

## THE DYNAMICAL MODEL OF THE HYDROGEN BOND. INCLUSION OF PROTON VIBRATIONS\*

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The recently proposed (*Mol. Phys.* 29, 1441 (1975)) dynamical model of the hydrogen bond is developed in order to include the  $X-H$  stretching vibration. It is shown that the polarization of the nonbonding electrons by proton vibration leads to the additional stabilization of the hydrogen bond, and to the diminution of the  $X-H$  stretching vibration frequency after formation of the hydrogen bond. These two effects are isotopically dependent, what is in agreement with experimental data. We present also the possible explanation of the great enhancement in the infrared absorption intensity of the  $X-H$  vibration, when the hydrogen bond is formed. Its origin is purely electronic and it is borrowed from the lowest antibonding  $n$ -electrons state, which is created during formation of the hydrogen bond. We get also in a natural way the term in expression for the ground-state dipole moment, which is responsible for the unusual changes in the total infrared absorption intensity of a hydrogen bond after deuteration.

### 1. Introduction

In a recent paper [1] the dynamic model of hydrogen bond, in which a special attention was paid to the interaction between the non-bonding electrons via the chemical bond, was formulated. This indirect mechanism was shown to lower the ground state energy of the non-bonding electrons by forming the correlated electronic pairs from the non-bonding electrons with the opposite spin from the opposite sides of the chemical bond. This interaction was shown to favour the formation of an asymmetric hydrogen bond and to lead to splitting of the ground state of the isolated non-bonding electronic pairs, creating therefore the lowest excited antibonding state of the non-bonding electrons.

In the above mentioned paper the influence of the proton vibrations on the properties of the hydrogen bond was not taken into account. We want to study this problem in detail in the present note because the motion of the proton has some important consequences for the properties of the hydrogen bond.

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In the next section of this note we are formulating the model Hamiltonian of the hydrogen bond in the second quantization formalism. Section 3 presents the transformation which gives the interaction between the non-bonding electrons via the proton vibration. In Section 4 we obtain the expression for the total interaction between the non-bonding electrons in which the  $\sigma$ -electrons and the proton vibration play a similar role. Section 5 is devoted to the problem of the infrared absorption intensity. The dipole moments in the adiabatic approximation are determined there. A brief discussion is presented in the last section

## 2. Hamiltonian of the hydrogen bond model

The total Hamiltonian of the molecular fragment X-H is given by

$$H = \frac{p_A^2}{2m} + \frac{p_B^2}{2m} + \frac{p^2}{2M} + U(x_A, x_B, q). \quad (1)$$

Here  $p_A, x_A; p_B, x_B$  denote the momenta and coordinates of the non-bonding and the  $\sigma$ -electrons of the chemical bond, respectively,  $q$  is the normal coordinate of the XH stretching vibration,  $m$  is the electronic mass,  $M$  is the reduced mass for the proton vibration, and  $U$  is the potential energy.

The electronic Hamiltonian of the chemical bond is defined by

$$h = \frac{p_B^2}{2m} + U(x_A, x_B, q), \quad (2)$$

and the solutions of the eigenvalue equation

$$h\psi_n(x_B; x_A, q) = E_n(x_A, q)\psi_n(x_B; x_A, q) \quad (3)$$

determine for the  $\sigma$ -valence electrons the eigenfunctions which depend parametrically on  $x_A$  and  $q$ .

If the coupling between the nuclear motions and that of the non-bonding electrons may be neglected, then the energy eigenvalues  $E_n$  of (3) can be written in the form

$$E_n(x_A, q) = \varepsilon_n(x_A) + \mathcal{E}_n(q).$$

This approximation for  $E_n$  was used in the previous paper [1]. It is clear, however, that in general some degree of coupling between this two motions must be allowed for as the proton vibration should polarize the non-bonding electrons in a similar way as the valence electrons do. It is also clear that the leading term describing such a coupling will be bilinear one in both coordinates. We put therefore

$$E_n(x_A, q) = \varepsilon_n(x_A) + \mathcal{E}_n(q) + \alpha_n x_A q, \quad (4)$$

where  $\alpha_n$  is a constant and we neglect in the present treatment any higher order coupling terms. The last two terms in (4), which form the potential energy for the nuclear movement, determine (within the harmonic approximation for  $\mathcal{E}_n(q)$ ) the vibrational wave

functions in the form of the harmonic oscillators shifted by  $\alpha_n x_A$  from the corresponding origin. Both the vibrational wave functions and the eigenvalues depend then parametrically on  $x_A$ . It will be more convenient, therefore, to shift the coupling term  $\alpha_n x_A q$  to the Hamiltonian determining the wave functions of the non-bonding electrons and to keep the following usual form

$$\left[ \frac{P^2}{2M} + \mathcal{E}_n(q) \right] \varphi_{n,m}(q) = \mathcal{E}_{n,m} \varphi_{n,m}(q) \quad (5)$$

of the vibrational energy eigenvalue equation.

