ХИМИЯ: ИТОГИ И ПЕРСПЕКТИВЫ

Dedicated to the memory of Professor Dr. Mikhail Iosifovich VINNIK

PROTON POLARIZABILITY OF HYDROGEN BONDS AND HYDROGEN BONDED SYSTEMS

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Представляем читателям нашего журнала обзорную статью известного немецкого химика профессора Георга Цунделя, которую он любезно согласился написать по предложению редколлегии.

Профессор, доктор Георг Цундель родился **17** мая **1931** года в немецком городе Тюбингене. Изучал физику в университетах Мюнхена и Франкфурта-на-Майне.

В 1961 году окончил Мюнхенский Университет имени Людвига Максимилиана с дипломной работой: «ИК- исследование ионного обмена на полистирольной основе». (IR investigation of ion exchange on polystyrene basis) (с оценкой summa cum laude).

С 1961 года возглавлял исследовательскую группу по изучению межмолекулярных взаимодействий и сольватации с использованием спектроскопических методов. Целью этих исследований было углубление понимания электрохимических и биологических процессов на молекулярном уровне. В 1964/1965 провел трехмесячную научную стажировку в Институте химической физики АН СССР (Москва) в группе профессора М.И.Винника**. В 1967 году



получил право читать лекции в Мюнхенском Университете. В **1970** году совместно с Е.Г.Вайдеманом открыл широкую протонную поляризуемость водородных связей (large proton polarizability of hydrogen bonds). С **1974** года был профессором Мюнхенского Университета. Читал четырехсеместровые курсы лекций: физические методы в биологии, биологические мембраны, транспортные процессы, биоэнергетика, биофизическая химия генетического вещества. Под руководством профессора Г. Цунделя выполнено **50** дипломных работ и **40** кандидатских диссертаций.

В 1972 принимал участие в организации "Berghof Foundation for Conflict Research". С тех пор является членом правления.

Хобби: лесоводство, сельское хозяйство, исследование конфликтов и миротворчества.

Имеет около 310 научных публикаций в международных журналах. В 1969 году – монография «Гидратация и межмолекулярное взаимодействие». В 1972 г. в издательстве Мир (Москва) издан расширенный русский перевод. В 1976 г. – один из редакторов трехтомника «Водородная связь» (North Holland Publ.Co.). Обзорная статья "Hydrogen Bonds with large Proton Polarizability and Proton Transfer Processes in Electrochemistry and Biology" (in Advances in Chemical Physics, Vol.111, pp.1-217. I.Prigogine and St.A.Rice Eds., John Wiley & Sons Inc., Chicago, 2000)

Редколлегия пользуется случаем поздравить автора с 70-летием и пожелать ему здоровья и творческих успехов.

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^{**} Автор посвятил эту статью памяти профессора М.И.Винника, которому 25 мая 2001 года исполнилось бы 80 лет. Краткие сведения об этом крупном советском физико-химике приведены сразу после статьи профессора Г.Цунделя.

Abstract

Hydrogen bonds with double minimum or broad flat proton potential well, respectively, show socalled proton polarizabilities which are about two orders of magnitude greater than polarizabilities of electron systems. These hydrogen bonds cause continua in the infrared spectra and vice versa their presence in systems is demonstrated by these continua. In aqueous acid solutions these continua are due to the hydrogen bond in $H_5O_2^+$ groups. Generally, all $BH^+\cdots B \leftrightarrows B\cdots H^+B$ and $AH\cdots A^- \leftrightarrows -A\cdots HA$ bonds, respectively, show great proton polarizabilities. Also heteroconjugated $AH\cdots B \leftrightarrows -A\cdots H^+B$ bonds with double minimum proton potential well show great proton polarizabili-

ties. The carboxylic acid – N base family of systems is discussed. The ΔpK_a (pK_a of the donor minus pK_a of the acceptor), at which the systems are symmetrical, are characteristic for the family of systems. The position of the proton transfer equilibria depends, however, also on the interactions of the hydrogen bonds with their environments. Hydrogen bonds with great proton polarizability are of considerable importance for molecular processes in electrochemistry and biology.

1. Introduction

At the beginning of the seventies we discovered that hydrogen bonds with double minimum proton potential well or with broad flat potential well show polarizabilities being about two orders of magnitude greater than polarizabilities connected with the distortion of electron systems. These polarizabilities are indicated by continuous absorptions in the infrared spectra. These polarizabilities arise due to shifts of the proton within these hydrogen bonds and are called proton polarizabilities. In the meantime this property of the hydrogen bonds was carefully studied. The important role of such bonds in electrochemistry and biology was clarified and discussed. These results have been summarized in several detailed review articles [1-4].

