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A Hellmann–Feynman Basis for the Determination of the Dependence of the Intramolecular X–H(D) Potential on the Hydrogen Bond Strength

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A Hellmann–Feynman Basis for the Determination of the Dependence of the Intramolecular X–H(D) Potential on the Hydrogen Bond Strength[#]

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Abstract

A novel theoretical method that enables extraction of the function describing the dependence of the decoupled X–H(D) intramolecular potential on the hydrogen bond strength from experimental frequency–structure correlation equations is proposed. The method is based on the Hellmann–Feynman theorem, using the perturbed anharmonic oscillator wavefunctions, and the conceptual approach of Sceats and Rice. Within the proposed method, other parameters obtained by empirical correlations have also exact physical meanings.

Motivation. The hydrogen bonding is beyond doubt one of the most interesting interactions from both fundamental and application viewpoints. A lot of experimental data have been collected so far regarding the spectroscopic manifestations of this interaction, among which the most important is the frequency downshift of the X–H stretching mode. A number of empirical correlations have been performed for the dependence of $\tilde{\nu}_{01,XH(D)}$ versus $R_{X...Y}$ in hydrogen bonded X–H...Y systems. However, there is still a lack of systematic theoretical basis for the empirical correlation functions which are widely applicable. Also, it would be especially interesting to extract the function describing the dependence of the intramolecular X–H(D) potential on the hydrogen bond strength obtained from experimental frequency–structure correlations.

Method. The Hellmann–Feynman theorem, in combination with the stationary perturbation theory in the non–degenerate case for the representation of anharmonic oscillator perturbed (by hydrogen bonding) wavefunction, is applied.

Results. It is shown that there is a solid theoretical basis for the empirical spectra–structure correlations in the case of hydrogen bonded systems. Moreover, on the basis of the derived theoretical model, "extraction" of the function describing the dependence of the intramolecular X–H(D) potential on the hydrogen bond strength becomes possible using experimental frequency–structure correlation data.

Conclusions. Within the conceptual approach of Sceats and Rice, a Hellmann–Feynman based theoretical model is derived, that enables determination of the function describing the dependence of the intramolecular X–H(D) potential on the hydrogen bond strength, derived from experimental frequency–structure correlations. Within the proposed method, other empirically obtained parameters have exact physical meanings as well. The proposed approach may serve to test the validity and physical basis of various model functions used for empirical correlations.

Keywords. Hydrogen bonding; Hellmann–Feynman theorem; frequency–structure correlations; intramolecular X–H(D) potential; Sceats–Rice model potential.

1 INTRODUCTION

The hydrogen bonding, as a very striking and biologically important interaction, has been studied, both theoretically and experimentally [2–18]. Various models have been proposed in order to rationalize the experimental observations. Many experimental data have been satisfactory explained within the "strong coupling theory" of Marechal and co–workers [3–9], as well as with its modifications [10]. Nowadays, with the enormous progress of *ab initio* and density functional methods, even subtle peculiarities of potential energy hypersurfaces of hydrogen bonded systems can be explored. A lot of experimental correlations among various quantities characterizing the hydrogen bonding interaction have been performed so far [11–14]. Since it has been shown that this interaction significantly affects the X–H(D) potential [15–20], special attention was paid to the dependence of the intramolecular X–H(D) potential on the parameters that characterize the hydrogen bond strength. The change in this potential due to the hydrogen bond formation may be treated within standard perturbation theoretical approaches [15,16]. On the other hand, the more phenomenological approach of Sceats and Rice [1] appears to be very useful in explaining the overtone spectra of Ice I [1], as well as in analyzing the spectral data for a series of methanol complexes with organic bases [21]. On the basis of the Sceats–Rice potential, a theoretical basis for the observed $\widetilde{\nu}_{01,OH} / \widetilde{\nu}_{01,OD}$ *vs* $\widetilde{\nu}_{01,OH}$ [17, 18] as well as $\widetilde{\nu}_{01,OH(D)}$ *vs* $R_{O...O}$ [19] correlations in solid crystalline hydrates was established. Recently, a more general perturbation theoretical method dealing with the $\widetilde{\nu}_{01,XH(D)}$ *vs* $R_{X...Y}$ correlations in hydrogen bonded X–H...Y systems was proposed [22].

