

Influence of the Environment on Proton Transfer in Symmetrical Hydrogen Bonds

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Symmetrical hydrogen bonds with a double minimum potential well or a largely flat potential are extremely easily polarisable, which leads to strong mutual interactions of such bonds and to interactions of the bonds with their environment. Particularly in the range of the rearrangement frequencies of the medium, the interactions depend to a marked extent on the fluctuation frequencies of the electromagnetic field and thus on the tunnelling frequency of the proton in the hydrogen bond. On the other hand, the tunnelling frequency decreases due to the interactions. The correlation of the proton movements in two adjacent symmetrical hydrogen bonds and the resulting decrease of the tunnelling frequency is studied for the lowest group of levels. In addition, the decrease of the tunnelling frequency due to the effect of ion and dipole fields is calculated. In the tunnelling approximation the result depends in both cases on simple dimensionless parameters and indicates delay of the proton transfer in the bonds, but not complete hindrance. The lingering times in the potential wells are simply connected in both cases with the transition frequencies of the systems.

I. Introduction

A continuous absorption is observed in the IR spectra in numerous aqueous and nonaqueous acid and base solutions¹ (further references in² and³) caused by protons or defect protons tunnelling in a double minimum potential well in hydrogen bonds $(\text{BH}\cdots\text{B})^+$, resp. $(\text{BH}\cdots\text{B})^-$. If the pKa value of the acceptor groups becomes low, as with the excess proton in H_5O_2^+ , the potential barrier may decrease so markedly that the lowest energy level already occurs above the barrier, so that one can no longer speak of tunnelling. But even then these systems have an extremely high polarisability (about 10^{-22} cm^3)^{3,4}, which results in three types of interaction: (a) a strong induced dipole interaction between the hydrogen bonds and the ions and dipole fields of the molecules of the medium⁵, (b) proton dispersion forces between the bonds⁶, and (c) coupling of the proton transitions in these bonds with intermolecular vibrations³. The dielectric constant ϵ of the medium surrounding the bonds is of significance for the strength of these interactions⁷. ϵ depends on the frequency at which the electromagnetic field transmitting the interactions fluctuates.

For the proton dispersion forces the dielectric constant is decisive at the frequency at which the protons

move in the hydrogen bonds. The frequency cannot simply be considered as equal to the tunnelling frequency of the protons in the isolated bonds, because the tunnelling frequency depends on the strength of the proton dispersion interaction. On the other hand, the proton dispersion forces decrease markedly when the tunnelling frequency lies in the range of the rearrangement frequencies of the molecules of the surrounding medium, as shown earlier⁷. The interplay between dispersion force and tunnelling movement is such that the dispersion force delays the tunnelling, which – acting contrary to the cause – results in weakening of the dispersion force.

The magnitude of the tunnelling frequency is also of significance for the induced dipole interaction between the ions and the symmetrical hydrogen bonds. This is due to the fact that the interaction is not purely static, but contains a fluctuating part caused by the tunnelling movement of the protons; the dielectric constant of the medium at the tunnelling frequency is decisive for this fluctuating part. A mutual dependence between the strength of the interaction and the frequency of the tunnelling movement occurs with the induced dipole interaction, too.

Due to the influence of the ion fields, the symmetrical double minimum potential of the undisturbed bonds becomes an asymmetrical potential. The problem of determining the tunnelling frequency of a particle in an asymmetrical double minimum potential has often been treated in publications. The movement of the particle

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was either handled from a semi-classical aspect using the WKB method⁸, or the splitting between the lowest state and the first excited state was divided into one part caused by the asymmetry of the potential well and one part which takes into account the removal of the degeneracy due to the tunnelling movement and yields the tunnelling frequency⁹. Finally, the tunnelling frequencies or the lingering times in the potential wells were calculated by numerical integration of the time-dependent Schrödinger equation for various potential wells¹⁰.

This paper likewise applies the latter method and shows that in the tunnelling approximation¹¹ the lingering times depend only on one dimensionless parameter resulting from the tunnelling frequency in the undisturbed symmetrical potential and the difference ΔV in height of the potential wells in the asymmetrical potential; furthermore, the lingering times do not depend on the special shape of the double minimum potential. The result conforms satisfactorily with the results of the computer calculations for various potential wells^{9,10}. In addition, it is shown that the frequency for the transition between the lowest state and the first excited state, well known to be the tunnelling frequency in the symmetrical potential well can easily be connected even in the unsymmetrical case with the tunnelling movement: this frequency is inversely proportional to the lingering time of the proton in the upper well.

II. Correlation of the proton movements due to proton dispersion forces

Just as the usual London dispersion forces occur due to a correlation of the movement of the electrons in neighbouring atoms or molecules, the proton dispersion forces are caused by a correlation of the proton movements in neighbouring hydrogen bonds; their extraordinary size is explained by the extraordinary polarisability of the symmetrical hydrogen bonds. The correlation of the proton movements can be demonstrated in detail in the tunnelling approximation in which only the two almost degenerate lowest levels are taken into account for each proton¹¹. To this end we investigate a system comprising two neighbouring hydrogen bonds, and calculate the stationary states, considering the coupling between the protons. We first briefly recapitulate the results from^{1,6} in simplified form. The correlation is then discussed, based on the correlation function defined in Equation (8).

In the tunnelling approximation the four states $|++\rangle$, $|--\rangle$, $|+-\rangle$ and $| - + \rangle$ are considered as a complete set of functions for the lower group of levels. Here, for instance, $|+-\rangle = |0+\rangle_1 |0-\rangle_2$ represents a product state previously⁶ designated as

$\psi_{0+0-}(x_1, x_2) = \psi_{0+}(x_1) \psi_{0-}(x_2)$, proton 1 occurring in the lowest state of even parity and proton 2 occurring in the first excited state of odd parity. The stationary states $|+\rangle$, $|-\rangle$, $|s\rangle$ and $|a\rangle$ of the lower group of levels of the system, taking the interaction between the two hydrogen bonds into consideration, can be expressed in this approximation as a linear combination of four states,

$$\begin{aligned} |+\rangle &= a_{1+} |++\rangle + a_{2+} |--\rangle, \\ |s\rangle &= (1/\sqrt{2}) (|+-\rangle + |-+\rangle), \\ |-\rangle &= a_{1-} |++\rangle + a_{2-} |--\rangle, \\ |a\rangle &= (1/\sqrt{2}) (|+-\rangle - |-+\rangle), \end{aligned} \quad (1)$$

when the interaction operator in the dipole-dipole approximation is used for the interaction between the bonds, as in⁶. For in this approximation, the symmetry of the interaction operator results in the fact that states of different parity or different symmetry with regard to exchange of the two proton coordinates do not combine

