta r/r\sim 1\%\) according to diffraction data. Within this rather modest uncertainty the proton transfer dynamics is isolated from the molecular frame and the transfer coordinate \(x\) is along the straight line between the two sites.

The potential barrier of \(\sim 5000\) cm\(^{-1}\) is very similar to that previously estimated for KHCO\(_3\) [52]. For both systems, transition from quantum to classical dynamics for protons can be excluded, even at room temperature. The estimated activation energy for the tautomerisation process [12,14,18,20,21,25,28–32] is about one order of magnitude less and cannot correspond to the potential barrier experienced by protons, as shown in Fig. 1. To the least, a potential barrier of \(\sim 500\) cm\(^{-1}\) for tautomerisation is much less than the zero-point energy for the \(\nu\ OH\) mode and should be totally insignificant for proton dynamics in the quantum regime.

The INS intensity of the \(0 \to 1\) transition is proportional to the scattering function \(S(Q,\omega)=|\int \Psi'_2(x)\Psi_1(x)\exp(\text{i}Qxx)\text{d}x|^2\). It depends strongly on the delocalisation degree of the wave functions, which can be estimated by numerical integration. Alternatively, within the two-level system...
approximation [18,118], the wave functions can be represented as:

\[ \Psi_{0\phi}(x) = \cos \phi \Psi_0(x - x_0) + \sin \phi \Psi_0(x + x_0), \]
\[ \Psi_{1\phi}(x) = -\sin \phi \Psi_0(x - x_0) + \cos \phi \Psi_0(x + x_0). \]

The harmonic wave functions \( \Psi_0(x \pm x_0) \) are eigenfunctions of the Hamiltonian obtained by second-order expansion of the potential function in the vicinity of the minima at \( \pm x_0 \). The angular parameter is determined as \( \tan 2\phi = v_0 / (v_{01} - v_0) \). With the experimental values we obtain \( \cos \phi \sim 1 \) and \( \sin \phi = \varepsilon \sim v_{01} / 2v_{01} \sim 1.80 \times 10^{-2} \). According to Table 4, the value for the angular parameter \( \phi \) is independent of the particular analytical function chosen for the potential. In addition, numerical integration of the computed wave functions gives virtually the same value. Therefore, about 2% of the wave function is delocalised. Compared to the symmetrical double minimum potential, the observed INS intensity for the 0 \( \rightarrow \) 1 transition is depressed by a factor \( \varepsilon^2 \sim 3 \times 10^{-4} \). Nevertheless, this band is observed with reasonable signal-to-noise ratio (Fig. 12), thanks to the great sensitivity of INS and high performances of the spectrometer.

Frequencies calculated for the OD stretching with the same potentials correspond to the bands observed at 2050 and 2205 cm\(^{-1}\) (Fig. 6) to within \( \sim 4\% \) accuracy. However, this coincidence is misleading because the calculated intensity ratio \( (I_{2050} / I_{2205} \sim 500) \) is quite different from the observed ratio of \( \sim 1.5 \). This difference is too large to be due to a dramatic change of the dipole moment derivative upon deuteration. As previously reported for KHCO\(_3\) and KDCO\(_3\) [52], a significant decrease of the potential barrier in the deuterated sample is more likely. Moreover, numerical calculations suggest a significant decrease of the potential asymmetry upon deuteration. Unfortunately, the 0 \( \rightarrow \) 1 transition is unknown and we have not enough information to determine all parameters accurately.

The potential function for the \( v \) OH/OD mode is an effective potential resulting from averaging the multidimensional potential for the whole crystal over the range of the hyper surface spanned by the other degrees of freedom, owing to zero-point motions. A decrease of the potential barrier upon deuteration is a consequence mainly of the restricted domain spanned by the bending OD modes compared to the hydrogenated analogues. The isotope effect suggests that the potential bar-
rrier and the asymmetry decrease as deformation of
the classical trajectory along the bending coordinates is depressed by deuteration. Consequently,
the top of the potential barrier along the classical
trajectory could be a saddle point.