The total electronic wave function of the molecular fragment X-H is now, by (3), (4), equal to

$$\psi = \sum_n X_n(x_A; q) \psi_n(x_B; x_A, q) \equiv \sum_n X_n |n\rangle, \quad (6)$$

where the function  $X_n$  satisfies the following set of equations

$$\begin{aligned} & \left[ \frac{p_A^2}{2m} + \varepsilon_n(x_A) + \alpha_n x_A q + \langle n | \frac{p_A^2}{2m} | n \rangle \right] X_n(x_A; q) \\ & + \sum_{n' \neq n} \left[ \frac{1}{m} \langle n | p_A | n' \rangle p_A + \langle n | \frac{p_A^2}{2m} | n' \rangle \right] X_{n'}(x_A, q) = E(q) X_n(x_A; q); \end{aligned} \quad (7)$$

If the off-diagonal terms and the  $\alpha_n x_A q$  coupling term in (7) can be neglected then the valence and non-bonding electrons are separable in the adiabatic sense. The eigenfunctions and the eigenvalues of the non-bonding electrons are then determined by

$$\left[ \frac{p_A^2}{2m} + \varepsilon_n(x_A) + \langle n | \frac{p_A^2}{2m} | n \rangle \right] X_n^i(x_A) = \mathcal{E}_n^i X_n^i(x_A). \quad (8)$$

Now we introduce the creation and annihilation operators  $B_n^+$ ,  $B_n$  for the valence electrons,  $A_i^+$ ,  $A_i$  for the non-bonding electrons and the  $b_n^+$ ,  $b_n$  operators for phonons (quanta of the X-H stretching vibrations) in the  $n$ -th state of the valence electrons. The operators  $B_n^+$ ,  $B_n$  and  $A_i^+$ ,  $A_i$  are determined on the basis of the single electronic solutions of (3), (8), respectively, and the  $b_n^+$ ,  $b_n$  operators are determined on the basis of solutions of (5) in which  $\mathcal{E}_n(q)$  is given in the harmonic approximation. These operators obey the standard anticommutation rules

$$\{B_n^+, B_{n'}\} = \delta_{n,n'}; \{A_i^+, A_j\} = \delta_{i,j}; \{B_n^+, A_i\} = 0, \quad (9)$$

and we assume also

$$[b_n, b_n^+] = 1, \quad (9a)$$

where the third equation in (9) follows from the assumption that no orbitals are common to the non-bonding and valence electrons. If we neglect, for simplicity, the off-diagonal

terms, quadratic in the momentum operator compared with the linear ones in (7), then the total Hamiltonian can be written in the following form

$$H = \sum_n \{ \mathcal{E}_n B_n^+ B_n + \omega_n (b_n^+ b_n + \frac{1}{2}) B_n^+ B_n \} + \sum_k \mathcal{E}_k A_k^+ A_k + \frac{1}{2} \sum_{\substack{n, n' \\ k, k'}} (V_{kk'}^{nn'} B_n^+ B_{n'} A_k^+ A_{k'} + (V_{kk'}^{n'n})^* B_n^+ B_n A_k^+ A_{k'}) + \sum_{k, k', n} \mathcal{V}_{kk'}^n A_k^+ A_{k'} B_n^+ B_n (b_n^+ + b_n), \quad (10)$$

where

$$V_{kk'}^{nn'} = \frac{1}{m} \langle n | p_A | n' \rangle_{x_B x_A} \langle k | p_A | k' \rangle_{x_A} \quad (11)$$

$$\mathcal{V}_{kk'}^n = \alpha_n \left( \frac{\hbar}{2M\omega_n} \right)^{1/2} \langle k | x_A | k' \rangle_{x_A}, \quad (12)$$

and where  $n$  and  $k$  indices number the states of the valence and non-bonding electrons, respectively. For simplicity of notation we have assumed also that  $\mathcal{V}_{kk'}^n$  are real;  $\omega_n$  denotes the frequency of the X-H stretching vibration in the  $n$ -th state of the valence bond electrons. It follows from (12) that the deuterium substitution in the molecular fragment X-H gives

$$(\mathcal{V}_{kk'}^n)_H^2 = \sqrt{2} (\mathcal{V}_{kk'}^n)_D^2. \quad (13)$$

In order to simplify our treatment we assume the  $\mathcal{E}_n(q)$  to be the same for all  $n$  (the same equilibrium distance and force constant for all valence electrons states), we assume further that  $\alpha_n$  does not depend on the index  $n$  and limits one of the indices  $n, n'$  to the ground state ( $n = 0$ ) of the valence electrons (the virtual transitions of the non-bonding electrons polarize much less the chemical bond than vice-versa [1]). The molecular Hamiltonian of the X-H fragment takes now the following final form

$$H = \sum_n \mathcal{E}_n B_n^+ B_n + \sum_k \mathcal{E}_k A_k^+ A_k + \omega (b^+ b + \frac{1}{2}) + \frac{1}{2} \sum_{kkn'} (V_{kk'}^{0n} B_0^+ B_n A_k^+ A_{k'} + (V_{kk'}^{n0})^* B_n^+ B_0 A_k^+ A_{k'}) + \sum_{k, k'} V_{kk'} A_k^+ A_{k'} (b^+ + b), \quad (14)$$

where the phonons do not depend on the  $n$  index as the phonons are supposed to be the same in the each energy state of the valence electrons.