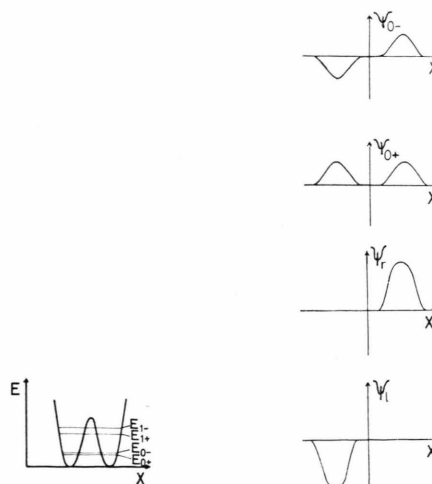


Fig. 1 a.

Fig. 1 b.

Fig. 1 a. Symmetrical double minimum potential.

Fig. 1 b. The wave functions of the two lowest energy states ψ_{0+} and ψ_{0-} and of the boundary structures ψ_r and ψ_l .

with each other. The symmetric state $|s\rangle$ and the anti-symmetric state $|a\rangle$ are thus eigenfunctions and the expansion amplitudes $a_{1\pm}$ and $a_{2\pm}$ result simply as solutions of a double-row secular problem.

The result for the expansion amplitudes is

$$a_{1\pm} = z/N_{\pm}, \quad a_{2\pm} = (1 \mp \sqrt{1+z^2})/N_{\pm} \quad (2)$$

with the abbreviations

$$z = p^2 g / (h \nu_0 \epsilon R^3), \quad (3)$$

$$N_{\pm} = \sqrt{z^2 + (1 \mp \sqrt{1+z^2})^2} \quad (4)$$

$$= \sqrt{2\sqrt{1+z^2}(\sqrt{1+z^2} \mp 1)}.$$

Here ν_0 , R , p , ϵ and g signify the following: ν_0 is the tunnelling frequency, R the distance between the two bond midpoints, p the transition moment between the lowest state 0^+ and the first excited state 0^- in an isolated bond, ϵ the dielectric constant of the medium at the frequency of the correlated movement of the two protons, and g a factor taking into consideration the mutual orientation of the two bonds ($-2 \leq g \leq +2$)⁶.

The eigenvalues

$$E_{\pm} = \mp h \nu_0 \sqrt{1+z^2}, \quad E_{s,a} = \pm h \nu_0 z, \quad (5)$$

belong to the states in Eq. (1) and are plotted in Fig. 2 as a function of the dimensionless variable z , that is, as a function of the distance and orientation of the two bonds. The splitting and shifting of the energy levels was discussed in detail in the earlier publications^{1,6}.

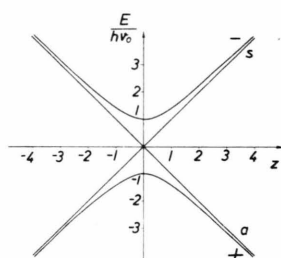


Fig. 2. The energy levels of the states $|+\rangle$, $|a\rangle$, $|s\rangle$ and $|-\rangle$ of a pair of hydrogen bonds plotted over the dimensionless variable $z = p^2 g / (h \nu_0 \epsilon R^3)$.

How are the proton movements correlated in the four states? As in the case of the customary dispersion forces, the mean dipole moment is zero for each of the two interacting systems in the stationary states. For example, Eq. (1) gives rise to

$$\langle + | e x_1 | + \rangle = 0 \quad (6)$$

that is, the disappearance of the mean dipole moment of the proton with the coordinate x_1 along the hydrogen bond 1 in the state $|+\rangle$. For substituting the expansion of Eq. (1) in Eq. (6), the following matrix elements are obtained

$$\begin{aligned} &\langle ++ | x_1 | ++ \rangle, \quad \langle -- | x_1 | -- \rangle, \\ &\langle ++ | x_1 | -- \rangle, \quad \langle -- | x_1 | ++ \rangle, \end{aligned} \quad (7)$$

which all disappear, since the dipole operator $e x_1$ has matrix elements differing from zero only between states

of opposite parity, and the interaction between the bonds only mixes states of the same parity⁶.

To show that the tunnelling movements of the protons in two neighbouring hydrogen bonds no longer occur independently, due to the influence of this interaction, a correlation function in an arbitrary state ψ is defined by

$$K_{\psi} = e^2 \langle \psi | x_1 \cdot x_2 | \psi \rangle / (p_1 \cdot p_2) \quad (8)$$

that is, essentially as the mean value of the scalar product of the dipole moments of both bonds in the state ψ . Division by $p_1 \cdot p_2$ serves to normalise the correlation function; p_1 and p_2 are the dipole moments in the bonds 1 and 2, when the protons are completely shifted in positive x_1 or x_2 direction. The amounts of these dipole moments are equal to the transition moment p between the lowest state and the first excited state of the proton in a single undisturbed hydrogen bond. $K > 0$ signifies that the dipole moments of both bonds are preferably parallel, $K < 0$ that they are preferably antiparallel. With strict correlation $K = +1$ or -1 .

