

# Hydrogen Bonding and Proton Transfer in PDMS and UV-LDMS

H.F. Kammer

*Fachbereich Physik  
and Institut für Chemie und Biologie des Meeres (ICBM)  
Universität Oldenburg, FRG*

## Abstract

Hydrogen bonding plays an important role in determining physical and chemical properties of many organic substances such as peptides or sugars. The specific behaviour of hydrogen bonds under the condition of an intensive electronic excitation, as given by the impact of a fast heavy ion or by UV-laser irradiation, will be discussed. There is some evidence for a mechanism which breaks hydrogen bonds selectively, promotes proton transfer reactions and thus enables the desorption of intact molecular ions.

## 1. Introduction

The investigation of hydrogen bonding is interesting in the context of this workshop, because

- hydrogen bonds (HBs) determine the physical and chemical properties of many substances which are of practical interest,
- the N-H and the O-H bond can interact strongly with excited electrons, which are produced by a fast projectile or laser light, because of their dipolar momenta,
- hydrogen bonds can have a strong influence on the absorption and fluorescence behaviour of aromatic molecules, which indicates another way of interaction with electronic excitation,
- protonization and deprotonization are important sources of molecular ion formation.

### 1.1. Properties of Hydrogen Bonds

HBs are placed at an intermediate position on the scale of atomic and molecular forces<sup>1</sup>: the ratio of the HB strength to the covalent bond strength is about 1:10 to

1:50. HBs can strongly influence intermolecular forces, e.g. in rising the boiling temperature of water or alcohols by a factor of about 10. In a hydrophilic environment they determine the relative coordination of molecules and (for biological matter) their secondary structure. To separate a molecule from its environment without destroying it, means therefore in many cases to break HBs without touching covalent bonds.

From positive and negative ion spectra it is obvious that proton transfer is an important mechanism (at least in PDMS) to produce *large* intact molecular ions. In a polar environment protonized and deprotonized molecules usually exist in chemical balance at room temperature, so (de-)protonization is a *soft* process compared to the breaking of a C-H bond. Despite of this, preformed ions are rarely observed in mass spectra; it seems that the conditions of the usual *cold chemistry* in the matrix are not conserved by the desorption process.

In PD as well as in UV-LD a local strong excitation of the electron system will, in general, influence all atomic forces. Its specific action on covalent bonds, however, is known at least as far as these bonds are understood in terms of simple two-electron physics (which holds for nearly all substances we deal with). Electrons can be removed from binding states by ionization or by being shifted to higher levels, which means that bonds can either be broken or (for aromatic systems) more or less slightly modified.

The specific influence of electronic excitation on HBs is more complex since hydrogen bonding can be understood only in terms of four-electron physics. The electronic state of a HB between OH and O is composed at least of three contributions\*:

1. the simple covalent state  $[-O-H] [O-]$  ,
2. the charge transfer state  $[-O]^- [H-O]^{+}$  ,
3. the ion state  $[-O]^- H^{+} [O-]$  .

Interatomic forces are usually composed of a covalent, a dispersive and an electrostatic contribution; none of them is negligible. For medium strong HBs this results in an effective potential curve with two local minima for the proton position of given O-positions, and an effective potential curve with respect to the O-O distance for the quantum mechanic ground state of the proton. The O-H bond has a relatively strong dipole momentum and is responsible for the high frequency bands in IR spectroscopy.

Due to the dipole character of the O-H stretching vibration, the cross section for its excitation by electron scattering is relatively large. From IR-measurements it is known that a variation of the position of the O-atoms of a HB-bound complex

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\*In this paper we talk about the O-H...O HB, but the OH...N, NH...O and NH...N pairs may be treated in an equivalent way.

**Table 1:** Blue (+) or red (-) shifts of optical transitions with substances dissolved in water or MeOH (unit:  $cm^{-1}$ )

Substance	$\nu_0$	Solvent		Tr.
		H <sub>2</sub> O	MeOH	
Nitrosobenzene	13,000	+ 50	+ 450	$n-\pi$
Pyrazine	31,500	+ 700	+ 1800	$n-\pi$
Pyridazine	29,450	+ 2440	+ 4000	$n-\pi$
Mesityl oxide	43,000	- 1000	- 1700	$n-\pi$
Mesityl oxide	30,760	+ 1000	+ 3200	$\pi-\pi$
Diazoetic ester	25,500	+ 800	+ 1500	$n-\pi$
Diazoetic ester	41,500	- 550	- 600	$\pi-\pi$

can have a strong influence on the frequency of the transition to the first excited level and its oscillator strength. So, vice versa, we can assume that an intensive excitation of this or higher modes will also influence the effective potential of the HB.

