A perturbation theoretical method for determination of the dependence of the intramolecular X–H(D) potential on the hydrogen bond strength

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A perturbation theoretical method is proposed that allows determination of the function describing the dependence of the intramolecular XH(D) potential on the hydrogen bond strength. Treating the XH(D) oscillators as mixed cubic–quartic oscillators in which the stretch–stretch couplings of the ν(X–H(D)) mode with the internal modes of the radical X may be neglected, and introducing the hydrogen bonding influence through the changes in the harmonic diagonal force constants (as proposed by Sceats and Rice [41]), it is possible to extract the analytical form of the function $k_{rr} = f(R_{X\ldots Y})$ from the experimental $\widetilde{\nu}_{XH(D)}$ versus $R_{X\ldots Y}$ correlations. The other parameters obtained by the empirical correlations, within this model, also have an exact physical meaning. The method is applicable to weak hydrogen bonds as well as to hydrogen bonds of intermediate strength, and, strictly speaking, to linear X–H(D)$\ldots$Y systems. However, extension to arbitrary geometry may be easily done.

1. Introduction

The hydrogen bond interaction as a general problem has received significant attention. Much work has been done in this field, from both theoretical and experimental viewpoints [42 and references therein]. Several theoretical approaches are currently in use in order to explain the experimentally observed peculiarities related to this phenomenon. It is widely accepted that in a hydrogen bonded X–H$\ldots$Y system, the X–H oscillator is coupled both to the low-frequency ν(X$\ldots$Y) mode [2,27–30,49,52], and to the various modes due to the radical X [22,46], the first one being of key importance for explanation of many properties of such complexes [46]. However, for weak and moderately strong hydrogen bonds, this coupling can be treated within the adiabatic approximation [30]. Another, in a sense more phenomenological, approach is that of Sceats and Rice [41]. In order to analyze the overtone spectrum of ice I, these authors adopted the following approach. The free (non-hydrogen-bonded) water molecule was

treated as a cubic–quartic anharmonic oscillator, with a potential of the form

$$\widehat{V} = \frac{1}{2}k_{rr}\left(\Delta r_1^2 + \Delta r_2^2\right) + \frac{1}{2}k_{\alpha\alpha}r_e^2\Delta\alpha^2 + k_{r\alpha}r_e\Delta\alpha(\Delta r_1 + \Delta r_2) + k_{rr'}\Delta r_1\Delta r_2$$
$$+ k_{rrr}\left(\Delta r_1^3 + \Delta r_2^3\right) + k_{rrrr}\left(\Delta r_1^4 + \Delta_2^4\right) \tag{1}$$

(using the usual notation [41]). It has been shown [41] that even in gas phase, the inclusion of only stretching anharmonicities is a good approximation to the true anharmonic potential. The terms of the type

$$k_{\alpha\alpha r}r_e\Delta\alpha^2(\Delta r_1 + \Delta r_2) \tag{2}$$

may, thus, be neglected. The only change in the anharmonic potential resulting from the hydrogen bonding interaction is in the force constant k_{rr} and the stretch–stretch interaction force constant $k_{rr'}$.

It follows from this assumption that in the case of a hydrogen bonded HDO molecule, one may completely include the effect of hydrogen bonding on the independent OH and OD oscillators through the changes in the corresponding diagonal harmonic force constants. This assumption should also be valid for other systems in which the stretch–stretch couplings of the X–H(D) group with some internal modes of the radical X in an X–H(D)...Y complex are negligible. It is important to mention at this point that the Sceats–Rice potential is, in fact, a second-order perturbation based expression derived from the Smith–Overend potential [51]. The assumption of Sceats and Rice has been successfully applied to the analysis of the overtone spectrum of ice I [41], for a series of methanol complexes with organic bases [39], as well as for a theoretical explanation of the observed $\widetilde{\nu}_{01,OH}/\widetilde{\nu}_{01,OD}$ versus $\widetilde{\nu}_{01,OH}$ correlations in solid hydrates [51]. In the latter work, the variational one-dimensional problem with a simple cubic–quartic potential was solved also with a modified Sceats–Rice potential, which explicitly accounts for the change in the equilibrium X–H distance in the course of hydrogen bonding.

In this work, starting with the Sceats–Rice assumption, we derive a perturbation theoretical method that enables extraction of the function describing the dependence of diagonal harmonic force constant on the X...Y distance from experimental data. Strictly speaking, the method is applicable to linear X–H(D)...Y complexes, in which the stretch–stretch couplings of the X–H mode with the internal modes of the radical X may be neglected.

