This article was downloaded by: [Tomsk State University of Control Systems and Radio]
On: 23 February 2013, At: 07:53
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

# The Theory of Proton Transfer in Hydrogen Bonded Solids

J. Amran Sussmann [a]

[a] Theoretical Physics Department, Israel Atomic Energy Commission Soreq Nuclear Research Centre, Yavne, Israel

Version of record first published: 28 Mar 2007.

To cite this article: J. Amran Sussmann (1972): The Theory of Proton Transfer in Hydrogen Bonded Solids, Molecular Crystals and Liquid Crystals, 18:1, 39-53

To link to this article: http://dx.doi.org/10.1080/15421407208083843

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.tandfonline.com/page/terms-and-conditions

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae, and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand, or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

*Molecular Crystals and Liquid Crystals.* 1972. Vol. 18, pp. 39–53
Copyright © 1972 Gordon and Breach Science Publishers
Printed in Great Britain

# The Theory of Proton Transfer in Hydrogen Bonded Solids†

J. AMRAN SUSSMANN

Theoretical Physics Department
Israel Atomic Energy Commission
Soreq Nuclear Research Centre
Yavne, Israel

*Received May* 5, 1971; *in revised form November* 22, 1971

**Abstract**—The quantum mechanical theory of ionic jumps is applied to the transfer of the proton between the potential minima of the hydrogen bond. Expressions for the phonon induced processes are given and extended to the photon induced ones. The effect of lattice accommodation is discussed. The available experimental data is reviewed in the light of the present theory.

**Résumé**—Nous appliquons dans cet article la théorie quantique de sauts atomiques au problème du déplacement du proton entre les deux minimum de potentiel de la liaison hydrogène. Nous donnons les expressions pour les procès induits par des phonons, aussi bien que pour ceux induits par des photons. Les effets de l'accommodation du réseau sont analysés. Les résultats expérimentaux disponibles sont revues, en face de la théorie ici présentée.

## 1. Introduction

The transfer of proton localization in the double well potential of the hydrogen bond is the direct cause of change in electric polarization in H-bonded ferroelectrics, and of loss of information in biological code carrying systems like the DNA molecule. It is also an essential step in the conductivity mechanism of certain protonic conductors as ice and in the change of optical absorption spectrum of photo- and thermochromic materials. This localization transfer will be analysed here along the lines of the quantum mechanical diffusion theory. It will be assumed that stationary localized states exist in both wells and that transitions between them are induced by interaction with either the phonon gas of the system or with photons incident on it from outside.

---

† Presented at the Second International Symposium on Organic Solid State Chemistry, Rehovolh, Israel, 1970.

Downloaded by [Tomsk State University of Control Systems and Radio] at 07:53 23 February 2013

Downloaded by [Tomsk State University of Control Systems and Radio] at 07:53 23 February 2013

## 2. The Static Potential

The hydrogen bond consists of a proton binding two negative ions. Only for very short bonds does the proton have a central localization. In the other cases it is asymmetrically placed as can be seen from X-ray and neutron diffraction experiments.(1) The potential felt by the proton is thus necessarily asymmetric and it is assumed to have two unequal minima. There is little straightforward experimental evidence for the second well, although its existence is necessary for the understanding of phenomena like the DC conductivity of ice. The most striking experiment in this direction is that of Plesser and Stiller(2) who did inelastic neutron scattering on paraelectric $KH_2PO_4$. Theoretical potential calculations have been performed for some particular situations, for instance, by Ladik(3) and Rein and Harris.(4) This and other similar work which has been reviewed by Bratoz,(5) yield potentials with two minima. The potential may become symmetrical, conserving the two minima if the configuration of the atom groups bonded by the proton is symmetrical. Even in such a situation we shall expect proton states localized in one well or the other because the symmetry is never perfect.(6) De-localization will only result if the transparency of the barrier becomes very high, a situation which can be expected for short bonds.