In order to calculate the correlation function K_{ψ} in the four stationary states of the lower group, ($\psi = +, -, s$ and a) of the interacting bond pair, we require in accordance with Eq. (1) the matrix elements of the operator $e^2 x_1 \cdot x_2$ with respect to the undisturbed states $|++\rangle$, $|--\rangle$, $|+-\rangle$ and $| - + \rangle$. On account of their parity, only the matrix elements

$$\begin{aligned} &e^2 \langle ++ | x_1 \cdot x_2 | -- \rangle \\ &= e^2 \langle -- | x_1 \cdot x_2 | ++ \rangle \\ &= e^2 \langle +- | x_1 \cdot x_2 | -+ \rangle \\ &= e^2 \langle -+ | x_1 \cdot x_2 | +- \rangle = p_1 \cdot p_2 \end{aligned} \quad (9)$$

remain, whilst all other matrix elements disappear. The matrix elements in Eq. (9) are obtained in detail, for instance, in accordance with

$$\begin{aligned} &e^2 \langle ++ | x_1 \cdot x_2 | -- \rangle \\ &= e^2 \int \psi_{0+}(x_1) x_1 \psi_{0-}(x_1) dx_1 \cdot \int \psi_{0+}(x_2) x_2 \psi_{0-}(x_2) dx_2 \\ &= p_1 \cdot p_2. \end{aligned} \quad (10)$$

These matrix elements then give rise, applying Eq. (1) and (2), to the correlation function K_{ψ} in the four stationary states $\psi = +, -, s$ and a of the interacting bond pair

$$K_{\pm} = 2 a_{1\pm} a_{2\pm} = \mp \frac{z}{\sqrt{1+z^2}}, \quad K_{s,a} = \pm 1. \quad (11)$$

In Fig. 3a, K_{ψ} is plotted as a function of z and thus of the distance between and the mutual orientation of the bonds.

Let us now consider two parallel adjacent hydrogen bonds as case (I) and two hydrogen bonds occurring along a straight line behind each other as case (II). In

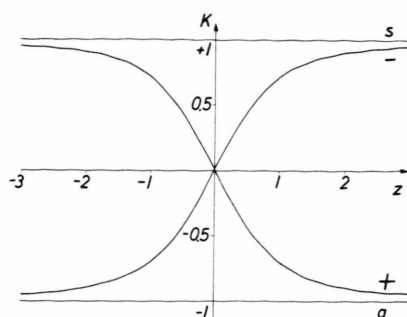


Fig. 3a. Correlation function of the states $|a\rangle$, $|+\rangle$, $|-\rangle$ and $|s\rangle$ plotted over $z = p^2 g / (h v_0 \epsilon R^3)$

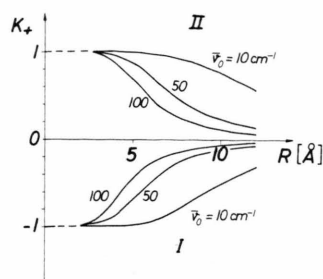


Fig. 3b. Correlation function of the state $|+\rangle$ plotted over the distance R between the midpoints of the hydrogen bonds for various tunnelling frequencies \bar{v}_0 . I. parallel bonds, II. collinear bonds.

case (I) $g = +1$ and thus $z > 0$. Thus, according to Fig. 3a, $K_+ < 0$ in the lowest state $|+\rangle$ of the bond pair; the two dipole moments are preferably antiparallel and thus attract each other, in conformance with the decrease in energy for the state $|+\rangle$ in Figure 2. Accordingly, the dipoles in the excited state $|-\rangle$ are preferably parallel and repel each other. When considering these statements, however, it must be taken into account that the dipole-dipole approximation is applicable only for electrically neutral systems. Since we are considering symmetrical hydrogen bonds in positively or negatively charged systems, the above statements are only valid when the pertinent ions of the other charge are included in the system. The larger z (that is, the smaller the distance between the bonds), the stronger is the correlation. The correlation for $z = 1$ amounts to $1/\sqrt{2} \approx 70\%$.

According to Eq. (3), the connection of the distance R between the bonds in Å to the dimensionless variable z is

$$z = 57.5 \frac{g}{R^3} \text{ Å}^3. \quad R = 3.86 \sqrt[3]{\frac{g}{z}} \text{ Å}. \quad (12)$$

when \bar{v}_0 is taken as 100 cm^{-1} , p as 2 Debye and ϵ as 3.5. The lower half of Fig. 3b plots the correlation for case (I) in the ground state $|+\rangle$ as a function of the distance, using these values and, in addition, for $\bar{v}_0 = 50$

and 10 cm^{-1} . This figure shows that the correlation is all the more far-reaching, the smaller the tunnelling frequency.

In case (II) of two collinear hydrogen bonds, $g = -26$, hence $z < 0$. According to Fig. 3a, in the ground state $|+\rangle$ the dipoles are now preferably parallel, which again results in an attracting force. Here, too, it must not be forgotten that the statement is only valid in the dipole-dipole approximation, that is, that altogether neutral systems must be considered.

In the two remaining states $|s\rangle$ and $|a\rangle$, the proton movements, according to Eq. (11), are correlated strictly independently of distance and orientation, in the symmetrical state $|s\rangle$ the dipole moments being oriented to the same side, in the antiparallel state $|a\rangle$ to opposite sides. The energies E_s or E_a in Eq. (5) are accordingly the classical interaction energies of two dipoles of the amount p . In the theory of intermolecular forces this interaction is designated resonance interaction¹² whereby the excitation energy is interchanged between the two systems.

The correlation in the states $|s\rangle$ and $|a\rangle$ is of course not strict up to infinite distances. This is not due to the tunnelling approximation or to the dipole-dipole approximation, since these become increasingly applicable for larger distances. The assumption, however, that the bond pair is in a stationary state, becomes more and more unrealistic, since the larger the distance becomes, the more time is required for the stationary states to occur. Finally this time becomes so great that no stationary state can occur at all, due to external disturbances.

III. Dependence of the tunnelling frequency on the proton dispersion forces

The proton dispersion forces cause a more or less strict correlation of the proton transfer in adjacent hydrogen bonds. It is readily understandable that this correlation hinders the proton transfer and thus leads to a lower tunnelling frequency.

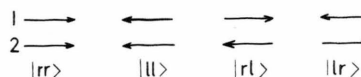


Fig. 4. Schematic presentation of the proton boundary structures of a pair of hydrogen bonds.