2. Theoretical model

Let us consider a cubic–quartic X–H(D) oscillator in which the stretch–stretch couplings with the internal modes of the radical X may be neglected (e.g., the HDO molecule). The Hamiltonian of such an anharmonic oscillator ("free" X–H(D) system)

with a reduced mass μ, in a one-dimensional approximation, can be written in the form [51]

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

The superscripts (0) refer to a state not perturbed by hydrogen bonding. The quantity Δr is defined as $r - r_0$, r and r_0 being the momentary and the equilibrium X–H(D) distance, respectively. According to the assumption of Sceats and Rice [41], later modified in some aspects by Wòjcik, Lindgren and Tegenfeldt [51], the whole effect of hydrogen bonding interaction with an atom Y may be introduced through a change in the diagonal harmonic force constant of this system. The other terms in the potential may be regarded as practically unchanged. The Hamiltonian (3), thus, takes the following form:

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

The whole increase in the anharmonicity of the X–H(D) mode due to the hydrogen bonding, according to this model, can be attributed to the increased amplitude of motion of the hydrogen atom. Let us now consider the relationship between k_{rr} and $k_{rr}^{(0)}$. Considering only linear hydrogen bonds, and particular proton donor X and proton acceptor Y, k_{rr} will depend on $k_{rr}^{(0)}$ and the hydrogen bond distance ($R_{\text{X}\dots\text{Y}}$). The previous statement is analogous to the assumption that the hydrogen bond strength is directly proportional to $R_{\text{X}\dots\text{Y}}$. For various X and Y, it would also depend on the effective charge on the proton acceptor atom.

In order to apply the stationary perturbation theory approach, it is convenient to write the function describing the dependence of k_{rr} on $R_{\text{X}\dots\text{Y}}$ (denoted by R further in the text) in the following form:

$$k_{rr} = k_{rr}^{(0)}\big[1 - f(R)\big]. \tag{5}$$

The function $f(R)$ should satisfy the following obvious requirements:

(a) $\lim_{R\to\infty} f(R) = 0$,

(b) $\max f(R) = f(R_0) = 1$,

(c) $\lim_{R\to R_0^+} f(R) = 1$,

(d) $f(R) \ll 1$, $R \gg R_0$, i.e., for consistency with the previous requirements,

$$\frac{\mathrm{d}f(R)}{\mathrm{d}R} < 0, \quad R \in (R_0, \infty),$$

(e) $f(R) = 0$, $R \in (-\infty, R_0)$ (values without physical meaning),

where R_0 is a constant, which may be regarded as some critical distance at which the X–H(D) oscillator no longer exists. However, the physical significance of this constant is not important at this point, because in this model, only weak and hydrogen bonds

of moderate strength are considered. Thus, only cases characterized by $R \gg R_0$ are of interest.

Within the previous assumptions, the parameter R will practically completely include the dependence of k_{rr} on the hydrogen bond strength for a given X and Y pair.

Combining (5) and (4), the Hamiltonian of the oscillator perturbed by hydrogen bonding takes the form

$$\widehat{H} = \widehat{H}^{(0)} - \frac{1}{2} k_{rr}^{(0)} f(R) \Delta r^2. \tag{6}$$

The second term in (6) is small, so it may be regarded as a small perturbation to the non-hydrogen-bonded oscillator. The perturbation operator is, in this case,

$$\widehat{V} = -\frac{1}{2} k_{rr}^{(0)} f(R) \Delta r^2. \tag{7}$$

It should be borne in mind that the unperturbed eigenvalue problem

$$\widehat{H}^{(0)} \big| \Psi_n^{(0)} \big\rangle = E_n^{(0)} \big| \Psi_n^{(0)} \big\rangle \tag{8}$$

refers to the cubic–quartic *anharmonic* oscillator. The energy of the nth level of the hydrogen-bonded system may be represented by the perturbation series

$$E_n = E_n^{(0)} + E_n^{(1)} + E_n^{(2)} + \cdots. \tag{9}$$

In order to calculate corrections of various orders to the energy spectrum of the unperturbed system, the matrix elements of the type

$$V_{mn} = \big\langle \Psi_m^{(0)} \big| \widehat{V} \big| \Psi_n^{(0)} \big\rangle \tag{10}$$

calculated in the basis $\{ | \Psi_n^{(0)} \rangle \}$ are required.