From the viewpoint of chemistry, the lowest
potential minimum in Fig. 13 corresponds to \( \text{I} \) and
the other minimum corresponds to isomers \( \text{III} \) or
\( \text{III}' \) in which one of the protons is transferred
along the hydrogen bond.

![Diagram of hydrogen bond]

For each state \( (n = 0 \text{ or } 1) \) the probabilities \( P_0(\text{I}) \), \( P_0(\text{III}) \) and \( P_0(\text{III}') \) are defined as the
squared wave functions integrated over the corre-
sponding domains. For example, \( P_0(\text{I}) = \int_1 \Psi_0^2(x) \sim 1 \) and \( P_0(\text{III}) = P_0(\text{III}') = \int_{\text{III}} \Psi_0^2(x) \sim \epsilon^2 \). Therefore, the states \( n = 0 \) and \( 1 \) are
virtually, but not exactly, pure species \( \text{I} \) and \( \text{III} \)
(\( \text{III}' \)), respectively. In the upper states
\( (n = 2, 3, \ldots) \) the wave functions are largely delo-
calised and isomers are no longer distinguishable.

The spectra at low temperature correspond to
virtually pure \( \text{I} \). At room temperature the relative
populations of \( \text{I} \) and \( \text{III} \) and \( \text{III}' \) are similar. As
there is no significant effect in the COO stretching
region (Fig. 3), it can be concluded that proton
transfer occurs without significant geometrical
change of the COO groups, in line with the esti-
mate of \( \sim 1 \) amu for the effective mass. The double
minimum function is the effective potential for the
mean geometry of the carboxylic groups. There is
no evidence that electrons follow adiabatically the
motions of protons.

6. Interconversion dynamics

In order to calculate the proton transfer rate as
a function of temperature we consider exclusively
the \( n = 0 \) and \( 1 \) states in the remainder of this
work. Contributions from higher states are negligi-
ble, even at 300 K.

6.1. The phonon-ground state

Owing to the decoupling of the proton dy-
namics in the tunnelling states the potential sur-
face for dimer interconversion is a function of
primarily the stretching coordinates \( (x_1, x_2) \) and the lattice coordinate \( R' \). The other coordinates can be ignored. The relevant eigenstates \( |n_1n_2\rangle \) are characterised with the three quantum numbers \( l, n_1 \) and \( n_2 \), associated to
\( R' \), \( x_1 \) and \( x_2 \), respectively.

As there is no coupling between protons, the
effective potential surface in the ground state of \( R' \)
can be represented with a simple addition of the
double minimum potentials for each coordinate.
The Hamiltonian is written as:

\[
H_0(x_1, x_2) = \frac{p_1^2}{2m} + \frac{p_2^2}{2m} + V_0(x_1) + V_0(x_2)
+ a_0(x_1 + x_2),
\]

where \( V_0(x) \) is the symmetric part of the potential
in Eq. (4). In the \( (x_1, x_2) \) plane, domains corre-
sponding to isomers \( \text{I} \) (\( -x_0, -x_0 \)), \( \text{II} \) (\( x_0, x_0 \)), \( \text{III} \)
and \( \text{III}' \) (\( \pm x_0, \mp x_0 \)) are separated by high potential barriers and can be regarded as well de
defined enti-
ties (see Fig. 14). This is in accordance with proton
ordering at low temperature. The three lower
eigenstates are at 0 for \( |000\rangle \), \( v_{01} \) for \( |001\rangle \) and
\( |010\rangle \), \( 2v_{01} \) for \( |011\rangle \). The wave functions
\( \Psi_{0ij}(x_1, x_2) = \Psi_{0i}(x_1)\Psi_{0j}(x_2) \) are simple products
of the wave functions \( \Psi_{0i}(x_i) \) given in Eq. (5) (see
Fig. 15). In the \( |000\rangle \) state the amplitude of the
wave function is \( \sim 1 \) for \( \text{I} \), \( \sim \epsilon \) for \( \text{III} \) or \( \text{III}' \) and \( \sim \epsilon^2 \)
for \( \text{II} \). In the degenerate states \( |010\rangle \) and \( |001\rangle \) the
wave functions have amplitudes of \( \sim 1 \) for \( \text{III} \) or
\( \text{III}' \), \( \sim \epsilon \) for \( \text{I} \) and \( \sim \pm \epsilon \) for \( \text{II} \). Finally, there is
the wave function in the state \( |011\rangle \) is \( \sim 1 \) for \( \text{II} \). There are
minor peaks for \( \text{III} \) and \( \text{III}' \) (\( \sim \epsilon \)) and negligible
amplitude for \( \text{I} \) (\( \sim \epsilon^2 \)).