Let us suppose now that on the opposite side of the chemical bond of the molecular fragment X-H there is a second group of the non-bonding localized on the atom Y. The Hamiltonian of the hydrogen bond -X-H ... Y can be written then as follows

$$H = \sum_n \mathcal{E}_n B_n^+ B_n + \sum_k \mathcal{E}_k^{(C)} C_k^+ C_k + \sum_k \mathcal{E}_k^{(A)} A_k^+ A_k + \omega (b^+ b + \frac{1}{2}) + \frac{1}{2} \sum_{kk'} [V_{kk}^{0n} (A_k^+ A_k + \varphi_{kk'}^{0n} C_k^+ C_k) B_0^+ B_n + \text{h.c.}] + \sum_{kk} \mathcal{V}_{kk} (A_k^+ A_k - \eta_{kk'} C_k^+ C_k) (b^+ + b), \quad (15)$$

where  $C_k^+$ ,  $C_k$  are the field operators for the non-bonding electrons located on the  $Y$  atoms and where  $V_{kk}^{0n(C)} = \varphi_{kk'}^{0n} V_{kk'}^{0n(A)}$ ,  $\mathcal{V}_{kk}^{(C)} = -\eta_{kk'} \mathcal{V}_{kk'}^{(A)}$  with  $\eta_{kk'} > 0$  and for the simplicity of notation the indices  $A, C$  are dropped. The factors  $\varphi$  and  $\eta$  are introduced in order to include the fact that the hydrogen bond may be formed between the different atoms  $X, Y$  and even for the same atoms may be asymmetric.

The relation  $\mathcal{V}_{kk}^{(C)} = -\eta_{kk'} \mathcal{V}_{kk'}^{(A)}$  holds, as the term  $\alpha_n x_A Q_n$  for the non-bonding electrons centered on  $A$  atom must be replaced by  $-\alpha_n x_C Q_n$  for the non-bonding electrons centered on  $B$  atom. The sign results from the fact that the both pairs of the non-bonding electrons are on the opposite side of the vibrating proton (the relative coordinates for the  $X$ -H and H... $Y$  distances measured with respect to the equilibrium position have different signs). The last equation (15) which determines the model Hamiltonian of the hydrogen bond forms the starting point for the later considerations.

### 3. Interaction between the non-bonding electrons via the vibrating proton

Now we will show that the last term in the Hamiltonian (15) leads to an attractive interaction between the non-bonding electrons of the  $A$  and  $C$  atoms. For this we are denoting by  $H_1$  the term

$$H_1 = \sum_{k,k'} \mathcal{V}_{kk'} (A_k^+ A_k - \eta_{kk'} C_k^+ C_k) (b^+ + b) \quad (16)$$

by  $H_e$  the fourth sum in (15) and by  $H_0$  all the remaining ones and we are looking for a unitary transformation  $\exp(iS)$ , where  $S$  is satisfying the equation

$$i [H_0, S] + H_1 = 0. \quad (17)$$

To satisfy this condition we put

$$S = \sum_{kk'} \{ [\varphi_A(kk') A_k^+ A_k + \varphi_C(kk') C_k^+ C_k] b + \text{h.c.} \}, \quad (18)$$

where

$$\varphi_A = \frac{iV_{kk'}}{\mathcal{E}_k^{(A)} - \mathcal{E}_{k'}^{(A)} - \omega}; \quad \varphi_C(k, k') = -\frac{i\eta_{kk'} V_{kk'}}{\mathcal{E}_k^{(C)} - \mathcal{E}_{k'}^{(C)} - \omega}, \quad (19)$$

then the transformed Hamiltonian takes the form

$$\tilde{H} = e^{iS} H e^{-iS} = H_0 + H_e + i[H_e, S] + \frac{i}{2} [H_1 S] + \dots \quad (20)$$

