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G. V. Yukhnevich^a

^a Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, Moscow, Russian Federation

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THE MECHANISM OF OCCURRENCE OF COOPERATIVE PROPERTIES IN CONJUGATE HYDROGEN BONDS

Key words: hydrogen bond, cooperative properties, force constants, vibrational spectra, molecular complexes.

G. V. Yukhnevich

Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, Leninskii prosp. 31, Moscow 117907, Russian Federation

ABSTRACT

The literature data on the change of ν_{HX} frequencies in hydrogen-bonded complexes of different structure are analysed. It is shown that the earlier found frequency dependencies can have a simple physical explanation. It consists in the fact that the XH-bond of any molecule, apart from its proton-donor and proton-acceptor properties, also has certain transmission abilities. It means that when hydrogen bonds are conjugated, to the proton-donor ability of any XH-group is always added a certain part (specific for this XH-group) of the proton-donor ability of the molecule, in relation to which this XH-group acts as a proton-acceptor. Similarly, the proton-acceptor property of XH-group is increased by a certain part (specific for this XH-

group) of the proton-acceptor ability of the molecule, in relation to which this XH -group acts as the proton-donor. The dependence of the proton-donor (proton-acceptor) ability on the bend of the angle adjacent to the hydrogen bond is found.

For the first time the concept of cooperativity of hydrogen bonds was advanced in the study of the structure of liquid water [1]. Actually it was reduced to a postulate, according to which the hydrogen bonds between the molecules in the complexes of the type (1) and (2) are always weaker, than the bonds between the same molecules in the complex (3).



It is known, that it is possible to judge the strength of hydrogen bonds in different molecular complexes from the values of the low-frequency band shifts of stretching vibrations of the corresponding $X-H$ groups - $\Delta\nu_{XH}$. For the first time the increase of $\Delta\nu_{XH}$ upon transition from the complex (1) to the complex (3) was registered in the study of spectra of alcoholic solutions [2]. The similar strengthening of H-bond was also found [3] in the interaction of the cation with the lone electron pair of the oxygen atom of the OH -group in the complex (1).

In the subsequent twenty years numerous theoretical and experimental research (considered in detail in [4]) have confirmed the cooperative character of hydrogen bonds. However due to complexity of the systems in consideration in none of these works, even in the most detailed one - [5], the

question about the mechanism of occurrence of the cooperative effect was not discussed. Therefore until recently no method was offered for the estimation of force constants of XH groups in an optional molecular system with conjugate hydrogen bonds. The ignorance of the dependence of dynamic properties of hydrogen bond on the structure of the molecular complex was making the study of its structure from vibrational spectra impossible.

In the present work an attempt is undertaken to elucidate the mechanism of occurrence of cooperative effects in systems with hydrogen bonds and to formulate a way of taking them into account. The basic attention thus is given to the consideration of conjugate or consecutive hydrogen bonds, in which the atom X of the proton-donor XH group of one hydrogen bridge is simultaneously the acceptor of a proton in the other hydrogen bridge (fig. 1, bonds b, c and d). Mutual influence of two parallel hydrogen bonds, when two proton-donor molecules interact with one base (fig. 1, bonds a and b), or when one proton-donor of the type $R(XH)_2$ interacts with two bases (fig. 1, bonds d and e), turns out to be one order of magnitude weaker [6]. Therefore in the present work it is not considered.

The proposed mechanism and the quantitative correlations, describing the mutual influence of conjugate hydrogen bonds, are mainly based on the results of works [7, 8]. The first of them has conclusively demonstrated, that in any complex (1) the shift $\Delta\nu_{X_iH}^j$ is proportional to the product of the proton-donor ability of the acid - A_{X_iH} and the proton-acceptor ability of the base - B_j , i.e., $\Delta\nu_{X_iH}^j = \alpha A_{X_iH} B_j$. The analysis of the results of work [8] in this context shows, that the frequency ν_{HF} of the complex (1) and the frequencies ν_{FH_a} and ν_{FH_b} of the complex (3) are related by strict linear dependencies (fig. 2, dash lines). It is necessary to emphasize, that the results

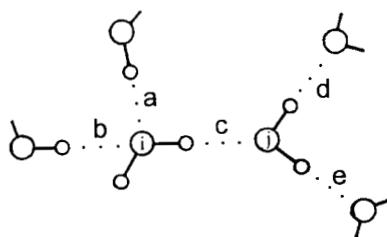


Fig. 1. A fragment of the liquid water structure.

