the P–C bond contribute essentially all of the increase in P–C overlap population upon allowing d character to the phosphorus. Thus, the sum of the values in parentheses for the P–C overlap in Table II add up to −0.004 for the σ-like orbitals (6a′, 7a′, and 9a′) while the corresponding sum for the π-like orbitals (8a′, 2a′′, 10a′, and 3a′′) is +0.210, with +0.164 being contributed to the latter from orbital 3a′′. These conclusions are borne out by a set of electron density difference maps (not shown) similar to Figures 3 and 4 representing the sum of the molecular orbitals which are π-like and the sum of those which are σ-like with respect to the P–C bond.

To summarize our work, methylenephosphorane and other phosphorus molecules which might be expected to exhibit the p_π–d_π bonding of classical electronic theory are found to have π-like orbitals even when d character is disallowed; but, when d character is included, the bonding in these molecular orbitals taken as a group is particularly enhanced. However, the electronic feedback upon allowing d character is often dominated by polarization effects,[24] which occur in all molecules without exception, when atomic orbitals of higher symmetry than those needed for the most simple description are included in the LCAO approximation.

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Extremely High Polarizability of Hydrogen Bonds

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Abstract: SCF–MO–LCGO calculations are performed for $H_5O_2^+$ as a model illustrating the properties of a symmetrical hydrogen bond with a double-minimum potential well. The potential curves for the proton in the hydrogen bond with and without electrical fields for various O–O distances are calculated, along with the dipole moments, polarizabilities, hyperpolarizabilities, and transition moments of the OH stretching vibrations in the hydrogen bond. The total dipole moment is almost twice as large as the contribution of the proton alone for displacements which are not too large. The relation between the dipole moment and the displacement cannot be approximated linearly. Thus hyperpolarizabilities are of importance. The most important result obtained is that the polarizability is about two orders of magnitude larger than usual polarizabilities. The polarizability of unsymmetric hydrogen bonds may also be considerably larger. The large polarizability causes three interaction effects: an interaction between symmetrical hydrogen bonds *via* proton dispersion forces, an induced-dipole interaction of the hydrogen bonds with the anions and the dipole fields of the solvation molecules, and an interaction between the transitions in the hydrogen bond and other, especially the intermolecular, vibrations. These interactions cause the strong continuous absorption which is observed in the ir spectra with liquid systems containing such hydrogen bonds. The smaller polarizability of unsymmetrical hydrogen bonds causes band broadening.

A continuous absorption was observed in the infrared spectrum on investigating acid and base solutions in the range of the fundamental vibrations[2] and in the range of the overtones,[3,4] as well as with acidic and basic polyelectrolytes.[5–8] This is caused in the acid solutions by $H_5O_2^+$ groupings and with bases by $H_3O_2^-$ groupings.[8] The continuum is not only observed in the presence of these bonds between water molecules but also in the case of many other liquid systems in which hydrogen bonds of type $BH^+\cdots B$ or $(AH\cdots A)^-$ are present.[9,10] It was possible to show that this continuum is caused by the special properties of these symmetrical hydrogen bonds with a double-minimum potential well in which the proton tunnels. Such hydrogen bonds are extremely polarizable.[11] This polarizability can be made plausible considering the distances between the energy levels and the symmetry of the wave functions in Figure 1. The wave function of the ground state E_{0+} of the tunneling proton is symmetric, that of the excited state, E_{0-}, is antisymmetric. If the first excited state is mixed with the ground state, an asymmetric charge distribution results. The first excited level of a tunneling proton is separated only slightly from the ground level. Thus, an extremely

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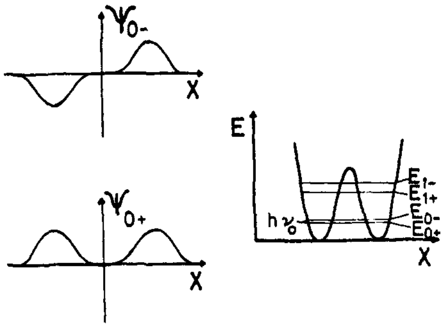

Figure 1. Schematic representation of a double-minimum potential well and the wave functions of the levels E_{0+} and E_{0-}.

small electrical field is sufficient for the first excited state to be mixed with the ground state. The high polarizability has three consequences. First, the electrical fields of anions and the dipole fields of solvate molecules in the neighborhood of the bonds polarize these bonds considerably. This is an induced-dipole interaction.[10] Secondly, these bonds exert a mutual influence on each other. Proton dispersion forces act between the bonds.[12] Thirdly, the OH stretching vibrations in these hydrogen bonds couple with low wave number transitions, especially the intermolecular vibrations as discussed in this paper. These three interactions shift the energy levels of the protons to a considerable extent. Since the strength of the interactions passes through a variety of values in a fluid, owing to the various distances and orientations between the groupings, a continuity of energy level shifts and thus the continuity of energy level differences occurs, which can be observed in the ir spectrum of systems with such hydrogen bonds.[8] Furthermore, the extremely high polarizability of these hydrogen bonds is the cause of the field-sensitive mechanism of the anomalously large proton conductivity.[11] In solids, tunneling movement of the Li^+ ions was postulated in particular for the movement of Li^+ in a KCl lattice. Many effects were observed which were thereby clarified. An extremely high degree of polarizability was explained analogously.[13-16] (See ref 13 for summary and further literature.) Subsequent to dielectric measurements of solutions of alcohol,[17-19a] and of complexes of phenols and triethylamine,[19b] a field-induced proton transfer in the hydrogen bond was discussed.

Only the proton in the bond was considered in our previous calculations of the polarizability of such hydrogen bonds.[11] However, it is of importance for the extent of the fluctuation of the charge center that the electrons move in the opposite direction on proton transfer. Hence, the charge center is shifted far more than the proton itself. In this paper, the polarizability of these hydrogen bonds is calculated, taking into consideration the electron shift induced by the proton transfer, using as an example $H_5O_2^+$.

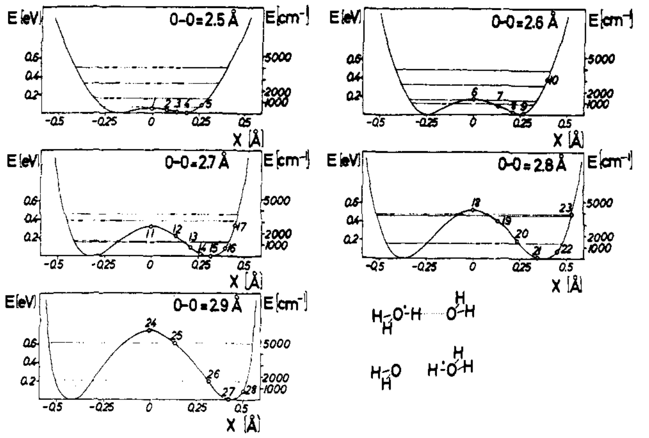

Figure 2. Potential wells for various O–O distances with the four lowest levels and the two proton boundary structures of the $H_5O_2^+$ group. The points indicated are calculated by the SCF treatment. The exact values are given in Table I. The geometry of $H_5O_2^+$: OH bond length in H_2O, 1 Å; H_2O bond angle, 110°; and the angle between the OH bond and the hydrogen bridge axis, 115°.