In order to calculate the tunnelling frequency as a function of the proton dispersion interaction, let us introduce a third particularly illustrative system in addition to the previously used two systems of orthonormal functions, the undisturbed states $|++\rangle$, $|--\rangle$, $|+-\rangle$, $| - + \rangle$ and the stationary states $|+\rangle$, $|-\rangle$, $|s\rangle$, $|a\rangle$ of a bond pair. The additional

systems consists of the four boundary structures of a bond pair indicated in Fig. 4. The arrows give the position of the protons and thus at the same time the direction of the dipole moments of the hydrogen bonds. $|rl\rangle = |r\rangle_1 |l\rangle_2$ signifies, for instance, that the proton in the first bond is shifted completely to the right (in positive x_1 direction) and in the second bond completely to the left (in negative x_2 direction). In the tunnelling approximation the boundary structures can be represented as simple superpositions of the stationary states⁴ (see Fig. 1b and Eq. (13)).

In order to see how the proton dispersion forces hinder the proton transfer in neighbouring hydrogen bonds, let us calculate how the boundary structure $|rl\rangle$, for instance, develops in the course of time. The time-dependent Schrödinger equation must be solved for this initial state. The result is given in Eq. (22), in which the time-dependent state is represented as a superposition of the four proton boundary structures.

The boundary structures must be expanded in the stationary states of a bond pair in order to integrate the Schrödinger equation. The expansion of these states in the undisturbed states can easily be given. Since with symmetrical hydrogen bonds with a double minimum potential having a high barrier, so that the wave functions of the two lowest levels penetrate the barrier only slightly, the following applies as a good approximation (for phase selection as in Fig. 1),

$$\begin{aligned} |r\rangle &= \frac{1}{\sqrt{2}} (|0+\rangle + |0-\rangle), \\ |l\rangle &= \frac{1}{\sqrt{2}} (|0+\rangle - |0-\rangle), \end{aligned} \quad (13)$$

so that, for instance,

$$|rl\rangle = |r\rangle_1 |l\rangle_2 = \frac{1}{2} (|0+\rangle_1 + |0-\rangle_1) (|0+\rangle_2 - |0-\rangle_2) \quad (14)$$

or, by multiplying out due to $|0+\rangle_1 |0+\rangle_2 \equiv |++\rangle$ etc.

$$|rl\rangle = \frac{1}{2} (|++\rangle - |--\rangle - |+-\rangle + |-+\rangle). \quad (15)$$

The three other boundary structures can likewise be represented as superpositions of the undisturbed states. All four equations can be summarised in the matrix equation

$$\begin{pmatrix} |rr\rangle \\ |ll\rangle \\ |rl\rangle \\ |lr\rangle \end{pmatrix} = \frac{1}{2} \begin{pmatrix} 1 & 1 & 1 & 1 \\ 1 & 1 & -1 & -1 \\ 1 & -1 & -1 & 1 \\ 1 & -1 & 1 & -1 \end{pmatrix} \begin{pmatrix} |++\rangle \\ |--\rangle \\ |+-\rangle \\ |-+\rangle \end{pmatrix}. \quad (16)$$

Since this is an orthogonal transformation, the inversion of these equations is obtained by transposing the matrix. Since the latter is symmetrical, the same matrix is obtained:

$$\begin{pmatrix} |++\rangle \\ |--\rangle \\ |+-\rangle \\ |-+\rangle \end{pmatrix} = \frac{1}{2} \begin{pmatrix} 1 & 1 & 1 & 1 \\ 1 & 1 & -1 & -1 \\ 1 & -1 & -1 & 1 \\ 1 & -1 & 1 & -1 \end{pmatrix} \begin{pmatrix} |rr\rangle \\ |ll\rangle \\ |rl\rangle \\ |lr\rangle \end{pmatrix}. \quad (17)$$

If Eq. (1) is also written in matrix form, the stationary states are obtained as a superposition of the four boundary structures by multiplying out the matrices:

$$\begin{pmatrix} |+\rangle \\ |-\rangle \\ |s\rangle \\ |a\rangle \end{pmatrix} = \frac{1}{2} \begin{pmatrix} a_{1+} + a_{2+} & a_{1+} + a_{2+} & a_{1-} - a_{2+} & a_{1-} - a_{2+} \\ a_{1-} + a_{2-} & a_{1-} + a_{2-} & a_{1-} - a_{2-} & a_{1-} - a_{2-} \\ \sqrt{2} & -\sqrt{2} & 0 & 0 \\ 0 & 0 & -\sqrt{2} & \sqrt{2} \end{pmatrix} \begin{pmatrix} |rr\rangle \\ |ll\rangle \\ |rl\rangle \\ |lr\rangle \end{pmatrix}. \quad (18)$$

Inverting the equations is again effected by transposing the matrix, as for the transition from Eq. (16) to Eq. (17), since this is likewise an orthogonal transformation.

$$\begin{pmatrix} |rr\rangle \\ |ll\rangle \\ |rl\rangle \\ |lr\rangle \end{pmatrix} = \frac{1}{2} \begin{pmatrix} a_{1+} + a_{2+} & a_{1-} + a_{2-} & \sqrt{2} & 0 \\ a_{1+} + a_{2+} & a_{1-} + a_{2-} & -\sqrt{2} & 0 \\ a_{1+} - a_{2+} & a_{1-} - a_{2-} & 0 & -\sqrt{2} \\ a_{1+} - a_{2+} & a_{1-} - a_{2-} & 0 & \sqrt{2} \end{pmatrix} \begin{pmatrix} |+\rangle \\ |-\rangle \\ |s\rangle \\ |a\rangle \end{pmatrix}. \quad (19)$$

Equations (18) and (19) are required when we treat the problem as to how a boundary structure changes in the course of time under the influence of the proton dispersion interaction.