## 3. The Dynamic Potential

The potential acting on a proton in a hydrogen bond has an important time dependent part, which will be responsible for inducing transitions between the eigenstates of the static part of the potential. This time dependent potential is a consequence of the motion of the ions and electrons in the crystal. As we are dealing with non metals, the electrons are not free and thus they contribute to the time dependent potential only through screening of the influence of the ions. In harmonic crystals, the motions of the ions can be described by phonons, and then the system is usually described as a particle in a static (average) potential and coupled to the phonons. In our case we have a strongly anharmonic element which is the hydrogen bond itself and thus the coupling between different protons cannot be described *a priori* by a particle–phonon type interaction only. We shall therefore discuss this interaction separately.

## 4. Interaction between hydrogen bonds

The matrix elements of the interaction Hamiltonian between bond I and II are

$$H_{\mathrm{I}j,\mathrm{I}k,\mathrm{II}l,\mathrm{II}m} = \langle \psi_j^{\mathrm{I}}\psi_l^{\mathrm{II}} \,|\, V_{\mathrm{int}} \,|\, \psi_k^{\mathrm{I}}\psi_m^{\mathrm{II}} \rangle \tag{1}$$

where $\psi$ are the wave functions of the proton in the non-interacting approximation. These matrix elements can be divided in two groups, the first lying on the diagonal $j = k$; $l = m$. These are the larger terms, the other ones being much smaller because of the small overlap between localized states (in the case of $j$ and $k$ belonging to different well) or to the decrease of $\langle \psi_j \,| l/r \,|\, \psi_k \rangle$ with growing $|j - k|$ for $j$ and $k$ in the same well. The diagonal terms can be tentatively written as

$$H_{\mathrm{I}_j\,\mathrm{I}_j\,\mathrm{II}_l\,\mathrm{II}_l} = H^{(l)}_{\mathrm{I}_{jj}} + H^{(l)}_{\mathrm{II}_{ll}} + H^{(l)}_{\mathrm{I}_j\mathrm{II}_l} \tag{2}$$

where the first two terms do not contribute to the coupling, each term being only dependent on one bond. Only the third term $H^{(l)}_{\mathrm{I}_j\mathrm{II}_l}$ does contribute to the interbond coupling. It will be responsible for the static coupling affecting the localization ordering of the hydrogen bonds. The dynamic coupling which leads to excitations in the ordered localization configurations will be caused by the off diagonal matrix elements, where the pairs of states $j$, $k$ and $l$, $m$ are localized in different wells. Such elementary excitations relative to the ordered localization configuration which may be called *bondions* were first discussed by de Gennes(7) and then by Kobayashi(8) and others.(9) Pelach(10) suggested a mechanism by which the static coupling can lead to a dynamical process of a non-coherent nature. A localization transfer in one bond changes the potential at neighbouring bonds where in consequence localization transfer may occur. Thus an initial perturbation of an ordered system expands or propagates. The interbond coupling acts through changing the potential felt by the proton but the actual localization transfer is a thermally induced process.

In this paper we shall be concerned with hydrogen bonded systems where hydrogen-bond interaction, if there is any, is only static. Such

Downloaded by [Tomsk State University of Control Systems and Radio] at 07:53 23 February 2013

Downloaded by [Tomsk State University of Control Systems and Radio] at 07:53 23 February 2013

situation may be the result of one or a combination of the following causes: large interbond distances, strong electronic screening and disordered bond geometry.

## 5. Phonon–Bond Interaction

Having taken care of the anharmonic part of the lattice bond interaction we are left with the harmonic part which can be described as caused by the lattice phonons.

The acoustic phonons produce two types of effects: they displace the whole bond rigidly which can be called the " shaking " interaction and they distort the configuration of the bond, an effect which can be described by the local strain. Because of the geometry of the bond sheer strain can be neglected. It can be seen from the phenomenological potential surfaces proposed by Reid(11) that a change in bond length causes a change in the height of the barrier, in the distance between the minima and in the energy difference between the minima. Numerical computations have been performed by Fischer, Hofacker and Sabin.(12) If we take the top of the barrier (different from the mid point of the bond) as origin, we get both symmetrical and antisymmetrical perturbation terms. The first may be termed barrier modulation and the second well depth modulation.