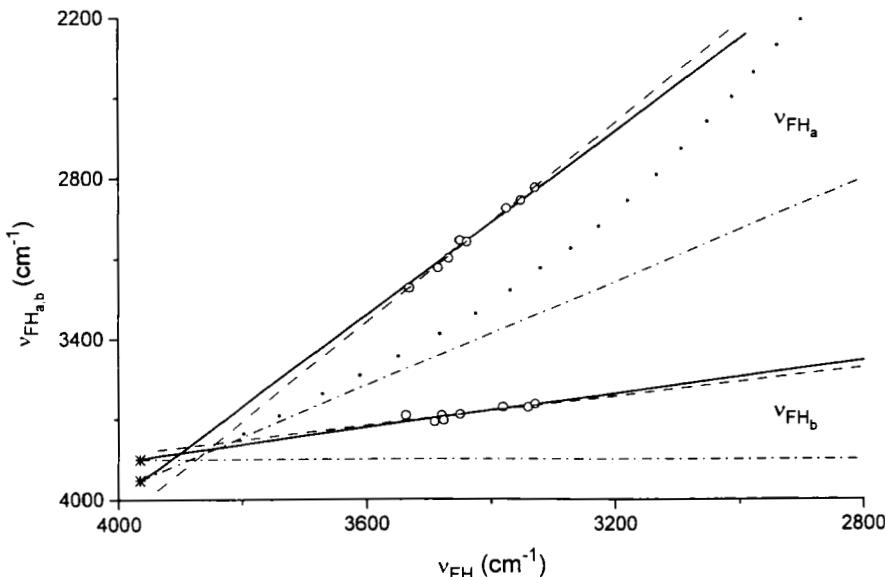


Fig. 2. Correlation of stretching vibration frequencies of the monomer and the dimer of hydrogen fluoride in complexes with the same base.

Open circles: experimental data from Ref. [7]; Dash lines: correlations made in Ref. [7]; Solid lines: correlations made in the present work, data from Ref. [9] are taken into account; Dash-dot lines: frequency behavior in the absence of the cooperative effect; Solid circles: behavior of ν_{FH_a} in the case of self-coordinated mutual strengthening of H-bonds.

of work [9], carried out much later by other authors (fig. 2, asterisks), have completely confirmed the linear character of the dependencies found in work [8]. Taking them into account has resulted in only a small (in the limits of the experimental spread of points) change in the slopes of the straight lines in fig. 2 - 1.72 and 0.34 instead of former 1.81 and 0.26.

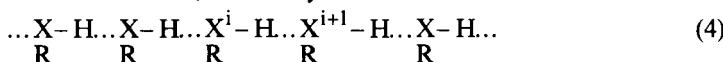
Let us try to analyze the nature of the phenomena, which cause the observed linear dependencies. It is obvious, that if hydrogen bonds were strictly additive, the vibration frequencies ν_{FH} of the complex (1) and ν_{FH_a} of the complex (3) with the identical bases Y would be equal. On the other hand, the frequency ν_{FH_b} of the complex (3) with any Y should remain constant (fig. 2, dash-dot line). Experimental results (fig. 2, solid lines), as we can see, obviously contradict with such assumption. They also testify that the assumption of self-coordinated mutual strengthening of hydrogen bonds of the complex (3) is incorrect, because in this case the dependence ν_{FH_a} on ν_{FH} [4] would have the form of a quadratic parabola (fig. 2, dot line).

At the same time, it follows from the experiment, that the excess of the actual strength of the hydrogen bond $H_a \dots Y - \Delta\nu_{FH_a}$ over its value, calculated according to the additive scheme, is always proportional to the proton-donor ability of the molecule FH_b . The analogous excess of the actual strength of the hydrogen bond $H_b \dots F_a$ over its value in the dimer $(HF)_2$ in all considered systems is proportional to the proton-acceptor ability of the molecule Y.

In other words, it is as if upon formation of hydrogen bond between any two molecules i and j (fig. 1), a certain fraction of the proton-donor ability of the molecule i is transferred to the base j (we will denote this part by K_A^j).