Within the conceptual approach of Sceats and Rice, and based on the Hellmann–Feynman theorem [23], a theoretical method enabling the extraction of the analytical form of the function that describes the dependence of the decoupled intramolecular X–H(D) potential on the hydrogen bond strength, from the experimentally obtained $\widetilde{\nu}_{01,XH(D)} = f(R_{X...Y})$ correlation equations is here proposed. The method is applicable to linear X–H(D)...Y complexes, in which the stretch–stretch couplings of the ν(X–H) mode with the internal modes of the radical X may be neglected. An extension to non–linear cases may be easily done. Within the proposed model, other parameters obtained by empirical correlations have an exact physical meaning as well.

2 THEORETICAL MODEL

The main assumption of the Sceats–Rice [1] approach is that the effect of hydrogen bonding on a water molecule in solid state can be modeled by modifying only the diagonal harmonic force constant k_{rr} and the stretch–stretch interaction force constant $k_{rr'}$ in the unperturbed potential, in internal coordinates [1], written as:

$$\hat{V} = \frac{1}{2}k_{rr}\left(\Delta r_1^2 + \Delta r_2^2\right) + \frac{1}{2}k_{\alpha\alpha}r_e^2\Delta\alpha^2 + k_{r\alpha}r_e\Delta\alpha\left(\Delta r_1 + \Delta r_2\right) + k_{rr'}\Delta r_1\Delta r_2 +$$
$$+ k_{rrr}\left(\Delta r_1^3 + \Delta r_2^3\right) + k_{rrrr}\left(\Delta r_1^4 + \Delta r_2^4\right)$$

The previous expression provides a sufficiently good description of the anharmonic potential even limiting to the above mentioned terms [24]. Thus, the terms of the type $k_{\alpha\alpha r}r_e\Delta\alpha^2\left(\Delta r_1 + \Delta r_2\right)$ can be neglected.

From the previous statement it follows that, in isotopically isolated HDO molecules, (or in general, X–H(D) hydrogen bonded species in which the interaction of the X–H(D) stretching mode with the internal modes of the radical X may be practically neglected), the whole effect of hydrogen bonding on the X–H(D) oscillators may be accounted for by the changes in the diagonal force constant k_{rr}.

Treating the unperturbed by hydrogen bonding X–H(D) oscillator as a cubic–quartic anharmonic system, its Hamiltonian can be written in the form:

$$\hat{H}^{(0)} = \frac{\hat{p}^2}{2\mu} + \frac{1}{2}k_{rr}^{(0)}\Delta r^2 + k_{rrr}^{(0)}\Delta r^3 + k_{rrrr}^{(0)}\Delta r^4 \tag{1}$$

where μ is the reduced mass, and $\Delta r = r - r_0$, r and r_0 being the actual and the equilibrium X–H(D) distance. Within the elaborated approach, the Hamiltonian of the system perturbed by the hydrogen bonding interaction, takes the form:

$$\hat{H} = \frac{\hat{p}^2}{2\mu} + \frac{1}{2}k_{rr}\Delta r^2 + k_{rrr}^{(0)}\Delta r^3 + k_{rrrr}^{(0)}\Delta r^4 \tag{2}$$

where the diagonal harmonic force constant k_{rr} depends on the hydrogen bond strength. If only linear X–H(D)...Y hydrogen bonds are considered, for a fixed pair (X, Y), the hydrogen bond strength depends only on the X...Y distance ($R_{X...Y}$) (of course, for another choice of the proton donor and the proton acceptor, it depends on other properties as well, such as the effective charge on the Y atom). In that case, k_{rr} is a function of $R_{X...Y}$ (denoted by R hereafter) only:

$$k_{rr} = f(R) \tag{3}$$

The hydrogen bond distance thus appears as a parameter in the Hamiltonian (2):

$$\hat{H} = \frac{\hat{p}^2}{2\mu} + \frac{1}{2}k_{rr}(R)\Delta r^2 + k_{rrr}^{(0)}\Delta r^3 + k_{rrrr}^{(0)}\Delta r^4 \tag{4}$$