Substituting the expression for the perturbation operator, the matrix elements (10) take the form

$$V_{mn} = -\frac{1}{2} k_{rr}^{(0)} f(R) \big\langle \Psi_m^{(0)} \big| \Delta r^2 \big| \Psi_n^{(0)} \big\rangle. \tag{11}$$

The corrections to the energy of various orders are thus easily obtained. The corresponding expressions are

$$E_n^{(1)} = f(R) \left[-\frac{1}{2} k_{rr}^{(0)} \big\langle \Psi_n^{(0)} \big| \Delta r^2 \big| \Psi_n^{(0)} \big\rangle \right], \tag{12}$$

$$E_n^{(2)} = f^2(R) \left[\frac{1}{4} \big(k_{rr}^{(0)} \big)^2 \sum_{m \neq n} \frac{|\langle \Psi_m^{(0)} | \Delta r^2 | \Psi_n^{(0)} \rangle|^2}{\hbar \omega_{nm}} \right], \tag{13}$$

$$E_n^{(3)} = f^3(R) \left[-\frac{1}{8} \big(k_{rr}^{(0)} \big)^3 \sum_{k \neq n} \sum_{m \neq n} \frac{\langle \Psi_n^{(0)} | \Delta r^2 | \Psi_m^{(0)} \rangle \langle \Psi_m^{(0)} | \Delta r^2 | \Psi_k^{(0)} \rangle \langle \Psi_k^{(0)} | \Delta r^2 | \Psi_n^{(0)} \rangle}{\hbar^2 \omega_{mn} \omega_{kn}} \right.$$

$$+ \frac{1}{8}\big(k_{rr}^{(0)}\big)^3 \big\langle \Psi_n^{(0)} \big| \Delta r^2 \big| \Psi_n^{(0)} \big\rangle \sum_{m \neq n} \frac{|\langle \Psi_n^{(0)} | \Delta r^2 | \Psi_m^{(0)} \rangle|^2}{\hbar^2 \omega_{mn}^2} \Bigg], \tag{14}$$

$$\vdots$$

The energy expression, thus, takes the form

$$E_n = E_n^{(0)} + f(R)f_n^{(1)} + f^2(R)f_n^{(2)} + f^3(R)f_n^{(3)} + \cdots, \tag{15}$$

where

$$f_n^{(1)} = -\frac{1}{2} k_{rr}^{(0)} \big\langle \Psi_n^{(0)} \big| \Delta r^2 \big| \Psi_n^{(0)} \big\rangle, \tag{16}$$

$$f_n^{(2)} = \frac{1}{4} \big(k_{rr}^{(0)}\big)^2 \sum_{m \neq n} \frac{|\langle \Psi_m^{(0)} | \Delta r^2 | \Psi_n^{(0)} \rangle|^2}{\hbar \omega_{nm}}, \tag{17}$$

$$f_n^{(3)} = -\frac{1}{8} \big(k_{rr}^{(0)}\big)^3 \sum_{k \neq n} \sum_{m \neq n} \frac{\langle \Psi_n^{(0)} | \Delta r^2 | \Psi_m^{(0)} \rangle \langle \Psi_m^{(0)} | \Delta r^2 | \Psi_k^{(0)} \rangle \langle \Psi_k^{(0)} | \Delta r^2 | \Psi_n^{(0)} \rangle}{\hbar^2 \omega_{mn} \omega_{kn}}$$

$$+ \frac{1}{8} \big(k_{rr}^{(0)}\big)^3 \big\langle \Psi_n^{(0)} \big| \Delta r^2 \big| \Psi_n^{(0)} \big\rangle \sum_{m \neq n} \frac{|\langle \Psi_n^{(0)} | \Delta r^2 | \Psi_m^{(0)} \rangle|^2}{\hbar^2 \omega_{mn}^2}, \tag{18}$$

$$\vdots$$

Since we consider weak hydrogen bonds (i.e., $f(R) \ll 1$), the terms that contain $f^2(R)$, $f^3(R)$ etc. in (13) may be neglected, and the energy expression reduces to

$$E_n = E_n^{(0)} + f(R)f_n^{(1)}. \tag{19}$$

The energy difference between the ground and the first excited vibrational state, on the basis of (19) is, thus,

$$E_1 - E_0 = E_1^{(0)} - E_0^{(0)}$$

$$- \frac{k_{rr}^{(0)}}{2} \Big[\big\langle \Psi_1^{(0)}(r) \big| \Delta r^2 \big| \Psi_1^{(0)}(r) \big\rangle - \big\langle \Psi_0^{(0)}(r) \big| \Delta r^2 \big| \Psi_0^{(0)}(r) \big\rangle \Big] f(R) \tag{20}$$

