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Ab initio Investigation of the Simultaneous Motion of Protons in the Hydrogen Bonds in the Cyclic Dimer of Formamide*

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The simultaneous motion of protons in interacting H-bonds plays an important role in biochemistry. By means of the simple example of the cyclic dimer of formamide some significant properties of the simultaneous motion of protons are discussed.

Starting from the calculations of Dreyfus, Maigret, and A. Pullman [9] an energy surface as well as a surface of dipole moment for the linear motion of the two protons is calculated point by point using a selfwritten program of the SCF-MO-LC (LCGO)-method and using a Gaussian basis set of intermediate size.

The resulting surface of total energy is further used to determine the states of vibration of the simultaneous motion of the protons. Whereas the surface of dipole moment is used to compute the relative transition intensities. These spectroscopic properties are finally used to find a criterion for estimating the kind of motion – mainly correlated or mainly independent.

Key words: Coupled H-bonds – Cyclic formamide dimer – Proton motion – Computed vibrational spectra.

1. Introduction

The importance of H-bonds in biochemical research is exemplified by the emphasis on the structure of peptides and nucleotides. Theoretical studies of these H-bonds deal mainly with structural properties and with energy curves corresponding to specific motions of the proton in the H-bond. Rein and Harris [1] as well as Löwdin [2] are using double well potentials for the discussion of the proton motion. However, Clementi and coworkers [3] have calculated energy curves with a single minimum in the case of base pairs of DNA. Even other theoretical investigations of many different H-bonds have never shown double well potentials by which sometimes the genetic code can be explained.

The theoretical investigation of an isolated H-bond or the motion of a single proton does not give in any case true results of dynamic nature because there are three different kinds of influences on a H-bond:

1) Coupled vibrations.
2) Electrical fields due to the surrounding molecules or ions.
3) H-bond – H-bond – interactions.

The order of magnitude of the effects 1) and 2) have been studied by means of the systems $H_2OHOH_2^+$ and $ClHCl^-$ [4 – 6]. Until now the effect 3) has been studied only in the cyclic dimer of formic acid, and only by means of the shape of potential curves [3, 7, 8]. In biochemistry the H-bond-H-bond-interaction will be of great importance because H-bonds are very close to each other in peptides

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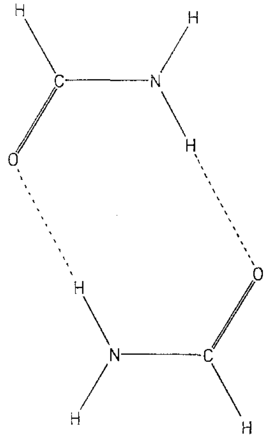

Fig. 1. Cyclic dimer of formamide

and nucleotides. A simple realistic unit of a peptide including two neighbouring H-bonds is the cyclic dimer of formamide. The starting point is a calculation for this system by Dreyfus, Maigret, and A. Pullman [9], who have examined the electronic structure using fixed positions of the atoms. In the present work an *ab initio*-treatment for different arbitrary proton positions under the constriction of linear H-bonds is improved.

In other words the two independent variables are the NH-distances in the two H-bonds. The aim of this treatment is the calculation of realistic spectroscopic data which will give a criterion for the kind of the proton motions involved. In particular the following questions should be clarified:

1) Are the motions of both H-bond-protons mutually independent or are they correlated?

2) If these motions are correlated, are they in phase or antiphase?

3) How are the spectroscopic differences referred to the monomeric formamide? Further questions deal with more or less familiar methods:

1) How is the accuracy of the second order perturbation theory in solving the Schroedinger equation for the nuclear motion?

2) Is the perturbation (anharmonicity) still small within H-bonds?

2. Method of Calculation

A selfwritten program for the nonempirical methods which may be called a theoretical spectrograph is subdivided into three parts:

1) The SCF-MO-LC (LCGO)-method which gives the total energy $V(q_1, q_2)$, the dipole moment $\mu(q_1, q_2)$ and the polarizability $p(q_1, q_2)$ pointwise. (q_1, q_2 are coordinates of nuclear motion)

2) The two-dimensional least square-method which yields analytical expressions of the form

$$\sum_{k,l} a_{kl} q_1^k q_2^l$$

for the representation of V, μ, and p.

3) The nuclear-CI-method for solving the 2-particle – Schroedinger equation of the nuclear motion. A second order perturbation calculation is also included.

The results using V are transition frequencies, IR-intensities by means of μ, Raman intensities by means of p, polarizabilities, including temperature dependency.