## 6. Phonon Induced Localization Transfer Mechanisms

We shall be interested in the problem of the particle transfer from a localized state on one side of the potential barrier to a localized state on the other side of the potential barrier. In addition to the static localization, which means a localization which is characteristic of the eigenfunctions for a given static potential, there is a different type of localization, a dynamical one, which results from the way in which the system is " prepared ". If we excite a particle under certain conditions, which will be stated later, the excitation of the particle leaves it not in a given eigenstate but in a linear combination of eigenstates, which is a wave packet and thus time-dependent. This is not a stationary state and will decay in time. This time evolution of the wave packet has been widely used in an attempt to describe a tunneling relaxation process. Such a description is necessarily incorrect because it does not contain any cause for randomization. It is based on a symmetrical double well potential, where one takes a linear combination of a symmetrical and an antisymmetrical solution, which is thus localized at $t = 0$ on one side.

From the symmetrical and antisymmetrical wave functions

$$\psi_s = \frac{1}{\sqrt{2}}(\psi_r + \psi_l)e^{-i(E_0-\delta)t/\hbar}$$

$$\psi_a = \frac{1}{\sqrt{2}}(\psi_r - \psi_l)e^{-i(E_0+\delta)t/\hbar} \tag{3}$$

we get the oscillating wave packet

$$\frac{1}{\sqrt{2}}(\psi_s + \psi_a) = \psi_r \cos\frac{\delta t}{\hbar} + i\psi_l \sin\frac{\delta t}{\hbar} \tag{4}$$

This wave packet oscillates back and forth, and therefore cannot lead to any type of relaxation. The time needed for the return of the particle is given by the energy splitting between the symmetrical and antisymmetrical states. The half period $h/2\delta$ has been interpreted as a relaxation time.

The reason why this approach has been accepted for so long as a description of a relaxation process lies in its analogy with the $\alpha$ decay of nucleae. There we really have a relaxation. The basic difference is that in the $\alpha$-decay an infinite volume is available for the particle outside the potential well, and therefore there is on the outside a continuum of states. In consequence of this, the time for the return of the particle into the well becomes infinite. A similar situation arises in the case of radiationless decay of an excited electronic state.(13) Again, what happens is that we have a nearly continuous density of states on the other side of the barrier, which leads to such a situation that the return time of the particle to its original state becomes long compared to the time necessary for other processes to take place. We can consider, therefore, that the particle is gone and does not return. This is not the case in our system, where we have a discrete set of levels, so that the particle, being in a dynamically localized state, which starts from one side, is able to go over and to come back again in a very short time.

After what was said above, it is clear that no proton transfer may occur in a purely static potential. We have to include therefore

Downloaded by [Tomsk State University of Control Systems and Radio] at 07:53 23 February 2013

Downloaded by [Tomsk State University of Control Systems and Radio] at 07:53 23 February 2013

time dependent perturbation into our picture. Two groups of such perturbations have to be considered: one being intrinsic to the lattice and in thermodynamical equilibrium therewith, and are typified by phonons, and the other coming from the exterior of the lattice and are typified by photons.

We shall consider first the phonon induced transitions. The classical Arrhenius type expression for the transition probability $W_{rl}$ from right to left is:

$$W_{rl} = \nu e^{-V/kT} \tag{5}$$

which contains only parameters characteristic of the static potential. As it will be shown by quantum mechanical considerations it is applicable only under specific conditions. Outside its region of applicability it must be substituted by expressions of a different kind.

We shall describe the different transition processes and give the expressions for the transition probabilities when the responsible agents are phonons. We shall start with the simplest process, which happens to be important at very low temperatures.

