

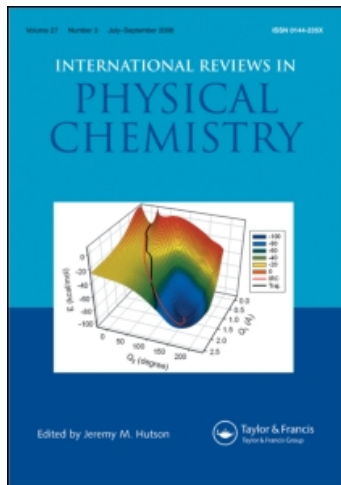
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Hydrogen bonding and quantum dynamics in the solid state

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Hydrogen bonding is of great importance to many fields in physics, chemistry and biology. However, a comprehensive view of this interaction is still far from being achieved. Recent developments of experimental techniques such as neutron diffraction, inelastic neutron scattering (INS), quasi-elastic neutron scattering (QENS) and nuclear magnetic resonance (NMR) T_1 measurements provide new information on the structure and dynamics of hydrogen bonds. The INS technique is unique to observing proton dynamics in the quantum regime. In the most favourable cases, potential functions for the proton motions are determined accurately and can be compared with those derived from other techniques or calculated with quantum chemistry methods. Two classical examples are presented to illustrate recent developments. First, tautomerism in centrosymmetric dimers is a prototypical example for proton transfer. The potential functions determined with vibrational spectroscopy or derived from QENS or NMR T_1 measurements are quite different. This is tentatively related to the characteristic time scale for each technique. Second, the strong symmetric hydrogen bond in the potassium hydrogen maleate is a model for the intermediate state in the proton transfer chemical reaction. The potential function for the proton determined with INS is quite different from the single minimum potential normally anticipated. The new concept of hydrogen bonding–antibonding vibrational state is emphasized. In all cases, advanced techniques yield a rather complex view of hydrogen bonds dominated by quantum effects that cannot be yet rationalized with the available theoretical tools of quantum chemistry.

1. Introduction

The concept of *hydrogen bond* appeared at the beginning of the twentieth century to account for chemical, spectroscopic, structural, thermodynamical and electrical properties. It was recognized that under certain conditions an atom of hydrogen is attracted by rather strong forces to two atoms, instead of only one, so that it may be considered to be acting as a bond between them. However, the location of the hydrogen atom and the physical origin of the binding energy long remained matters of controversies. The hydrogen bond was for some time thought to result from the formation of two covalent bonds by the hydrogen atom. However, with the development of the quantum-mechanical theory of valence, this view was abandoned. Pauling [1] wrote in his renowned book: ‘it is now recognized that the hydrogen atom, with only one stable orbital (the 1s orbital), can form only one covalent bond, that the hydrogen bond is largely ionic in character, and that it is formed only between the most electronegative atoms.’ Consequently, hydrogen bonds can be described as involving resonance among the three structures $X-H \dots Y$, $X-H^+ \dots Y^-$ and $X^- \dots H^+Y$.

In a premonitory view, Pauling [1] emphasized the main motivations for physicists, chemists and biologists to study hydrogen bonds in a great variety of systems in different states: ‘Because of its small bond energy and the small activation energy involved in its formation and rupture, the hydrogen bond is especially suited to play

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a part in reactions occurring at normal temperatures. It has been recognized that hydrogen bonds restrain protein molecules to their native configurations, and I believe that as the methods of structural chemistry are further applied to physiological problems it will be found that the significance of the hydrogen bond for physiology is greater than that of any other single structural feature.'

During these early times, the techniques available to characterize hydrogen bonds at the chemical bond level were essentially X-ray diffraction, infrared and Raman spectroscopy. Modelling was on a semiempirical basis. Unfortunately, it was not possible to determine the position of the binding proton with X-rays and the interpretation of the vibrational spectra was, and still is, largely hampered by the complexity of interactions between photons and matter [2–4].

Since these times, experimental techniques and computer-based data acquisition, storage and analysis have made spectacular progress. X-ray diffraction, infrared and Raman spectroscopy and nuclear magnetic resonance (NMR) are routinely used with excellent definition and resolution. The arrival of intense neutron sources has had a dramatic impact on hydrogen-bonding studies in the solid state. Nowadays, the locations of hydrogen atoms in crystals are determined with neutron diffraction, and vibrational spectroscopy can be performed with inelastic neutron scattering (INS) techniques. With quasi-elastic neutron scattering (QENS), diffusional jumps of protons can be measured over a large range of time scales. In the gas phase, hydrogen-bonded clusters have been widely studied in supersonic molecular beams coupled to laser spectroscopy, time-of-flight mass spectroscopy and optical spectroscopy in the infrared and microwave domains. Extreme cooling depopulates rotational levels, enables large concentration of aggregates to be formed and simplifies the spectral analysis.