The development in time of a state $|\psi\rangle$ is given in the Schrödinger picture by

$$|\psi\rangle_t = e^{-iHt/\hbar} |\psi\rangle_{t=0} = 0. \quad (20)$$

The effect of the time displacement operator $e^{-iHt/\hbar}$ on a state, can be given directly when the state can be ex-

panded in the eigenstates of H . Equation (19) effects this for the boundary structures in the tunnelling approximation. If, for instance, $|rl\rangle$ is selected as the initial state at a time $t = 0$, the following state results at the time t :

$$\begin{aligned} |rl\rangle_t &= \frac{1}{2} [(a_{1+} - a_{2+}) e^{-iE_+ t/\hbar} |+\rangle \\ &\quad + (a_{1-} - a_{2-}) e^{-iE_- t/\hbar} |-\rangle - \sqrt{2} e^{-iE_s t/\hbar} |s\rangle]. \end{aligned} \quad (21)$$

Substituting the stationary states by the boundary structures according to Eq. (18) the following results:

$$\begin{aligned}
 |rl\rangle_t = & \frac{1}{4} [(a_{1+} - a_{2+})^2 e^{-iE_+ t/\hbar} \\
 & + (a_{1-} - a_{2-})^2 e^{-iE_- t/\hbar} + 2e^{-iE_a t/\hbar}] |rl\rangle \\
 & + \frac{1}{4} [(a_{1+} - a_{2+})^2 e^{-iE_+ t/\hbar} \\
 & + (a_{1-} - a_{2-})^2 e^{-iE_- t/\hbar} - 2e^{-iE_a t/\hbar}] |lr\rangle \\
 & + \frac{1}{4} [(a_{1+}^2 - a_{2+}^2) e^{-iE_+ t/\hbar} \\
 & + (a_{1-}^2 - a_{2-}^2) e^{-iE_- t/\hbar}] (|rr\rangle + |ll\rangle).
 \end{aligned} \quad (22)$$

Equation (22) shows how the other boundary structures are mixed in the course of time with the boundary structure $|rl\rangle$. The coefficients in this equation can easily be expressed by the dimensionless variable z using Eq. (2) and (4).

$$\begin{aligned}
 (a_{1\pm} - a_{2\pm})^2 &= 1 \pm \sqrt{\frac{z^2}{1+z^2}}, \\
 a_{1\pm}^2 - a_{2\pm}^2 &= \pm \sqrt{\frac{1}{1+z^2}}.
 \end{aligned} \quad (23)$$

Let us now consider the case of extremely strong interaction. For $z \rightarrow \infty$, $(a_{1-} - a_{2-})^2$ and $a_{1\pm}^2 - a_{2\pm}^2$ approach zero and $(a_{1+} - a_{2+})^2$ approaches 2. In addition, according to Equation (5), E_+ moves toward $E_a = -h\nu_0 z$. Thus admixture of the states $|rr\rangle$, $|ll\rangle$ and $|lr\rangle$ does not occur in this limiting case:

$$\begin{aligned}
 |rl\rangle_t &= e^{-iHt/\hbar} |rl\rangle \sim e^{-iE_a t/\hbar} |rl\rangle = e^{i2\pi z\nu_0 t} \\
 &\text{for } z \rightarrow \infty.
 \end{aligned} \quad (24)$$

Hence the boundary structure $|rl\rangle$ becomes a quasi-stationary state with the energy $E_a = -h\nu_0 z$; the interaction hinders the proton transfer.

In reality, the interaction is indeed weaker and the proton transfer is not hindered but only delayed. In order to make this statement quantitative, the expressions in Eq. (23) are expanded in powers of $1/z$.

$$\begin{aligned}
 (a_{1\pm} - a_{2\pm})^2 &= 1 \pm \left(1 - \frac{1}{2z^2}\right) + 0\left(\frac{1}{z^3}\right), \\
 a_{1\pm}^2 - a_{2\pm}^2 &= \pm \frac{1}{z} + 0\left(\frac{1}{z^3}\right).
 \end{aligned} \quad (25)$$

Likewise, according to Equation (5),

$$E_{\pm} = \mp h\nu_0 \left(z + \frac{1}{2z}\right) + 0\left(\frac{1}{z^2}\right), \quad E_{s,a} = \pm h\nu_0 z \quad (26)$$

is obtained for the energy eigenvalues. Substituting this in Eq. (22) and omitting all terms of $0(1/z^2)$ or less, the

following is obtained:

$$\begin{aligned}
 |rl\rangle_t &= \frac{1}{2} e^{-i2\pi z\nu_0 t} (e^{i\pi\nu_0 t/z} + 1) |rl\rangle \\
 &+ \frac{1}{2} e^{i2\pi z\nu_0 t} (e^{i\pi\nu_0 t/z} - 1) |lr\rangle \\
 &+ \frac{1}{4z} (e^{-iE_+ t/\hbar} - e^{-iE_- t/\hbar}) (|rr\rangle + |ll\rangle) + 0\left(\frac{1}{z^2}\right).
 \end{aligned} \quad (27)$$

The admixed boundary structures $|rr\rangle$ and $|ll\rangle$ are of $0(1/z)$. Except for these terms a periodic transition occurs between the boundary structures $|rl\rangle$ and $|lr\rangle$, which signifies a correlated proton transfer in hydrogen bonds lying close to each other ($z \gg 1$), whereby the dipole moments are always antiparallel. At the time

$$\tau = z/\nu_0 \quad (28)$$

the state $|rl\rangle$ has become state $|lr\rangle$. Since the period of this process is 2τ , the tunnelling frequency $\nu_t = 1/(2\tau) = \nu_0/(2z)$ is depressed by the factor $1/2z$.

This result is remarkable in that, since

$$\nu_t = 1/(2\tau) = (E_- - E_+)/\hbar \quad (29)$$

in the case of strong coupling ($z \gg 1$), the reduced tunnelling frequency can be read directly from the level scheme (Fig. 2) – in fact from the energy difference between the first excited state of the hydrogen bond pair and the ground state. The connection between the energy level difference in Eq. (29) and the tunnelling frequency also applies for the case of weak coupling ($z \rightarrow 0$), where the energy level difference approaches $h\nu_0$. This suggests defining the tunnelling frequency by Eq. (29) in the intermediate coupling range, too. For

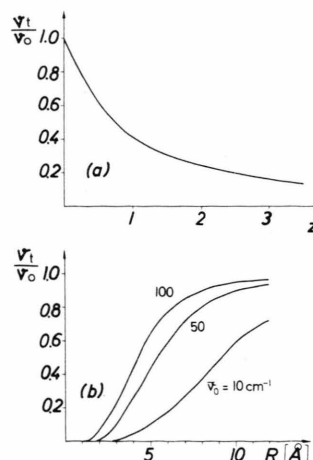


Fig. 5a. Decrease of the tunnelling frequency ν_t by the proton dispersion interaction between a pair of hydrogen bonds depending on $z = p^2 g/(h\nu_0 \epsilon R^3)$.