Let us consider a weakly asymmetric double well potential. The ground state of the system will be localized in the lowest well (let us assume it is the left one) and let us further assume that the first excited state is localized in the other well. If the energy splitting $\Delta$ between them is smaller than the maximum phonon energy $k\theta$ available, a transition may be induced by a single phonon absorption (respectively emission). The transition probability for such a process assuming a Debye spectrum is given by$^{(13)}$

$$W_{lr} = C \coth \Delta/2kT \tag{6}$$

with

$$C = \begin{cases} \dfrac{\beta^2\lambda^2\Delta^3}{2\pi\hbar^4\rho c^5} & \text{for barrier modulation} \\[2ex] \dfrac{2\beta^2\lambda^2\Delta\,\delta^2}{\pi\hbar^4\rho c^5} & \text{for well depth modulation} \end{cases} \tag{7}$$

where $\beta$ is the coupling constant between the elastic strain at the site of the bond and the change in the potential$^{(6,14)}$ it induces, $\lambda$ is the overlap integral between $\psi_r$ and $\psi_l$, the wave functions localized at right and left, $\rho$ is the density of the crystal and $c$ the sound velocity. The above expressions (6) and (7) have been experimentally confirmed and the constants involved can be obtained from independent experimental evidence.(15,16) This process is called single phonon induced tunneling. If $\Delta > k\theta$, more than one phonon is necessary for the transition and this expression (6) is no longer applicable. This will be especially the case when the asymmetry of the double well potential is considerable. Many phonons will now have to be involved in the excitation process. Expressions for such a process will be given later.

The process which comes next in order of increasing complexity is that of a transition, accompanied by an inelastic scattering of one phonon. It leads to a transition probability whose temperature dependence is $T^7$ for $T < \theta$ and $T^2$ for $T > \theta$. The range of temperature where this process takes over from the single phonon process will depend on the details of the model.(6) Expressions for many phonon induced tunneling have been recently obtained by Pirc and Gosar,(17) and Flynn and Stoneham.(18)

Pirc and Gosar used a polaron-like approach and obtained the following expression in the absence of lattice accommodation, i.e. when the potential is independent of the localization of the particle

$$W = \frac{6T\Gamma^2}{\pi\hbar k T_\alpha^{\,2}} \exp[-2J - T^2/T_\alpha^{\,2}] \frac{\Delta U/kT}{\exp(\Delta U/kT) - 1} \cdot \left\{1 + \sum_{n=0}^{\infty} \frac{(12T^2/T_\alpha^{\,2})^n}{(2n+1)!(n+1)!} \prod_{m=1}^{n} \left[\left(\frac{\Delta U}{2\pi kT}\right)^2 + m^2\right]\right\} \tag{8}$$

Flynn and Stoneham obtained expressions for multi-phonon induced tunneling in the limit of very large numbers of phonons and obtained an expression of the form

$$W = \frac{1}{4h} \left| J_{\text{lim}} \right|^2 \frac{1}{\sqrt{E_{ac}}} \exp(-E_{ac}/kT) \tag{9}$$

where $E_{ac}$ is the accommodation energy of the lattice, not the potential barrier height. Consider now a process of excitation which involves a very large number of phonons. One can show (14,19) that the general form of $W_{li}$ is given by:

$$W_{li} = \nu_0 \mathrm{e}^{-V/kT} \qquad \text{for } T < \theta \tag{10}$$

$$W_{li} = \nu_0 \left(\frac{T}{\theta}\right)^{V/k\theta} \mathrm{e}^{-V/2kT} \qquad \text{for } T > \theta \tag{11}$$

Downloaded by [Tomsk State University of Control Systems and Radio] at 07:53 23 February 2013