The potential surface presented in Fig. 14 does
not account for the simultaneous transfer of the
two protons of a dimer. The reaction path be-
tween \( \text{I} \) and \( \text{II} \) along the diagonal has no physical
meaning and potential functions previously proposed (see Fig. 1) should not be regarded as a cut of the potential surface along this line. The distance between the two minima ($\sqrt{2R} \sim 1$ Å) does not correspond to any real distance between proton sites and the barrier is $\sim 10000$ cm$^{-1}$. Interconversion between I and II due to uncorrelated transfer of protons occurs exclusively via III or III$'$. In order to calculate the proton transfer rate, the evolution of the quantum system is represented with the time-dependent wave function whose expansion in terms of the eigenfunctions depends on the initial conditions [118,119]

$$
\Phi_0(x_1, x_2, t, T) = \exp(iE_0t/\hbar) \left\{ e_{000} \Psi_{000\phi} + [c_{010} \Psi_{010\phi} + c_{001} \Psi_{001\phi}] \right\} \\
\times \exp(i\omega_{01}t + \theta_1) + c_{001} \Psi_{011\phi} \exp(i2\omega_{01}t + \theta_2).
$$

(7)

The $c_{ijk}$ are implicit real function of the temperature (Boltzmann population factors of the states) and $\omega_{01} = \nu_{01}/\hbar$. The time-phases $\theta_1$ and $\theta_2$ are arbitrary. They disappear in the final result and can be ignored. The proton transfer rate is given by the time evolution of the probability density

$$
|\Phi_0(x_1, x_2, t, T)|^2 = \Gamma_{00} + 2c_{000} \Psi_{000\phi} [c_{010} \Psi_{010\phi} + c_{001} \Psi_{001\phi}] \cos(\omega_{01}t) \\
+ 2c_{001}c_{010} \Psi_{000\phi} \Psi_{011\phi} \cos(2\omega_{01}t) \\
+ 2c_{011} \Psi_{011\phi} [c_{010} \Psi_{010\phi} + c_{001} \Psi_{001\phi}] \cos(\omega_{01}t).
$$

(8)

The harmonic oscillations are quantum beats. As $c_{010} = c_{001}$, we can distinguish three contributions.

$$
\Gamma_{01} = \Psi_{000\phi} \left[ \Psi_{010\phi} + \Psi_{001\phi} \right] \\
= \frac{1}{2} \sin \phi \cos^3 \phi \left[ \Psi_0^2(x_1 - x_0) \Psi_0^2(x_2 + x_0) - \Psi_0^2(x_1 + x_0) \\
\times \Psi_0^2(x_2 + x_0) + \Psi_0^2(x_1 + x_0) \Psi_0^2(x_2 - x_0) \\
- \Psi_0^2(x_1 + x_0) \Psi_0^2(x_2 + x_0) \right] \\
+ \frac{1}{2} \sin^3 \phi \cos \phi \left[ \Psi_0^2(x_1 - x_0) \Psi_0^2(x_2 - x_0) \\
- \Psi_0^2(x_1 + x_0) \Psi_0^2(x_2 - x_0) + \Psi_0^2(x_1 - x_0) \\
\times \Psi_0^2(x_2 - x_0) - \Psi_0^2(x_1 - x_0) \Psi_0^2(x_2 + x_0) \right].
$$