2. Infrared continua and RAYLEIGH wings in the RAMAN spectra

With aqueous acid and base solutions long time ago continua have been observed by Suhrmann and Breyer in the overtone region of the infrared spectra [5]. Later with the same systems Wicke, Eigen and Ackermann [6] found infrared continua in the fundamental region (Fig. 1A). Zundel et al. [7] observed these continua with acidic polyelectrolytes and Zundel and Metzger [8] proved that these continua are caused by $H_5O_2^+$ groups in the case of aqueous acid solutions. All studies with polyelectrolyte membranes are summarized in ref. [9]. Such a continuum observed with polystyrenesulfonicacid is shown in Fig. 1B.

The corresponding effect in the RAMAN spectrum is intense elastic scattering at the excitation line – so-called RAYLEIGH wings – shown in Fig. 2 [10].



Fig.1A. IR spectra of pure water (dashed line) and of an aqueous HCl solution (solid line).



Fig.1B. IR spectra of a polystyrenesulfonic di membrane, thickness 5 μ m (solid line) and for comparison, Na⁺ salt of this membrane (dashed line). [Taken from ref. 9].



Fig.2A. The central Lorentzians of aqueous HCl solutions at 293 K as a function of the acid concentration: c = 0 (solid line), c = 1.0 mole·dm⁻³ (dashed line), 3.1 mole·dm⁻³, (dotted line), 6.0 mole·dm⁻³, (dashed dotted line), c = 12.3 mole·dm⁻³ (dashed double dotted line).



Fig.2B. The central Lorentzians of aqueous DCl solutions at 293 K as a function of the acid concentration: c = 0 (solid line), c = 1.0 mole·dm⁻³ (dashed line), 3.1 mole·dm⁻³ (dotted line), 6.0 mole·dm⁻³ (dashed dotted line), c = 12.3 mole·dm⁻³ (dashed double dotted line) [Taken from ref. 10].

3. Reasons of these infrared continua

3.1. $H_5O_2^+$ group

To clarify the reasons of these IR continua we studied 5 µm thick membranes of polystyrenesulfonicacid [7-9].

Figure 3 shows the intensity of these continua as a function of the dissociation dearee of of the - SO₂OH groups for various polystyrenesulfonic acid membranes. The intensity of these continua increases in proportion to the degree of dissociation.

Figure 4 shows the number of water molecules \tilde{n} present per dissociated -SO₂OH group. The extrapolation of these curves demonstrates that the dissociation may occur if two water molecules are present per dissociated proton.

Both results, taken together, demonstrate that the excess proton with two water molecules, i.e. $H_5O_2^+$ is responsible for these IR continua [8,9]. In the $H_5O_2^+$ groups a so-called homoconjugated hydrogen

bond $BH^+ \cdots B \leftrightarrows B \cdots H^+ B$ is present.

The homoconjugated bonds are built up between the same type of groups, in this case water molecules. whereby excess protons form the hydrogen bonds. These hydrogen bonds are structurally symmetrical. Thus, when they are considered in isolation from their environments symmetrical proton potentials are present within these hydrogen bonds.

Figure 5 shows the H₂O scissor vibration of a highly concentrated aqueous solution of a strong acid. If one H₂O scissor vibration is ob- ciation [Taken from ref. 8]. served [11]. Hence, the excess pro-



Fig.3. Absorbance of the continuum as a function of α . the degree of dissociation [Taken from ref. 8].



two or less than two water mole- Fig.4. Number, \tilde{n} , of water molecules available to the cules are present per proton, only excess proton as a function of α , the degree of disso-

ton influences both water molecules of $H_5O_2^+$ to the same extent. Thus, the excess proton fluctuates in $H_5O_2^+$ with a frequency larger than the IR frequencies, i.e. with about 10^{13} Hz.

Figure 6 shows the IR spectrum of a hydrated polystyrenesulfonicacid membrane. The spectrum drawn with the dotted line is the one of the membrane at 292 K and that drawn with the solid line is that of the sample at 85 K. Thus, the continua of these homoconjugated hydrogen bonds are almost independent of the temperature [12]. By the latter result the supposition that the continuum has anything to do with the thermal fluctuations was invalidated.



Fig.5. H_2O scissor vibration of aqueous solutions of a strong acid. Ratio of moles water per mole acid: 2:1 (solid line), 3:1 (dotted line), 5:1 (dashed line). Pure water (dashed-dotted line) for comparison. [Taken from ref. 11].



Fig.6. IR spectra of polystyrenesulfonicacid, hydrated at 33% relative air humidity, at 292 K (dotted line), and 85 K (solid line). [Taken from ref. 12].

3.2. The great proton polarizabilities of hydrogen bonds

It seemed highly probable that these IR continua have something to do with the very fast fluctuation of the protons in the hydrogen bonds. Therefore, we solved the Schrodinger equation for the proton motion within a double minimum proton potential (Fig. 7A). Furthermore, we added to this Schrodinger equation a term $-\mu F$, dipole moment of the hydrogen bond times electrical field strength. This term takes into account the local electrical fields present in solutions [13].

The wavefunction of the proton groundstate in such a potential is symmetrical, while that of the first excited state is antisymmetrical as illustrated in Fig. 7A. We built a basis set by adding or subtracting both wavefunctions (Fig. 7B).