Calculations for $H_5O_2^+$ groupings by the SCF–MO–LCGO method[20,21] resulted in an equilibrium distance of the O atoms of 2.39 Å. At this distance, an extremely low barrier in the double-minimum potential well is present. According to calculations by the CNDO/2 method,[22,23] the barrier in the equilibrium distance has even disappeared completely. These calculations concern "free" $H_5O_2^+$. In the case of acid solutions, however, the $H_5O_2^+$ is linked with its environment *via* hydrogen bonds in the network of the solvate structure. Therefore, the water molecules of the $H_5O_2^+$ become polarized since they form extremely strong hydrogen bonds with their environment.[8] Thus, the O–O distance increases and the barrier in the hydrogen bond between the O atoms of the $H_5O_2^+$ is raised. This expansion of the O–O distance as the hydration of the $H_5O_2^+$ increases is illustrated by the X-ray structure investigations of Lundgren and Olovsson.[24-27] They find an O–O distance of 2.41 Å with $H_5O_2^+Cl^-$.[25] With $H_5O_2^+Cl^-H_2O$, the smallest O–O distance already amounts to 2.43 Å,[26] with $H_7O_3^+H_9O_4^+$-$2Br^-H_2O$, the O–O distances in the hydrogen bonds linked to the water molecules by H_3O^+ groupings of the $H_7O_3^+$ amount to 2.465 and 2.498 Å and in $H_9O_4^+$ groupings to 2.495, 2.587, and 2.588 Å.[27] Lee and Kaplow[28] observed distances of 2.56, 2.68, and 2.75 Å on X-ray investigation of hydrous HCl solutions. They write the following on this subject: "These O–O distances are probably related to the presence of excess protons in the water, and moreover, appear to be shorter as the concentration of protons increases." Naturally, this influence of further water molecules

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on the $H_5O_2^+$ grouping cannot be taken directly into consideration in our calculations. We therefore consider the special properties of the hydrogen bonds in dependence on the O–O distance. These calculations can thereby serve as a general model illustrating the properties of a symmetrical hydrogen bond with a double-minimum potential well.

(I) Method of Calculation

Both fragments of $H_5O_2^+$ (see Figure 2) were assumed to be pyramidal, with the two water molecules in the trans position.[24,29] One energy curve each for the proton movement between the two O atoms was calculated point by point for the five different O–O distances, 2.5, 2.6, 2.7, 2.8, and 2.9 Å. At least six points were calculated for each of the symmetrical energy curves. The SCF–MO–LC (LCGO) method (we used the SCF program from Dr. G. H. F. Diercksen, Max Planck Institute for Astrophysics, Munich, Germany) was applied,[30–33] whereby 67 spherical Gaussians, which were contracted to 46 basis group functions, served to describe the electron distribution of the $H_5O_2^+$ system. The energy curves obtained in this way for the proton movement are double-minimum potential wells (Figure 2). In conjunction with the calculated dipole moment curves (Figure 3), these can supply all required spectroscopic data. The values obtained from this calculation are given for the individual points in Table I.

Numerous methods were attempted previously to deal with the movement of a particle in the double-minimum potential well.[34–38] The three factors which are of importance for a symmetrical double-minimum potential well are the height of the barrier, the distance of the energy minima, and the force constant of the energy minima. By means of three points near the minimum of energy, we may calculate this minimum, the distance of both minima, and the force constant. A fourth point in the middle of the hydrogen bond gives, together with the minimum of energy, the potential barrier. A useful analytical representation of the potential must therefore comprise at least four free parameters. For this reason, even polynominals of the fourth degree or two Morse curves are not sufficient to represent such potential wells. Our own investigations have shown that at least six items of information are required to specify a symmetrical double-minimum potential well, if the four lowest energy levels are to be consistent. For this reason, the previously proposed modification of the linear-combination method of oscillator eigenfunctions[39] was applied, which allows the use of any number of points on the energy curve. The entire range of the position coordinate is divided into partial ranges in which the potential is approximated piecewise by polynomials.

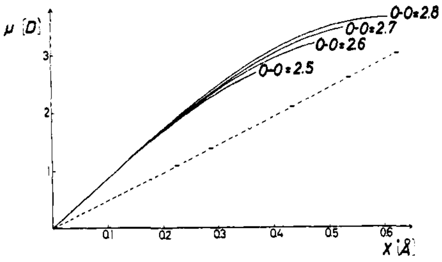

Figure 3. Dipole moment of the hydrogen bond as a function of the displacement of the proton from the center of the bond for various O–O distances (Å): (——) total dipole moment, (----) contribution of the proton alone.

Table I. Total Energy, Energy Level, and Transition Moments

Total Energy (au) of the Calculated Points

Point	Proton position, au	Total energy	Point	Proton position, au	Total energy
1	0	−151.55761	15	0.60	−151.54690
2	0.15	−151.55811	16	0.75	−151.54337
3	0.25	−151.55907	17	0.85	−151.53458
4	0.35	−151.55926	18	0	−151.52043
5	0.50	−151.55652	19	0.25	−151.52457
6	0	−151.54726	20	0.45	−151.53227
7	0.25	−151.55009	21	0.65	−151.53909
8	0.40	−151.55268	22	0.85	−151.53685
9	0.50	−151.55347	23	1.00	−151.52089
10	0.75	−151.54046	24	0	−151.50515
11	0	−151.53471	25	0.25	−151.50956
12	0.25	−151.53833	26	0.60	−151.52569
13	0.40	−151.54267	27	0.80	−151.53248
14	0.50	−151.54548	28	0.95	−151.53008

Energy Levels, cm^{-1}

	O–O distance, Å			
Level	2.5	2.6	2.7	2.8
0+	508.31	938.70	1153.79	1286.79
0−	1267.48	1272.09	1206.90	1290.31
1+	2593.34	2612.65	3048.10	3741.42
1−	3976.05	3937.86	3646.83	3822.63

Transition Moments,[a] D

	O–O distance, Å			
Transition	2.5	2.6	2.7	2.8
0+ ⟶ 0−	1.211544 (0.697917)	1.615994 (0.942583)	2.248941 (1.347881)	2.745533 (1.690592)
0+ ⟶ 1+	0 (0)	0 (0)	0 (0)	0 (0)
0+ ⟶ 1−	0.054589 (0.068271)	0.221868 (0.171842)	0.455492 (0.332266)	0.472658 (0.377284)
0− ⟶ 1+	1.233623 (0.751234)	1.133918 (0.693602)	0.738665 (0.489774)	0.501114 (0.391680)
0− ⟶ 1−	0 (0)	0 (0)	0 (0)	0 (0)
1+ ⟶ 1−	1.426379 (0.903192)	1.412764 (0.866166)	1.735601 (1.060280)	2.314677 (1.437222)

[a] Values in parentheses represent contribution of the proton alone.