Fig. 5b. The same plotted over the distance R of two parallel hydrogen bonds for various tunnelling frequencies.

negative z , as for instance in the case of collinear hydrogen bonds ($g = -2$), a shall be replaced by s in Eq. (29), as shown in Fig. 2. Accordingly, the general result is:

$$\nu_t/\nu_0 = \sqrt{1 + z^2} - |z|. \quad (30)$$

ν_t/ν_0 is plotted in Fig. 5a as a function of the dimensionless variable z . Expressing z according to Eq. (12) by the distance R , the decrease in tunnelling frequency plotted in Fig. 5b results for the special case of two parallel adjacent hydrogen bonds.

Figure 5 shows that the proton transfer occurs even when interaction is very strong. It can also be seen that proton transfer is hindered all the more at larger distances, the smaller the tunnelling frequency is.

IV. Influence of inner electrical fields on the tunnelling frequency

Similarly as in the previous section, the question of how ion or dipole of solvent molecules affect the tunnelling frequency or, more generally, how large the tunnelling frequency is in an asymmetrical double minimum potential, can be dealt with in the tunnelling approximation by tracing the development in time of a proton boundary structure. The symmetry of hydrogen bonds between like partners is more or less strongly disturbed by the fields of adjacent ions in solutions and crystals. The ion fields, approximated by a homogenous field with the component F in the bond axis, gives rise to an asymmetrical potential, as sketched in Fig. 6, whereby

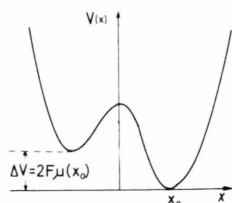


Fig. 6. Potential well in a homogenous electrical field F .

$\mu(x_0)$ is the dipole moment of a proton boundary structure which is almost the same size as the transition moment p between the first excited state $|0-\rangle$ and the

lowest state $|0+\rangle$ as long as the potential has a marked barrier.

In the tunnelling approximation the ground state $|+\rangle$ and the first excited state $|-\rangle$ of the proton in the potential disturbed by ion fields (not to be confused with the stationary states of a bond pair in section 2 and 3!) are represented as linear combinations of the undisturbed states $|0+\rangle$ and $|0-\rangle$:

$$\begin{pmatrix} |+\rangle \\ |-\rangle \end{pmatrix} = \begin{pmatrix} c_{1+} & c_{2+} \\ c_{1-} & c_{2-} \end{pmatrix} \begin{pmatrix} |0+\rangle \\ |0-\rangle \end{pmatrix}. \quad (31)$$

Here the expansion amplitudes are

$$c_{1\pm} = -\frac{\zeta}{N_{\pm}}, \quad c_{2\pm} = \frac{1 \mp \sqrt{1 + \zeta^2}}{N_{\pm}} \quad (32)$$

with the abbreviations

$$\zeta = \frac{2F\mu(x_0)}{h\nu_0} = \frac{\Delta V}{h\nu_0}. \quad (33)$$

$$N_{\pm} = \sqrt{\zeta^2 + (1 \mp \sqrt{1 + \zeta^2})^2} \\ = \sqrt{2\sqrt{1 + \zeta^2}(\sqrt{1 + \zeta^2} \mp 1)}. \quad (34)$$

The pertinent energy eigenvalues are

$$E_{\pm} = \mp \frac{h\nu_0}{2} \sqrt{1 + \zeta^2}. \quad (35)$$

The dimensionless parameter ζ is a measure of the asymmetry and acts as a coupling constant between the proton movement and the fields. It replaces the parameter z from the previous section, which was a measure of the strength of the coupling between the protons in two adjacent hydrogen bonds.

As in section 3, the tunnelling frequency is calculated by solving the time-dependent Schrödinger equation and thus determining how a proton boundary structure develops in the course of time. The outcome of the calculation is Eq. (41) for the state $|r\rangle_t$ at time t , resulting from the boundary structure $|r\rangle$ at $t = 0$.

In order to solve the time-dependent Schrödinger equation, we first expand as in Eq. (13), the boundary structures $|r\rangle$ and $|l\rangle$, whereby the proton is shifted completely to the right (in field direction), or completely to the left (contrary to field direction), in the eigenstates of the symmetrical potential, and vice-versa. In matrix form

$$\begin{pmatrix} |r\rangle \\ |l\rangle \end{pmatrix} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix} \begin{pmatrix} |0+\rangle \\ |0-\rangle \end{pmatrix}, \quad \begin{pmatrix} |0+\rangle \\ |0-\rangle \end{pmatrix} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix} \begin{pmatrix} |r\rangle \\ |l\rangle \end{pmatrix}. \quad (36)$$

Substituting this in Eq. (31), the relationship between the eigenstates in the asymmetric potential and the boundary structures are obtained.

$$\begin{pmatrix} |+\rangle \\ |-\rangle \end{pmatrix} = \frac{1}{\sqrt{2}} \begin{pmatrix} c_{1+} + c_{2+} & c_{1+} - c_{2+} \\ c_{1-} + c_{2-} & c_{1-} - c_{2-} \end{pmatrix} \begin{pmatrix} |r\rangle \\ |l\rangle \end{pmatrix}, \quad \begin{pmatrix} |r\rangle \\ |l\rangle \end{pmatrix} = \frac{1}{\sqrt{2}} \begin{pmatrix} c_{1+} + c_{2+} & c_{1+} - c_{2+} \\ c_{1-} + c_{2-} & c_{1-} - c_{2-} \end{pmatrix} \begin{pmatrix} |+\rangle \\ |-\rangle \end{pmatrix}. \quad (37)$$

The development in time of the proton boundary structure $|r\rangle$ is obtained analogously to Eq. (21):

$$|r\rangle_t = \frac{1}{\sqrt{2}} [(c_{1+} + c_{2+}) e^{-iE_+ t/\hbar} |+\rangle + (c_{1-} + c_{2-}) e^{-iE_- t/\hbar} |-\rangle]. \quad (38)$$