Both the structure (geometry) and the dynamics (potential functions) have been analysed for many hydrogen-bonded systems. It is not possible to give here a review of all the work in this field. There have been numerous texts, monographs and compilations dealing with hydrogen bonds over the years [1, 4–11]. Much of this literature has taken the viewpoint of the crystallographer or the spectroscopist with an emphasis placed on the structural aspects of hydrogen-bonded complexes in their equilibrium geometries or their modes of internal vibration. Quantum-chemical calculations offer a rich source of supplementary information.

It has been largely confirmed that hydrogen bonding is ubiquitous. It can stabilize a broad range of configurations from the simple $XH \dots Y$ entities to the most extended multidimensional structures. Cooperative processes appear with chemical moieties that can simultaneously act as both an acceptor and a donor. Such species can be either ions, for example carboxylates, carbonates, phosphates and arsenates, or molecular moieties such as water, amides, peptide units ($-\text{CONH}-$) and proteins. Molecules containing several donor (acceptor) residues with specific spatial organization play a key role in molecular recognition, base pairing in nucleic acids, etc.

Despite the spectacular amount of knowledge accumulated during the last 50 years a comprehensive view of hydrogen-bonding phenomena is still far from being achieved. Unfortunately, it is impossible to obtain unambiguous estimates of the specific contribution of hydrogen bonds in complex systems because the bond energy is in the same range as other weak interactions, such as van der Waals or dispersion, and thermal energy at room temperature. Moreover, in many solvents, including the very important case of water, there are many different hydrogen bonds that cannot be unravelled easily. For aggregates in the gas phase, rotational structures are

complicated by anharmonic motions with large amplitudes when potential minima are multiple and shallow. It is then necessary to use sophisticated methods to take into account the strong coupling between intramolecular and intermolecular degrees of freedom. Predissociation (i.e. dissociation following vibrational excitation) is a serious limitation for high-resolution rovibrational spectroscopy. The lifetime of excited states is shortened and line broadening is observed.

Consequently, although most experimental and theoretical studies give bond energies in the range 2–5 kcal mol⁻¹ [12], in nice agreement with earlier estimates, these values should be treated with caution. It has been speculated that the binding energy might be much greater, but the proposal that hydrogen bonding could contribute up to 10–20 kcal mol⁻¹ to the stabilization of intermediates in enzyme-catalysed reactions [13] has generated some controversy [14].

Hydrogen bonds are still difficult to model because there is no unique way to partition the binding energy resulting from simultaneous changes in the electronic and vibrational wavefunctions upon hydrogen bond formation [15]. The basis of the interaction in hydrogen bonds is still regarded as essentially electrostatic in nature, but each particular experimental or theoretical approach highlights a different view. Structural studies emphasize the geometrical characteristics (bond lengths and angles) [16]. NMR and QENS are mainly concerned with dynamics over rather long time scales (typically longer than about 10⁻¹⁰ s) [17] while vibrational and rotational spectroscopy are dominated by quantum effects [18]. Quantum chemistry is hampered by the complexity of treating thermal and quantum fluctuations in complex systems with a high accuracy [15]. Nevertheless, all approaches agree that the strength, the length and the symmetry are correlated properties of hydrogen bonds. In simple systems XH...Y, the potential energy for the motion of the hydrogen atom along the hydrogen bond (usually referred to as the stretching motion) has two minima corresponding to the schematic structures XH...Y and X⁻...H⁺Y. Dynamics are thus directly related to proton transfer, an important phenomenon in many fields of physics, chemistry and biology. According to this chemical view, the top of the potential barrier between the two minima corresponds to the transition state X...H...Y. In the most general case the two minima are not equivalent and key parameters for proton transfer dynamics are the distance *R* between the two wells, the barrier height *E_a* and the potential asymmetry ΔU . Only in symmetric systems AH...A, can the two wells be equivalent and proton transfer may be mediated by tunnelling [12, 16–18]. Indeed in shorter hydrogen bonds the distance between the two minima can decrease to such an extent that the potential barrier between them may disappear. Only a single well remains and this symmetric structure is often regarded as mimicking the ‘intermediate state’ for proton transfer in chemical reactions or biological processes [13].