The Schrödinger equation, using atomic units, may be written as follows

$$\left(-\frac{1}{2m}\frac{d^2}{dx^2} + \sum_l\sum_k a_{kl}x^k\right)\psi(x) = E\psi(x) \qquad (1)$$

The a_{kl}'s are the coefficients of the polynomial which

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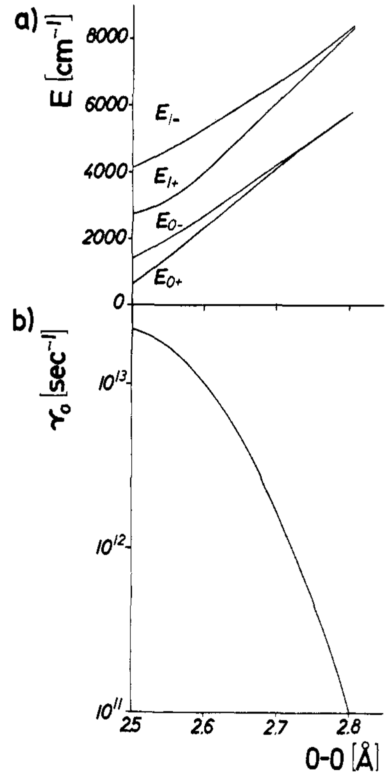

Figure 4. Energy levels in a symmetrical double-minimum potential well and ν_0 (ν_0 tunneling frequency) plotted as a function of the O–O distance.

represents the potential energy in the lth interval of the position coordinate x. In order to solve eq 1, the wave functions of the proton are represented as linear combinations of L oscillator eigenfunctions with respect to the potential minima x_i ($i = 1, 2$; $j = 1, 2, \ldots, L$).

$$\varphi_j^{ni}(x - x_i) = \sqrt{\frac{1}{2^n n!}\sqrt{\frac{\lambda_j}{\pi}}}e^{1/2\lambda_j(x-x_i)^2}\left(\frac{-1}{\sqrt{\lambda_j}}\right)^n\cdot\frac{\mathrm{d}^n e^{-\lambda_j(x-x_i)^2}}{\mathrm{d}(x - x_i)^n} \tag{2}$$

λ_j and x_i are in principle free variational parameters. In the case of the harmonic oscillator[40]

$$\lambda_j = \sqrt{mf}/\hbar \tag{3}$$

In the above equation f represents the force constant of the harmonic oscillator. The basis functions, eq 2, are thus variable as regards position (x_i) as well as shape (λ_j). The λ_j's are calculated for small n in eq 2 by means of the force constant f of the potential minima according to eq 3. For larger n, the force constant of the harmonic potential enveloping the double-minimum potential well is used. Values between these two force constants are also used for certain intermediate n. An advantage of this procedure is the fact that the lower states—and only these are of interest—are consistent especially rapidly as the basis functions increase in number. In this case, 10 basis functions are sufficient to calculate the four lowest states, while 40–120 functions were required by previous methods.

The coefficients c_r of the linear combinations of the functions in eq 2 to describe proton states are obtained by means of the secular problem.

$$\sum_{r=1}^{L}(H_{sr} - ES_{sr})c_r = 0 \tag{4}$$

H_{sr} is the energy matrix, calculated with the aid of eq 1, and S_{sr} is the overlapping matrix of the basis eq 2. We obtain an energy level scheme E_t and the related eigenfunctions

$$\psi_t = \sum_{r=1}^{L}c_{rt}\varphi_r \tag{5}$$

By means of the eigenfunctions in eq 5, dipole moments, polarizabilities, and transition moments can be calculated.

(II) Numerical Results

Figure 2 shows the potential curves of the proton in the hydrogen bond for various O–O distances. Figure 4 gives the energy levels of the proton as well as the tunneling frequency dependent on the O–O distance. Table I indicates the results of the SCF calculation, the positions of the energy levels, and the transition moments.

(A) Dipole Moment of the Hydrogen Bond. Figure 3 shows the total dipole moment of the bond with respect to the center of the bond depending on the position of the proton in the bond. The broken curve indicates the contribution of the proton to the dipole moment (see eq 9) and the solid one gives the total dipole moment. The total dipole moment is almost twice as large as the contribution of the proton for displacements which are not too great. This is due to the fact that the electrons shift in the opposite direction on displacement of the proton. The center of the charge thus shifts to a far greater extent than the proton.

This was taken only formally into consideration in the previous calculations by selecting a correspondingly longer distance between the potential minima.[11]

The effect of an external homogeneous electrostatic field F on the hydrogen bond in the O–O direction was now calculated in the following way. The Hamiltonian in eq 1 is given the additional term

$$W = -\mu(x)F \tag{6}$$

where $\mu(x)$ is the total dipole moment of the system, as shown in Figure 3. The change in the potential curves due to the electrical field is given in Figure 5. Figure 6 shows the four lowest energy levels in dependence on the electrical field strength.

Ten basis functions were again used to calulate the four lowest proton states in the hydrogen bond with a field. The dipole moment μ_t induced in the bond for the individual states t was calculated with the aid of the resulting eigenvectors.

$$\mu_t(F) = \int\psi_t^*(x, F)\mu(x)\psi_t(x, F)\mathrm{d}x \tag{7}$$

The shape of $\mu(x)$ in Figure 3 shows that the curve cannot be approximated linearly in the entire range containing both potential minima. Thus, in the expansion of $\mu(x)$ which is usually truncated after the linear term, the cubic term must be taken into account. Of course, the same is true with the transition moments.