Downloaded by [Tomsk State University of Control Systems and Radio] at 07:53 23 February 2013

where $\theta$ is the Debye temperature of the lattice, $V$ is the energy of the excited state and $\nu_0$ is a frequency which depends very strongly on a coupling between the phonon and the proton. Although expression (10) resembles the classical expression, it is fundamentally different from it because $\nu_0$ is not a function of the static potential alone. Expression (11) on the other hand looks very different from the classical dependence, but when plotted in the usual way as $\log W$ versus $1/T$ it gives a nearly linear plot with a small upward curvature. If we approximate it by an Arrhenius-like plot around $T = T_0$

$$W = \nu_{ef} e^{-V_{ef}/kT} \tag{12}$$

we get

$$\nu_{ef} = \nu_0 \left(\frac{T}{\theta}\right)^{V/k\theta} e^{-V/kT_0} \tag{13}$$

$$V_{ef} = V(\tfrac{1}{2} + T_0/\theta) \tag{14}$$

It should be noticed that even when $\nu_0 < 10^{13}$ (which is the normal situation, as will be shown later) $\nu_{ef}$ may be many orders of magnitude larger than the classical value of $10^{13}$.

The deviation of this expression from the exact exponential temperature dependence can explain the general behaviour of the anomalous diffusion in BCC mutals(19) without recurring to complex diffusion mechanisms. Furthermore expression (13) presents a way to explain both the anomalously small and anomalously large pre-exponential factors which have been found experimentally and which can in no way be explained by the classical model. This process is active when the double well potential is strongly asymmetric as well as in the localization transfer process which we are going to consider next.

Another possible transition process which has to be considered is that of excitation of the proton to an intermediate state lying above both the localized initial and final states. Due to the form of the proton-felt potential such an intermediate level will be delocalized to a smaller or larger extent, whether lying above or below the top of the barrier. Thus, after excitation, the particle will decay either back to the state localized at the left, or to the state localized at the right. The probabilities of the two decay processes will be of the same order of magnitude whenever $\Delta/kT$ is not very large. Thus the transition probability can be written approximately as

$$W_{lr} = W_{li} \frac{W_{ir}}{W_{ir} + W_{il}} \tag{15}$$

and if we assume as we did before that the fraction in the above expression is of the order of magnitude of 1 and insensitive to the temperature, the transition probability will be mainly determined by the form of the excitation probability $W_{li}$. Whenever this excitation involves the absorption of many phonons we have to use expressions (10) and (11) for both $W_{li}$ and $W_{ri}$ leading to

$$W_{lr} = \frac{\nu_{li}\nu_{ri}}{\nu_{li} + \nu_{ri}} \, \mathrm{e}^{-(E_i - E_e)/kT} \tag{16}$$

for $T < \theta$ and

$$W_{lr} = \frac{\nu_{li}\nu_{ri}}{\nu_{li}\left(\frac{T}{\theta}\right)^{\Delta V/2k\theta} \mathrm{e}^{+\Delta V/2kT} + \nu_{ri}\left(\frac{T}{\theta}\right)^{-\Delta V/2k\theta} \mathrm{e}^{-\Delta V/2kT}} \cdot \left(\frac{T}{\theta}\right)^{V/2kT} \mathrm{e}^{-(V + \Delta V/2)/kT} \tag{17}$$

for $T > \theta$ where

$$V = \frac{2E_i - E_l - E_r}{2} \quad \text{and} \quad \Delta V = \frac{E_r - E_l}{2}$$

The third class of transition processes is the most complicated one from the quantum mechanical point of view—but it is the one which leads to the classical expression. It is called the tunneling bottleneck process, because a tunneling-like behaviour is the rate determining step in it.

If two or more levels are broadened to such an extent that the line width $\Gamma$ is larger that the splitting $\Delta$ between them, no transition is possible to one of them separately (unless when selection rules exclude one of them). Any transition from the ground state goes into a phase-correlated linear combination of these wave functions. Such a linear combination of states of different energy is a wave packet which necessarily changes in time. The change in time has three causes: (a) decay of the wave packet which has a half life of

Downloaded by [Tomsk State University of Control Systems and Radio] at 07:53 23 February 2013

Downloaded by [Tomsk State University of Control Systems and Radio] at 07:53 23 February 2013