Simultaneously, the certain fraction of the proton-acceptor ability of the base j (K_B^i) is transferred to the proton-donor molecule i. Thus, in both cases the

fractions of transferred proton-donor and proton-acceptor abilities (we will call them transmission factors) turn out to be influenced by the properties of the "accepting" molecule, along the covalent XH bond of which this transfer occurs. In this case in a chain, formed by identical molecules RXH:



the proton-donor as well as the proton-acceptor ability of XH groups of each of them will be different. Indeed, if the proton-donor ability of the first molecule RX-H in the chain (4) is A_{XH} , then for the second molecule it will be $A_{\text{XH}} + K_{\text{A}}^{\text{XH}} A_{\text{XH}}$, for the third one $A_{\text{XH}} + K_{\text{A}}^{\text{XH}} (A_{\text{XH}} + K_{\text{A}}^{\text{XH}} A_{\text{XH}})$, and so on. The proton-acceptor ability of the molecules in the chain will change in the similar way, if we begin to consider them from the right. Thus, the proton-donor ability of the i -th molecule turns out to be influenced by the properties of all molecules located to the left of it in the chain, and the proton-acceptor ability of the $i + 1$ -st molecule - by the properties of all molecules located to the right of it.

For the calculation of ν_{XH} frequencies of such or any other chain we must know its geometry and the force constants of all its bonds. For this purpose from the frequency shifts of stretching vibrations $\Delta\nu_{\text{XH}}$ of XH bonds we must go to the decreases of their force constants - ΔK_{XH} (the difference between the force constants of free - K_{XH}^{f} and bonded - K_{XH}^{b} XH-groups). Such approach does not cause difficulties since even with the shifts of several hundred cm^{-1} , $\Delta\nu_{\text{XH}}$ and ΔK_{XH} change proportionally to each other [10]. Therefore all laws, derived for $\Delta\nu_{\text{XH}}$ [5, 7, 8], remain valid when we express ΔK_{XH} . Even the absolute values of transmission abilities of XH bonds - K_{A}^{XH} and K_{B}^{XH} remain constant.

In this case, if we have an infinite chain of any identical molecules or a cyclic oligomer with non-strained hydrogen bonds, the cooperative effect should be equal to the product of the sums of infinite geometrical progressions, in which the factors of the progressions are the transmission factors K_A and K_B . As the result of this the decrease of the force constant in an infinite chain or in a non-strained cycle K_{XH}^∞ ($K_{XH}^{\text{mon}} - K_{XH}^\infty$) will be equal to the decrease of the force constant of an open dimer - ΔK_{XH}^2 multiplied by $(1 - K_A^{XH})^{-1} (1 - K_B^{XH})^{-1}$. Being applied to the clusters of hydrogen fluoride, for which the transmission factors are determined the most accurately ($\nu_{(HF)_2} = 3868 \text{ cm}^{-1}$ [9], $K_A^{\text{HF}} = 0.72 \pm 0.03$, and $K_B^{\text{HF}} = 0.34 \pm 0.02$ [5]), such approach for the cyclic pentamer $(HF)_5$ predicts the frequency - 3453 cm^{-1} , while its experimental value is 3455 cm^{-1} [11]. From this example it is obvious, that in the case of the complexes with non-strained bonds the found mechanism of cooperative properties of hydrogen bonds allows to calculate the frequencies of their vibrations with rather good accuracy.

For the offered approach to be applicable to a complex of any structure, it was necessary to find the dependence of hydrogen bond strength on the extent of its bending. It can be done by comparing the force constants of HF bonds of the cyclic pentamer and the trimer. The conclusion about absence of any appreciable strain of hydrogen bonds of a pentamer $(HF)_5$ follows from the analysis of the equilibrium configuration of the dimer $(HF)_2$ [12], in which the angle between molecules HF is equal to 107° ($H-F \dots H = 122^\circ$ and $F \dots H-F = 165^\circ$). Since the angle between HF molecules in the cyclic trimer $(HF)_3$ is equal to 60° , the sum of angles $F \dots H-F$ and $H-F \dots H$ is 47° less than the sum of their equilibrium values. As a consequence, the effective (for the strained

trimer) values A_{HF} and B_{HF} must decrease. On this stage we do not know, how each of them will decrease, but it is easy to determine, how their product and, hence, the strength of H-bond will decrease. For this purpose we will use the semi-empirical model of the description of dynamic and eletrooptical properties of hydrogen bond [10]. From the frequencies of stretching vibrations of the trimer (3712 cm^{-1}) and the pentamer (3455 cm^{-1}) it is easy to find their force constants - $K_{HF}^3 = 12.883 \times 10^6\text{ cm}^{-2}$ and $K_{HF}^5 = 10.864 \times 10^6\text{ cm}^{-2}$. From the obtained data it follows, that in comparison with the monomer ($K_{HF}^1 = 14.847 \times 10^6\text{ cm}^{-2}$) the force constant of XH bond of the pentamer under the influence of hydrogen bonds decreases 2.028 times more than the force constant of the trimer.