Note that, the equilibrium distance r_0 depends on the hydrogen bond strength as well, but since the derivative dr_0/dR is negligibly small, it may be practically neglected (as in the original approach of Sceats and Rice). According to the Hellmann–Feynman theorem,

$$\frac{dE_n}{dR} = \left\langle \frac{\partial\hat{H}}{\partial R} \right\rangle = \left\langle \Psi_n(r,R)\left|\frac{\partial\hat{H}}{\partial R}\right|\Psi_n(r,R) \right\rangle \tag{5}$$

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where E_n is the energy of the n–th level of the perturbed anharmonic oscillator, while $\Psi_n(r,R)$ is the corresponding wavefunction that depends parametrically on R. Since the hydrogen bonding interaction effects may be treated as a perturbation to the energy spectrum of the free anharmonic oscillator, $\Psi_n(r,R)$ may be represented with the perturbation series:

$$\Psi_n(r,R) = \Psi_n^{(0)}(r) + \Psi_n^{(1)}(r,R) + \Psi_n^{(2)}(r,R) + \cdots \tag{6}$$

where $\Psi_n^{(0)}(r)$ is the unperturbed anharmonic oscillator wavefunction, while the successive perturbation corrections are denoted by $\Psi_n^{(i)}(r,R)$. In order to calculate these successive corrections, it is suitable to split the Hamiltonian (4) into a part referring to the non hydrogen bonded X–H(D) system and the perturbation. The simplest way to do this is to represent the function $k_{rr}(R)$ in the form:

$$k_{rr}(R) = k_{rr}^{(0)} \left[1 - \varphi(R) \right] \tag{7}$$

where the function $\varphi(R)$ must satisfy several logical requirements. Since for large values of R k_{rr} tends to $k_{rr}^{(0)}$, the condition:

$$\lim_{R \to \infty} \varphi(R) = 0 \tag{8}$$

obviously holds. Further,

$$\max \varphi(R) = \varphi(R_0) = 1 \tag{9}$$

where R_0 may be regarded as some critical distance, for which the X–H(D) oscillator does not longer exist. The model is limited to weak and medium strong hydrogen bonds, where the values of R are significantly larger than R_0. Otherwise, $\varphi(R) << 1$ must hold.

The expression (7) and the previous discussion, allows one to write the Hamiltonian (4) in the form:

$$\hat{H}(r,R) = \hat{H}^{(0)}(r) - \frac{1}{2} k_{rr}^{(0)} \cdot \varphi(R) \cdot \Delta r^2 \tag{10}$$

Applying the stationary perturbation theory with the perturbation operator:

$$\hat{V}(r,R) = -\frac{1}{2} k_{rr}^{(0)} \cdot \varphi(R) \cdot \Delta r^2 \tag{11}$$

the successive corrections to the unperturbed wavefunction are straightforwardly calculated using the matrix elements [23]:

$$V_{mn} = \left\langle \Psi_m^{(0)} \left| \hat{V} \right| \Psi_n^{(0)} \right\rangle = -\frac{1}{2} k_{rr}^{(0)} \cdot \varphi(R) \cdot \left\langle \Psi_m^{(0)} \left| \Delta r^2 \right| \Psi_n^{(0)} \right\rangle \tag{12}$$