Fig.7. A: Double minimum proton potential and wave functions ψ_{0+} and ψ_{0-} , of the two lowest states. B: The wave functions ψ_r and ψ_l [Taken from ref. 13].

$$\psi_r = \frac{1}{\sqrt{2}} (\psi_{0+} + \psi_{0-}), \ \psi_l = \frac{1}{\sqrt{2}} (\psi_{0+} + \psi_{0-}).$$
(1)

If c_{\pm} are the coefficients of the wave functions $\psi_{0\pm}$ and ψ_{0-} , the coefficients of ψ_r and ψ_1 are

$$a_r = \frac{1}{\sqrt{2}}(c_+ + c_-), \quad a_l = \frac{1}{\sqrt{2}}(c_+ - c_-).$$
 (2)

The weights of the proton limiting structures G_r and G_l are:

$$G_r = a_r^2, \quad G_l = a_l^2.$$
(3)

 G_1 gives the weight of the structure O⁺H··O, i.e. when the proton is on the left, and G_r the weight when it is on the right-hand side, i.e. the weight of the structure O··H+O. In the Schrodinger equation we introduced a term $-\mu F$, hence we got these weights as a function of the electrical field strength in hydrogen bond direction.

In this way we obtained the important result that hydrogen bonds having a double minimum proton potential show polarizabilities as result of shifts of the proton within these bonds [13]. The unexpected fact that these so-called proton polarizabilities are about two orders of magnitude higher than the usual polarizabilities arising by distortion of electron systems was considered highly unusual and noteworthy.

The fact of so great proton polarizabilities does, however, become understandable in the light of the following consideration (see Fig. 7A). For a double minimum proton potential the groundstate is symmetrical while the first excited state is antisymmetrical. These two states E_{0+} and E_{0-} are very close. Thus, even small electrical fields can admix the first excited state to the groundstate and in this way induce an asymmetrical charge distribution, i.e. result



Fig.8: The dependence of the shift of the energy levels in a hydrogen bond with a tunneling proton on the electrical field F (tunneling approximation, i.e. only the two lowest levels are considered) [Taken from ref. 13].

in polarization. The shift of the energy levels $E_{0\tau}$ by the electrical field F is

$$E_{0\mp} = \pm \sqrt{\left(\frac{1}{2}hv_0\right)^2 + (F\mu)^2}$$
(4)

Here, v_0 is the tunneling frequency and μ the maximum induced dipole moment of the hydrogen bonds. The lowest level is lowered and the first excited level is raised as illustrated by Fig.8.

To clarify whether this is really the case we performed ab initio self consistent field (SCF) studies of $H_5O_2^+$ [14,15]. The calculations give the O-O distance in the gas phase. This distance is much increased because of the environment, as is known from various experimental

results [16-18]. Therefore we artificially increased this distance to 2.55-2.65 A with these calculations. We obtained the energy surface and the dipole moment surface μ . Using these surfaces we solved the Schrodinger equation for the proton motion, again adding the term μF (dipole moment surface μ times electrical field strength), to take into account the influence of the local electrical fields *F* in the solutions.

From these calculations proton polarizabilities about two orders of magnitude greater than the usual polarizabilities due to distortion of electron systems were obtained [14,15].

Figure 9 shows these proton polarizabilities as a function of the electrical field strength and of the temperature. These polarizabilities decrease significantly if the hydrogen bonds are polarized. The upper scale ΔV is the difference between the two minima, i.e. a measure of the asymmetry induced by the external electrical fields.

Using the calculated transition moments, and assuming a reasonable electrical field strength distribution and a hydrogen bond length distribution, we calculated the IR continua. In Fig. 10A the IR continuum calculated in this way is compared with the experimental IR continuum, Fig. 10B. The extent of the agreement is highly satisfactory [19].

We performed now the following experiment [20]. We added neutral salts to a HCI solution in which the HCI concentration was kept constant. Figure 11 shows the intensity of the continuum as a function of the neutral salt concentration. This Figure shows that the intensity of the continuum decreases if LiCl is added. Thus, when Li⁺ ions are present in the solution the local electrical fields at the hydrogen bonds with



Fig.9. The proton polarizability α of the hydrogen bond in the H₅O₂⁺ group at various temperatures in degrees Kelvin, plotted against the field strength *F* and against ΔV , the energy difference between the two minima; also shown is the tunneling approximation in the case of 300 K (dotted line) [Taken from ref. 14].



Fig.10. Infrared continuous absorption of $H_5O_2^+$. (A) Calculated continuum. Mean field strength $\overline{F} = 5 \times 10^6 \text{ V/ cm}$. Molarity x layer thickness (in μ m) = 100. (B) that of a 13 mole·dm⁻³ aqueous HCl solution at 21°C, layer thickness 8 μ m; (solid line), along with H₂O shown for comparison (dashed line). [Taken from ref. 19].

great proton polarizability are stronger than those found in the pure acid solutions. The opposite is true when alkylammonium ions are present.