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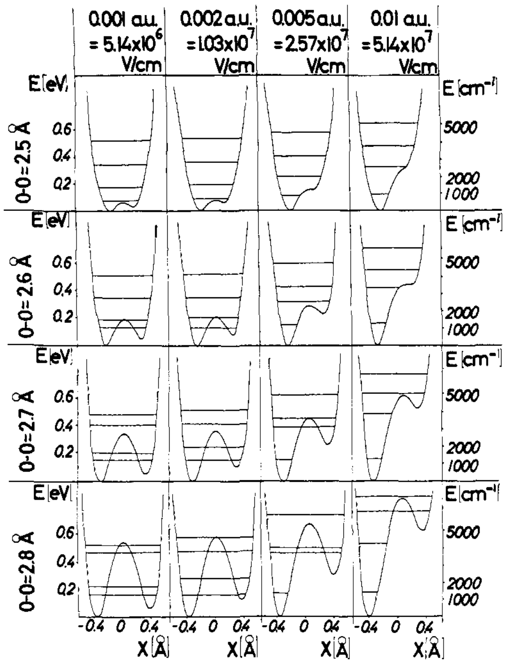

Figure 5. Potential wells for various field strengths at the hydrogen bond and various O–O distances.

$$\mu_{st} = \frac{d\mu(x)}{dx}\int \psi_s^*(x)x\psi_t(x)dx + \frac{1}{6}\frac{d^3\mu(x)}{dx^3}\int \psi_s^*(x)x^3\psi_t(x)dx \quad (8)$$

Thus, the intensity is no longer proportional to $(d\mu/dx)^2$.

These dipole moments for the ground state and the first excited state are plotted in Figure 7. In the first excited state, the dipole moment is induced opposite to the field direction with fields not too large. The direction of the induced dipole moment of the first excited state is reversed at field strength 3.5 × 10^7 V/cm. The dipole moment for various temperatures by taking the thermal average, as in ref 11, is also plotted. The dipole moment is in all cases relative to the dipole moment of the proton boundary structure, that is, to the total dipole moment p_m obtained if one considers the proton as localized in a minimum of the potential curve of the proton in the hydrogen bond without a field. Since the minimum shifts, due to the field, to the outside, μ/p_m can become >1 with extremely large fields, especially if the wells of the potential curves are flat. This is quite evident in the case of the O–O distance of 2.5 Å.

Since the induced dipole moment of the hydrogen bond is more than two orders of magnitude larger than in cases in which the main contribution is only due to the electrons (for instance, in the free water molecule, the dipole moment is 0.004 D in an external field of 5 × 10^7 V/cm[41]), the direct influence of the external field on the electrons could be neglected. The dipole operator in eq 6 for the proton is correspondingly

$$\mu(x) = e\int d^3r_1 \ldots d^3r_N \Psi^*(\mathbf{r}_1, \ldots, \mathbf{r}_N, x) \times \left(-\sum_{i=1}^{N} x_i + x\right)\Psi(\mathbf{r}_1, \ldots, \mathbf{r}_N, x) = \mu_{el}(x) + ex \quad (9)$$

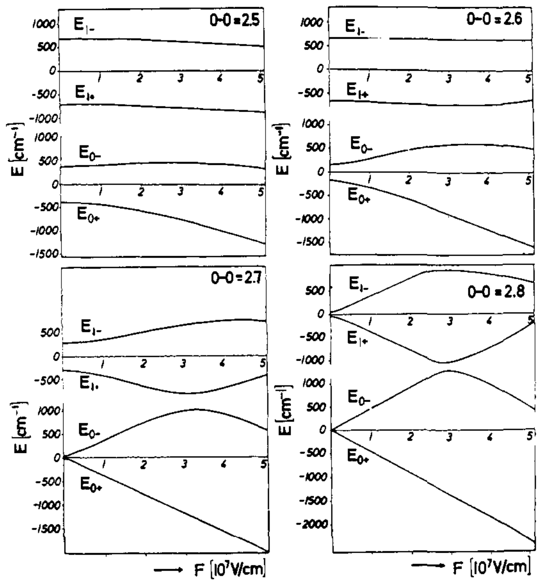

Figure 6. The four lowest energy levels plotted over the field strength at the hydrogen bridge. The distance between the zero points of the lower and upper levels is the calculated one.

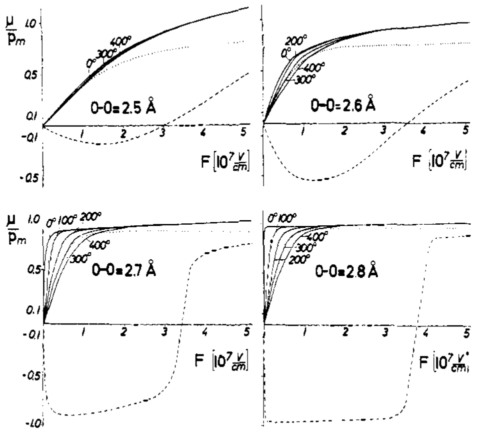

Figure 7. Induced dipole moments in the hydrogen bond for various temperatures in degrees Kelvin and various O–O distances in units of dipole moment p_m of the proton boundary structure plotted against the field strength: (-----) dipole moment of the first excited state, (·····) tunneling approximation in the case 300°K.

$\mathbf{r}_1, \ldots, \mathbf{r}_N$ are the electron coordinates and $\Psi(\mathbf{r}_1, \ldots, \mathbf{r}_N, x)$ the wave functions of the electrons with the proton fixed. μ_{el} is the contribution of the electrons shifted in the opposite direction from the H nucleus. The field dependence of Ψ was neglected.

The earlier calculations in the so-called tunneling approximation[11] only took the two lowest levels into account. In this calculation, the dipole moment could be expressed by the formula

$$\mu(F, T) = p\frac{Z}{\sqrt{1 + Z^2}}\tanh\left(\frac{h\nu_0}{2kT}\sqrt{1 + Z^2}\right) \quad (10)$$

$$Z = \frac{2p}{h\nu_0}F$$

Setting p equal to the transition moment between the states 0+ and 0−, as obtained in the present calculation, one gets the dotted curves shown in Figure 7. An appreciable deviation occurs for field strengths

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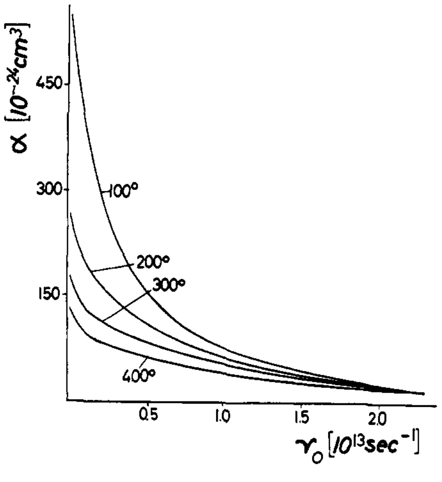

Figure 8. The polarizability as a function of the tunneling frequency for various temperatures in degrees Kelvin.

greater than about 5 × 10^6 V/cm. This can also be seen on considering the symmetry of the contributions of the ground state and the first excited state. For in the tunneling approximation, the first excited energy level E_{0-} is shifted to the same extent upward as the level E_{0+} downward, in contrast to the present calculation for larger field strengths (Figure 6). This shows that the tunneling approximation is valid only for fields which are not too large.