The corresponding expressions are:

$$\Psi_n^{(1)}(r, R) = \varphi(R) \cdot \left[-\frac{1}{2} k_{rr}^{(0)} \sum_{m \neq n} \frac{\left\langle \Psi_m^{(0)} \middle| \Delta r^2 \middle| \Psi_n^{(0)} \right\rangle}{\hbar \omega_{nm}} \Psi_m^{(0)}(r) \right] \tag{13}$$

$$\Psi_n^{(2)}(r, R) = \varphi^2(R) \cdot \left\{ \frac{(k_{rr}^{(0)})^2}{4} \left[\sum_{m \neq n} \sum_{k \neq n} \frac{\left\langle \Psi_m^{(0)} \middle| \Delta r^2 \middle| \Psi_k^{(0)} \right\rangle \left\langle \Psi_k^{(0)} \middle| \Delta r^2 \middle| \Psi_n^{(0)} \right\rangle}{\hbar^2 \omega_{nk} \omega_{nm}} \Psi_m^{(0)}(r) - \right.\right.$$

$$\left.\left. - \sum_{m \neq n} \frac{\left\langle \Psi_n^{(0)} \middle| \Delta r^2 \middle| \Psi_n^{(0)} \right\rangle \left\langle \Psi_m^{(0)} \middle| \Delta r^2 \middle| \Psi_n^{(0)} \right\rangle}{\hbar^2 \omega_{nm}^2} \Psi_m^{(0)}(r) + \frac{1}{2} \Psi_n^{(0)}(r) \sum_{m \neq n} \frac{\left| \left\langle \Psi_m^{(0)} \middle| \Delta r^2 \middle| \Psi_n^{(0)} \right\rangle \right|^2}{\hbar^2 \omega_{nm}^2} \right] \right\} \tag{14}$$

$$\Psi_n^{(3)}(r, R) = \varphi^3(R) \cdot \left\{ \cdots \right. \tag{15}$$

etc.

On the other hand, the derivative $\dfrac{\partial \hat{H}}{\partial R}$ is given by:

$$\frac{\partial \hat{H}}{\partial R} = -\frac{1}{2} k_{rr}^{(0)} \Delta r^2 \frac{d\varphi(R)}{dR} + \text{smaller terms} \tag{16}$$

In the previous expression, the dropped smaller terms include the derivative of the equilibrium X–H distance r_0 on the parameter R, which is practically negligible.

The Hellmann–Feynman expression thus takes the form:

$$\frac{dE_n}{dR} = \left\langle \Psi_n(r, R) \middle| \frac{\partial \hat{H}}{\partial R} \middle| \Psi_n(r, R) \right\rangle = -\frac{1}{2} k_{rr}^{(0)} \frac{d\varphi(R)}{dR} \left\{ \left\langle \Psi_n^{(0)}(r) \middle| \Delta r^2 \middle| \Psi_n^{(0)}(r) \right\rangle \right.$$

$$+ \varphi(R) \cdot \left[-\frac{1}{2} k_{rr}^{(0)} \sum_{m \neq n} \frac{\left\langle \Psi_m^{(0)}(r) \middle| \Delta r^2 \middle| \Psi_n^{(0)}(r) \right\rangle \left\langle \Psi_n^{(0)}(r) \middle| \Delta r^2 \middle| \Psi_m^{(0)}(r) \right\rangle}{\hbar \omega_{nm}} \right.$$

$$\left. -\frac{1}{2} k_{rr}^{(0)} \sum_{m \neq n} \frac{\left\langle \Psi_n^{(0)}(r) \middle| \Delta r^2 \middle| \Psi_m^{(0)}(r) \right\rangle^* \left\langle \Psi_m^{(0)}(r) \middle| \Delta r^2 \middle| \Psi_n^{(0)}(r) \right\rangle}{\hbar \omega_{nm}} \right] \tag{17}$$