These results demonstrate again that one important reason for the appearance of the continua is the induced dipole interaction between the hydrogen bonds having a great proton polarizability and the local electrical fields in solutions.

But there are also other interaction effects of homoconjugated hydrogen bonds with their environments as discussed in the next paragraph.

3.3. Interaction of polarizable bonds with phonons and polaritons in their environments

The interaction of hydrogen bonds with great proton polarizability with the thermal bath was treated by Hayd and Zundel in ref. [21].

3.4. Continua calculated in this way

IR continua calculated in this way are shown in Fig. 12 (see ref. 21), in the upper part for a mean hydrogen bond length of 2.7 A, and in the lower part for a mean hydrogen bond length of 2.8 A. The dotted spectra have been obtained without phonon coupling. For the spectra drawn with the long dashed line the coupling constant is 0.5. and for the spectra drawn with the solid line the coupling constant is 1.0. These calculated spectra show that the intensity of the continua increases strongly due to the coupling of the hydrogen bonds with great proton polarizability with the phonons of the thermal bath. This effect is particularly important for longer hydrogen bonds with great proton polarizability. In the case of shorter polarizable hydrogen bonds the coupling with the phonons of their environments is less important, since their proton polarizability is smaller.



Fig.11. Absorbance of the continuum caused by $H_5O_2^+$ as a function of the concentration of added neutral salt [Taken from ref. 20].



Fig.12. Calculated IR spectra of easily polarizable $O^+H^-O \leftrightarrows O^-H^+O$ bonds, coupled with the phonons of the thermal bath (dashed lines) without coupling, having a coupling constant of 0.5 (broken lines), and a coupling constant of 1.0 (solid lines). A: Bond length 2.7. B: bond length 2.8 A [Taken from ref. 21].

3.5. Continua in non-aqueous systems

When a strong acid is added to alcohol an intense continuum arises, as shown in Fig. 13A. When a strong acid is added to dimethylsulfoxide [23] an intense continuum is found, too, as shown in Fig. 13B. In the latter case the SO⁺H^{...}OS \Rightarrow SO^{...}H⁺OS bonds are strong, easily polarizable hydrogen bonds.



Fig.13A. IR spectra of non-aqueous systems (completely water-free): *p*-toluene sulfonic acid solutions in CH₃OH (at 30°C) having a layer thickness of 10 μ m. Spectrum 1 concentration 1.96 mole dm⁻³, spectra 1 to 11 decreasing concentration, while spectrum 12 is pure alcohol [Taken from ref. 23].



Fig.13B. The IR spectra of non-aqueous systems (completely water-free) of p-toluenesulfonic acid solutions in dimethylsulfoxide (DMSO) (at 30°C), having a layer thickness of 10 μ m. Spectrum 1 shows a saturated solution (3.29 mole·dm⁻³), spectra 1 to 8 decreasing concentration, and spectrum 9 pure DMSO [Taken from ref. 23].

If one protonates N-methylimidazole [24] an intense IR continuum arises, indicating that

the N⁺H···N \leftrightarrows N···H⁺N bonds formed between the N-methylimidazole molecules show also very great proton polarizability. Figure 14 shows the intensity of the IR continuum of an aqueous N-methylimidazole solution as a function of the degree of protonation [24]. In the range of 0–50% protonation hydrogen bonds with great proton polarizability are formed between N-methylimidazolium and N-methylimidazole. After 50% protonation the continuum again decreases and has vanished almost completely at 100% protonation. The reason is that at 100% protonation all N-methylimidazole molecules are protonated, almost no non-protonated N-methylimidazole molecules are available as acceptors. Therefore, almost no N⁺H···N \leftrightarrows N···H⁺N bonds can be formed. After 100% protonation the intensity of the con-

 $N^+H^-N \rightarrow N^-H^+N$ bonds can be formed. After 100% protonation the intensity of the continuum increases strongly again, since the excess protons form now $H_5O_2^+$ groups with water molecules. The results obtained for the N-methylimidazole and dimethylsulfoxide systems are particularly interesting. They show that for the appearance of the continua to occur, the groups forming the polarizable hydrogen bonds must not be cross-linked with their environment via further hydrogen bonds [23,24].

3.6. Deuteron bonds and deuteron polarizabilities

Let us now consider deuteron bonds [22], i.e. we compare the IR continuum caused by $H_5O_2^+$ with the respective IR continuum caused by $D_5O_2^+$. The spectrum drawn with the solid line in Fig. 15 is the spectrum of a HCl solution in H_2O , the one drawn with the dashed line is that of a DCl solution in D_2O . The continuum caused by $H_5O_2^+$ begins at the v(OH) vibration, and the $D_5O_2^+$ continuum at the v (OD) vibration. Furthermore, the intensity of the $D_5O_2^+$ continuum is only about half of that caused by $H_5O_2^+$. Thus, the deuteron polarizability of deuteron bonds is about half of the proton polarizability are determined by the same transition moments.