HBs can be regarded as *partial* (incompletely dissociated) proton transfer complexes<sup>2</sup> where the donor- and the acceptor molecule are not separated completely from each other. An electronic excitation of one of the molecules at a position close to the HB will generally affect its strength; this has been observed since the 1950's where absorption and fluorescence behaviour have been studied using different solvents. As an example the transition of an electron in an atomic (not binding) to an anti-binding state in an aromatic ring ( $n-\pi$ ) can cause a reduction of electron density in the nodal plane and thus weaken the HB, as discussed by Pimentel<sup>4</sup> as early as 1957. The spectroscopic manifestation of this interaction is a *blue-shift* of the transition when the molecule is investigated in a polar medium (as compared to the behaviour in an aliphatic solvent). In other cases, the opposite may occur that the HB formed by the excited state becomes stronger, thus leading to a *red shift*. Blue shifts are usually stronger than red shifts. On the chemical level one can observe stronger or weaker changes of the acidity/basicity of the molecule when excited (which is expressed quantitatively by a change of the pKs value). *In the  $^1(\pi^*\pi)_1$  state of aromatic compounds basic sites are often more basic and acidic sites more acidic than in the ground state. If both such functional groups are present, it may occur that a molecule in its fluorescing ( $\pi^*\pi$ ) state exists either as a cation or as an anion, but there is no pH value in aqueous solution at which it is neutral ...*<sup>2</sup>. Tab. 1 shows some values listed in Ref.<sup>4</sup>.

## 1.2. Physical Conditions in PDMS and UV-LDMS

In PDMS the initial energy deposition occurs by ionization and excitation of electronic states by the projectile within a certain short range and time as discussed in<sup>6,7</sup>. Coupling within the electron system is much stronger than coupling between electrons and molecular vibrational modes, so in a first phase electronic energy is distributed over a larger area before interaction with molecular motion becomes important. In resonant UV-LDMS the laser light excites very intensively and selec-

tively levels with (usually) a large oscillator strength, i.e. strong transition dipolar momentum and thus also strong coupling to other transitions by radiationless interaction.

With a wave number of about  $3500\text{ cm}^{-1}$  of the transition from the ground to the first excited state the O–H stretching vibration has the highest frequency of all molecular vibrational modes which are observed in *usual* organic substances. In a dipole approximation the cross section for an electron being scattered inelastically is

$$\sigma(v) = \frac{8\pi\hbar\lambda^2}{3M_{\text{red}}\Omega} \frac{v_{\text{B}}^2}{v^2} \operatorname{arccosh} \sqrt{\frac{m_e v^2}{2\hbar\Omega}} .$$

$\lambda$  is the dipole momentum, divided by the binding distance,  $M^*$  is the reduced mass and  $\Omega$  the oscillator frequency ( $v_{\text{B}} = e^2/\hbar$ ). Since the mass of the proton is small in comparison to the mass of other atoms which are usually present in organic molecules, the O–H stretching vibration consists mainly of proton motion, i.e. the normal mode is nearly the same as the vibration of a single mass. When electrons are scattered by the O–H dipole, energy is transferred to other vibrational modes mainly by Fermi-resonances<sup>1</sup>, but there is no coupling to direct transitions. This means that, if the density of O–H bonds is large, a certain subsystem is formed which receives energy from excited electrons faster than the rest of the molecular lattice can do. If enough time is left to the system (as in IR-LD) this energy will, of course, be distributed to all degrees of freedom.

As suggested in<sup>12</sup>, electronic energy can be transported over a wide range by exciton diffusion before being transformed (trapped) into molecular motion, destruction or chemical reactions. So the interdependence between electronic excitation and HBs, which has been studied up to now mainly from a photochemical point of view, may become important.