$h/\Gamma$, (b) its time evolution as a wave packet, which in our case leads to back and forth motion between the two wells with a frequency of $\Delta/h$ where $\Delta$ is the typical splitting between the levels which make up the wave packet, and (c) the loss of phase correlation between the components of the wave packet due to transitions between the components themselves. The description of this evolution is simple when only two levels (one symmetric and one antisymmetric) are involved. It is then clear that the excitation from a ground state localized say in the left well, will go to a wave packet localized at time $t = 0$ on the left. The particle then may decay back to the ground state within a time $h/\Gamma$ or " tunnel " over to the right within a time $h/\Delta$. We put the word tunneling between quotation marks because this " tunneling " may occur well above the potential barrier and not necessarily below its top. As we had to assume that $\Gamma > \Delta$, the probability of falling down is much larger than that for going over to the other side, and thus we may write in a crude approximation

$$W_{lr} = W_{li} \frac{\Delta/h}{W_{il} + \Delta/h} \tag{19}$$

which leads, with

$$\Delta \ll \Gamma = hW_{il} = hW_{li} e^{V/kT} \tag{20}$$

to

$$W_{lr} \frac{1}{2\pi} \frac{\Delta}{\hbar} e^{-V/kT} \tag{21}$$

which is equivalent to the classical expression (5). The derivation presented here is not an exact one but the exact treatment$^{(19)}$ leads to the similar expression

$$W_{lr} = 0.225 \frac{\Delta}{\hbar} e^{-V/kT} \tag{22}$$

in the meaningful region of $0.5 < \Delta/\Gamma < 2$.

In the temperature region where the tunneling bottleneck process takes over, the $\log W$ versus $1/T$ has a downward curvature. The justification of the name comes from the fact that were it not for the interference between the two transition paths, each through a different intermediate state, one half of the excited particles would fall down on the right hand side, leading to a much larger transition probability.

## 7. Photon Induced Transitions

In studying photon induced transitions, the same three classes of processes have to be considered. The mechanism of the processes will not be altered but the temperature dependence will be basically different as the incident photon density is independent of the temperature of the lattice. The single photon induced proton transition, which is an electric analogue to the spin magnetic resonance has already been described previously.(20) Although it has not yet been observed for hydrogen bonds, it is well known in the case of the electric resonance of $OH^-$ centre in alkali halides.(21) It has been shown that the asymmetry of the potential well must be necessarily small in order not to decrease the transition matrix element too drastically. Such transitions are thus to be expected for nearly symmetrical hydrogen bonds and resonance is expected to fall between the microwave and the infrared region of the spectrum. Raman processes have not been considered.

In the photon induced Orbach type process the photon leads to excitation to an intermediate non-localized state, from where the particle falls down either to the left or to the right due to interaction with the phonons. If the potential is not too asymmetric, so that the two downfall probabilities are comparable, the transition probability will be given by half the photon induced excitation probability. In contrast to the previous paragraph, we do not have to consider many photon processes as no cut-off exists for photon energy. If the wave function on right and left are of similar character and the intermediate excited state is either symmetrical or antisymmetrical, we get for the case of an asymmetrical potential well

$$W_{lr(\text{photon})} = W_{ll(\text{photon})} \frac{1}{1+\exp(\Delta V/kT)} \tag{23}$$

It is in the tunneling bottleneck controlled process that electromagnetic radiation can lead to a new phenomenon. Narrow excited states can be broadened if the resonant electromagnetic field is intense enough. Thus, a process which for weak illuminations is of

Downloaded by [Tomsk State University of Control Systems and Radio] at 07:53 23 February 2013

Downloaded by [Tomsk State University of Control Systems and Radio] at 07:53 23 February 2013

the Orbach type can change over to the tunneling bottleneck type, by increasing the illumination intensity, leading first to a limitation of the transition probability and if the intensity grows further, it leads to a reduction of the transition probability.