In the modern view of hydrogen bonding, determining the potential functions experienced by protons is of fundamental importance. Owing to the difficulty of measuring the binding energy, this is the only way to characterize accurately hydrogen bonds. Moreover, potential functions determined from experiments can be compared with those calculated with quantum chemistry. Consequently, proton transfer, the simplest chemical reaction in which quantum effects can prevail, has become a key issue in the modern approach to hydrogen bonding.

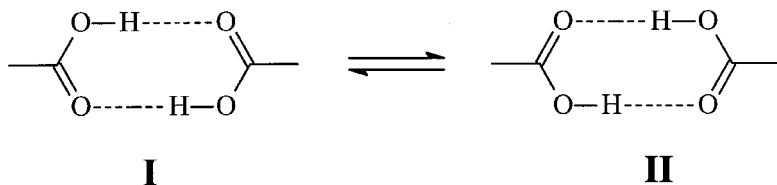
Among the experimental techniques, only vibrational and rotational spectroscopies provide direct information on proton dynamics in the quantum regime. Many hydrogen-bonded systems have been thoroughly investigated with infrared and

Raman techniques, but the interpretation of these spectra is hampered by the lack of theoretical frameworks accounting for band shapes and intensities [16]. These difficulties are largely avoided by exploiting INS spectroscopy, which has been successfully used to observe quantum effects in hydrogen bonds [18]. In the most favourable cases, it is possible to determine the potential function experienced by the binding proton. At the very least, such studies are useful in evaluating the accuracy of proposed model potentials and often lead to alternative models.

In order to illustrate this historical evolution we have chosen to present below two typical examples which emphasize the importance of quantum effects in hydrogen bonds: first, experimental determinations of double-well potentials for proton transfer in centrosymmetric cyclic dimers and, second, single minimum potentials for very short and symmetric hydrogen bonds.

2 Proton transfer and tautomerism

For an isolated centrosymmetric cyclic dimer the tautomeric forms **I** and **II** are equivalent and a symmetric double-well potential is anticipated for simultaneous transfer of the two protons:



In crystals, however, intermolecular interactions may destroy the potential symmetry (figure 1). During the past 50 years, two prototypical systems containing centrosymmetric dimers, namely benzoic acid ($\text{C}_6\text{H}_5\text{COOH}$) and potassium hydrogen carbonate (KHCO_3) have been thoroughly investigated with various techniques. However, as strange as it may seem, quite different pictures have emerged for proton dynamics and it is not yet clear whether the difference is real or not.

2.1. Benzoic acid

The infrared spectra at various temperatures (from room temperature to liquid helium) reveal the existence of two molecular forms which could correspond to tautomers [20]. The tautomerization reaction was further studied by NMR T_1 relaxation [17, 21–23], QENS [23, 24], optical spectroscopy techniques [25] and neutron diffraction [26].

Neutron diffraction performed on single crystals at various temperatures reveals that the O...O distance of 2.608 Å at 20 K increases to 2.629 Å at 175 K. The bridging protons are delocalized over two sites separated by 0.70 Å at 20 K (0.78 Å at 178 K). The population of the most stable form decreases from 0.87 (20 K) to 0.62 (175 K). The energy difference between the two tautomers is $\Delta H^0 = 40 \pm 3 \text{ cm}^{-1}$ ($0.12 \pm 0.01 \text{ kcal mol}^{-1}$).

The ‘phonon-assisted tunnelling’ model was proposed to interpret NMR and QENS data in terms of proton transfer rate [19]. The concerted transfer of the two protons is supposed to be governed by a double-well potential along a collective coordinate ξ (figure 1). This collective coordinate is rather complex. In addition to the proton positions, it involves the coordinates of the other atoms of the skeleton, as in the tautomerism process not only do the protons migrate but also the skeleton is