## 2. Change of the Effective Intermolecular Potential

### 2.1. Excitation of the O–H Stretching Vibration

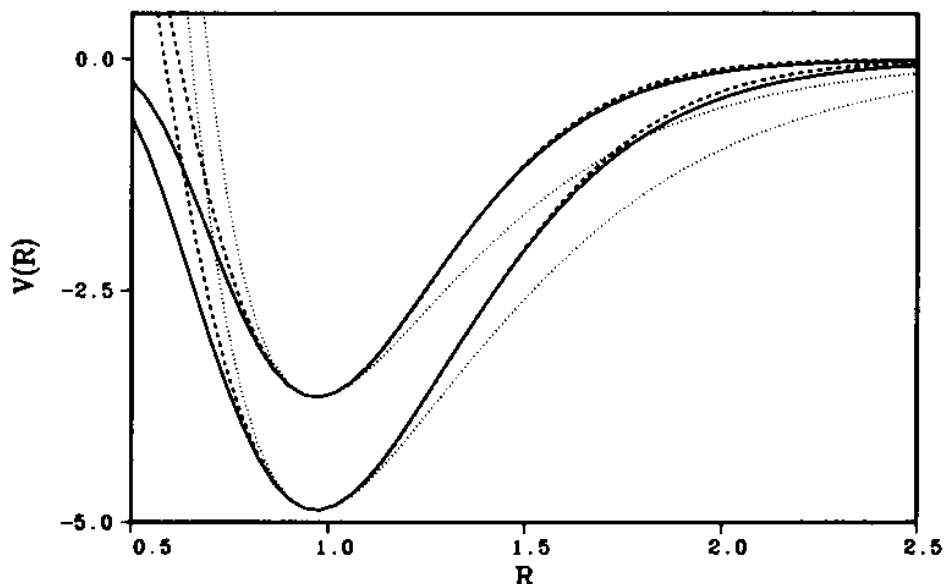
Instead of starting from first principles we use an empiric potential to describe the forces in a HB, which has been introduced by Lipincott and Schroeder<sup>11</sup> and used with some modifications by Reid<sup>9</sup>:

$$V(R, r) = W \exp\{-CR\} - \frac{U}{R^6} + V_{\text{L}}(r, 1) + V_{\text{L}}(R - r, \alpha) - \alpha D$$

where

$$V_{\text{L}}(x, \beta) = D\beta \left[ 1 - \exp \left\{ -\lambda \frac{(x - d)^2}{2x\beta} \right\} \right] .$$

$R$  is the O–O and  $r$  the O–H distance; the parameters  $W = 3.42 \cdot 10^5\text{ eV}$ ,  $C = 5.0\text{ \AA}^{-1}$ ,  $U = 11.26\text{ eV\AA}^6$ ,  $D = 4.87\text{ eV}$ ,  $\lambda = 9.18\text{ \AA}^{-1}$ , and  $d = 0.97\text{ \AA}$  were taken



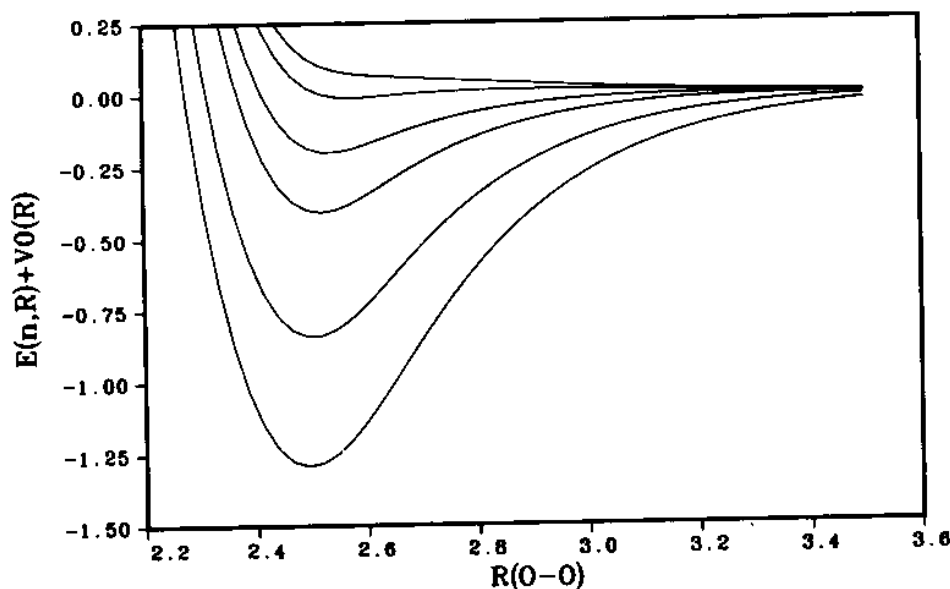
**Figure 1:** Lipincott–Schroeder (line), Morse (dotted) and modified Morse (dashed) potential with identical depth and force constant at equilibrium position for  $\alpha$  values 1 and 0.7.