A rather lengthy algebra of the commutators leads to the result

$$\begin{aligned} \tilde{H} = & \sum_n \mathcal{E}_n B_n^+ B_n + \sum_k \mathcal{E}_k^{(C)} C_k^+ C_k + \sum_k \mathcal{E}_k^{(A)} A_k^+ A_k \\ & + \tilde{\omega} (b^+ b + \frac{1}{2}) + \frac{1}{2} \sum_{kk'} [V_{kk}^{0n} (A_k^+ A_k + \varphi_{kk'}^{0n} C_k^+ C_k) B_0^+ B_n + \text{h.c.}] \end{aligned}$$

$$\begin{aligned}
& + \sum_{\substack{kk' \\ pp'}} \frac{\mathcal{V}_{pp'} \mathcal{V}_{kk'} \omega}{(\mathcal{E}_p^{(A)} - \mathcal{E}_{p'}^{(A)})^2 - \omega^2} (A_k^+ A_k A_p^+ A_{p'} - \eta_{kk'} C_k^+ C_k A_p^+ A_{p'}) \\
& + \sum_{\substack{kk' \\ pp'}} \frac{\mathcal{V}_{pp'} \mathcal{V}_{kk'} \omega}{(\mathcal{E}_p^{(C)} - \mathcal{E}_{p'}^{(C)})^2 - \omega^2} (\eta_{pp'} \eta_{kk'} C_k^+ C_k C_p^+ C_{p'} - \eta_{pp'} C_p^+ C_{p'} A_k^+ A_k), \quad (21)
\end{aligned}$$

where we have neglected the term resulting from the commutator  $i[H_e, S]$  as they contribute to the energy in the order  $V^2 \mathcal{V}^2$  at least. In (21) the term

$$\tilde{\omega} = \omega - \sum_{kk'} \frac{2|\mathcal{V}_{kk'}|^2 (\mathcal{E}_{k'}^{(A)} - \mathcal{E}_k^{(A)})}{(\mathcal{E}_{k'}^{(A)} - \mathcal{E}_k^{(A)})^2 - \omega^2} A_k^+ A_k - \sum_{kk'} \frac{2|\eta_{kk'} \mathcal{V}_{kk'}|^2 (\mathcal{E}_{k'}^{(C)} - \mathcal{E}_k^{(C)})}{(\mathcal{E}_{k'}^{(C)} - \mathcal{E}_k^{(C)})^2 - \omega^2} C_k^+ C_k \quad (22)$$

is the frequency of the X-H stretching vibration renormalized by the interaction of non-bonding electrons with the vibrating proton. The difference of the X-H stretching frequency before and after the hydrogen bond formation (which is measured as the corresponding difference in the positions of the infrared absorption gravity centres) is, by (22), equal to

$$\Delta\omega = -4 \sum_k \frac{|\eta_{k0} \mathcal{V}_{k0}|^2 (\mathcal{E}_k^{(C)} - \mathcal{E}_0^{(0)})}{(\mathcal{E}_k^{(0)} - \mathcal{E}_0^{(C)})^2 - \omega^2} < 0, \quad (23)$$

as  $\sum C_0^+ C = 2$  in the ground electronic state and  $\mathcal{E}_k^{(C)} - \mathcal{E}_0^{(C)} > 0$ . The hydrogen bond formation shifts, therefore, the infrared absorption spectrum towards longer wavelengths and this shift is changed after the substitution of hydrogen by deuterium

$$\Delta\omega_H = \sqrt{2} \Delta\omega_D. \quad (24)$$

These conclusions are in a qualitative agreement with the experimental observations [2].

The following part of the Hamiltonian

$$H_2 = - \sum_{\substack{kk' \\ pp'}} \frac{\eta_{kk'} \mathcal{V}_{pp'} \mathcal{V}_{kk'} \omega}{(\mathcal{E}_p^{(A)} - \mathcal{E}_{p'}^{(A)})^2 - \omega^2} C_k^+ C_k A_p^+ A_{p'} - \sum_{\substack{kk' \\ pp'}} \frac{\eta_{pp'} \mathcal{V}_{pp'} \mathcal{V}_{kk'} \omega}{(\mathcal{E}_p^{(C)} - \mathcal{E}_{p'}^{(C)})^2 - \omega^2} C_p^+ C_{p'} A \quad (25)$$

describes the interaction between the non-bonding electrons of the A and C atoms via the virtual exchange of the X-H stretching vibrational quanta (phonons). The interaction described by (25) is attractive for the ground electronic state, where one of the indices  $p, p'$  is equal to 0 and  $|\mathcal{E}_p^{(AC)} - \mathcal{E}_0^{(AC)}| > 0$ . This interaction parallels, therefore, the leading interaction between the non-bonding electrons via the chemical bond introduced in the previous paper [1].