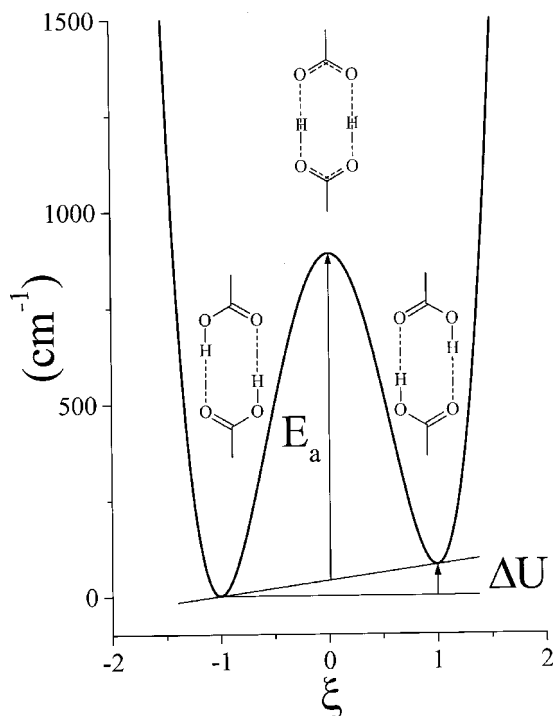


Figure 1. Schematic view of the tautomerism mechanism and effective potential for concerted proton transfer in benzoic acid. (After [19].)

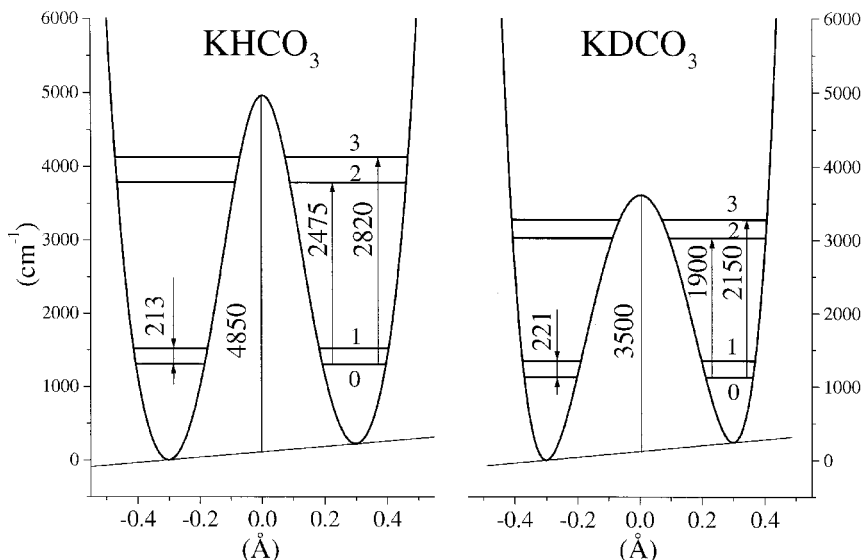


Figure 2. Potential functions for the proton and deuteron stretching modes in KHCO_3 and KDCO_3 . (After [31].)

rearranged. For example, the CO single and double bonds are interchanged and interatomic distances change correspondingly. The complexity of the reaction coordinate is such that it cannot be defined totally on the basis of experimental data. Modelling of the multidimensional potential surface is necessary [17, 22, 27]. However,

the reaction path is largely dependent on the quantum chemistry method and on the number of degrees of freedom under consideration. In addition, the break in the symmetry of the two wells due to the crystal field cannot be represented with an isolated dimer. Similarly, the asymmetry ΔU is modulated via linear coupling with acoustic modes: $\delta(\Delta U) = a \delta\rho(\mathbf{R})$. (a is a coupling constant and $\delta\rho(\mathbf{R})$ is the density fluctuation of the crystal, regarded as an elastic medium, at the position \mathbf{R} , which is the centre of symmetry of the dimer.) Because of this extreme complexity, the transfer rate between the two tautomers at thermal equilibrium is phenomenologically represented with thermally activated jumps over a barrier and tunnelling due to the delocalization of the wavefunction over the two wells. The estimated potential asymmetry of 57 cm^{-1} [23] is not too far from neutron diffraction results. The model-dependent barrier height is found to be in the range $400\text{--}500 \text{ cm}^{-1}$ ($1.2\text{--}1.5 \text{ kcal mol}^{-1}$) [17, 22–24].