Fig.14. Absorbance of the IR continuum of an aqueous imidazole solution as a function of the protonation [Taken from ref. 24].



Fig.15. The IR spectra of various solutions having a layer thickness of 12.5 μ m, at a temperature 293 K, 3.4 mole dm⁻³ HCl in H₂O (solid line), 3.6 mole dm⁻³ DCl in D₂O (dashed line), pure H₂O (dotted line) and pure D₂O (dashed-dotted line). [Taken from ref. 22].

3.7. Negatively charged hydrogen bonds with large proton polarizability

We have seen that homoconjugated $B^+H\cdots B \leftrightarrows B\cdots H^+B$ bonds show large proton polarizabilities. The question now arises whether the homoconjugated negatively charged $AH\cdots A^- \leftrightarrows A\cdots HA$ bonds show also great proton polarizabilities [25-27].

In Fig. 16A the IR spectrum of a strongly basic ion exchanger is given. The fixed ions are trimethylammonium ions. With the hydrated base an intense IR continuum is observed. One can prove that this IR continuum is caused by the OH···O⁻ \Rightarrow ⁻O···HO bonds in H₃O₂⁻ groups. Thus, these groups which contain a hydrogen bond with great proton polarizability are present in aqueous, strongly basic systems.

Figure 16B shows that also for aqueous KOH solutions an intense IR continuum is observed. Its intensity increases in proportion to the KOH concentration if it is not too high. Figure 16C shows that also negatively charged hydrogen bonds, formed if alcoholate is added to alcohol, cause intense IR continua, demonstrating that the $OH\cdots O^{-} \leftrightarrows O\cdots HO$ bonds built up in these systems show great proton polarizability, too. Thus, also negatively charged homoconjugated hydrogen bonds show great proton polarizability.



Fig.16.

A: IR spectra of a basic polyelectrolyte membrane at $25 \,^{\circ}$ C, about 10μ m thick, hydrated at 90% relative air humidity, poly(*p*-trimethylammonium)styrene hydroxide (lower line), and poly(*p*-trimethylammonium) styrene iodide (upper line). [Taken from ref. 27].

B: IR spectra of aqueous solutions of KOH at 28°C. The numbers shown in the figure are mole dm⁻³ KOH. Layer thickness 15 μ m. [Taken from ref. 25].

C: IR spectra. CH_3OK . The numbers shown in the figure are the concentrations in mole dm⁻³ in methanol [Taken from ref. 25].

In summary we can state: All $BH^+ \cdots B \leftrightarrows B \cdots H^+ B$ bonds as well as all $AH \cdots A^- \leftrightarrows A \cdots HA$ bonds, respectively, i.e. all homoconjugated hydrogen bonds show proton polarizabilities being about two orders of magnitude greater compared with polarizabilities due to distortion of electron systems. These proton polarizabilities are indi-

cated by continua in the IR spectra and by intense RAYLEIGH wings (elastic scattering) at the excitation line when RAMAN spectra are taken. Vice versa the presence of easily polarizable hydrogen bonds in systems is indicated by this effect.

4. Heteroconjugated $AH \cdots B \leftrightarrows A \cdots H^+B$ hydrogen bonds

The question arises whether the heteroconjugated $AH \cdots B \implies -A \cdots H^+B$ bonds with a double minimum proton potential also show great proton polarizabilities.

Huyskens gave the following definitions of a family of systems with heteroconjugated hydrogen bonds [28,29]. 1. All systems of a family have the same hydrogen bond donor AH, and all acceptors B are also similar molecules. They differ only with regard to the pK_a of B, or 2. the acceptor B is always the same, and the donors AH are similar molecules which differ only in their pK_a values. The Δ pK_a value is defined as pK_a of the acceptor B minus the pK_a of the donor AH.

4.1. The carboxylic acid – N base family of systems

The first family we studied was the carboxylicacid – N base family with $OH \cdots N \rightleftharpoons O \cdots H^+N$ hydrogen bonds [30,31]. The percent proton transfer can be determined in these systems from bands of the carboxylic group.

Figure 17 shows that the v (C=O) stretching vibration of the -COOH groups is observed at about 1715 cm⁻¹, and the asymmetrical stretching vibration of the $-CO_2^-$ ions, v_{as} (CO₂⁻) at about 1570, and the symmetrical ones at about 1400 cm⁻¹, respectively. In the IR spectrum one can distinguish between the non-polar and the polar structure. This shows that the fluctuation of the protons in these hydrogen bonds is slightly slower than in the homoconjugated hydrogen bonds [30-34]. However, this fluctuation is still so fast that in the far infrared no separate bands of a hydrogen bond vibration of the non-polar and the polar structure can be observed. All 1:1 carboxylic acid + N base mixtures were studied without solvent. All these mixtures are liquids at room temperature.