from Reid’s and Lipincott’s papers and were found by fitting to well-known values from molecular spectroscopy. The parameter  $\alpha$  defines the symmetry of the HB:  $\alpha = 1$  would mean a symmetric HB. In order to do quantum mechanical calculations using a harmonic oscillator wave function base, we replaced the *Lipincott potential* function by a modified *Morse* function

$$V_{\text{M}}(x, \beta) = D\beta \left[ 1 - \exp \left\{ -\sqrt{\frac{\lambda}{2d\beta}} (r - d) - \frac{\sigma^2}{2\sqrt{\beta^3}} (r - d)^2 \right\} \right]^2$$

where  $\sigma^2/2 = 1 \text{ \AA}^2$ . As shown in Fig. 1 the difference between Lipincott’s and our curve is only visible in the range of small  $r$  where the steeper Morse shape looks more reasonable than the original form. The reason for this approach is that Lipincott’s potential is general and fitted in good agreement with the properties known for many molecules. A simple Morse potential (same depth and force constant) gives significantly different HB binding energies because of its different asymptotic behaviour for larger distances.

Since we deal with a system containing a lot of energy we have to look for excited vibrational states. The effect of HBs to the IR spectra (frequency shift) suggests that there may also be some effects of vibrational level excitation to the behaviour

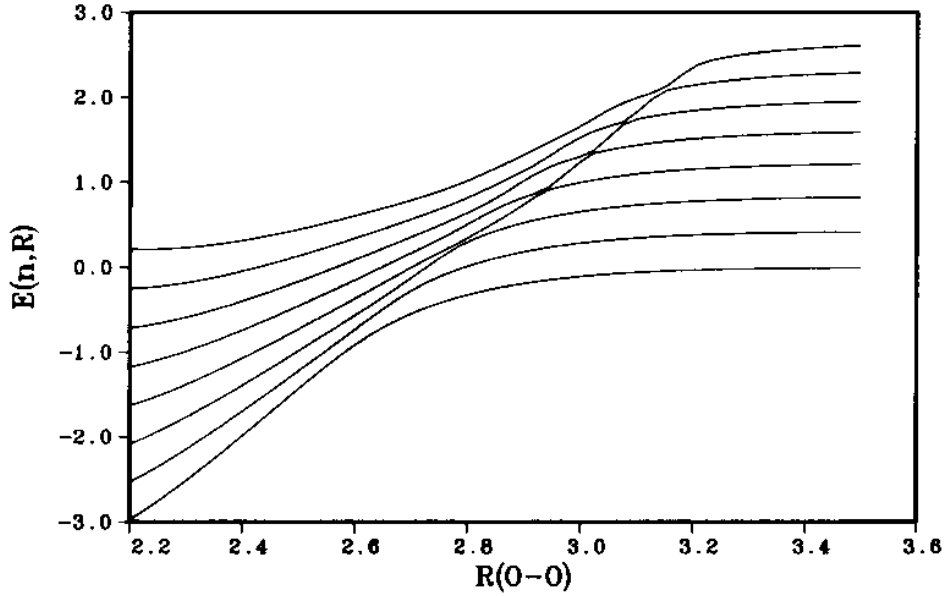


**Figure 2:** Effective HB potentials for different  $\alpha$  values (0.675, 0.7, 0.75, 0.8, 0.9 and 1.0), calculated quantum mechanically. For  $\alpha < 0.68$  the repulsive forces exceed the attractive contributions.