Let us assume, that the weakening of the hydrogen bond due to its bending is proportional to some degree of a cosine of the bending angle. It is now unknown how each of the angles $F\ldots H-F$ and $H-F\ldots H$ changes upon bending of the hydrogen bridge. Therefore it is expedient to consider two extreme cases: when angles $F\ldots H-F$ and $H-F\ldots H$ decrease by the same value - 23.5° ; and when all deformation fall on less rigid (approximately 4 times) angles $F\ldots H-F$ [10]. In the first case we obtain the dependence in the form $\cos^4(\Delta\angle F\ldots H-F) \times \cos^4(\Delta\angle H-F\ldots H)$, which leads to the ratio $\Delta K^5/\Delta K^3 = 1.999$. In the second case we obtain the dependence $\cos^2(\Delta\angle F\ldots H-F)$, leading to the value of this ratio 2.150. The second form of the expression of the value of weakening of the hydrogen bond upon its bending turns out to be not less accurate, but physically more justified. Therefore, probably, it is this form that must be recommended for practical use until the moment when the force constants of such angles will be determined more accurately. Thus, the offered approach can be extended also to systems with strained H-bonds,

making it possible to apply it for the study of the structure of practically any hydrogen-bonded complexes.

It is believed that in cryogenic solutions and in matrixes (Ar, Kr, Xe, N₂) the molecule RXH is held by nonspecific van der Waals interaction, essentially different from directed hydrogen bonds. Such notion is seemingly supported by the results of the latest spectral studies [13, 14]. The latter shows that the frequency ν_{RXH}^b of the complex RXH...Y depends on whether it is in a gas phase, in a cryogenic solution or in a matrix, i.e. not only on the properties of the interacting particles, but also on the properties of the medium as a whole (Table 1).

Actually this fact cannot form the basis for such a conclusion. This fact can be equally explained in the context of the above-stated notion of the cooperative character of directed conjugate hydrogen bonds. Indeed, it is now already reliably established that all spectral exhibitions of the formation of the hydrogen-bonded and van der Waals complexes (changes in the position, intensity, half-width, and the form of the contour of the band ν_{HX}) completely coincide [13,14]. It allows to assert that upon interaction of the molecule RXH with an atom of noble (or inert) gas Y, a directed bond is also formed, and the strength of this bond is proportional to the proton-acceptor ability of the gas atom - B_Y^a . As was specified above, due to the cooperative properties of conjugate intermolecular hydrogen bonds, the proton-acceptor ability of the atom Y in the cryogenic solution - B_Y^l and in the matrix - B_Y^m will always be higher than in the gas phase - B_Y^g . Moreover, in the liquid and in the solid phase, where the mutual arrangement of particles is not identical, their proton-acceptor properties must also be different. Since in the solid phase the bond between atoms is stronger than in the liquid, B_Y^m must be higher than B_Y^l .

TABLE 1
Frequencies of stretching vibrations of the HF molecule in complexes FH...Y
(according to the data of Ref. [14])

State	Y							
	--	Ne	Ar	Kr	Xe	N_2	CO_2	OC
gas	3961.6		3951.8	3943.9	3932.2	3918.2	3909.3	3844.0
cryogenic solution			3943.9		3902			
matrix		3953.0	3919.5			3881.5	3870.1	3789.3

The results of experimental research, as can be seen from the presented table, completely confirm the derived consequence. Indeed, in all cases the correlation $v_{\text{XH}}^g > v_{\text{XH}}^l > v_{\text{XH}}^m$ is satisfied. Such conformity proves once again, that the interaction of proton-donor molecules with atoms of noble gas must be considered as a weak hydrogen bond [13, 14]. The found explanation of the reasons of the frequency change v_{XH}^b upon transition of the complex RX-H...Y from the gas phase into the solution and into the matrix simultaneously poses a new question. Indeed, if the proton-acceptor ability of one atom of noble gas can be partially transferred to the other atom, then it to some extent must be also transferred to any proton-acceptor molecule in the same cryogenic solution (matrix). It is impossible to tell, along which bonds and to which extent it will be transferred, but it is obvious that as a result of such transfer it must increase. Thus, two conclusions follow.