4. The total indirect interaction between non-bonding electrons in a hydrogen bond

We are now in the position to perform the second unitary transformation in order to eliminate from (21) the terms non-diagonal in the operators of the valence electrons. Denote

$$\bar{H} = \exp(S_1) \tilde{H} \exp(-S_1), \quad (26)$$

$$S_1 = \frac{1}{2} \sum_{kk'} (S_{kk}^{0n(A)} + S_{kk}^{0n(C)}) + \text{h.c.}, \quad (27)$$

$$S_{kk}^{0n(A)} = \varphi^A(kk', 0n) A_k^+ A_k B_0^+ B_n \quad (28)$$

$$\varphi^A(k, k', 0, n) = \frac{iV_{kk'}^{0n(A)}}{\mathcal{E}_k^{(A)} - \mathcal{E}_{k'}^{(A)} - \omega_n}, \quad \omega_n = \mathcal{E}_n - \mathcal{E}_0, \quad (29)$$

and similar equation holds for  $S_{kk}^{0n(C)}$  and  $\varphi^C(kk, 0n)$ . The canonical transformation (26)–(29) satisfies the condition

$$i[H_0, S_1] + H_e = 0. \quad (30)$$

The transformed Hamiltonian is therefore given by

$$\bar{H} = H_0 + H_f + \frac{i}{2} [H_e, S_1] + i[H_f, S_1], \quad (31)$$

where  $H_f$  denotes the two last terms in (21). The commutator  $[H_f, S_1]$  leads to the terms which contribute to the energy in the order of  $V^2\mathcal{V}^2$  at least, and we may neglect this term, as we did before with the commutator  $[H_e, S]$ . In calculation of the commutator  $[H_e, S_1]$  we neglect all terms non-diagonal in the operators of the valence electrons and also the non-diagonal terms bilinear in the operators of the non-bonding electrons, as they contribute to the energy in higher orders of perturbation.

In the transformed Hamiltonian we neglect further the indirect interaction between the non-bonding electrons located in the same atom as such an interaction via the chemical bond or vibrating proton is small compared with the direct Coulomb repulsion at the same atom. We also do not write in the formulae the term giving only the energy renormalization for the valence electrons, which are here of no interest for us. Then, for the ground state of the chemical bond with two paired electrons ( $\sum B_0^+ B_0 = 2, \sum_{n \neq 0} B_n^+ B_n = 0$ ), we obtain the following Hamiltonian describing the indirect interaction of the non-bonding electrons  $A, C$  located at the atom  $X$  and  $Y$ :

$$H_{A-C} = \sum_k \mathcal{E}_k^{(A)} A_k^+ A_k + \sum_k \mathcal{E}_k^{(C)} C_k^+ C_k - \sum_{\substack{kk' \\ pp'}} \frac{\eta_{kk'} \mathcal{V}_{pp'} \mathcal{V}_{kk'} \omega}{(\mathcal{E}_p^{(A)} - \mathcal{E}_{p'}^{(A)})^2 - \omega^2} C_k^+ C_k A_p^+ A_{p'} - \sum_{\substack{kk' \\ pp'}} \frac{\eta_{pp'} \mathcal{V}_{pp'} \mathcal{V}_{kk'} \omega}{(\mathcal{E}_p^{(C)} - \mathcal{E}_{p'}^{(C)})^2 - \omega^2} C_p^+ C_{p'} A_k^+ A_k$$

$$\begin{aligned}
& + \frac{1}{2} \sum_{k, k_1, k_2, k_3} \frac{V_{kk}^{0n(A)} V_{kk}^{*n0(C)}}{(\mathcal{E}_k^{(A)} - \mathcal{E}_{k_1}^{(A)})^2 - \omega_n^2} A_k^+ A_{k_1} C_{k_2}^+ C_{k_3} \\
& + \frac{1}{2} \sum_{\substack{k_2 k_2 \\ k_3, n}} \frac{V_{kk_1}^{*n0(A)} V_{k_2 k_3}^{0n(C)}}{(\mathcal{E}_{k_2}^{(C)} - \mathcal{E}_{k_3}^{(C)})^2 - \omega_n^2} A_k^+ A_{k_1} C_{k_2}^+ C_{k_3}. \quad (32)
\end{aligned}$$

Now, we choose from (32) only the leading terms which describe the interactions corresponding to the virtual oscillations of the electronic density of the non-bonding electrons occurring on the opposite sides of the chemical bond only in phase or out-of-phase [1]. We pick out, therefore, only an interaction between the correlated pairs in a similar manner as in the BCS theory. Therefore, from the indices  $kk_1pp_1$  and  $kk_1k_2k_3$  only the two different ones may occur. This can be done if we put

$$A_k^+ A_{k_1} C_{k_2}^+ C_{k_3} = \delta_{kk_2} \delta_{k_1 k_3} A_k^+ A_{k_1} C_k C_{k_1} + \delta_{k_1 k_2} \delta_{kk_3} A_{k_1} C_{k_1}^+ C_k^+ + \delta_{kk_1} \delta_{k_2 k_3} A_k^+ A_{k_1} C_{k_2}^+ C_{k_3}. \quad (33)$$