The geometry as well as the Gaussian basis set for the cyclic dimer of formamide are mainly taken from [9]. The atomic basis set was $(4^s, 2^p/1^s)$ which was contracted to $(2^s, 1^p/1^s)$. The least square method was constricted to $k+l \leqq 4$ in the case of the energy surface and to $k+l \leqq 3$ in the case of the dipole moment which was sufficient for up to the first overtones. In order to solve the 2-particle- Schroedinger equation for the nuclear motion, the coordinates of motion which were used are the normal modes and not the primary internal atomic distances. From this we gain the advantage that the coupling of the motions occurs only in the potential energy and only in terms with $k+l \geqq 3$ $(k, l \neq 0)$. Neglecting these coupling terms the Schroedinger equation will be separable. For each of the normal coordinates 30 configurations $\varphi^n(q)$ are sufficient for consistent results up to the second overtone (n is the vibrational quantum number). The effect of neglecting this coupling will be discussed later. Further more a 2-particle treatment including coupling terms in the potential energy is performed. $\binom{16}{2} = 120$ configurations of the type

$$\varphi_1^m(q_1) \cdot \varphi_2^n(q_2)$$

with $m+n \leqq 16$ are sufficient for consistent results up to the first overtones which includes the 6 lowest states

$$00, 10, 01, 20, 11, 02$$

if such an assignment of the states is possible at all. The application of normal modes yields a further advantage. As already stated the coupling of the motions in the potential energy occurs through terms with $k+l \geqq 3$. By this it is determined in most cases that there are dominating coefficients in the CI-expansion, at least for the lower states. By means of these dominating coefficients the resulting states are labeled by quantum numbers mn as long as no Fermi resonance occurs [5, 6].

The Hartree equations of two coupled linear harmonic oscillators may be solved exactly, but the resulting wave function is identically equal to that of the uncoupled problem. [10] By means of this fact the above stated configurations may be denoted as solutions of the Hartree-method so that there is in some sense a parallelism to corresponding well-known methods for the electron motion. The Hartree-method alone, however, has not the same importance for the nuclear motion as it has for the motion of the electrons.

3. Results and Discussion

1. Formamide (Monomer)

The systems in question are the formamide molecule as well as the cyclic dimer of formamide. There are two reasons to discuss the results of the monomeric formamide, too. At first the accuracy of the methods should be checked by comparing the calculated molecular properties with measurements in the vapour phase and in the liquid state. On the other hand we will study the spectroscopic differences of the NH-stretching modes concerned with the formation of H-bonds. With the formamide molecule both the NH-distances have been varied independently keeping all the other distances and angles fixed. The following potential energy surface has been determined:

Table 1 a. Coefficients [a.u.] corresponding to $s^k a^l$ of the potential energy surface for the NH-stretching modes in the formamide molecule. (s symmetrical-, a antisymmetrical-coordinate)

l \ k	0	1	2	3	4
0	0.0	0.0	0.32897	−0.24852	0.20417
1	0.0	0.0	0.0	0.0	
2	0.36494	−0.71518	0.62366		
3	0.0	0.0			
4	0.14242				

The result for the dipole moment surface is as follows:

Table 1 b. Coefficients $\boldsymbol{d}_{kl}$ [a.u.] corresponding to $s^k a^l$ of the dipole moment surface for the NH-stretching modes in the formamide molecule

l \ k	0	1	2	3
0	0.0	−0.24259	−0.04654	
	0.0	0.00633	−0.00450	
1	−0.08315	−0.03108		
	0.17728	0.45260		
2	−0.21306			
	−0.04727			
3	0.16509			
	0.41661			

The coefficient $\boldsymbol{d}_{00}$ was set arbitrarily to zero. The results of different methods of computation as well as the measured values are given in Table 1 c.

Table 1 c. Spectrum of the NH-stretching modes of formamide. PT (I): Perturbation theory, 1-particle treatment; I: Nuclear-CI (30 config.), 1-particle treatment; II: Nuclear-CI (120 config.), 2-particle treatment; Exp: Experimental values

Transition	Frequency (cm^{-1})				IR-intensity			
	PT (I)	I	II	Exp	PT (I)	I	II	Exp
00–10	2981	2989	2967	3435 (vap)	8.386	8.394	8.612	m.s.
00–01	3291	3291	3211	3545 (vap)	6.342	6.342	7.284	m.s.
00–20	5949	5981	5943	–	0.002	0.008	0.006	–
00–11	–	–	6143	6138 (liq)	–	–	0.312	m.
00–02	6620	6620	6411	6565 (liq)	0.287	0.287	0.141	m.