(9)

The term proportional to $\sin \phi \cos^3 \phi$ accounts for single proton transfer between I and III(III$'$) (Fig. 16(a)). If at $t = 0$ the two protons are localised at
Fig. 15. Schematic view of the wave functions in the phonon-ground state ($l = 0$, right-hand side) and in the phonon-excited state ($l = 1$, left-hand side). The quantum numbers $n_1$ and $n_2$ refer to the proton-stretching coordinates $x_1$ and $x_2$, respectively. The wave functions were factorised as $\Psi_1(x_1, x_2)$ with $\Psi_1(x) = \cos \phi \exp[-(x + x_0)^2 / 0.01] + \sin \phi \exp[-(x - x_0)^2 / 0.01]$ and $\Psi_2(x) = -\sin \phi \exp[-(x + x_0)^2 / 0.01] + \cos \phi \exp[-(x - x_0)^2 / 0.01]$ with $\sin \phi = 0.1$ and $\cos \phi = 0.995$. For the sake of clarity the amplitude of the minor components is about 10 times greater than in the case depicted in Fig. 13. Wave functions in the $l = 1$ state are superpositions of $\Psi_{11}^{\text{II}} = \Psi_{01}^{\text{II}}(x_1, x_2)$ and $\Psi_{10}^{\text{II}} = \Psi_{02}^{\text{II}}(x_1 - \phi_1(x_1, x_2))$. 

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Fig. 16. The time-dependent contributions to the density probability for protons obtained for superposition of the $|000\rangle$ and $|010\rangle$ or $|001\rangle$ states (a and b), $|000\rangle$ and $|011\rangle$ states (c), $|010\rangle$ or $|001\rangle$ and $|011\rangle$ states (d and e). (f) is the time dependent superposition of (a) and (b). The density probability undergoes harmonic oscillations at frequency $f_{01}$ (a, b, d, e and f) and $2f_{01}$ (c). $\varepsilon$ is the delocalisation degree of the wave functions (see Fig. 15).
(say) $I$, a proportion $\sin \phi \cos^3 \phi$ of the dimers is converted into $III(III')$ at time $t = \pi/\omega_{01}$. Then, Eq. (8) gives the proton transfer rate of $4\sin \phi \cos^3 \phi f_{01} \sim 4\epsilon f_{01}$ or $4f_{01}$ (with $f_{ij} = v_{ij}/\hbar$) that is independent of the potential asymmetry. However, the potential asymmetry still appears in the Boltzmann population factor for the states.

The term proportional to $\sin^3 \phi \cos \phi$ in Eq. (9) accounts for single proton transfer between $I$ and $III(III')$ (Fig. 16(b)). The rate is $\sim 4\epsilon^3 f_{01}$ or $4\epsilon^2 f_{01}$.

All together, the two contributions account for interconversion between $I$ and $II$. The rate is that of the limiting step, namely $4\epsilon f_{01}$. This interconversion process corresponds to uncorrelated proton transfer via coherent tunnelling, which is different from the simultaneous transfer of the two protons in $I$.

The second term

$$\Gamma_{02} = \Psi_{00\phi} \Psi_{01\phi}$$

$$= \sin^2 \phi \cos^2 \phi$$

$$\times \left\{ \begin{array}{l}
\Psi_0^2(x_1 + x_0) \Psi_0^2(x_2 + x_0) \\
+ \Psi_0^2(x_1 + x_0) \Psi_0^2(x_2 + x_0) \\
- \Psi_0^2(x_1 - x_0) \Psi_0^2(x_2 + x_0) \\
+ \Psi_0^2(x_1 - x_0) \Psi_0^2(x_2 - x_0) \\
\end{array} \right\}$$

accounts for harmonic oscillation at frequency $2f_{01}$ between a superposition of $I$ and $II$, on one hand, and a superposition of $III$ and $III'$, on the other (see Fig. 16(c)). The transfer rate for a single proton is $8\sin^2 \phi \cos^2 \phi v_{01} \sim 8\epsilon f_{01}$ and the interconversion rate is $\sim 4\epsilon^2 f_{01}$.