(B) The Polarizability of Hydrogen Bonds. The polarizabilities depending on ν_0 for four different temperatures are plotted in Figure 8. The polarizability of the symmetric hydrogen bond is approximately two orders of magnitude higher than usual electron polarizabilities, and thus extremely large. The polarizability also indicates that the direct influence of the outer field on the electrons is negligible, as was already mentioned during discussion of the dipole moments, for the polarizability of the H_2O molecule[42-44] is approximately two orders of magnitude less than that of the hydrogen bonds.

The high increase of polarizability as the tunneling frequency decreases, that is, as the O–O distance increases, is caused by the fact that the antisymmetric state ψ_{0-} is mixed more and more with the ground state. The polarizability thereby increases strongly when the barrier in the double-minimum potential well rises and, on the other hand, the polarizability becomes considerably less when the barrier disappears.

In the tunneling approximation, the following formula is obtained for the polarizability (eq 43 from ref 11).

$$\alpha(T) = \frac{p^2}{kT}\frac{\tanh y}{y}$$

$$y = \frac{h\nu_0}{2kT} \tag{11}$$

When the values p and ν_0 from the present calculations are substituted in ref 11, the deviations always remain below 3%.

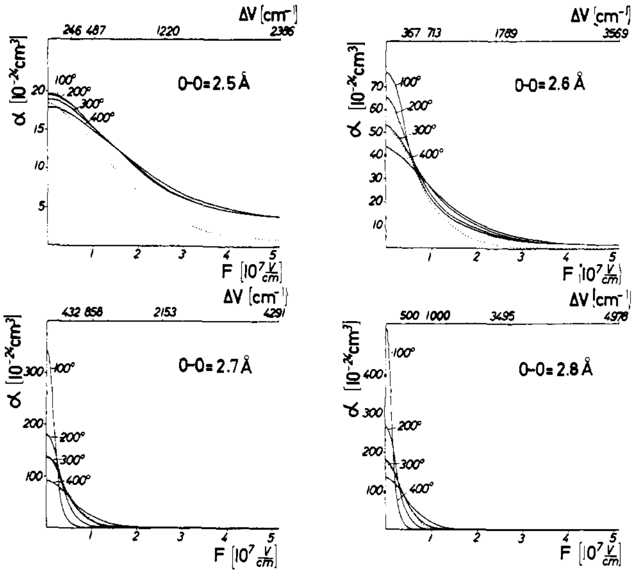

Figure 9. The polarizability of the hydrogen bridge for various temperatures in degrees Kelvin and various O–O distances, plotted against the field strength F and against ΔV, the energy difference between the two minima; (·····) tunneling approximation in the case of 300°K.

The dependence of polarizability on the field is plotted in Figure 9, that is, the derivation of the entire dipole moment with respect to the field. Furthermore, the energy difference ΔV of the minima in the double-minimum potential well caused by the field is indicated. As the field increases, the polarizability decreases, since the distance between the levels increases. At large field strengths, however, the polarizability does not decrease to the same extent as with the tunneling approximation,[11] which is especially noticeable in the case of small O–O distances.

The polarizabilities of the hydrogen bond with fields of approximately 10^7 V/cm are still about one order of magnitude larger than the usual polarizabilities. With these fields, the double-minimum potential wells are already rather unsymmetrical (Figure 5). This relatively high polarizability is caused, however, by the fact that the proton can still tunnel from one well to the other in the ground state (Figure 5).

With field strength of 2.5 × 10^7 V/cm in the cases of the O–O distances between 2.5 and 2.6 Å, the polarizabilities of the hydrogen bonds are still larger than the usual polarizabilities. In these cases, the proton cannot transfer in the ground state, but in the first excited state. This is shown in Figure 5. At least the first excited level occurs near an inflection of the potential well. Under these conditions, the proton in the ground state can penetrate further into the potential barrier when the field strength is increased, which causes the relatively high polarizability, even if the second minimum is strongly raised. However, the following condition must be fulfilled. The product of field strength times transition moment must be comparable with the energy level difference of both states in order that the first excited state can still be mixed with the ground state to a considerable extent.

The polarizability is maintained at larger field strengths the smaller the O–O distance and the higher the temperature. In comparison, the polarizability for large O–O distances is largest in the case of small fields

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(42) R. Moccia, *Theor. Chim. Acta*, **8**, 192 (1967).

(43) G. P. Arrighnini, M. Maestro, and R. Moccia, *Chem. Phys. Lett.*, 1, 242 (1967).

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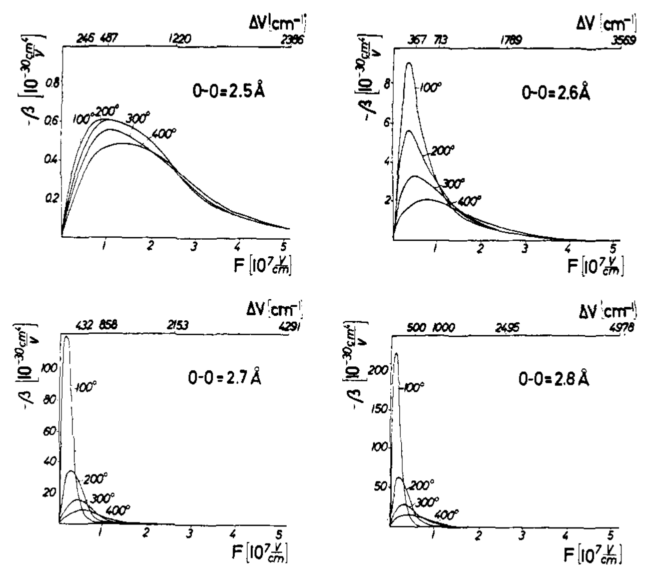

Figure 10. The hyperpolarizability of the hydrogen bridge for various temperatures in degrees Kelvin and various O–O distances, plotted against the field strength F and against ΔV, the energy difference between the two minima.

or considerably symmetric potential wells, since the two lowest levels are then closest together.

(C) Hyperpolarizability of Hydrogen Bonds. The finding that the dipole moments of the hydrogen bonds do not rise linearly with the field indicates that the usual polarizability is not sufficient to describe the field influence, but that hyperpolarizabilities[45] play an important role. The hyperpolarizability is the second derivative of the dipole moment with respect to the field, that is, the value β in the expansion of the dipole moment in $F - F_0$ at a certain field F_0.

$$\mu(F) = \mu(F_0) + \alpha(F - F_0) + \frac{1}{2}\beta(F - F_0)^2 \quad (12)$$

The necessity of observing hyperpolarizabilities is easy to imagine, since when the potential wells become asymmetric, the hydrogen bonds must be polarizable differently in both directions alongside the bond. This cannot be described by a linear field term and hence not by α.