of the HBs. Investigating this question requires a quantum mechanical calculation of the eigenvalues of the Hamiltonian for the proton depending on  $R$ . The resulting ground state gives the *effective potential* for the partner molecules connected by HB. This implies that a *Born-Oppenheimer* approximation is applied to the proton motion, as compared to the motion of the whole molecules. This should be justified by the ratio of the observed oscillation frequencies (about 1:30 for  $\text{H}_2\text{O}\cdots\text{H}_2\text{O}$ , see<sup>9</sup>). Assuming a Hamiltonian

$$H = p^2/2M + V(R, r)$$

for the proton we use the harmonic oscillator wave functions (centered at  $r = d$  and for the same frequency  $\omega_0$ ) to calculate the matrix elements of  $H$  (as in<sup>10</sup>, but using a different potential) and obtain the eigenvalues by diagonalization of the matrix using a subroutine from the IMSL library. The advantage of the Morse potential (and the potential with the gaussian modification) is that the matrix elements can be calculated analytically from algebraic relations and without solving the Schrödinger equation. This enables the use of 50 states (or more, but this would not improve the accuracy further) with little computer time. For harmonic oscillator function



**Figure 3:** Excited vibrational levels  $E_n(R)$  for  $\alpha=0.75$  depending on  $R$ .

matrix elements  $|\mu\rangle, |\nu\rangle$

$$\langle \mu | f(X) | \nu \rangle = \frac{1}{\sqrt{\mu! \nu!}} \left( \frac{\partial}{\partial \chi} \right)^\mu \left( \frac{\partial}{\partial \eta} \right)^\nu [\exp\{\chi \eta\} \langle 0 | f(x_0(\chi + \eta) + X) | 0 \rangle]$$

at  $\chi, \eta = 0$  with  $x_0 = \sqrt{\hbar/2M\omega_0}$ . The latter matrix element can be calculated analytically because the potential contains only Gauß type functions  $f$  (or exponential functions, for a pure Morse potential). The result has the form

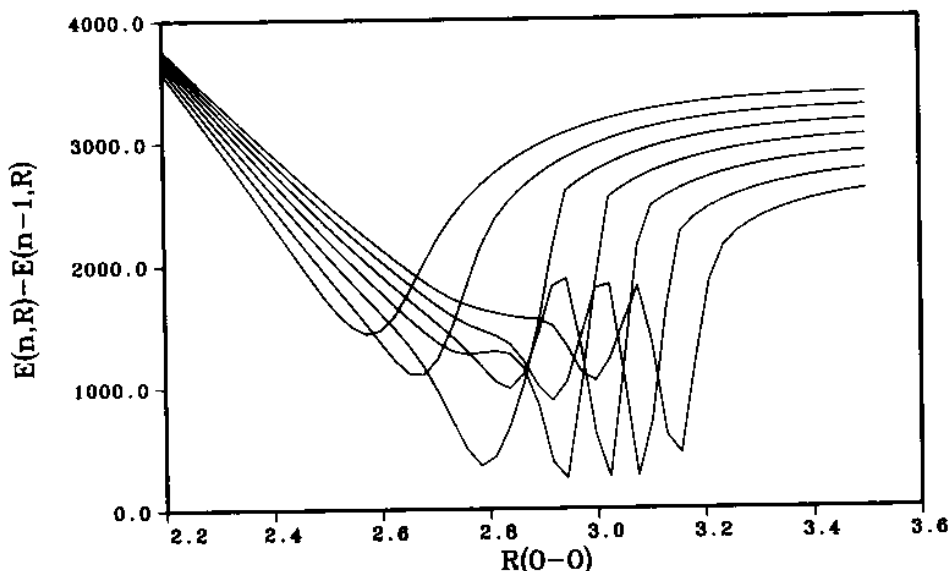
$$B_{0,0} = \exp\{\chi \eta + \Gamma(\chi + \eta) - \Lambda^2(\chi + \eta)^2/2\}.$$

The partial derivatives are calculated recursively by the relation

$$B_{\mu,\nu} = \frac{\Gamma}{\sqrt{\nu}} B_{\mu,\nu-1} + (1 - \Lambda^2) \sqrt{\frac{\mu}{\nu}} B_{\mu-1,\nu-1} - \Lambda^2 \sqrt{\frac{\nu-1}{\nu}} B_{\mu,\nu-2}.$$

The result gives the well-known behaviour of  $E_0(R)$ , the effective intermolecular potential representing (with respect to  $\alpha$ ) more or less strong HBs. Fig. 2 shows some curves; Lipincott found that a bond exists only if  $\alpha$  exceeds a certain value.