## 8. The Accommodation of the Potential

In the previous sections we assumed that the static potential felt by the proton is constant. This is not always the case. Three cases have to be considered depending on whether the potential changes before, after or during the proton transfer process.

A change in potential prior to the proton transfer has to be a result of external factors as for instance an electronic excitation. Such changes of potential have been calculated by Ladik.(12) If the change is a sudden one (as compared with photon transfer times) the proton may find itself in an excited state and even on the wrong side of the potential barrier, and subsequently the system must decay into the ground state.

In the two other cases no external causes exist for the change of the potential. In order to understand the phenomena, we have to go back to the Born–Oppenheimer-like approximation which we assumed at the beginning. We separated the motion of the proton (in analogy to that of the electrons) from that of the heavy ions of the lattice. An equilibrium configuration for the cores is thus obtained which in its turn determines the potential, for the proton (electrons). If a different state—say, an excited one—is assumed for the proton (electrons), a different equilibrium configuration results for the lattice and therefore a different potential for the proton. This leads, in molecular physics, to the Franck–Condon behaviour. In our case, it means that a different potential for the proton should be computed for each protonic state—self-consistently. We have to consider both the magnitude of the change of potential and the time necessary for the rearrangement of lattice which produces it. Thus relaxation of the lattice, which can be more properly designated by the new term *accommodation*, is an irreversible process whereby energy is dissipated into the phonon heat-bath of the lattice. We shall designate its relaxation time by the name of accommodation time. If the accommodation time is long compared to the proton transfer time, the proton transition will occur in a practically constant potential just as we described it in the previous sections. Only after the proton transfer will the accommodation occur.

In the third case two possibilities must be considered. If the accommodation time is much shorter than the proton transfer time (for a given situation) the potential accommodates immediately and therefore we have to use a potential calculated by an adiabatic approximation, appropriate to that transition. This potential can be considered as constant during the proton transfer. No accommodation will occur after the transfer. This seems to be the case in nearly all normal problems of diffusion. If the accommodation and transfer times are comparable, a new and different treatment is required. It can be shown for instance, that an effective mass for the proton has to be used which may be very different from its normal mass.

One special case of accommodation has recently been worked out by Cohan(22) who considered an accomodating asymmetric double well potential, where the asymmetry changes with time. He showed that the accommodation increases the transition probability.

## 9. Available Experimental Results

Unfortunately the experimental data available on the localization transfer of protons in hydrogen bonds is very poor. Schmidt and Uehling(23) have shown that in the paraelectric phase of $KD_2PO_4$ there is a process of relaxation due to random motion of protons along the bond. The relaxation time of this process has been obtained to be

$$W \cong 10^{13} \exp(-0.078\,\mathrm{eV}/kT)$$

and it can be interpreted as a proton localization transfer process in a slightly asymmetric double well potential. The asymmetry of the potential even above the Curie temperature seems to be confirmed by neutron scattering experiments of Plesser and Stiller.(2) Another explanation cannot be disconsidered where the hydrogen bond is assumed to be on the average symmetrical (in the paraelectric phase) but undergoing oscillations due to coupling with the $PO_4$ tetrahedra.(24) In this picture the relaxation process above could be identified as a transition between the symmetrical and anti-

Downloaded by [Tomsk State University of Control Systems and Radio] at 07:53 23 February 2013

Downloaded by [Tomsk State University of Control Systems and Radio] at 07:53 23 February 2013

symmetrical state. Independently of the nature of the initial and final state, the process under consideration is most probably a multiphonon induced excitation process.

Another system presenting proton transfer in hydrogen bond is ice. The rate determining process in DC conductivity is a localization transfer in a symmetrical double well potential. Experiments yield that the mobility has zero activation energy and a very large isotope effect. This problem has been discussed in detail previously(6) and it was shown that we are dealing with a tunneling process involving a very small number of phonons. Proton conductance in water has been discussed previously(25) and shown to involve proton localization transfer. The quantitative analysis should be reviewed in the light of the present theory.