Expressing the stationary states on the right-hand side of the equation by the boundary structures using Eq. (37) gives:

$$|r\rangle_t = \frac{1}{2} [(c_{1+} + c_{2+})^2 e^{-iE_+ t/\hbar} + (c_{1-} + c_{2-})^2 e^{-iE_- t/\hbar}] |r\rangle + \frac{1}{2} [(c_{1+}^2 - c_{2+}^2) e^{-iE_+ t/\hbar} + (c_{1-}^2 - c_{2-}^2) e^{-iE_- t/\hbar}] |l\rangle. \quad (39)$$

The following results from Eqs. (32) and (33) for the coefficients in this equation:

$$(c_{1\pm} + c_{2\pm})^2 = 1 \pm \frac{\zeta}{\sqrt{1 + \zeta^2}}, \quad c_{1\pm}^2 - c_{2\pm}^2 = \pm \frac{1}{\sqrt{1 + \zeta^2}}. \quad (40)$$

These relations and the eigenvalues from Eq. (35) yield

$$|r\rangle_t = \left(\cos \pi \nu_0 \sqrt{1 + \zeta^2} t + i \frac{\zeta}{1 + \zeta^2} \sin \pi \nu_0 \sqrt{1 + \zeta^2} t \right) |r\rangle + i \frac{1}{\sqrt{1 + \zeta^2}} \sin \pi \nu_0 \sqrt{1 + \zeta^2} t |l\rangle. \quad (41)$$

Eq. (41) describes the periodic transition between the two potential wells. Thus the interpretation of ν_0 as the tunnelling frequency follows as usual for the symmetrical potential well ($\zeta = 0$) (see below).

The squares of the modulus of the amplitudes in front of the states $|r\rangle$ and $|l\rangle$ are designated as weights G_r resp. G_l of the two boundary structures. Eq. (41) gives

$$G_l(t) = \frac{1}{1 + \zeta^2} (\sin \pi \nu_0 \sqrt{1 + \zeta^2} t)^2, \quad (42)$$

$$G_r(t) = 1 - G_l(t).$$

$G_l(t)$ and $G_r(t)$ are plotted in Fig. 7 as functions of the time. The first maximum for $G_l(t)$ occurs at the time

$$T = \frac{1}{2 \sqrt{1 + \zeta^2} \nu_0} = \frac{\tau_0}{\sqrt{1 + \zeta^2}}. \quad (43)$$

In the symmetrical potential ($\zeta = 0$), the maximum is equal to 1; the proton has transferred at the time $\tau_0 = 1/(2 \nu_0)$ to the left-hand potential well. τ_0 is the lingering time in a well of the symmetrical potential and the meaning of ν_0 as the tunnelling frequency follows from $\nu_0 = 1/(2 \tau_0)$. In the asymmetrical potential ($\zeta \neq 0$), the probability of finding the proton in the higher well is at no time equal to 1, but $1/(1 + \zeta^2)$, if the proton was localised at a certain time ($t = 0$) in the lower well.

In an asymmetric potential a longer lingering time (τ_r) is expected in the deeper right-hand well than in the higher left-hand one (τ_l). This is a direct consequence of the equilibrium condition

$$\frac{\bar{G}_l}{\tau_l} = \frac{\bar{G}_r}{\tau_r}, \quad (44)$$

in which \bar{G}_l and \bar{G}_r are the weights averaged over a period.

$$\bar{G}_l = \frac{1}{2} \frac{1}{1 + \zeta^2}, \quad (45)$$

$$\bar{G}_r = 1 - \frac{1}{2} \frac{1}{1 + \zeta^2} = \frac{1 + 2\zeta^2}{2(1 + \zeta^2)}.$$

Evidently $G_r \geq G_l$, whereby the equal sign only applies for the symmetrical case $\zeta = 0$, so that $\tau_r \geq \tau_l$ as expected.

Equations (44) and (45) define the ratio of τ_r to τ_l only. The absolute values are calculated as follows: the time interval $0 < t < T$ is considered, where, according to Fig. 7, $G_l(t)$ increases and $G_r(t)$ decreases.

Since the increase of $G_l(t)$ is not constant with respect to time, the following applies

$$\dot{G}_l(t) = w_r(t) G_r(t) \quad (46)$$

with a transition probability $w_r(t)$ from the right to the left depending on the time. Averaging over the interval T under consideration and substituting $w_r(t)$ by the mean value $1/\tau_r$ gives

$$\bar{\dot{G}}_l^T = \frac{1}{T} \int_0^T \dot{G}_l(t) dt = \frac{1}{T} \int_0^T w_r(t) G_r(t) dt = \alpha \frac{\bar{G}_r(t)^T}{\tau_r}. \quad (47)$$

whereby α is a factor which is yet to be determined. According to Fig. 7, the mean value of $G_r(t)$ over the half period $0 < t < T$ is, due to the symmetry, equal to the mean value over a whole period, so that we can write $\bar{G}_r(t)^T = \bar{G}_r$ and can apply Equation (45).

$$\bar{\dot{G}}_l(t)^T = \frac{\alpha}{\tau_r} \left(1 - \frac{1}{2} \frac{1}{1 + \zeta^2} \right). \quad (48)$$

On the other hand, the direct calculation of the left-hand side of the equation using Eq. (42) supplies

$$\bar{\dot{G}}_l(t)^T = \frac{1}{T} \frac{1}{1 + \zeta^2} = \frac{1}{\sqrt{1 + \zeta^2}} \frac{1}{\tau_0}. \quad (49)$$

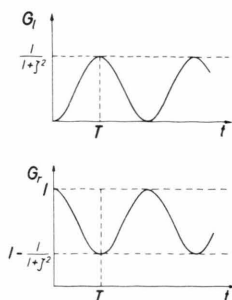


Fig. 7. Weights of the proton boundary structures G as functions of time in an asymmetrical potential well.

Comparing the right-hand sides of Eq. (48) and (49) gives

$$\tau_r = \frac{1 + 2\zeta^2}{\sqrt{1 + \zeta^2}} \tau_0, \quad (50)$$

whereby the numerical value of α is chosen such that $\tau_r \rightarrow \tau_0$ for $\zeta \rightarrow 0$. Equation (50) shows that in the tunnelling approximation the ratio of τ_r to τ_0 depends only on the dimensionless parameter $\zeta = \Delta V/(h\nu_0)$ and, furthermore, is independent of the exact shape of the double minimum potential.

$$\tau_l = \frac{1}{1 + 2\zeta^2} \tau_r = \frac{1}{\sqrt{1 + \zeta^2}} \tau_0 \quad (51)$$

follows from Eqs. (44), (45) and (50) for the lingering time in the higher (left) potential well. On account of Eq. (35) this is related directly to the excitation energy of the first excited state in the asymmetrical potential.

$$\tau_l = \frac{1}{2} \frac{h}{E_- - E_+}. \quad (52)$$

The lingering time in the higher potential well is inversely proportional to the transition frequency between the ground state and the first excited state.