The hyperpolarizability β as a function of the field or the energy difference ΔV of the potential minima is plotted in Figure 10. The hyperpolarizability, depending on the field, passes through a maximum which shifts toward smaller field strengths and sharpens simultaneously as the O–O distance increases.

The behavior of the hyperpolarizability with the field can easily be understood by considering the dipole curves in Figure 10. With large O–O distances, *i.e.*, large barrier and small tunneling frequency in the undisturbed potential well, small fields are already sufficient to shift the proton almost completely. Hence the polarizability curves in Figure 9 decrease as rapidly as the O–O distance increases. Thus, the hyperpolarizability differs significantly from zero only in the small range of maximum slope. With small O–O distances, the decrease of the polarizability occurs only in the case of larger fields; it is not as strong and extends over a greater range.

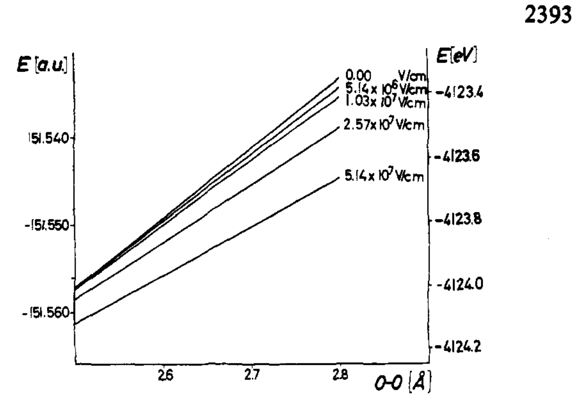

Figure 11. Total energy of the hydrogen bond plotted against the O–O distance.

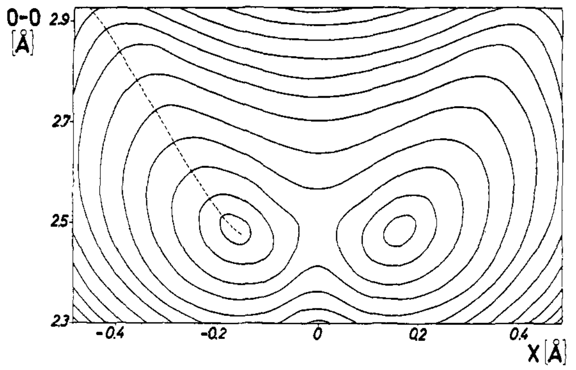

Figure 12. Schematic representation of the energy surface for the proton movement and the O–O vibration of the hydrogen bridge. The dashed curve indicates the calculated positions of the minima.

(D) Total Energy Dependence on the O–O Distance. The dependence of total energy of the $H_5O_2^+$ in the ground state on the O–O distance is plotted in Figure 11 for fields of different strengths. With increasing field strengths, the slope of the curves is diminished, *i.e.*, the energy is a little less dependent on the O–O distance. Consequently, strong fields weaken the hydrogen bond, which results in a shorter lifetime of the bond due to the fields of neighboring ions.

(E) Criticisms of the One-Dimensional Treatment. The considerations in the previous sections did not take into account that the proton movement is not independent of the O–O vibration. The energy surface for both these modes of vibration is given schematically in Figure 12. Here, as discussed in the introduction, it is assumed that the energy minimum occurs at an O–O distance where a double-minimum potential well is present in the hydrogen bond. In the harmonic approximation, two normal vibrations occur in each minimum orthonormal to one another. Figure 11 illustrates that these normal vibrations are neither pure O–O vibrations nor pure proton vibrations. Most previous considerations did not take this fact[34–38] into account. Batuev[46] was the first to discuss this. Haas and Hornig[47] attempted to take this effect into account by averaging over various O–O distances. Bratož and Hadži[48] consider this coupling formally through anharmonic terms and thus explain band widening on the formation of hydrogen bonds. A quantitative treat-

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(45) A. D. Buckingham, *Quart. Rev., Chem. Soc.*, 13, 183 (1959).

(46) M. I. Batuev, *Zh. Fiz. Khim.*, 23, 1399 (1949).

(47) C. Haas and D. F. Hornig, *J. Chem. Phys.*, 32, 1763 (1960).

(48) S. Bratož and D. Hadži, *ibid.*, 27, 991(1957).

ment of this problem was given by Maréchal and Witkowski.[49] They, however, assumed the O–O vibration to be slow as compared with the proton movement and dealt with the latter in the Born–Oppenheimer approximation. Their paper was not concerned with a double-minimum potential well, and the proton movement could thus be assumed to be a harmonic vibration.

A two-dimensional treatment of the problem would be required for an exact consideration of the coupling of the O–O vibration with the proton vibration. The first attempt at such a treatment was made by Singh and Wood[50] for a given analytical potential surface.

However, nothing of significance as far as the polarizability is concerned will be changed as long as two minima in the potential surface exist and any path from one minimum to the other leads over a high barrier.[50a]

(III) Unsymmetric Hydrogen Bonds

The unsymmetric potential wells shown in Figure 5 can be considered as a model for hydrogen bonds between different groups, for an external field F_0 leads to a potential well, as may occur in an $AH^+\cdots B$ bond. In order to obtain the polarizability of these bonds, the zero point in Figure 9 must therefore be shifted toward $F = F_0$.

With a double-minimum potential well with an asymmetry corresponding to a field $F_0 = 10^7$ V/cm, the polarizability at room temperature has indeed sunk but still remains about one order of magnitude larger than customary electron polarizabilities. If the asymmetry is still larger, so that only an inflection or a second minimum in the potential well relatively close to the first excited level occurs, as for instance with O–O distances between 2.5 and 2.6 Å and $F_0 = 2.5 \times 10^7$ V/cm, the polarizability is still larger than usual polarizabilities. The polarizability with these unsymmetric bonds changes to varying degrees in both axis directions. This is evident considering the unsymmetric potential curve.

Forces between hydrogen bonds are likewise caused, even if these are smaller than those between the symmetric bonds. Forces between these bonds thus do not lead to a continuous absorption in solutions but cause a more or less strong widening of the bands of the XH stretching vibrations in the hydrogen bonds (see part D of the following section).

Prevailing Calculations and Experimental Facts

(A) Solutions. As discussed in detail in the introduction, a continuous absorption[1–9] is found in the ir spectra of acid solutions and polyelectrolytes in the presence of symmetrical hydrogen bonds with a double-minimum potential well. This is due to the three interaction effects mentioned, which for their part result from the large polarizability of these symmetrical hydrogen bonds. In solutions, the distances and orientations between the hydrogen bonds and also the distances between the hydrogen bonds, the anions, and the solvate molecules pass through a variety of values. Hence, a variety of energy level shifts is obtained, and thus a variety of energy level differences is observed as a continuous absorption. A further cause is the variously strong coupling with the intermolecular vibrations (part C of this section).