2.2. Potassium hydrogen carbonate

In the potassium hydrogen carbonate (KHCO_3) crystal the hydrogen bond is slightly shorter than in benzoic acid. The O...O distance is 2.587 \AA , or 2.607 \AA for KDCO_3 . At 298 K, protons are disordered between two sites located at approximately $\pm 0.3 \text{ \AA}$ off centre from the hydrogen bond, with population ratio of about 1:4 [27]. Unfortunately, systematic neutron diffraction measurements at various temperatures are not available. In contrast with the benzoic acid crystal, only one NMR study on KDCO_3 has been reported [27] and we are not aware of any published QENS study.

Proton dynamics in the quantum regime has been thoroughly investigated with vibrational spectroscopy techniques [29–32]. Tunnelling for proton transfer is best observed for the stretching vibration along the reaction path. In infrared and Raman spectroscopy, this mode gives broad bands, with several submaxima between 1800 and 3500 cm^{-1} , compatible with quasisymmetric double-minimum potentials (figure 2) [31]. KHCO_3 was one of the very first examples where INS spectra have yielded a totally unforeseen picture for hydrogen bond dynamics [32]. First, the INS spectrum cannot be represented with conventional harmonic force fields and normal modes. The proton dynamics are almost totally decoupled from the heavy atoms. They are better represented with localized modes in a ‘fixed’ (laboratory) referential frame. From this standpoint, KHCO_3 can be regarded as a crystal of protons so weakly coupled to the surrounding atoms that the framework of carbonate and K^+ ions can be virtually ignored. Second, the potential barrier of 4850 cm^{-1} for KHCO_3 is about one order of magnitude greater than that obtained for benzoic acid. This value is imposed by the observed $\nu \text{ OH}$ frequency. In contrast with this, a weak barrier of about 500 cm^{-1} should be absolutely incompatible with the OH stretching frequency. Third, the ‘tunnelling’ transition for the quantum transfer of a single proton was observed at 216 cm^{-1} with the INS technique, very close to the value of 213 cm^{-1} proposed from the optical spectra. To our knowledge, this was the first observation ever reported of proton tunnelling for a hydrogen bond in the crystalline state. The band is surprisingly sharp (full width at half-maximum, about 10 cm^{-1}). This confirms that the proton transfer is largely decoupled from the heavy-atom dynamics, in line with the remainder of the spectrum. Therefore, the potential asymmetry is largely static in nature. Tunnelling transitions observed in various hydrogen bonds are quite similar [33].

The ‘phonon-assisted tunnelling’ model, which supposes a large modulation of the potential asymmetry via coupling with acoustic modes must be rejected. This model applied to NMR measurements on KDCO_3 [27] gives an activation energy of about 480 cm^{-1} , which is almost one order of magnitude smaller than the potential barrier

derived from vibrational spectroscopy (3500 cm^{-1} in figure 2). This difference is beyond experimental errors. On the other hand, NMR gives similar activation energies for KDCO_3 and benzoic acid, as anticipated from the similar strengths of their respective hydrogen bonds. It can be thus concluded that different activation energies for proton transfer are probed by different techniques. Unfortunately, tunnelling transitions for the deuterium bond are not easily observed with INS.

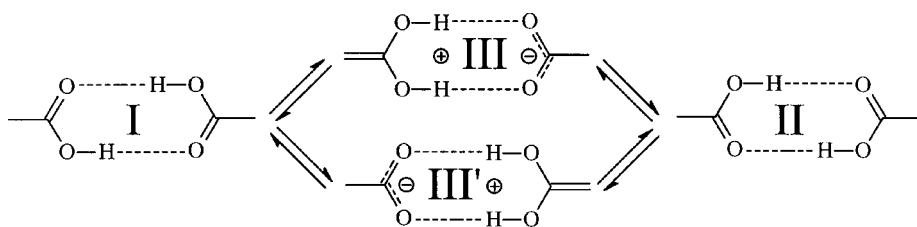
2.3. Future prospects

Great confusion will arise if the phonon-assisted tunnelling and the spectroscopic models are supposed to deal with the same physical reality. Indeed the apparent conflict is frustrating and we believe that a major goal for further experimental and theoretical works is to overcome this conflict.

We suspect that the concerted transfer of two protons within a dimer is not realistic because the two protons are not so strongly coupled as to form a quasirigid entity. Indeed, vibrational spectra show that the coupling is of the order of a few reciprocal centimetres and certainly negligible compared with the activation energy for proton transfer. Therefore, uncorrelated proton transfer is certainly a major contribution to the tautomerization rate.