At first, one should notice the general result that the calculated frequencies deviate by about 10% from the measured values [11]. This is understandable in view of the small *ab initio*-basis set. However, this basis set is sufficient in accuracy to give the correct sequence of wavenumbers of the types of transition. The splittings between symmetric and antisymmetric transitions are comparably large. The frequencies of the three methods are in relatively good agreement with each other. Differences between the one- and the two-dimensional treatment are sometimes of the same order of magnitude as that between the perturbation theory and the one-dimensional treatment. The combination transition 00–11 results only when coupling of vibrations is taken into account (method II). The calculated IR-intensities are also in good qualitative agreement with experiments as long as any comparison is possible at all. Both the fundamental NH-stretching modes have almost the same intensities. The smallest of the three overtones is very weak in intensity in respect to the two others. The reason for this is seen in the very small electric anharmonicity in Table 1b.

2. *Cyclic Dimer of Formamide*

The potential energy surface for the motion of the two H-bond-protons in the cyclic dimer of formamide has the following coefficients:

Table 2a. Coefficients [a.u.] corresponding to $s^k a^l$ of the potential energy surface for the H-bonded protons in the cyclic dimer of formamide. (s in phase-, a *anti* phase-coordinate)

k l	0	1	2	3	4
0	0.0	0.0	0.14260	−0.23483	0.11660
1	0.0	0.0	0.0	0.0	
2	0.19100	−0.54243	0.69351		
3	0.0	0.0			
4	0.10000				

This energy surface is represented in Fig. 2.

Considering this energy surface the harmonic approximation seems to fail here already for the ground state because the amplitude of the zero-point vibration extends to the third level line ($\sim 1200\,\mathrm{cm}^{-1}$). The shape of the potential energy curve for the in phase-motion of both protons is similar to corresponding energy curves which have been obtained in the case of base pairs in DNA by Clementi [3]. Beside a single minimum near the N-atoms the energy curves have only a weak shoulder at that place where a second minimum near the O-atoms would have been expected. Considering the potential energy surface the proton motions seem to be almost uncoupled for small amplitudes of vibration due to the circular level line near the minimum. For higher states of vibration the in phase-motion predominates. A more precise and sensitive criterion are the calculated frequencies for the motions in question which are represented in Table 2c. The dipole moment surface which is responsible for the IR-intensities is given in Table 2b and in Fig. 3 (x-component).

Table 2b. Coefficients d_{kl} [a.u.] corresponding to $s^k a^l$ of the dipole moment surface for the H-bonded protons in the cyclic dimer of formamide

l \ k	0	1	2	3
0	0.0 0.0	0.0 0.0	0.0 0.0	0.0 0.0
1	1.01236 −2.48341	0.83694 −2.70704		
2	0.04135 −0.09784			
3	−0.09950 0.29613			

The y-component has a quite similar shape. The electrical anharmonicity which causes, together with the mechanical anharmonicity, the overtones is indicated by the curvature of the level lines. In Table 2c the calculated frequencies as well as the corresponding IR-intensities of the formamide dimer are listed.

Table 2c. Calculated spectrum of the H-bonded NH-stretching modes of the cyclic dimer of formamide

Transition	Frequency (cm^{-1})			IR-intensity		
	PT (I)	I	II	PT (I)	I	II
00–10	1832	1779	1701	0.0	0.0	0.001
00–01	2501	2501	2254	1159.013	1159.030	1210.043
00–20	3372	3109	3086	0.0	0.0	0.0
00–11	–	–	3885	–	–	0.569
00–02	5052	5054	4382	0.105	0.105	0.009
10–01	–	–	553	–	–	0.022
10–11	–	–	2184	–	–	0.499
01–02	–	–	2128	–	–	0.007

There are larger differences between the one- and the two-particle treatment due to the relatively strong influence of the vibrational coupling in H-bonds. Further combination transitions and higher fundamental transitions (10–11) are present at a temperature of 300 °K. All of them do not exist within the one-particle approximation. The frequencies in Table 2c also show that the second order perturbation theory is no longer a useful method for H-bonded systems. This concerns only the in phase-motion and in particular the overtones. The breakdown of the second order perturbation method was already supposed by Sandorfy [12]. The fundamental transition of the anti phase-mode which is the dominating transition has a wavenumber of 2254 cm^{-1}. The calculated frequencies and intensities are represented once more in Fig. 4.