The present calculations also show that the induced-dipole interaction plays a significant part in shifting the energy levels (Figure 6). This induced-dipole interaction implies attractive forces. It would be conceivable that the symmetrical hydrogen bonds are so strongly polarized by the anion fields that, in comparison to the induced-dipole interaction, the proton dispersion forces no longer play a part. This, however, is not the case. For with fields of 10^7 V/cm, the symmetry of the potential well is indeed already considerably disturbed (Figure 5) and the induced dipole moments are, especially for large O–O distances, already very large (Figure 7); the proton with these fields, however, can still transfer by tunneling, although it is already considerably shifted to one side. In solutions, the fields at the hydrogen bonds are usually of this order of magnitude. Hence, the proton dispersion forces[8,12] as well as the induced-dipole interaction[10] between the anions and these hydrogen bonds and between the dipole fields of the solvate molecules and the hydrogen bonds are of significance and cause the observed ir continuum. Furthermore, the large polarizability causes the field-sensitive mechanism of the anomalous proton conductivity.[11]

(B) Crystals. No varieties of distances and orientations between the hydrogen bonds and ions and between the hydrogen bonds themselves are present in crystals. Furthermore, the ions will often be far nearer to the hydrogen bonds. If the fields of the ions in crystals did not compensate to a large extent at "symmetrical" hydrogen bonds, one or a few types of hydrogen bonds with strongly deformed potential curves would occur (Figure 5). Due to the various field strengths at the bonds, these potential curves would vary from crystal to crystal even if, as here, it were a case of identical bonds. A good example of this is provided by the crystals containing $H_5O_2^+$ investigated by Williams, *et al.*[29,51–53] These authors observe quite different proton density distributions in the hydrogen bonds according to the structure of the crystal with $H_5O_2^+$. In particular, when the anions are arranged symmetrically, as in $HAuCl_4{\cdot}4H_2O$, a symmetric double-minimum potential well can be observed.[29] Hence in a certain crystal with "symmetrical" hydrogen bonds, no continuum is observed, but considerably broad bands.

The $NH^+\cdots N$ bonds in the semiprotonated double helix of the salts of the polycytidylic acid illustrate a similar situation. In the latter, the hydrogen bonds polarize each other to such an extent that proton transfer is very rare. In this case, a very wide band is observed.[54]

(C) Coupling of the Stretching Vibration of the Hydrogen Bonds with Other Vibration Transitions. The high

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[49] Y. Maréchal and A. Witkowski, *J. Chem. Phys.*, **48**, 3697 (1968).

[50] T. R. Singh and J. L. Wood, *ibid.*, **50**, 3572 (1969).

[50a] Note Added in Proof. Meanwhile calculations with the two-dimensional potential surface have affirmed that this is correct.

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[53] J. M. Williams and S. W. Peterson, Collected Abstracts of the 8th General Assembly and International Congress of the International Union of Crystallography, Aug 1969.

[54] G. Zundel, W. D. Lubos, and K. Koelkenbeck, *Biophys. J.*, in press.

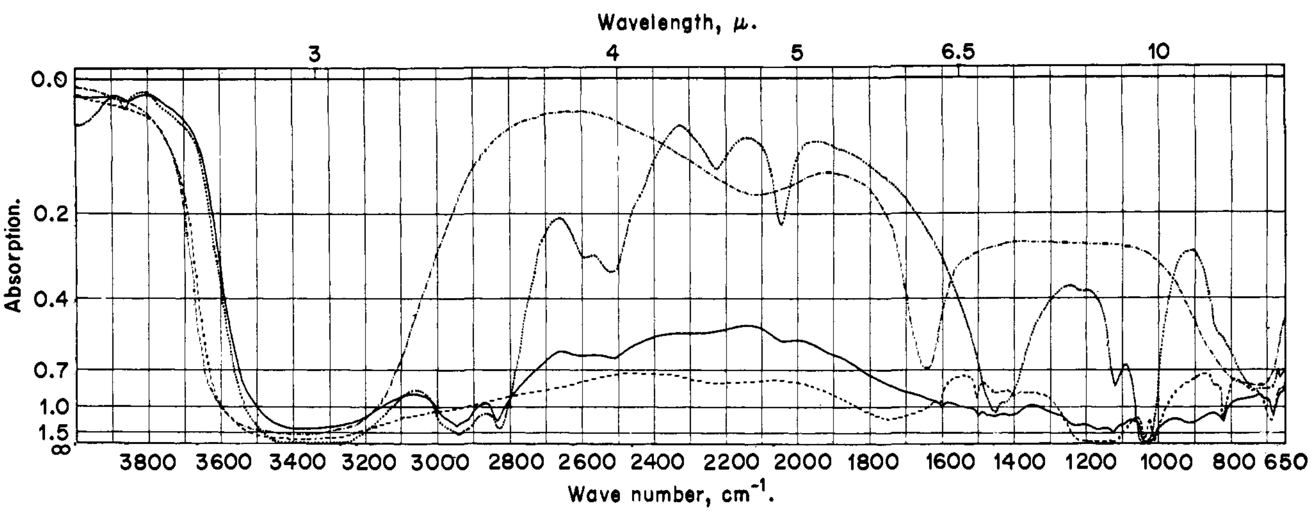

Figure 13. Ir spectra: (—·—·—) water, (- - - - - -) *p*-toluenesulfonic acid solution in water, (· · · · · ·) methanol, (———) *p*-toluenesulfonic acid solution in methanol.

polarizability, however, causes not only a strong coupling between the hydrogen bonds *via* proton dispersion forces and a large induced-dipole interaction between the hydrogen bonds and the ions and the dipole fields of solvation molecules, but also a strong coupling with other vibrations, especially intermolecular ones. The classical conception links each vibration with an oscillating dipole moment whose field induces an extremely large dipole moment in the hydrogen bonds, due to the high polarizabilities. In quantum mechanics, the transition moment oscillating with the frequency of the vibration corresponds to the oscillating dipole, and the coupling with the dipole moment induced in the hydrogen bond corresponds to a coupling of the transition moments. This is especially strong when the wave numbers of these transitions are of comparable size.

Since the transition frequencies of the stretching vibration pass through a variety of values, due to the interaction of the bonds *via* the proton dispersion forces and due to induced-dipole interaction, this conformity occurs in the case of many different vibrations. It may accordingly be expected that the coupling with transitions of small wave numbers is especially strong, that is, that a coupling with the intermolecular vibrations, in particular, is effected.