The phonon-assisted tunnelling mechanism is largely phenomenological in nature. The function along the reaction coordinate ξ in figure 1 is not directly related to the proton motions. The positions of the minima do not correspond to real atomic locations and the effective mass is largely unknown. The tunnelling matrix element is an *ad hoc* parameter to account for deviation from the Arrhenius law. Therefore, the double-minimum function is not the potential determining the proton transfer dynamics. It is a phenomenological representation of the proton transfer rate.

As opposed to this, the potential functions in figure 2 are entirely determined from observed transitions and diffraction data. Quantum effects are fully accounted for. There is no evidence for significant coupling with other modes. The coordinate corresponds to the transfer of a single proton between **I** and **III** and **III'** along the stretching direction:



This could be an elementary step in the tautomerism process resulting from uncorrelated proton transfer. The potential asymmetry in figure 2, corresponds to the energy difference between **III** or **III'** and **I**. It has not the same physical meaning as the energy difference ΔU between **II** and **I** in figure 1. It is tempting to suppose that the real intermediate state in figure 1 should be **III** and **III'**. If this were the case, the activation energy E_a ($\approx 500\text{ cm}^{-1}$) should be compared with the potential asymmetry $\nu_{01} \approx 220\text{ cm}^{-1}$ in figure 2. The values are effectively of the same order of magnitude but further work is needed to account for the significant difference between them. Therefore, it is not yet clear whether potentials derived from spectroscopy can account for dynamics on the time scale of NMR and QENS. In future research, full

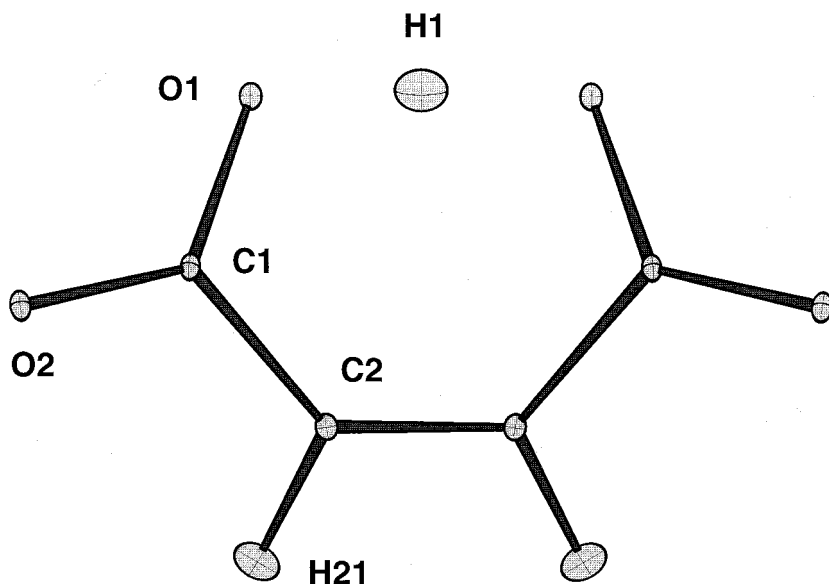


Figure 3. Schematic view of the monoanion of the maleic acid at 4 K. (After [37].)

measurements with all relevant techniques should be performed on the same systems. Most probably, more complex models must be sought for.

3. The quantum nature of strong symmetric hydrogen bonds

Strong (i.e. very short) symmetric hydrogen bonds have always fascinated chemists and physicists and FHF^- entities in the KHF_2 crystal are archetypal linear centrosymmetric three atom systems [1]. The $\text{F} \dots \text{F}$ distance is about 2.26 Å and the enthalpy of formation is suspected to be as large as about 58 kcal mol⁻¹. For pioneering spectroscopists the complexity of the infrared spectra was surprising [34]. For example, Ketelaar [3] in 1948 analysed the isomorphous RbHF_2 crystal and isotopic mixtures $\text{KHF}_2/\text{KDF}_2$ to conclude that the spectrum is due to virtually isolated FHF^- entities. Consequently, the great number of observed transitions was tentatively attributed to a double well potential. However, further neutron diffraction [35] and INS work [36] established that the potential has a single minimum and is virtually harmonic. The complexity of the infrared spectrum is due mainly to electrical anharmonicity. This is a further illustration of how difficult the interpretation of the infrared spectra of strong hydrogen bonds in solids can be.