It is also easy to see that the last term in (33) gives a zero contribution as  $\mathcal{V}_{pp} = V_{kk}^{0n} = 0$ . Therefore, we obtain finally

$$H_{AC} = \sum_k (\mathcal{E}_k^{(A)} A_k^+ A_k + \mathcal{E}_k^{(C)} C_k^+ C_k) + \sum_{kk_1} \bar{V}(k, k_1) (A_k^+ A_{k_1} C_k^+ C_{k_1} + A_k^+ A_{k_1} C_{k_1}^+ C_k), \quad (34)$$

where we have denoted

$$\begin{aligned}
\bar{V}(k, k_1) &= - \frac{\eta_{kk_1} |\mathcal{V}_{kk_1}|^2}{(\mathcal{E}_k^{(A)} - \mathcal{E}_{k_1}^{(A)})^2 - \omega^2} - \frac{\eta_{kk_1} |\mathcal{V}_{kk_1}|^2}{(\mathcal{E}_k^{(A)} - \mathcal{E}_{k_1}^{(C)})^2 - \omega^2} \\
&+ \frac{1}{2} \sum_n \frac{\varphi_{kk_1}^{0n} |V_{kk_1}^{0n}|^2 \omega_n}{(\mathcal{E}_k^{(A)} - \mathcal{E}_{k_1}^{(A)})^2 - \omega_n^2} + \frac{1}{2} \sum_n \frac{\varphi_{kk_1}^{0n} |V_{kk_1}^{0n}|^2 \omega_n}{(\mathcal{E}_k^{(C)} - \mathcal{E}_{k_1}^{(C)})^2 - \omega_n^2}. \quad (35)
\end{aligned}$$

For a symmetrical hydrogen bond  $\eta_{kk_1} = \varphi_{kk_1}^{0n} = 1$  and  $\mathcal{E}_k^{(C)} = \mathcal{E}_k^{(A)}$ . As a final simplification of (35) we introduce a cut-off Hamiltonian, defined by

$$\begin{aligned}
V(k, k_1) &= -V < 0 \text{ for all } |\mathcal{E}_k^{(i)} - \mathcal{E}_{k_1}^{(i)}| < \bar{\omega}, \\
V(k, k_1) &= 0 \text{ for all } |\mathcal{E}_k^{(i)} - \mathcal{E}_{k_1}^{(i)}|_{i=A,C} > \bar{\omega}. \quad (36)
\end{aligned}$$

The effective interaction between the non-bonding electrons (described by (34), (35)) is composed, therefore, of two parts. One part results from the indirect interaction via the X-H stretching vibration. This last one is isotopically dependent. For  $|\mathcal{E}_k^{(i)} - \mathcal{E}_{k_1}^{(i)}| > \omega$  the signs of this interactions are the same, therefore, the X-H stretching vibration gives additional attraction between the correlated pairs of the non-bonding electrons located on the opposite sides of the hydrogen bond. Assuming the interaction between non-bonding electrons resulting from nuclear vibrations to form 30% of the total interaction in the hydrogen bond [3], we may expect the isotopic substitution of hydrogen by the deuterium to diminish the total interaction to about 90% of its primary value.



The diagonalization of the Hamiltonian (34) can be performed in a similar manner as in the previous paper [1], however, the meaning of the  $V$  parameter is now somewhat different. We may conclude, as before [1], that from the Hamiltonian obtained here the existence of a low energy excited state of the non-bonding electrons results, which is created simultaneously with the ground state, from the nearly degenerate ground states of the two isolated pairs of the non-bonding electrons. The proton vibration increases the splitting between the ground and excited states of the hydrogen bond.

### 5. Intensity of infrared absorption of hydrogen bond

The interaction between the correlated pairs of non-bonding electrons splits, as it was shown in the previous paper [1], nearly degenerate states of the isolated pairs of  $n$ -electrons into two states: the ground and the excited one, which differ in the inversion symmetry interchanging  $A$  and  $C$  electrons. The splitting between this two levels, for not too strong hydrogen bonds, is equal to a fraction of the mean valence excitation energy. The asymmetric stretching vibration in the  $X-H...Y$  hydrogen bond can, therefore, strongly mix this states, as the Born-Oppenheimer separation of the non-bonding electrons, and the proton vibration is no longer possible. These two states separated by  $2(\Delta_0^2 + \eta_0^2 + \delta_0^2)^{1/2}$  (notation of [1] is used), differ in the electronic density distribution and possess the following dipole moments

$$\begin{aligned}\vec{\mu}_{00} &\sim -\eta_0(\eta_0^2 + \Delta_0^2)^{-1/2}, \\ \vec{\mu}_{11} &\sim \Delta_0(\eta_0^2 + \Delta_0^2)^{-1/2},\end{aligned}\quad (37)$$

where  $\vec{\mu}_{00}$ ,  $\vec{\mu}_{11}$  denote the permanent dipole moments of the ground and the excited states, respectively;  $\vec{\mu}_{01}$  is the transition dipole moment, allowed by symmetry, between these two states. As the energy separating this two non-bonding electronic states can be of the order of a vibrational quantum, therefore, the nonadiabatic interaction between these two states, with the help of the stretching vibration, can occur.