The consequences of this coupling can be seen directly in the spectra. In Figure 13, for instance, is illustrated the fact that the bands for the torsion vibrations of the H_2O molecules disappear at 710 cm^{-1} and that of the methanol molecules disappear at 655 cm^{-1} as the acid concentration increases, that is, as the number of polarizable bonds increases. The OH bending vibration of the methanol at 1425 cm^{-1} is subjected to extensive smearing. In contrast, the H_2O scissors vibration at 1640 cm^{-1} only widens. The same is true in both cases for the stretching vibrations occurring at still higher wave number values.

The fact that the water band disappears at 2120 cm^{-1} as the acid concentration increases also fits extremely well into this picture. This is usually assigned (see ref 8, p 32 ff) to a combination vibration in which a torsion vibration of the water molecules participates. Since the latter can couple strongly with the stretching vibration of the proton in the hydrogen bond, it can no longer combine with another vibration.

The coupling with the intermolecular vibrations is an important reason for the fact that the integral absorbance of the continuous spectrum compared with that of ir bands is usually so large, for the intensity of the intermolecular vibrations due to the coupling merges with the continuum. A second important reason for the large intensity is the relatively large transition moments of the stretching vibrations in the symmetrical hydrogen bond.

(D) Broadening of the Ir Bands. While the extremely large polarizability of the symmetric hydrogen bonds with a double minimum cause the ir continuous absorption in solutions, the smaller polarizabilities of unsymmetric hydrogen bonds with an inflection or a second minimum in the potential well are a reason for forces causing strong band broadening.

Such broadening is sometimes found, for instance, with NH stretching vibrations in hydrogen bonds. Foldes and Sandorfy[55] concluded on considering the anharmonicity in the NH···N bond of secondary NH groups that in these hydrogen bonds the potential wells are of the above-mentioned shape. Shulman[56] considers that, with polynucleotides, an unsymmetric double-minimum potential well occurs in the hydrogen bond between the N_3 of the thymine and the N_1 of the adenine. Numerous SCF calculations[57-60] provide other and contradictory results with respect to this potential well. The problem with these calculations, however, is the fact that base pairs are treated in isolation from their environment. The hydration of the DNA and the stacking of the base pairs certainly influence the potential well in these hydrogen bridges decisively. Extreme broadening is indeed observed with the band of the NH stretching vibration of this hydrogen bond as well as with the band of the corresponding hydrogen bond between guanine and cyto-

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sine base pair. This broadening is independent of temperature.[54] The interaction causing the polarizability is largely independent of temperature for short unsymmetric hydrogen bonds (Figure 9).

The proton dispersion interaction between neighboring hydrogen bonds, the induced dipole interaction with ions and dipoles of solvate molecules and, in addition, the coupling with intermolecular vibrations are responsible for the widening caused by the polarizability. The band widening caused by polarization corresponds to the band-widening effect which Bratož and Hadži[48] base on the anharmonicity. For, according to this paper, a high degree of anharmonicity always involves high polarizability.

The second band-widening mechanism discussed by these authors[48] is independent of the polarizability and corresponds to the coupling of the stretching vibrations with the bond vibration discussed in section IIE. Maréchal and Witkowski[49] calculated the profile of the wide band of the carboxylic acid dimers in the gaseous state and that of the imidazole in the solid state based on this mechanism.

Symmetric hydrogen bonds with a potential without a barrier should also exhibit a relatively large polarizability, even if this is considerably less than with the double-minimum potential wells. Such a potential well is present in the $(FH\cdots F)^-$ ion.[21,23,61] In this case, an extremely wide intensive band is indeed observed[62] which becomes very much sharper and loses intensity on investigating the $(FH\cdots F)^-$ ions well diluted in KCl. This suggests that the widening is based on the kinds of interaction caused by the polarizability of the hydrogen bond.

Acknowledgments. We wish to take this opportunity to thank Professor H. Preuss for many valuable discussions and for making the SCF program available. We are indebted to the Leibniz Computing Center of the Bayerische Akademie der Wissenschaften for providing the computing time and to the DFG for a grant for one of us (H. P.).

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Self-Consistent Field Studies of Glycine and Glycylglycine. The Simplest Example of a Peptide Bond[1a]

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Abstract: *Ab initio* SCF and limited CI treatments of the ground state and certain $\pi \rightarrow \pi^*$ excited states of glycine, $^+NH_3CH_2COO^-$, and glycylglycine, $^+NH_3CH_2CONHCH_2COO^-$, are reported for the two molecules in their equilibrium ground-state geometries. Orbital energies of glycine and glycylglycine are analyzed to elucidate the effect of the charged sites in the molecules, and it is found that certain of these effects can be reproduced by a simple point-charge model. Mulliken population analyses for the two molecules are performed and polarization parameters are obtained for localized orbitals which represent lone pairs, bonds and 1s orbitals in the two molecules. It was found that the description of the peptide bond corresponded to only very weak three-center π bonding and that the highest energy π orbital of the peptide region which is highly localized on the nitrogen is involved in the intense $\pi \rightarrow \pi^*$ absorption band.

In recent years it has become practicable to perform *ab initio* self-consistent-field (SCF) calculations on reasonably large molecules. Therefore, it is appropriate to apply this method, insofar as is possible at the present time, to problems of biological significance. In particular, a study of the peptide linkage is of considerable interest. Eventually it may be possible to extend such calculations to proteins by means of a model in which only a certain section of the protein is treated exactly, the rest of the molecule and other effects such as those due to the solvent and other nearby molecules and ions being represented approximately. In the present work a study is presented of glycine, $^+NH_3CH_2COO^-$, and the simplest dipeptide, glycylglycine, $^+NH_3CH_2CONHCH_2COO^-$, as isolated molecules in the gas phase. The zwitterion form of these molecules is considered since in aqueous solutions at biological pH's the molecules are believed to exist predominately in this form.[2] Although a theoretical treatment which ignores all effects except intramolecular electronic effects must be viewed with a great deal of caution as far as extrapolation to molecular systems in solution is concerned, it is still felt that the results obtained in the present work may be of value to the fundamental understanding of polypeptides. Of specific interest would be the following information: an analysis of the electron distribution in the peptide bond, the nature and energy of electronic transitions originating in the region of the peptide bond, the changes in gross electronic structure (if any) which take place upon formation of glycylglycine from glycine, the effect of the charged regions of the zwitterion upon the gross

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(1) (a) Research supported by NSF Grant No. GP-18121; (b) Alfred P. Sloan Fellow.

(2) W. Hückel, "Theoretical Principles of Organic Chemistry," Vol. II, Elsevier, New York, N. Y., 1958, pp 150–157.