The monoanion of maleic acid in the crystal of potassium hydrogen maleate is another classic example of a symmetric intramolecular hydrogen bond (figure 3). X-ray diffraction at room temperature shows that the $\text{O} \dots \text{H} \dots \text{O}$ bond is extremely short, with an $\text{O} \dots \text{O}$ length of about 2.44 Å, and symmetry considerations mean that the proton is located at the centre [38]. Experiments using several techniques are in general agreement that this strong hydrogen bond is, at least statistically, symmetrical [39]. Single-crystal neutron diffraction confirms that the proton of the hydrogen maleate ion remains centred at all temperatures from 4 K to 300 K and the $\text{O} \dots \text{O}$ distance remains virtually unchanged apart from a tiny expansion of 0.01 Å [37].

On the other hand, NMR studies in solution converge to the conclusion that hydrogen maleate and many other monoanions of diacids exist as pairs of asymmetric

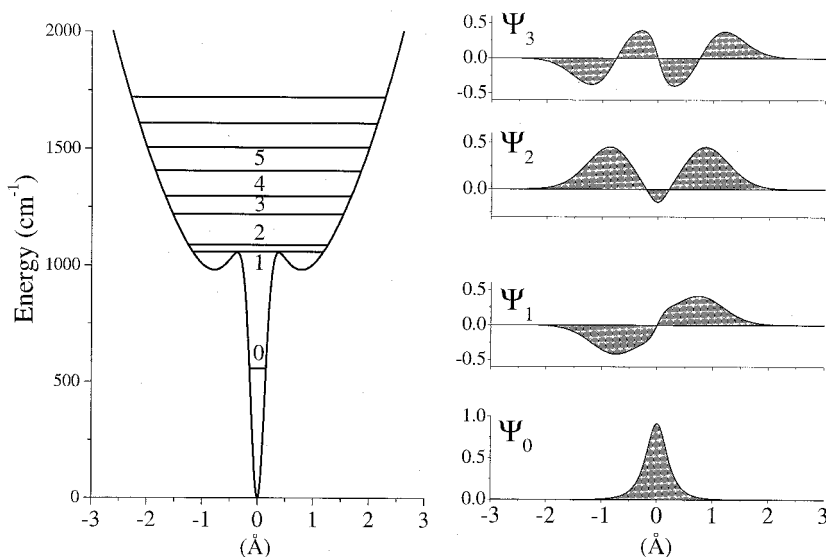
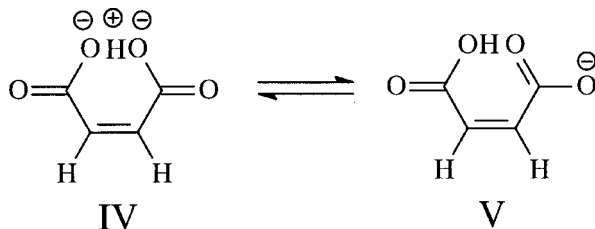


Figure 4. Potential function (left) and wavefunctions (right) for the proton stretching mode of the maleate monoanion at 20 K. (After [37].)

equilibrating tautomers within a double-well potential [12, 40]. This was claimed as ‘a remarkably simple counterexample to the prevailing hope that a crystal structure describes the solution structure’ [40].

INS spectra of powdered samples at 20 K are extremely complex but the assignment scheme could be established after examination of specifically deuterated samples and single crystals [37]. At least five transitions (between 500 and 1000 cm^{-1}) are due to the local dynamics of the proton-stretching mode. The potential presented in figure 4 was determined from the observed frequencies and their intensities. This potential is consistent with the symmetry-related selection rules in the infrared and with previously reported frequency shifts upon deuteration.

This potential does not fit the conventional single well anticipated for this hydrogen bond. It is a superposition of a central well, rather narrow, and a double well with minima located at approximately ± 0.8 Å off-centre. The energy gain upon hydrogen bond formation reaches a maximum when the proton is centred in the totally symmetric structure **IV**. Electrostatic interaction with the two negatively charged oxygen atoms can be as large as about 40 kcal mol^{-1} and vanishes rapidly for even small displacements of the proton away from its central position. This can be regarded as a consequence of the rearrangement of the electric charges as pictured schematically in :



Surprisingly, whereas the covalent OH bond in **V** is anticipated to be about 1 Å, the