$$+ \varphi^2(R) \cdot \left[\frac{1}{4} (k_{rr}^{(0)})^2 \sum_{m \neq n} \sum_{m' \neq n} \frac{\left\langle \Psi_n^{(0)}(r) \middle| \Delta r^2 \middle| \Psi_m^{(0)}(r) \right\rangle \left\langle \Psi_{m'}^{(0)}(r) \middle| \Delta r^2 \middle| \Psi_n^{(0)}(r) \right\rangle \left\langle \Psi_m^{(0)}(r) \middle| \Delta r^2 \middle| \Psi_{m'}^{(0)}(r) \right\rangle}{\hbar^2 \omega_{nm} \omega_{nm'}} + \cdots \right] + \cdots \right\}$$

or, in a more compact form:

$$\frac{dE_n}{dR} = -\frac{1}{2} k_{rr}^{(0)} \frac{d\varphi(R)}{dR} \cdot \left[c_{0n} + c_{1n} \cdot \varphi(R) + c_{2n} \cdot \varphi^2(R) + \cdots \right] \tag{18}$$

$$dE_n = -\frac{1}{2} k_{rr}^{(0)} \cdot \left[c_{0n} + c_{1n} \cdot \varphi(R) + c_{2n} \cdot \varphi^2(R) + \cdots \right] \cdot d\varphi(R) \tag{19}$$

which gives, by integration:

$$E_n = C_n - \frac{1}{2} k_{rr}^{(0)} \cdot \left[c_{0n} \cdot \varphi(R) + c_{1n} \cdot \frac{\varphi^2(R)}{2} + c_{2n} \cdot \frac{\varphi^3(R)}{3} + \cdots \right] \tag{20}$$

The energy difference between the ground and the first excited vibrational state is, accordingly:

$$E_1 - E_0 = (C_1 - C_0) - \frac{1}{2} k_{rr}^{(0)} \cdot \left[(c_{01} - c_{00}) \cdot \varphi(R) + \frac{(c_{11} - c_{10})}{2} \cdot \varphi^2(R) + \frac{(c_{21} - c_{20})}{3} \cdot \varphi^3(R) + \cdots \right] \tag{21}$$

or, expressed in terms of the wavenumber of the corresponding vibrational transition:

$$\widetilde{v}_{01} = \frac{(C_1 - C_0)}{hc} - \frac{1}{2} k_{rr}^{(0)} \cdot \left[\frac{(c_{01} - c_{00})}{hc} \cdot \varphi(R) + \frac{(c_{11} - c_{10})}{2hc} \cdot \varphi^2(R) + \frac{(c_{21} - c_{20})}{3hc} \cdot \varphi^3(R) + \cdots \right] \tag{22}$$

If only the first–order perturbation corrections of the wavefunction are accounted for, the previous expression reduces to the form:

$$\widetilde{v}_{01} = \frac{(C_1 - C_0)}{hc} - k_{rr}^{(0)} \frac{(c_{01} - c_{00})}{2hc} \cdot \varphi(R) \tag{23}$$

$$\widetilde{v}_{01} = A - B \cdot \varphi(R) \tag{24}$$

On the other hand, the experimental data [11–15] regarding the dependence of the wavenumber corresponding to the $1 \leftarrow 0$ vibrational transition on the hydrogen bond strength, show that the dependence of $\widetilde{v}_{01}$ on R may be successfully fitted with a function of the type:

$$\widetilde{v}_{01} = \widetilde{v}_{01}^{(f)} - K \cdot \exp(-aR) \tag{25}$$

where the constant $\widetilde{v}_{01}^{(f)}$ refers to a free X–H(D) oscillator. Obviously, the experimentally derived correlation equations allow a direct determination of the function describing the dependence of the intramolecular X–H(D) potential on the hydrogen bond strength. It follows that the function $\varphi(R)$ is often of the type $\exp(-aR)$, and the dependence of the harmonic diagonal force constant on R, within the first–order perturbation theory, may be successfully described by the function:

$$k_{rr}(R) = k_{rr}^{(0)}[1 - \exp(-aR)] \tag{26}$$

Further, the empirically obtained coefficient K is equal to the difference:

$$\frac{k_{rr}^{(0)}}{2hc} \left[\left\langle \Psi_1^{(0)}(r) \middle| \Delta r^2 \middle| \Psi_1^{(0)}(r) \right\rangle - \left\langle \Psi_0^{(0)}(r) \middle| \Delta r^2 \middle| \Psi_0^{(0)}(r) \right\rangle \right] \tag{27}$$