Let us suppose, that the above mentioned two electronic states form a complete basis of the non-bonding electronic wave functions in the adiabatic treatment. Denoting by  $|0\rangle$ ,  $|1\rangle$  the ground and the first excited  $n$ -electronic state in the hydrogen bond, respectively, we get

$$\frac{d}{dq} \vec{M}_0 = \frac{d}{dq} \langle 0 | \vec{M} | 0 \rangle = 2 \langle 0 | \vec{M} | 1 \rangle \langle 1 | \frac{d}{dq} | 0 \rangle, \quad (38a)$$

$$\frac{d}{dq} \vec{M}_1 = \frac{d}{dq} \langle 1 | \vec{M} | 1 \rangle = 2 \langle 1 | \vec{M} | 0 \rangle \langle 0 | \frac{d}{dq} | 1 \rangle, \quad (38b)$$

$$\frac{d}{dq} \vec{M}_{01} = \frac{d}{dq} \langle 0 | \vec{M} | 1 \rangle = \langle 0 | \vec{M} | 0 \rangle \langle 0 | \frac{d}{dq} | 1 \rangle + \langle 1 | \vec{M} | 1 \rangle \langle 1 | \frac{d}{dq} | 0 \rangle. \quad (38c)$$

Here, we have assumed that  $d\vec{M}/dq = 0$ , and that only electronic wave functions depend on  $q$ -coordinate. Let us denote

$$\langle 1 | \frac{d}{dq} | 0 \rangle = \lambda \quad (39)$$

which, for simplicity, we will assume to be independent of  $q$ . We get in such a way the set of differential equations that should be satisfied by the dipole moments  $M_0, M_1, M_{01}$ . A similar treatment for the case of the adiabatic approximation in vibronic coupling problems was presented by Fulton in [4]. This set has the following form:

$$\frac{d\vec{M}_0}{dq} = 2\lambda\vec{M}_{01}, \quad \frac{d\vec{M}_1}{dq} = -2\lambda\vec{M}_{01}, \quad \frac{d\vec{M}_{01}}{dq} = -\lambda\vec{M}_0 + \lambda\vec{M}_1, \quad (40)$$

the solutions being

$$\begin{aligned} \vec{M}_{01} &= \vec{A} \cos 2\lambda q + \vec{B} \sin 2\lambda q, \\ \vec{M}_0 &= \vec{A} \sin 2\lambda q - \vec{B} \cos 2\lambda q + \vec{C}, \\ \vec{M}_1 &= -\vec{A} \sin 2\lambda q + \vec{B} \cos 2\lambda q + \vec{C}. \end{aligned} \quad (41)$$

We note that

$$\vec{M}_{01}(q=0) = \vec{\mu}_{01}, \quad \vec{M}_0(q=0) = \vec{\mu}_{00}, \quad \vec{M}_1(q=0) = \vec{\mu}_{11}. \quad (42)$$

Therefore, we get

$$C = 0.5(\vec{\mu}_{00} + \vec{\mu}_{11}), \quad B = 0.5(\vec{\mu}_{11} - \vec{\mu}_{00}), \quad A = \vec{\mu}_{01}, \quad (43)$$

where according to Eq. (37)

$$C \sim \frac{\Delta_0 - \eta_0}{2(\Delta^2 + \eta_0^2)^{1/2}}, \quad B \sim \frac{\Delta_0 + \eta_0}{2(\Delta^2 + \eta_0^2)^{1/2}} \quad (44)$$

We can write now

$$\begin{aligned} \vec{\mu}_{00} &= \vec{\mu}_{00}^0 + \vec{\mu}_{00}^1 Q + \dots, \\ \vec{\mu}_{01} &= \vec{\mu}_{01}^0 + \vec{\mu}_{01}^1 Q + \dots, \\ \vec{\mu}_{11} &= \vec{\mu}_{11}^0 + \vec{\mu}_{11}^1 Q + \dots, \end{aligned} \quad (45)$$

where  $Q$  denotes the  $X\dots Y$  distance. The physical sense of (45) is clear as  $\Delta$  must depend on  $Q$ , as  $(\Delta^2 + \eta^2)^{1/2}$  is the energy of a hydrogen bond, and this energy (which strictly speaking is the attractive part of the total  $X\dots Y$  interaction energy only) must of course depend on the  $X\dots Y$  distance. So we get finally

$$\vec{M}_0 = \vec{\mu}_{00}^0 + \vec{\mu}_{00}^1 Q + 2\lambda\vec{\mu}_{01}^0 q + (\vec{\mu}_{11}^0 - \vec{\mu}_{00}^0)\lambda^2 q^2 + (\vec{\mu}_{11}^1 - \vec{\mu}_{00}^1)\lambda^2 Q q^2 + 2\lambda\vec{\mu}_{01}^1 Q q + \dots \quad (46a)$$