The third term

$$\Gamma_{03} = \left[ \Psi_{00\phi} + \Psi_{01\phi} \right] \Psi_{011\phi}$$

$$= \frac{1}{2} \sin \phi \cos^3 \phi$$

$$\times \left\{ \begin{array}{l}
\Psi_0^2(x_1 - x_0) \Psi_0^2(x_2 - x_0) \\
- \Psi_0^2(x_1 - x_0) \Psi_0^2(x_2 + x_0) \\
+ \Psi_0^2(x_1 + x_0) \Psi_0^2(x_2 - x_0) \\
- \Psi_0^2(x_1 + x_0) \Psi_0^2(x_2 + x_0) \\
\end{array} \right\}$$

compares to $-\Gamma_{01}$ after permutation of the proton coordinates (compare Figs. 16(d) and (e) with (a) and (b), respectively). The single proton transfer rate is proportional to $4f_{01}$ and the interconversion rate is proportional to $4\epsilon^2 f_{01}$.

A combination of the two terms proportional to $\sin \phi \cos^3 \phi$ in $\Gamma_{01}$ and $\Gamma_{03}$ gives a rate proportional to $4f_{01}$ for dimer interconversion (compare to a superposition of Figs. 16(a) and (d)).

Finally, we obtain the temperature dependent proton transfer rate via thermally activated tunnelling involved in interconversion of isolated dimers:

$$k_{l-h} = 4f_{01} \left\{ e^{\frac{2}{\epsilon f_{01}}} \exp (-v_{01}/kT) + (e^2 + e + 1) \exp (-2v_{01}/kT) \right\}. \quad (12)$$

This rate is totally determined by the shape of the potential function for proton transfer, without any contribution from the crystal lattice ($\Delta L = 0$). This “intrinsic” interconversion rate vanishes at low temperature and this is at variance from the observation for benzoic acid. In the next section we consider coupling with phonons to remove this discrepancy.

### 6.2. Phonon-excited state

The system is represented with a superposition of the two forms ($I$ and $II$) with equal probability (see Section 3.4). The potential for each form is similar to that represented in Eq. (6) but with opposite signs for the linear terms. The total Hamiltonian is a superposition of two terms $H_0^I$ and $H_0^H$, respectively, and we suppose there is no coupling term between them.

$$H_I = H_0^I \oplus H_0^H,$$

$$H_0^I(x_1^I, x_2^I) = \frac{p_1^I}{2m} + \frac{p_2^I}{2m} + V_0(x_1^I) + V_0(x_2^I) + a_0(x_1^I + x_2^I),$$

$$H_0^H(x_1^H, x_2^H) = \frac{p_1^H}{2m} + \frac{p_2^H}{2m} + V_0(x_1^H) + V_0(x_2^H) - a_0(x_1^H + x_2^H). \quad (13)$$

Coordinates $x_1$ and $x_2$ correspond to protons labelled 1 and 2, respectively. Superscript $I$ and $II$ refer to isomers $I$ and $II$, respectively. For each Hamiltonian there are three distinct states: $|100\rangle$
at \( v_{\text{IR}} \), \(|110\rangle\) and \(|101\rangle\) at \( v_{\text{IR}} + v_{01} \) and \(|111\rangle\) at \( v_{\text{IR}} + 2v_{01} \), respectively. For each state with twofold degeneracy the wave function is a superposition of 
\[
\Psi_{n_1 n_2}^f = \Psi_{0(1/2\pm)}(x_1, x_2) \quad \text{and} \quad \Psi_{n_1 n_2}^b = \Psi_{0(1/2\mp)}(x_1, x_2),
\]
respectively (see Fig. 15). The interconversion rate between the two degenerate forms is proportional to the proton transfer rate within a dimer \( (2f_{00}) \) and to the probability for interconversion given by the overlap integral for the wave functions \( (2\nu^2) \).