There is still further experimental evidence but it is of an indirect nature. It refers to proton jumps in double well potentials which are *not* hydrogen bonds. Under this heading we could mention the orientational relaxation of $OH^-$ substitutional centers in alkali halides, inter bond proton jumps in ice and in $KH_2PO_4$ as well as the family of protonic conductors as for instance imidazol and borax(26) and finally tautomeric conversions in biological molecules.

Photochromic and thermochromic behaviour in general involves proton localization transfer,(27) if not basically, then as a stabilization process for a more extensive change in molecular configuration. No measurements are however available which can be directly related to the rate of localization transfer of the proton. It is hoped that the existence of a detailed theory will stimulate the search for more extensive parallel results.

## REFERENCES

1. Hamilton, W. C. and Ibers, J. A., *Hydrogen Bonding in Solids*, Benjamin Inc., 1968.
2. Plesser, Th. and Stiller, H., *Solid State Comm.* **7**, 323 (1969).
3. Ladik, J., Quantum Chemistry Group, Uppsala, Preprint QB 8 (1963).
4. Rein, R. and Harris, F. E., *J. Chem. Phys.* **41**, 3393 (1964).
5. Bratoz, S., in *Advances in Quantum Chemistry* **3**, 209 (1967).
6. Sussmann, J. Amran, *Phys. Kond. Mat.* **2**, 146 (1964).
7. de Gennes, P. G., *Solid State Comm.* **1**, 132 (1963).
8. Kobayashi, K., *Phys. Letters* **26A**, 55 (1967); *J. Phys. Soc. Japan* **24**, 497 (1968); *J. Phys. Soc. Japan* **25**, 1147 (1968).

9. Brout, R., Muller, K. A. and Thomas, H., *Solid State Comm.* **4,** 507 (1966). Villain, J. and Stamenkovic, S., *Phys. Stat. Sol.* **15,** 585 (1966).
10. Cinader, G., Zamir, D. and Pelach, I., *Solid State Comm.* **6,** 435 (1968).
11. Reid, C., *J. Chem. Phys.* **30,** 182 (1959).
12. Fischer, S. F., Hofacker, G. L. and Sabin, J. R., *Phys. Kondens. Materie* **8,** 268 (1969).
13. Englman, R. and Jortner, J., Mol. Phys. **18,** 145 (1970).
14. Sussmann, J. Amran, *J. Phys. Chem. Sol.* **28,** 1643 (1967).
15. Silsbee, R., *J. Phys. Chem. Sol.* **28,** 2525 (1967).
16. Pfister, G. and Kanzig, W., *Phys. Kond. Mater.* **10,** 231 (1969).
17. Pirc, R. and Gosar, P., *Proceedings of the XIVth Colloque Ampere* 1966, Ed. R. Blinc, North Holland, Amsterdam, p. 636 (1967).
18. Flynn, C. P. and Stoneham, A. M., *Phys. Rev.* **1B,** 3966 (1970).
19. Sussmann, J. Amran, *Annales de Physique* **6,** 135 (1971).
20. Sussmann, J. Amran, in *Physics of Ice*, Plenum Press, 1969, p. 541.
21. Estle, T. L., *Phys. Rev.* **176,** 1056 (1968).
22. Cohan, N. V., *Phys. Stat. Sol.* (*b*) **45,** 139 (1971).
23. Schmidt, V. H. and Uehling, E. A., *Phys. Rev.* **126,** 447 (1962).
24. Sussmann, J. Amran, to be published.
25. Conway, B. G., Bockris, J. O'M. and Linton, Hedda, *J. Chem. Phys.* **24,** 834 (1956).
26. Giesekhe, E. W. and Glasser, L., *J. Phys. Chem.* **71,** 2573 (1967). Chan-Henry, R. and Glasser, L., to be published.
27. Cohen, M. D. and Flavian, S., *J. of the Chem. Soc.*, pp. 317, 321 (1967).

Downloaded by [Tomsk State University of Control Systems and Radio] at 07:53 23 February 2013