Fig. 3 shows some excited levels (up to  $n = 8$ ) for  $\alpha = 0.75$ , Fig. 4 the level spacing. The decrease in the transition frequencies, as observed in experiments<sup>3</sup>

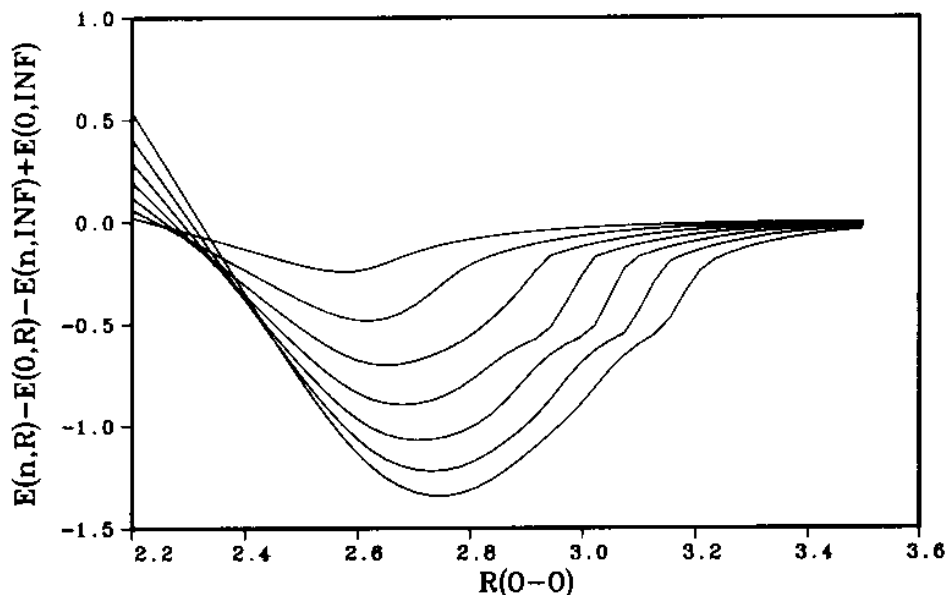


**Figure 4:** Level spacing ( $E_n(R) - E_{n-1}(R)$ ) for  $\alpha = 0.75$  depending on  $R$  for  $n = 1$  to 8. ( $E_1 - E_0$ ) starts with  $3500 \text{ cm}^{-1}$  for large  $R$  (O-H bond without other interactions); the other transition frequencies shown below.

with decreasing  $R$  is visible (however,  $n > 4$  is probably not of practical interest), but there is no significant change in binding strength for the higher levels. The main effect of a transition to excited vibrational levels is obviously a small increase in the equilibrium distance or (if molecular positions are kept) an effective repulsive force between molecules. In Fig. 5 the additional (relative) potential contributions from excited states  $\{E_n(R) - (E_0(R)) - [E_n(\infty) - E_0(\infty)]\}$  are displayed. The repulsive forces lie in the range of some  $\text{eV}/\text{\AA}$  for  $R < 2.5 \text{ \AA}$  (see Fig. 6).