It is, thus, possible to obtain the term $\left\langle \Psi_1^{(0)}(r) \middle| \Delta r^2 \middle| \Psi_1^{(0)}(r) \right\rangle - \left\langle \Psi_0^{(0)}(r) \middle| \Delta r^2 \middle| \Psi_0^{(0)}(r) \right\rangle$ from the correlation data, if the unperturbed force constant $k_{rr}^{(0)}$ is known. On the other hand, if one calculates the matrix elements $\left\langle \Psi_n^{(0)}(r) \middle| \Delta r^2 \middle| \Psi_n^{(0)}(r) \right\rangle$ in the basis of the eigenfunctions of a Morse–type oscillator, it is also principally possible to obtain the value for $k_{rr}^{(0)}$ from experimental data for a

particular series of compounds. On the other hand, the term:

$$\frac{(C_1 - C_0)}{hc} \tag{28}$$

obviously corresponds to the wavenumber of the unperturbed (by hydrogen bonding) X–H(D) oscillator. In fact, many discussions have been devoted to the choice of the constant $\tilde{\nu}_{01}^{(f)}$ in empirical correlations [11,19]. Although the previously mentioned choice is principally incorrect [11,12,19,22], it is, however, the simplest one for a large number of systems. Especially in case of solid crystalline hydrates, it is impossible to achieve experimentally the situation of an O–H(D) oscillator, that does not take part in hydrogen bonding and is in the same crystalline environment as the hydrogen bonded ones [19,22]. It is thus easier to take the wavenumber for free H_2O(HDO), or, in general X–H(D) species as a reference point in correlations. The theoretical approach elaborated in this work gives a further support to the statement that a better choice instead of $\tilde{\nu}_{01}^{(f)}$ should be the corresponding value for an unbounded oscillator, in exactly the same crystalline environment.

On the other hand, if all terms in the perturbation series are retained, the dependence of the $\tilde{\nu}_{01}$ value on the parameter R is given by the following expression:

$$\tilde{\nu}_{01} = A - B \cdot \varphi(R) - C \cdot \varphi^2(R) - D \cdot \varphi^3(R) - \cdots \tag{29}$$

It is well known [11, 12] that the $\tilde{\nu}_{01}$ values correlate very well with R in cases of weak and medium strong hydrogen bonds. However, for stronger hydrogen bonds, the correlation between these parameters is much worse. Obviously, this theoretical approach suggests a deeper fundamental reason for such experimental findings. In cases for which the perturbation theory is still applicable, but the perturbation is not very small, inclusion of the higher–order terms from the perturbation series may be significant. The last equation is a method for testing the model functions used for correlations. Namely, instead of the functions of type (25) one may use the following ones:

$$\tilde{\nu}_{01} = \tilde{\nu}_{01}^{(f)} - K \cdot \frac{1}{R - a} \tag{30}$$

Expanding the interval of the R values, and including the higher order perturbation correction terms, the empirical model function providing a deeper physical meaning should allow a better correlation with the experimental data.

3 CONCLUSIONS

Within the conceptual approach of Sceats and Rice, a Hellmann–Feynman based theoretical model is derived, that enables determination of the function describing the dependence of the intramolecular X–H(D) potential on the hydrogen bond strength, derived from experimental frequency–structure correlations. Within the proposed method, other empirically obtained

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