First, calculating frequency shift v_{XH}^b of the complex (1) in the solution (matrix), it is necessary to compare it with the frequency of the monomer RXH in the gas. The comparison of the frequency v_{XH}^b of the complex with the frequency of the monomer RXH in the same solution (matrix), as it is

frequently done in the literature (see for example [15]), is essentially incorrect, because in this case the frequency of one complex is compared with the frequency of the other, though a weaker one, but still the hydrogen-bonded complex. Second, in the cryogenic solution (matrix) the fraction of the proton-acceptor ability of the molecules of the solvent, transmitted to the molecule Y, will depend not only on their chemical nature, but also on possible steric hindrances. Therefore the quantitative correlation of values of the shifts $\Delta\nu_{XH}$ obtained in different cryogenic solutions (matrixes) can strongly vary. Indeed, if one reconsiders the results of work [15] in this context, it turns out that they lead to the value of the transmission factor - K_A^{HF} (factor of cooperativity) 0.74 ± 0.21 . This result completely conforms with the data of other authors [5, 8], and the scatter actually turns out to be higher. Thus any dependence of the factor of cooperativity on the strength of the hydrogen bond [15] in these data can not be observed.

Thus, the offered mechanism of cooperative character of intermolecular bonds enables to study a structure of any self-associates and complexes, for the molecules of which the transmission factors and the proton-donor properties are known. Moreover, the developed approach allows to find the specified characteristics of the molecules without the analysis of large sets of experimental data. The values K_A^{XH} , K_B^{XH} , and A_{RXH} can be determined practically for any molecule, for which spectra of its monomer, dimer and open trimer, accurately measured in the gas phase, are known. Generally speaking, for the molecules DOH, CH₃OH, HCl, HBr, and HI the values of these factors are available in the literature (fig. 3, solid lines). However, the data, on the basis of which they were obtained, do not conform with the results of later measurements [16, 17] (fig. 3, asterisks). Therefore, at the

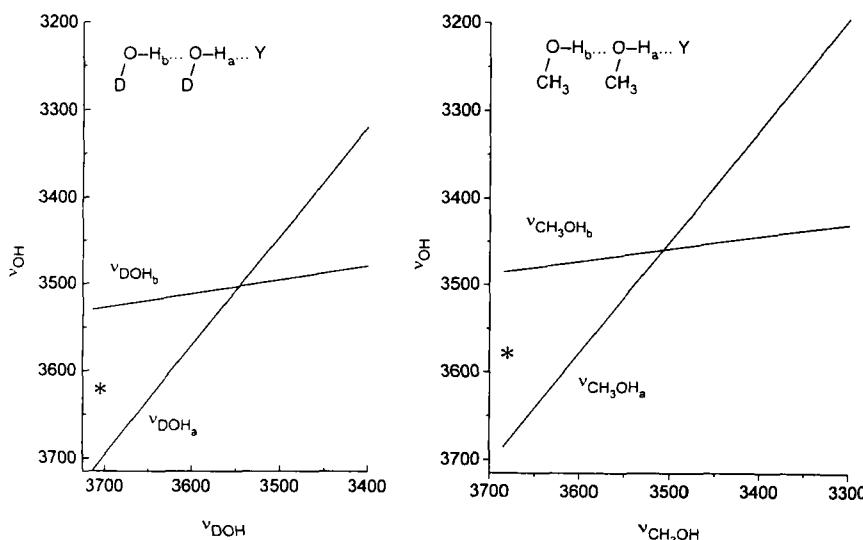


Fig. 3. Correlation of ν_{OH} frequencies of the monomer and the dimer of (a) CH_3OH and (b) DOH in complexes with the identical base. Solid lines - according to the data of Ref. [8], asterisks - according to the data of Refs. [15, 16].

moment it is impossible to tell, in which cases it is possible to use these factors.

Unfortunately, the question about the value of the decrease of the stretching vibration frequency of the free XH group as a result of strengthening of its proton-donor properties is still an open question. Even in the dimer this decrease can be rather significant (for $(HF)_2$ it is equal to 31 cm⁻¹). Therefore at the analysis of the values of the shifts of frequencies in the complexes of the type (3) the frequency of vibration ν_{XH_b} must be compared with the frequency of the monomer RXH, and the frequency ν_{XH_a} - with the frequency of the free XH-group of the dimer $(RXH)_2$. In complexes of any form the vibration frequencies of all free XH groups - ν_{XH}^f - are determined

by the composition and the structure of the complex as a whole, and consequently for each XH group its frequency must be estimated individually. It is possible that finding a way of such an estimation for an optional XH group of any complex will become one of the basic problems of the hydrogen bond spectroscopy in the near future.

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