## 2.2. Electronic Excitation and Proton Transfer

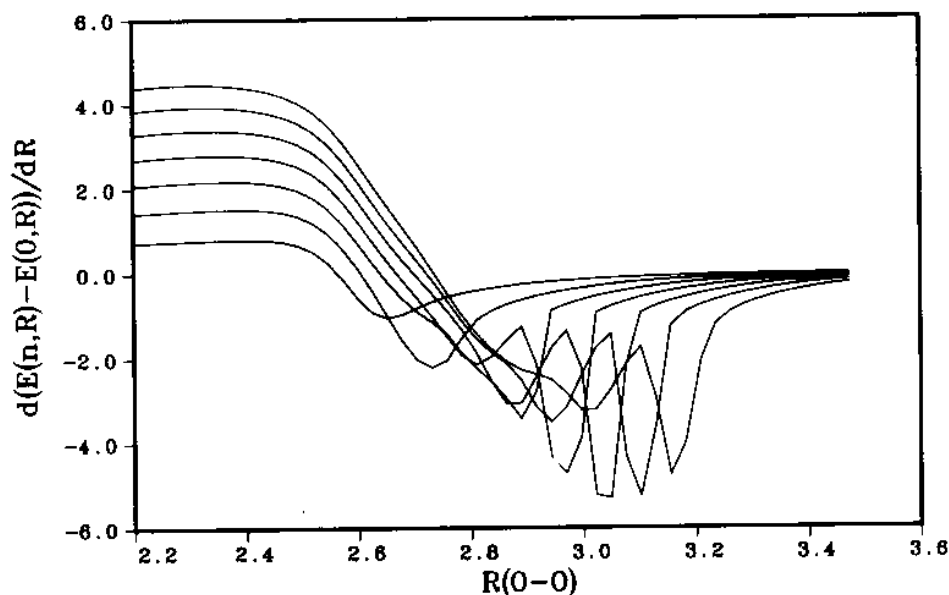
In the previous section we found that vibrational excitation of the HB, despite its effective coupling with the electron system, probably does neither give rise to intensive HB breaking, nor to proton transfer and thus charge separation. Its main effect are short-range repulsive forces, which may contribute to desorption in a way comparable to the *popcorn*-mechanism<sup>8</sup>. This may explain some differences between IR-LD on the one hand and UV-LD and PD on the other: IR irradiation directly excites the O-H stretching vibration very strongly, while UV irradiation and fast heavy ions release their energy mainly to electrons; in the first case ionization is weaker and energy is in the first place led to molecular heat.



**Figure 5:** Relative effective potential contribution from excited vibrational states.

As shown by Pimentel in a quite general way (see above) the effective forces acting in a HB are changed if electronic transitions occur in one of the molecules involved in the HB. We may describe the excitation energy by an additional energy  $\epsilon_0$ , representing the *free molecule* excitation energy and a change of the parameters in the Lipincott potentials.

In Pimentel's paper the Franck-Condon-principle is applied only to the position of the molecules, i.e. it is implicitly assumed that the proton stays in a vibrational ground state when an electronic transition takes place. This is usually sufficient for conditions where vibrational states are not almost not populated and where the relaxation of the molecule with some solvent makes the difference between absorption and fluorescence light frequency. Here we have to take into account that  $R$  and  $r$  are variable and that an electronic Franck-Condon transition depends both on the relative position of the molecules and the position of the proton. As an example we looked at the situation for  $\alpha = 0.8$  and a hypothetic modification of the O-H bond with  $\alpha^* = 0.75$  and  $d^* = 1.1d$  ( $\epsilon_0$  is out of scale). Fig. 7 shows the effective potential of the proton before and after the electronic transition takes place. Obviously, a Franck-Condon-transition from a vibrational state will lead to a stronger blue shift than from the ground state, and proton tunneling after the electronic transition will become more efficient proportional to the amount of proton energy — as compared to the remaining potential dwell. Proton tunneling frequencies<sup>5</sup> can range from  $10^3$  to  $10^8 \text{ ns}^{-1}$ .