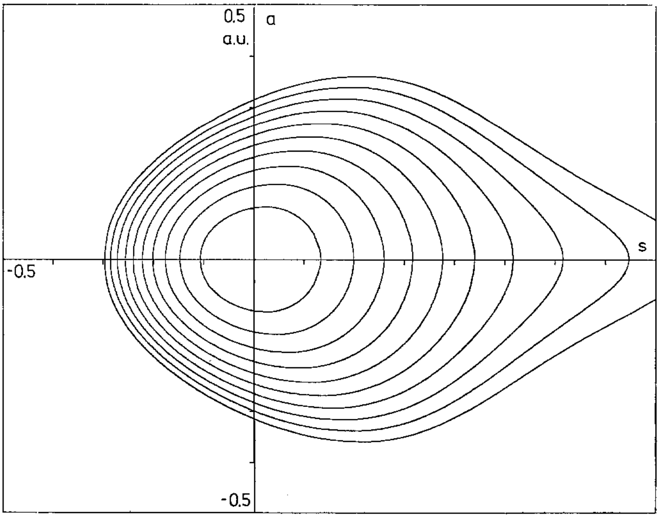

Fig. 2. Potential energy surface for the coupled motion of H-bonded protons in the cyclic dimer of formamide. The energy levels are drawn at 400 (400) 4000 cm^{-1}. (*s* in phase-, *a anti* phase-coordinate)

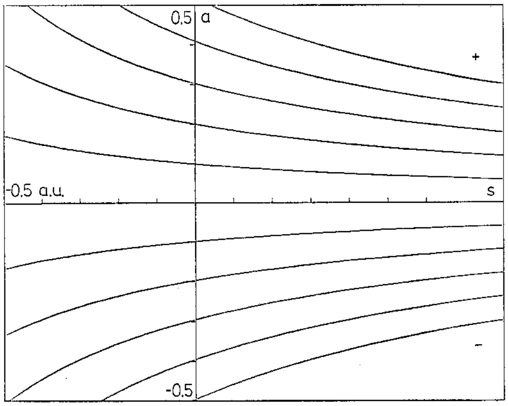

Fig. 3. *X*-component of the dipole moment surface for the coupled motion of H-bonded protons in the cyclic dimer of formamide. The levels are drawn at -1.27 (0.254) 1.27 *D*; the zero level line is the *s*-axis

The ratios of intensity are indicated by a different thickness of the lines. The IR-spectrum of formamide in the liquid state shows the doublet of free NH_2-groups (3545, 3435 cm^{-1}) as well as a broad band at about 3300 cm^{-1} due to H-bonded NH-groups. The chain association predominates in contrast to cyclic associations, otherwise the very intensive anti phase-vibration of both NH-bonds shall occur in the spectra. However, in peptides there is an additional NH-absorption in the range of 3080 cm^{-1} which is unexplained until now. An interaction effect of two equal NH-bonds have been supposed to explain absorption at 3300 and at 3080 cm^{-1} [13, 14]. Probably, the calculated anti phase transition is an ex-

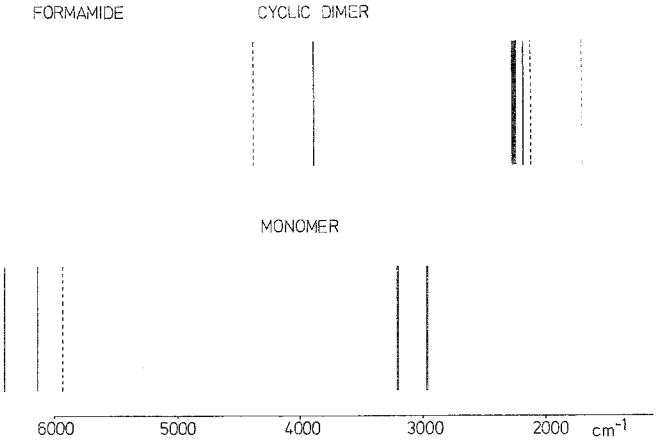

Fig. 4. Calculated spectra for the NH-stretching modes

planation for the additional NH-absorption, taking into account that H-bonds in peptides are much more distorted than in the present idealized system.

Finally two additional results should be noticed. The increase of the NH-distances due to the formation of H-bonds was calculated to be 0.08 Å. A dimerization energy of 11.5 kcal/mole was obtained.

All numerical calculations were performed in the Universitaets-Rechenzentrum Stuttgart on the CDC 6600. I thank Mr. K.Bernhart for plotting the figures and Mr. Haye for reading the manuscript.

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