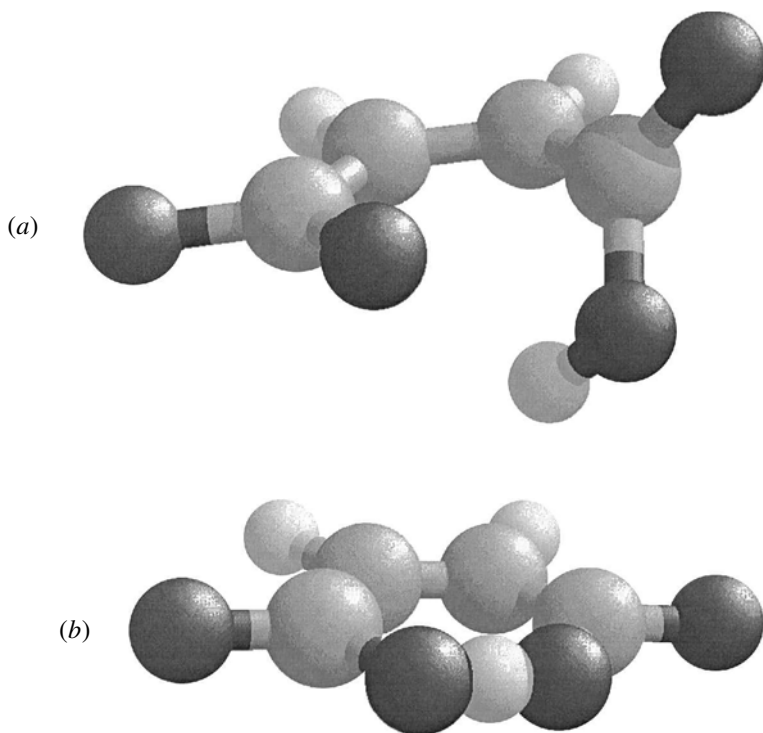


Figure 5. Schematic representation of the interconversion of the maleate ring: (a) opened structure in the excited states of the proton stretching mode; (b) planar structure in the ground state. (After [37].)

two upper minima seen in figure 4 correspond to extremely short OH distances, each of about 0.4 \AA . Minima occur at these positions because the oxygen atoms can move away from the midplane, by at least $\pm 0.8 \text{ \AA}$, so as to keep the OH distance within a reasonable range (figure 5). The triple-well potential is thus related to the interconversion of the maleate ring. The effective potential along the stretching coordinate presented in figure 4 is a snapshot of the proton dynamics before the rotation of the carboxylic group creates asymmetry in the potential surface.

The potential energy function of figure 4 gives a rather modest dissociation energy of about 500 cm^{-1} ($1.5 \text{ kcal mol}^{-1}$), which is probably a balance between the energy gain upon hydrogen bond formation and the energy cost to stabilize the strained planar *cis* configuration of the maleate ion (about 2500 cm^{-1}) [38]. This is a clear example of a very strong hydrogen bond that is nonetheless easily dissociated by thermal activation and probably solvent effects. The dissociation energy can be seen as a consequence of the quantum nature of the hydrogen bond. In the vibrational ground state the probability distribution of the proton (as given by the square of the wavefunction Ψ_0^2 in figure 4) is well localized at the centre. In contrast with this, the probability distribution for excited vibrational states (Ψ_n^2 in figure 4) is largely localized off centre. Then, only V is possible and the hydrogen bond is broken. In other words, the proton ground state is ‘hydrogen bonding’ while excited states are ‘hydrogen antibonding’.

4. Conclusion

The examples presented above illustrate the continuity of research on hydrogen bonding. The main intuition that guided the pioneering work has been totally confirmed. Hydrogen bonding is of primary importance in many scientific fields and is essentially electrostatic in nature. However, the prevailing hope that hydrogen bonds could be represented with rather simple semiempirical potentials and valence bond theory belongs to the past. Quantum effects related to the light mass of the hydrogen atom and to the complex nature of the potential surface were largely overlooked in early works. Nowadays, quantum effects are at the forefront of research and generate dramatically complex views of hydrogen bonding. Modelling, even based on the most advanced quantum-chemical methods, is still very far from being satisfactory, in spite of increasing computer power. Clearly, it is not yet possible to put together measurements performed with different techniques and theoretical models. Co-operative research involving expertise in many complementary disciplines is a key for further developments. Given the great importance of hydrogen bonds, progress in understanding these interactions provides a better understanding of complex phenomena of strategic interest for solid-state and material science, chemical reactivity and biological processes.

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