Fig.17. IR spectra, region 4000-600 cm⁻¹: acetic acid + metylimidazole (solid line), acetic acid+n-propylamine (dashed line), acetic acid + 2-methylpyrazine (dotted line). [Taken from ref.31].

Figure 17 shows the IR spectra of three extreme examples. In the 1:1 acetic acid + 2-methylpyrazine system an intense v (C=O) vibration indicates that the proton is localized at the carboxylic acid group, i.e. only the non-polar structure of the OH···N \Rightarrow -O···H+N equilibrium has weight. In the acetic acid + n-propylamine system an intense v_{as} (CO₂⁻) band and a v_s (CO₂⁻) band indicate that the protons are localized at the amine molecules, i.e. only the polar proton limiting structure O⁻···H+N has weight. In the acetic acid + me-

thylimidazole system these three bands have comparable intensity. Thus, both proton limiting structures have almost comparable weight. An intense continuum demonstrates that the

OH···N \leftrightarrows -O···H⁺N bonds show great proton polarizability. A double minimum proton potential is present within these hydrogen bonds. Thus, also heteroconjugated AH···B \leftrightarrows -A···H⁺B hydrogen bonds with double minimum proton potential show great proton polarizability.

In Fig. 18 (dashed line) the % proton transfer are shown as a function of the $\Delta p K_a$. For the systems with smaller $\Delta p K_a$ the deeper well of the double minimum is still at the acid. For the systems with $\Delta p K_a$ of about 2.3 both wells are on the average comparably deep, and for those of higher $\Delta p K_a$ the deeper well is at the N base. The curve, drawn with the solid line, represents the absorbance of the IR continuum. In the region around 50% proton transfer the

OH…N \Rightarrow ⁻O…H⁺N bonds show great proton polarizability, since an intense IR continuum is observed for these systems. These results show that 50% proton transfer is not observed at $\Delta pK_a = 0$ but for this family of systems at $\Delta pK_a^{50\%} = 2.3$.



Fig.18. Carboxylic acid – N base systems with N bases with additional hydrogen bond donor group showing the degree of transfer of the proton to the N base in % (dashed line), and the absorbance of the continuum in the region of higher wavenumbers (solid line). (b) Acetic acid + pyrazole, (c) acetic acid + 2-methanolpyridine, (e) acetic acid + 3- aminopyridine, (f) acetic acid + imidazole, (k) acetic acid + 2-ethylimidazole, (m) formic acid + 2-ethylimidazole, (o) acetic acid + n-propylamine, (p) formic acid + n-propylamine [Taken from ref. 31].

4.2. $\Delta p K_a^{50\%}$ value with various families of systems

These $\Delta p K_a^{50\%}$ values at which the systems are symmetrical are characteristic for the families of systems and depend on interaction effects influencing the symmetry.

Such values are summarized in the Table. With these systems the $\Delta p K_a^{50\%}$ values are found between 1.3 and 5.3. They have been measured by various researchers using a variety of methods.

In respect to the carboxylicacid – N base systems in Fig. 19 the curve, drawn as dashed line, represents the proton transfer curve already known, and the curve, drawn as solid line, is the case in which no hydrogen bond donor groups are present at the respective N bases. Thus, 50% proton transfer is only found at $\Delta p K_a^{50\%} = 4.0$, i.e. the transfer equilibrium is shifted in favor of the non-polar structure. The smaller $\Delta p K_a^{50\%}$ value 2.3 for the systems with N bases having additional hydrogen bond donor groups can be understood as follows: The additional NH groups build up an NH…O hydrogen bond to the second O atom of the carboxylic group. The carboxylicacid OH group becomes more acidic because of this additional hydrogen bond, favoring the transfer of the proton to the N-base.

Similar results are obtained with octylamine – substituted phenol and octylamine-substituted thiophenol systems [32-34].

system family		Apr 50%	colvent	mathad	rof
donor	acceptor	Δρκασον	Solvent	methou	IEI.
substituted phenols	n-propylamine	3.25	CD ₃ CN	IR	32
substituted phenols	octylamine	3.6	CCl ₄	IR	33
pentachlorophenol	substituted pyridines	1.6	CCl ₄	IR	33
3,4-dichloro- thiophenol	substituted pyridines	2.4	none	IR	34
substituted phenols	triethylamine	5.3	C ₆ H ₆	dipole	35
substituted phenols	substituted pyridines	3.5	C ₆ H ₆	dipole	36
substituted phenols	(L-lys) _n	2.2		IR	37
carboxylic acids	pyridine	3.5	CHCl ₃	IR	38
substituted benzoic acids	pyridine	3.7	C ₆ H ₆	dipole	39
carboxylic acids	pyridine	4.5	C ₆ H ₆	dipole	40
carboxylic acids	aromatic N bases (no self-solvation)	4	none	IR	31
carboxylic acids	aromatic N bases (self-solvation possi- ble)	2.3	none	IR	31
carboxylic acids	substituted pyridines	2.6	CH ₃ CN	IR	41
carboxylic acids	(CH ₃) ₃ NO	2.76	CH ₃ CN	IR	42
CF ₃ COOH	substituted pyridine N oxides	1.68	C ₆ H ₆ , C ₆ H ₅ Cl, C ₂ H ₄ Cl ₂ , CHCl ₃	IR, NMR	43
CF ₃ COOH	substituted quinoline N oxides	1.62	C ₆ H ₆ ,C ₆ H ₅ CI, C ₂ H ₄ Cl ₂ , CHCl ₃	IR, NMR	44
CF ₃ COOH	substituted pyridines	5.2	C ₆ H ₆ , C ₆ H ₅ Cl, CH ₂ Cl ₂ , C ₂ H ₄ Cl ₂ , CH ₃ CN	NMR, IR	45-47
CF ₃ COOH	substituted pyridine N oxides	1.32	CH ₂ Cl ₂	NMR, IR	47
(L-glu) _n	aromatic N bases	2.0		IR	48
carboxylic acids	(L-his) _n	2.8		IR	49
(L-cys) _n	N bases	2.0		IR	50