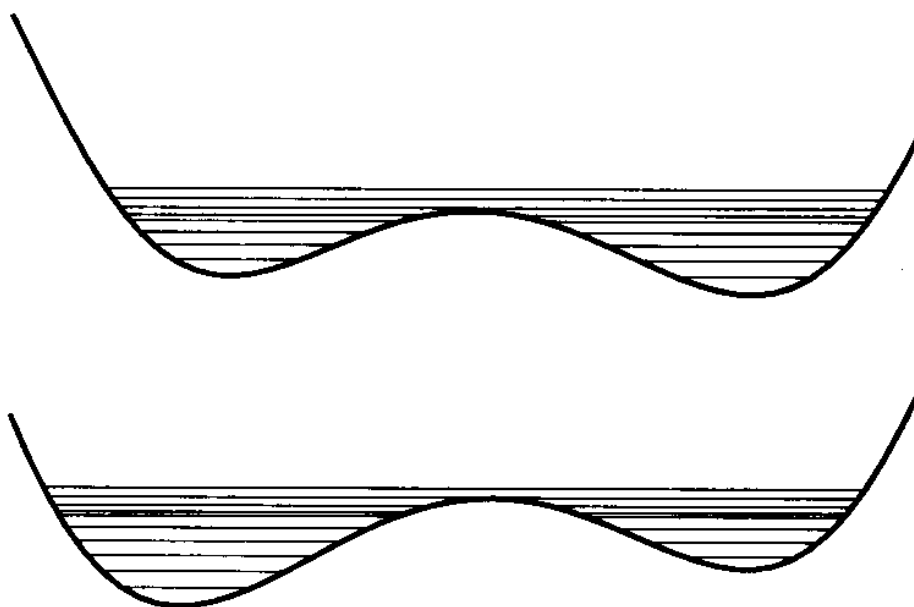
**Figure 6:** Effective force contributions from excited vibrational states for  $\alpha = 0.75$ .

The blue or red shift of some substances, compared to the energy of the HB gives some information about the possible strength of the effect. This means that there is a good chance to form proton transfer complexes, for many of the listed molecules if bound to a partner molecule which *fits* their behaviour (i.e. blue-shift molecules to basic and red-shift molecules to acidic sites).

### 3. Practical Consequences for Matrix Preparation

The theoretical considerations above have shown that there is not a *general* tendency of HBs to promote proton transfer, to break under the conditions of PD or UV-LD and thus enable ion desorption. But the obvious differences between different matrices and targets in desorption suggest that the molecular properties as discussed above should play a role and be worth of a systematic experimental checking.

Up to now the influence of HBs on electronic transitions and vice versa have mainly been investigated from a photochemical point of view. Particularly, in PD we have to take into account that excited states may play a role which is not accessible to photochemical experiments because of the different way of excitation. Where different transitions have different tendencies in their influence on the pKs values, the level density of the excited states will become important (which is in favour of  $(\pi-\pi)$ -transitions).



**Figure 7:** Effective potentials of the proton in electronic ground state and electronic excited state, unchanged  $R_{O-O}$ . A Franck-Condon transition from an excited vibrational state has a stronger blue shift than from the ground state and can enable an immediate transfer of the proton to the new potential minimum.

Generally, an enhancement of electronically stimulated proton transfer complex formation should take place in a matrix which forms many HBs and contains aromatic acids, bases or alcohols<sup>†</sup> Especially, the latter are known to show a strong blue shift and can strongly change their proton affinity when excited. The formation of proton transfer complexes with the molecule should be one criterium among others (good mixing with probe molecules, no chemical destructive reactions, no disturbance of the mass spectrum in the interesting range) for the selection of a certain matrix substance.

There are two arguments in favour of many HBs. On the one hand, in a usual (solid) matrix the fast relaxation after excitation, which is responsible for the effects in polar solvents, cannot take place. Instead, if a molecule has enough polar partners to rearrange with, an equivalent effect may take place. This is an argument in favour of small molecules (or molecules with *mobile* functional groups), but it is still an open question how far the reduction of the mobility of molecules caused by a rigid solid lattice would support the formation of states which would be suppressed

<sup>†</sup>This is with respect to the functional groups attached to the aromatic system, e.g. the hydroxyle or carboxyle group.

if *relaxation to anywhere* was allowed. It is possible that this difference between solvent and solid state environment results in a pressure increase, which means that the energy of the system can be reduced by expansion only, if rearrangement of solvent molecules is impossible.

On the other hand, many HBs can interact with each other by forming a phonon band where energy is transferred via dipole-dipole-interaction<sup>13</sup>, since we found above that vibrational excitation *in connection with* electronic excitation should give fastest proton transfer reactions. Finally, the more O-H bonds are present, the stronger they can interact with excited electrons and receive energy, which may cause different (destructive) effects if transferred to other processes.

#### 4. Acknowledgement

This work was supported by the Bundesministerium für Forschung und Technologie under grant No. MFU 05798.

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