This scheme is quite different in nature from that anticipated for the symmetrized potential surface obtained by simple addition of \( H_I^1 \) and \( H_0^b \), which cancels the linear terms \( a_0 \) in the potential function. The energy levels would be at \( v_{\text{IR}} \), \( v_{\text{IR}} + v_{00} \) and \( v_{\text{IR}} + 2v_{00} \). The wave functions would be symmetric and antisymmetric combinations of the wave functions of the symmetric double minimum potential \( V_0 \). In this case, the \( 0 \rightarrow 2 \) transition would be infrared inactive and the \( v \) OH profile would be dramatically changed. Symmetrisation of the potential surface upon thermal population of the phonon states is incompatible with the very weak temperature effects on the OH stretching bands.

The “intrinsic” \((\Delta l = 0)\) proton transfer mechanisms in the phonon-exicted state, similar to those in Eq. (12), do not contribute to the interconversion rate since the two forms have equal probabilities in each state. Interconversion occurs exclusively via energy transfer to the phonon mode that couples the two regimes. We can distinguish three “extrinsic” mechanisms. First, interconversion may occur upon one-quantum phonon absorption/emission \((\Delta l = \pm 1)\), without any energy transfer to the stretching modes. This thermally activated rate can be treated as in Eq. (2) [18]. However, the potential asymmetry \( \Delta U \) is now replaced by the lattice mode frequency \( v_{\text{IR}} \). The “up” rate is proportional to the Bose factor \( n(v_{\text{IR}}) = \exp(v_{\text{IR}}/kT) - 1 \). The “down” rate for stimulated and spontaneous emission is proportional to \( n(v_{\text{IR}}) + 1 \). The sum of the “up” and “down” rates is \( 2n(v_{\text{IR}}) + 1 = \coth(v_{\text{IR}}/2kT) \) and the interconversion rate is: \( 4\nu^2 f_{00} \coth(v_{\text{IR}}/2kT) \).

The second mechanism can be represented with a projection of the degenerate wave function in the \(|100\rangle\) state onto the wave functions in the \( l = 0 \) states

\[
\Phi_{100}(t) = \frac{1}{\sqrt{2}} \exp(-iE_0 t/\hbar) \times \{ \Psi_{000} + \Psi_{011} \exp(i4\pi\omega_{01} t) + \nu \Psi_{010} + \Psi_{001} \exp(i2\pi\omega_{01} t) \}.
\]

Neglecting the terms proportional to \( \nu \) we obtain the time-dependent density probability

\[
|\Phi_{100}(t)|^2 \approx \Psi_{000} \Psi_{011} \cos(4\pi\omega_{01} t).
\]

This is proportional to \( f_{02} \) (see Eq. (10) and Fig. 16(c)). The system initially in the state \(|100\rangle\) at \( v_{\text{IR}} \) oscillates between a superposition of \(|000\rangle + |011\rangle\), on one hand, and a superposition of \(|010\rangle + |001\rangle\), on the other, with mean energy \( v_{01} \). The thermally activated rate is then \( 4\nu f_{00} \exp[-(v_{01} - v_{\text{IR}})/kT] \). Similarly, a projection of the wave function in the state \(|111\rangle\) at \( v_{\text{IR}} + 2v_{01} \) onto the wave functions in the \( l = 0 \) state gives the same rate as Eq. (14). However, the probability for this process is strongly depressed by the population factor for the upper state, namely \( \exp[-(v_{\text{IR}} + 2v_{01})/kT] \).