Table I. $\Delta p K_a^{50\%}$ values in the case of various families of systems (taken from reference 4)

According to Huyskens [28,29] the proton transfer equilibrium constant K_{PT} and the percent proton transfer in a family of systems are connected by the equation

$$\ln K_{PT} = \zeta \cdot \Delta p K_a - \delta \tag{5}$$

where ζ and δ are constants characteristic of a family and the solvent in which the family is studied.

In Fig. 20 $\ln K_{PT}$ is shown as a function of the $\Delta p K_a$ for the above mentioned family of systems. A linear relation is observed which is in agreement with equation (5). $\Delta p K_a^{50\%}$ is obtained from the point of intersection of this curve with the abscissa.



Fig.19. Carboxylic acid – N base systems, showing the degree of proton transfer to the N base in %; shown are systems with N bases without additional hydrogen bond donor groups (solid line), and systems with N bases with additional hydrogen bond donor groups (dashed line), for comparison. (d) Acetic acid + pyridine, (g) acetic acid + N-methylimidazole, (h) acetic acid + 2,4,6-trimethylpyridine, (i) formic acid + N-methylimidazole, (l) monochloroacetic acid + N-methylimidazole, (n) dichloroacetic acid + N-methylimidazole, (n) dichloroacetic acid + N-methylimidazole [Taken from ref. 31].



Fig.20. Log K_{PT} of the systems octylamine + substituted phenols plotted as a function of the $\Delta p K_a$. (1) 4-chlorophenol, (2) 3-chlorophenol, (3) 3,4-dichlorophenol, (4) 3,5-dichlorophenol, (5) 2,4-dichlorophenol (6) 2,3-dichlorophenol, (7) 2,3,4-trichlorophenol, (8) 2,4,5-trichlorophenol, (9) 2,3,5-trichlorophenol, (10) 2,4,6-trichlorophenol, (11) penta-chlorophenol [Taken from ref. 33].

4.3. Non-specific and specific interactions of polarizable hydrogen bonds with their environments

In what follows the dependence of the position of the proton transfer equilibria on nonspecific and specific interaction effects of hydrogen bonds with their environments is discussed [51].

Examining the nonspecific effect, Figure 21 shows results obfor the tained 2,4,6-trichlorophenol + triethylamine system in various solvents. The values of the $\ln K_{PT}$ are shown as a function of the Onsager parameter [52] $P_0 =$ $(\epsilon - 1)/(\epsilon + 2)$, where ϵ is the dielectric permittivity of the solvents. The Onsager parameter determines the SOcalled non-specific interactions, i.e. the interactions of the hydrogen bonds with the so-called reaction field [53]. The reaction field is the field arising from the orientation of



Fig.21. Logarithm of the proton transfer equilibrium constant of the system 2,4,6-trichlorophenol + triethylamine as a function of the Onsager parameter $P_0 = (\epsilon - 1)/(2\epsilon + 1)$. Solvents shown are (1) methyl-cyclohexane, (2) tetrachloromethane, (4) trichloroethene, (5) chloroform, (6) chlorobenzene, (7) trichloroethane, (8) butylchloride, (9) dibromomethane, (10) dichloromethane, (11) 1,2-dichloroethane [Taken from ref. 51].

the dipoles of the solvent molecules induced by the dipole of the hydrogen bonds. Besides this interaction effect, there are the so-called specific interactions of groups of the solvents with groups of the hydrogen-bonded partners. The most important ones are interactions of CH acidic groups with π -electrons of phenols or with the carbonyl O atom of carboxylic acid groups.