The tunnelling movement from the right-hand to the left-hand well and vice-versa occurs over the period $\tau_r + \tau_l = 2\tau$. The tunnelling frequency ν_t hence follows from the mean lingering time τ according to

$$\tau_t = \frac{1}{2\tau}, \quad \tau = \frac{1}{2} (\tau_r + \tau_l). \quad (53)$$

From Eqs. (50) and (51) we obtain for the mean lingering time

$$\tau = \sqrt{1 + \zeta^2} \tau_0. \quad (54)$$

τ , τ_r and τ_l are plotted in Fig. 8a as a function of the parameter $\zeta = \Delta V/h\nu_0$. If the asymmetry of the potential is produced by fields, the connection between ζ and the field strength F in the direction of the hydrogen bond is given according to Eq. (34) by

$$\zeta = 0.606 \cdot 10^{-6} F [\text{V/cm}], \quad F = 1.65 \cdot 10^6 \zeta \text{ V/cm} \quad (55)$$

when the same values are chosen as in Eq. (12) for the

tunnelling frequency and for the transition moment p , which differs only slightly for potential wells with marked barriers from the dipole moment of the proton boundary structure $\mu(x_0)$.

The tunnelling frequency ν_t is plotted as a function of the field strength, using these values and in addition $\bar{\nu}_0 = 10 \text{ cm}^{-1}$, in Fig. 8b. The field of a single-charged ion on the bond axis at a distance of 5 \AA amounts to $0.9 \cdot 10^7 \text{ V/cm}$, when the charge is screened by the factor $1/3.5$. According to Fig. 8b, the tunnelling frequency is then reduced by the factor $1/5$ only. It is clear that the proton transfer still occurs even with very large fields i.e. in cases in which the potential well is already strongly deformed³. With considerably larger fields the tunnelling approximation is invalidated and the tunnelling frequency sinks more rapidly than as shown in Fig. 8b.

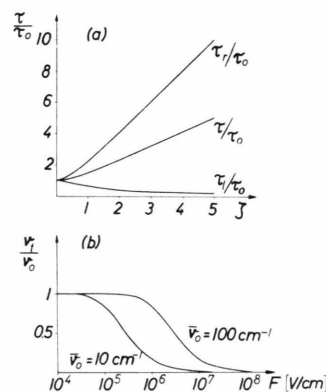


Fig. 8a. Lingering time τ plotted over the dimensionless parameter $\zeta = \Delta V/(h\nu_0)$.

τ_r : lingering time in the lower well,
 τ_l : lingering time in the higher well,
 τ : mean lingering time.

Fig. 8b. Tunnelling frequency ν_t plotted over electrical field strength F for two tunnelling frequencies.

The results obtained with the simple formula (54) for the mean lingering time comply excellently with the results of the computer calculations in¹⁰. Taking the values for τ_0 from the curves for $\Delta V = 0$, lingering times are obtained with Eq. (54) for $\Delta V = 5, 20$ and 100 cm^{-1} which are the same within the accuracy with which the curves can be read. Deviations occur for $\Delta V = 500$ and 1500 cm^{-1} ; these are cases, however, for which no great degree of accuracy is claimed¹⁰ and for which the tunnelling approximation becomes increasingly inaccurate.

IV. Conclusions

The calculation have shown that the interaction between the polarisable hydrogen bonds as well as the

induced dipole interaction of these hydrogen bonds with fields from their environment cause the tunnelling frequency to sink. The proton fluctuation, however, is not completely hindered even by strong fields (approx. 10^7 V/cm). The decrease of the tunnelling frequency, however, causes the latter to approach the rearrangement frequencies of the solvent molecules. It was shown in⁷ that the interactions discussed disappear to a large extent in the range of the rearrangement frequencies of the solvent molecules as the tunnelling frequency decreases. This is due to the fact that the solvent molecules now follow the fluctuating fields, thus weakening them. When the tunnelling frequency has sunk to such an extent, an interplay between the fall of the tunnelling frequency due to these interactions and the weakening of this interaction and vice-versa occurs.

Experimental findings have demonstrated that as the tunnelling frequency decreases, the IR continuum and the interaction indicated hereby actually disappear². Hydrogen bonds of the type $(\text{BH} \cdots \text{B})^+$ were studied. If the acceptor groups B have a relatively low pK_a value, the potential barrier is extremely low and the tunnelling frequency thus extremely high. In the limiting case, e.g. in "free" H_3O_2^+ not linked further via hydrogen bonds, the barrier even disappears to a large extent^{13,14}. As the pK_a value of the acceptor groups B increases, the barrier in the potential well rises, since both acceptor groups attract the proton strongly. The tunnelling frequency thus becomes increasingly lower. Hydrous solutions of N bases with pK_a values between 0 and 12 were then studied. Here it was shown that the IR continuum and thus the interactions disappear when the pK_a values > 8 . Hence, in the case of substances with pK_a values > 8 , the tunnelling frequency accordingly becomes so small that at 25°C it reaches the range of the rearrangement frequencies of the H_2O molecules, due to the decrease already discussed². The above-mentioned interplay is certainly significant, in particular for substances with pK_a values between 6 and 9 in hydrous solutions.

An IR investigation of N base molecules adsorbed at silica gel provided confirmation of the role ascribed to the rearrangement processes¹⁵. $(\text{NH} \cdots \text{N})^+$ bonds form at the surface between the base molecules. Contrary to the findings obtained in hydrous media, however, in these systems an intensive IR continuum is observed even when the base molecules have pK_a values of about 11. The interactions do not disappear in this case even with considerably smaller tunnelling frequencies, since the rearrangement processes at the surface are effected considerably more slowly than in hydrous media.

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