Finally, the state \(|111\rangle\) can be represented with a superposition of \(|000\rangle\) and \(|011\rangle\). According to Eq. (11) the corresponding interconversion rate is \( 4\nu f_{00} \exp[-(v_{\text{IR}} + 2v_{01})/kT] \).

The total proton transfer rate related to “extrinsic” interconversion \((\Delta l \neq 0)\) is then

\[
K_{1l-1l} = 4\nu f_{00} \left\{ \nu^2 \coth(v_{\text{IR}}/2kT) + \nu \exp[-(v_{01} - v_{\text{IR}})/kT] + (1 + \nu) \exp[-(2v_{01} + v_{\text{IR}})/kT] \right\}.
\]

For \( \nu \ll 1 \) we obtain

\[
K_{1l-1l} \approx 4\nu f_{00} \left\{ \nu^2 \coth(v_{\text{IR}}/2kT) \right. \left. + \nu \exp[-(v_{01} - v_{\text{IR}})/kT] \right. \left. + \exp[-(2v_{01} + v_{\text{IR}})/kT] \right\}.
\]

This is formally identical to the empirical temperature dependence for the proton correlation time measured with NMR and QENS in BA-h\(_6\) [31]:

\[
\tau_c^{-1} = \{ 1.72 \times 10^8 \coth(43/T) + 10^{10} \exp(-180/T) + 6.3 \times 10^{11} \exp(-600/T) \} \text{s}^{-1}.
\]

A straightforward comparison of Eqs. (16) and (17) gives \( f_{00} = 1.57 \times 10^{11} \text{s}^{-1}, \quad v_{01} = 5.25 \text{ cm}^{-1} \).
\( \varepsilon = 1.6 \times 10^{-2}, \varepsilon^2 = 2.7 \times 10^{-4}, v_p = 57 \text{ cm}^{-1} \) and \( v_{01} = 173 \text{ cm}^{-1} \). These values are virtually identical to those derived above from the spectra \((v_{01} = 6 \text{ cm}^{-1}, \varepsilon^2 = 3 \times 10^{-4}, v_p = 54 \text{ cm}^{-1} \) and \( v_{01} = 172 \text{ cm}^{-1} \)). This remarkable agreement demonstrates that NMR, QENS and vibrational spectroscopy forward different views of the same phenomena: the interconversion of dimers via thermally activated tunnelling of uncorrelated protons with an effective mass of 1 amu. The proton transfer rate measured with NMR and QENS is twice the interconversion rate.

There is no visible contribution from the “intrinsic” interconversion mechanisms represented with Eq. (12). At low temperature this contribution is negligible compared to Eq. (16). At high temperature, the rates given by both equations are on the same order but the rather large occupation number of phonon-excited states \( n(v_p) \) hides the “intrinsic” contribution from the phonon-ground state.

The crucial role of the phonon mode in the interconversion mechanism is thus confirmed by vibrational spectroscopy but proton tunnelling is not assisted by phonons. All techniques converge to the conclusion that the potential function for protons and the related frequencies \( v_{01} \) and \( v_{01} \) are temperature invariant. On the other hand, the energy difference between the two forms \( \Delta U(R') \), which is different in nature from \( 2v_{01} \), remains largely unknown. Presumably \( \Delta U_0 \) is much greater than \( v_p \) and the thermally activated interconversion process depends exclusively on the phonon frequency.

It may sound paradoxical to conclude that interconversion occurs via excitation/relaxation of phonons and, at the same time, that proton dynamics are totally isolated from the lattice dynamics. However, this is a logical consequence of the superposition of Hamiltonian \( H_0^I \) and \( H_0^{II} \) which leaves unchanged the potential function for protons. Vibrational spectra impose the concept of coherent superposition because they probe directly the wave function and symmetrisation of the potential functions can be excluded. In contrast to this, the diffraction techniques probe probabilities proportional to the squared wave function averaged over time and space. Mixtures of \( \text{III} \) and \( \text{III}' \) are not distinguished from mixtures of \( \text{I} \) and \( \text{II} \) and proton disorder can be understood within the framework of classical thermodynamics. The time scale for NMR and QENS is too long to give a snapshot of the wave function. The symmetrisation of the potential function cannot be excluded. Data can be tentatively analysed in terms of stochastic disorder and semiclassical models. However, significant deviation due to quantum effects cannot be avoided and remains largely unexplained. Only vibrational spectroscopy techniques give access to the fundamental parameters \( (v_{01} \) and \( v_{00} \)) bridging the gap between classical, semiclassical and quantum dynamics.