In Fig. 21 the solvents 1,2,7 and 8 cause mainly non-specific interactions, as shown by the linear relation between $\ln K_{PT}$ and the reaction field. By the reaction field the

OH…N \Rightarrow O…H+N equilibria are shifted in favor of the polar structure. The systems in which the proton transfer is greater than expected, relative to the non-specific interaction, i.e. the reaction field, are systems with solvents with CH acidic groups. 4 is chloroform, 5 chlorobenzene, 9 dibromomethane, 10 and 11 dichloromethane and 1,2-dichloroethane, respectively. All these solvents have strongly CH acidic groups. Consequently, the specific interaction of the CH acidic groups of the solvent with the π -electrons of the phenols cause a strong addi-

tional shift. Thus, due to non-specific as well as specific interactions the OH···N \leftrightarrows O···H⁺N equilibria are shifted in favor of the polar structure. Therefore the proton transfer equilibrium is determined by intrinsic and extrinsic factors [54]. Fig.22 shows that the proton transfer equilibria are shifted with decreasing temperature in favor of increasing transfer [51].

In summary we can state: also heteroconjugated i.e. $AH \cdots B = A \cdots H^+B$ bonds show great proton polarizability if double minimum proton potentials are present within these bonds. The $\Delta pK_a^{50\%}$ of a family of systems is characteristic for the family and is in addition determined by the environment of the hydrogen bonds.

4.4. The energy surfaces

We already know from our experimental results that also heteroconjugated $AH \cdots B \leftrightarrows ^{-}A \cdots H^{+}B$ bonds show great proton polarizability. Is it possible to prove this result by a theoretical treatment?

Using the ab initio SCF procedure we calculated the energy surface, the dipole moment surface μ , the proton polarizability and the line spectra for heteroconjugated hydrogen bonds [55]. It is already known that in the gas phase usually only the non-polar proton limiting structure is realized. The ab initio SCF results correspond to the behavior of the bonds in

gas phase. Therefore, we studied the extreme system $HBr-NH_2CH_3$. It is well known from data in the literature, that the protons may transfer in this system to a certain degree from BrH to the amine also in gas phase [56-60].

First we calculated the energy and dipole moment surfaces by using an ab initio SCF



Fig.22. IR spectra of acetic acid + trimethylamine in various solvents, concentration of the complex c = 0.07 mole dm⁻³ (ten-fold excess of amine). Layer thickness = 200 µm (A) in trichloroethane at 26° (solid line), at 0° (dashed line) and at -25° (dashed-dotted line) and (B) in dibromomethane at 27° (solid line), at -8° (dashed line) and at -49° (dashed-dotted line) [Taken from ref. 51].

treatment. The energy surface is shown in Fig. 23. The ordinate of the energy surface is the vibrational coordinate and the abscissa the proton coordinate. Even if no electrical field is present a double minimum proton potential is found in the BrH…N \leftrightarrows Br⁻…H⁺N bonds. The well of the proton potential at the N atom is slightly deeper.

To this surface a term $-\mu$ (BrN,BrH)x *F* is added. This term represents the dipole moment surface multiplied by the electrical field strength. The term $-\mu F$ takes into account the local electrical fields from the environments of the hydrogen bonds.

Figure 24A and B show that negative fields lower the well at Br at room temperature, the double minimum is largely symmetrical at a field strength of -5.10^6 Volt/ cm. Figure 24C and D show that the left well vanishes and the proton becomes localized at the nitrogen if the field is changed in opposite direction.



Fig.23. Energy surface, where the coordinates are the two vibrational modes BrH and BrN. [Taken from ref. 55].

Figure 25 shows the proton polarizability as a function of the electrical field strength and of the temperature. If the double minimum proton potential is largely symmetrical the proton polarizability is even at room temperature almost two orders of magnitude higher than the usual polarizabilities due to distortion of electron systems.

Figure 26 shows the calculated line spectra as a function of the electrical field strength. As with the homoconjugated hydrogen bonds, the lines shift as a function of the electrical field strength. Some lines vanish, other lines arise. Thus, if a distribution of local electrical fields is present due to this induced dipole interaction an IR continuum arises, as observed.



This theoretical treatment confirms that heteroconjugated $AH \cdots B = A \cdots H^+B$ bonds may show great proton polarizability if a double minimum proton potential is present within these hydrogen bonds.

Fig.24. Energy surface after addition of the surface $-\mu_{x-}(BrN, BrH) \ge F$, where $\mu_{x}(BrN, BrH)$ is the dipole moment surface and F the electrical field strength in the direction of the hydrogen bond. Distance between two lines amounts 300 cm⁻¹. Field strengths shown are (A) -1.4 $\ge 10^{7}$; (B) -1.0 $\ge 10^{7}$ V/ cm;(C) F = 1.0 $\ge 10^{7}$; (D) F = 1.4 $\ge 10^{7}$ V/ cm [Taken from ref. 55].



Fig.25. Proton polarizabilities as a function of the electrical field. Parameter, temperature in Kelvin. [Taken from ref. 55].



Fig.26. Relative absorption intensities of the transitions in the wavenumber range $0-1600 \text{ cm}^{-1}$ as a function of the electrical field strength. [Taken from ref. 55].

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