$$\vec{M}_{01} = \vec{\mu}_{01}^0 + \vec{\mu}_{01}^1 Q - 2\vec{\mu}_{01}^0 \lambda^2 q^2 + \lambda(\vec{\mu}_{11}^0 - \vec{\mu}_{00}^0)q + \lambda(\vec{\mu}_{11}^1 - \vec{\mu}_{00}^1)Q q + \dots \quad (46b)$$

$$\vec{M}_1 = \vec{\mu}_{11}^0 + \vec{\mu}_{11}^1 Q - 2\lambda\vec{\mu}_{01}^1 Q q + (\vec{\mu}_{00}^1 - \vec{\mu}_{11}^1)\lambda^2 q^2 + (\vec{\mu}_{00}^0 - \vec{\mu}_{11}^0)\lambda^2 Q q^2 + \dots \quad (46c)$$

Equation (46a) gives all the terms which are responsible for the infrared intensity. The following term is responsible for the far infrared absorption:

$$\vec{M}_{\text{fir}} = \vec{\mu}_{00}^1 Q, \quad (47a)$$

for the infrared absorption corresponding to the creation of the  $X\dots Y$  vibrational quantum is responsible for the following one:

$$\vec{M}_{\text{ir}(1)} = 2\lambda \vec{\mu}_{01}^0 q, \quad (47b)$$

whereas for the overtone:

$$\vec{M}_{\text{ir}(2)} = (\vec{\mu}_{11}^0 - \mu_{00}^0) \lambda^2 q^2, \quad (47c)$$

of course the relation

$$\lambda \left| \frac{\vec{\mu}_{11}^0 - \vec{\mu}_{00}^0}{2\vec{\mu}_{01}^0} \right|^2 < 1 \quad (48)$$

must hold, as the overtone intensity in the infrared spectrum of hydrogen bond is always smaller than that of the fundamental. For  $\lambda < 1$  we can neglect all terms of higher orders in  $\lambda$ , and, therefore, also in  $q$ . We can conclude, that the adiabatic coupling between the two lowest non-bonding electron states in a hydrogen bond via the  $X$ -H stretching vibration can be responsible for the great increase of the infrared intensity after formation of the hydrogen bond. It will be proportional to the *electronic* transition moment to the anti-bonding state, which will arise from mixing of the ground  $n$ -electronic state with highly excited states of great density via the chemical bond and the vibrating proton. We note also that Eq. (46a) possesses the term

$$\vec{M}_{\text{el.an.}} = 2\lambda \vec{\mu}_{01}^1 Qq, \quad (49)$$

which results here in a very natural way and was postulated by Bournay and Marechal [5] in order to explain the observed unusual changes in the total infrared absorption intensities of a hydrogen bond after the isotopic substitution. It was called by them "the electrical anharmonicity" and can play also a role in the far infrared spectrum [6]. It was shown recently, that the dynamical coupling between  $q$  and  $Q$  modes in hydrogen bond can also produce such anharmonicity, but of the wrong order of magnitude [7]. We believe that the term  $\vec{\mu}_{01}^1$ , which is, in principle, of electronic nature, can give the proper order of magnitude for the observed electrical anharmonicity

The influence of the non-bonding electron interaction, via the vibrating proton, on the infrared intensities can be estimated only when we get the dependence of  $\vec{\mu}_{01}^0$  on  $\Delta_0$  which should increase with increasing  $V$ . If  $\vec{\mu}_{01}^0 \sim \Delta_0$  then this coupling can increase this intensity, if only the diminution of  $\lambda$  (because of the greater energy gap  $2(\Delta_0^2 + \eta_0^2)^{1/2}$ ) is not too big.

### 6. Summary

We have shown in this paper how to extend the dynamical model of hydrogen bond proposed by Witkowski [1] in order to include the proton vibration. The stretching vibration of  $X-H$  group leads to additional indirect attraction between non-bonding electrons located on opposite sides of the hydrogen bridge, and this stabilizes additionally hydrogen bond. At the same time the frequency of the stretching  $X-H$  mode slightly drops down. This is in qualitative agreement with results obtained by Anderson and Lippincott [3]. These effects are isotopically dependent, and the substitution of hydrogen by deuterium should lead to slight diminution of hydrogen bond energy. This agrees with the experiments of Singh and Rao [8].

It was suggested that the source of large intensity enhancement of  $X-H$  stretching mode, after formation of hydrogen bond, can result from a strong vibronic coupling of the two lowest non-bonding electron states, splitted by indirect interactions via  $\sigma$ -electrons of  $X-H$  chemical bond and proton vibration. In such a case the intensity would be borrowed from intense Rydberg-type transitions in lone pairs of  $X$  and  $Y$  atoms of the  $X-H...Y$  hydrogen bond.

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