The concept of coherent superposition lies at the heart of the profound difference between quantum mechanics and classical physics. Quantum coherence is best observed for isolated quantum objects (like photons or atoms) in environments specially designed to minimise dissipation. In complex systems quantum coherence for a subsystem is rapidly lost via interaction with the many degrees of freedom of the surrounding environment [120]. For example, quantum entanglement on a very short time scale has been evidenced for protons with the neutron Compton scattering technique [121–124].

The benzoic acid crystal could be a representative example where long-lived quantum coherence is related to phonon excitation and survives at room temperature. This is not in conflict with the expectation of fast quantum decoherence in complex systems because in the benzoic acid crystal coupling is specific to a unique or a very limited number of phonon modes. It transpires that the subsystem of coordinates \( \{ R',x_1,x_2 \} \) is perfectly isolated from the other degrees of freedom. Presumably, space and time coherency of the phonon-excited states and superposition of \( H_0^I \) and \( H_0^{II} \) are intimately intricate and macroscopic quantum coherence could occur in the benzoic acid crystal.

7. Conclusion

Vibrational spectra emphasise the quantum nature of proton transfer and interconversion dynamics in the benzoic acid crystal. The concept of
tautomerism referring to a chemical equilibrium between two forms is replaced by the concept of quantum superposition that has no equivalent representation in classical mechanics. The salient characteristics of interconversion dynamics are rationalised.

1. The asymmetric double minimum potential for the proton-stretching mode is determined from observed frequencies ($v_{01}$, $v_{02}$ and $v_{03}$), distance between proton sites and intensity ratio.

2. The transfer of a single proton in a dimer is uncoupled to the molecular frame. The effective mass is 1 amu and the transfer coordinate is along the straight line between the two sites. There is no evidence for qualitative change of the topology of the chemical bonding during proton transfer.

3. The potential barrier of $/C_{24}^{5000}$ cm$^{-1}$ is much greater than thermal energy. The quantum regime prevails over the whole temperature range. The tunnelling matrix element $v_{0t}$ and the delocalisation degree of the wave function $v_{R0}$ are the key parameters for the proton transfer rate via coherent tunnelling.

4. Proton dynamics along the stretching coordinate are uncorrelated. The potential surface for the interconversion of the two protons is obtained by simple addition of the potentials along each stretching coordinate.

5. The proton transfer rate via thermally activated tunnelling is calculated with a coherent superposition of states. The analytical function depends solely on $f_{0t}$ and $v$. The “intrinsic” interconversion rate vanishes at low temperature.

6. The Raman spectra reveal that interconversion is also a consequence of the excitation of a particular phonon at $v_R$. In the phonon-ground state dimers are ordered in a unique configuration throughout the crystal. The excited states correspond to a coherent superposition of the two degenerate configurations. Quantum coherence occurs for a subset of coordinates $\{R',x_1,x_2\}$ perfectly isolated from the other degrees of freedom.

7. The analytical function for the interconversion rate as a function of temperature depends on $f_{0t}$, $v_{01}$ and $v_R$. The remarkable agreement with NMR and QENS data demonstrates that the quantum regime applies over very large dynamical ($10^8$–$10^{12}$ s$^{-1}$) and temperature ranges. Tunnelling and coherent superposition of configurations survive at room temperature.

The demonstration of quantum coherence in the benzoic acid crystal could be a key to understand a large class of phenomena related to proton ordering/disordering in solids.

References