or, expressed in terms of the wavenumber for the corresponding fundamental transition,

$$\widetilde{\nu}_{01} = \widetilde{\nu}_{01}^{(0)} - \frac{k_{rr}^{(0)}}{2hc} \Big[\big\langle \Psi_1^{(0)}(r) \big| \Delta r^2 \big| \Psi_1^{(0)}(r) \big\rangle - \big\langle \Psi_0^{(0)}(r) \big| \Delta r^2 \big| \Psi_0^{(0)}(r) \big\rangle \Big] f(R). \tag{21}$$

The last equation describes the dependence of the experimentally measured wavenumber of the $1 \leftarrow 0$ transition on the hydrogen bond length R. Much effort has been done in order to establish empirical correlations between these two quantities [5,18, 24,32,33,38]. It has been shown that for a great variety of systems, experimental data can be successfully modeled with a function of the type

$$\widetilde{\nu}_{01} = \widetilde{\nu}_{01,f} - A \exp(-aR), \tag{22}$$

where the quantity $\widetilde{\nu}_{01,\mathrm{f}}$ is the value referring to a non-hydrogen-bonded ("free") system.

Equations (21) and (22), thus, enable determination of the function $f(R)$ for particular series of compounds, from experimentally obtained correlation equations. According to the experimental data, it often has the following form:

$$f(R) = \exp(-aR). \tag{23}$$

Further, the constant A is equal to the quantity

$$\frac{k_{rr}^{(0)}}{2hc}\big[\big\langle \Psi_1^{(0)}(r)\big|\Delta r^2\big|\Psi_1^{(0)}(r)\big\rangle - \big\langle \Psi_0^{(0)}(r)\big|\Delta r^2\big|\Psi_0^{(0)}(r)\big\rangle\big]. \tag{24}$$

If the diagonal harmonic force constant for the unperturbed system is known, an experimental determination of the difference

$$\big\langle \Psi_1^{(0)}(r)\big|\Delta r^2\big|\Psi_1^{(0)}(r)\big\rangle - \big\langle \Psi_0^{(0)}(r)\big|\Delta r^2\big|\Psi_0^{(0)}(r)\big\rangle$$

through the constant A is possible.

It should be pointed out that the usage of the gas-phase wavenumbers in such empirical correlations has been a subject of many discussions [32,37], at least for solid crystalline hydrates. It is even intuitively clear that a more representative value for these systems would be the one for an oscillator placed in exactly the same crystal surrounding, which does not take part in hydrogen bonding. The model derived in this work further supports the previous statement. However, since such a situation (non-hydrogen-bonded system in a particular crystal environment) is practically inaccessible experimentally, the usage of the gas-phase values yields useful approximation.

Inclusion of higher-order energy corrections in (19) and (20) leads to the following relation between $\widetilde{\nu}_{01}$ and R:

$$\widetilde{\nu}_{01} = \widetilde{\nu}_{01}^{(0)} - Af(R) + Bf^2(R) + Cf^3(R) + \cdots, \tag{25}$$

where the constants B and C are given by

$$B = \frac{1}{4}\big(k_{rr}^{(0)}\big)^2\left[\sum_{m\neq 1}\frac{|\langle\Psi_m^{(0)}|\Delta r^2|\Psi_1^{(0)}\rangle|^2}{\hbar\omega_{1m}} - \sum_{m\neq 0}\frac{|\langle\Psi_m^{(0)}|\Delta r^2|\Psi_0^{(0)}\rangle|^2}{\hbar\omega_{0m}}\right], \tag{26}$$

$$C = -\frac{1}{8}\big(k_{rr}^{(0)}\big)^3\left[\sum_{k\neq 0}\sum_{m\neq 0}\frac{\langle\Psi_0^{(0)}|\Delta r^2|\Psi_m^{(0)}\rangle\langle\Psi_m^{(0)}|\Delta r^2|\Psi_k^{(0)}\rangle\langle\Psi_k^{(0)}|\Delta r^2|\Psi_0^{(0)}\rangle}{\hbar^2\omega_{m0}\omega_{k0}}\right.$$

$$\left. - \big\langle\Psi_1^{(0)}\big|\Delta r^2\big|\Psi_1^{(0)}\big\rangle\sum_{m\neq 1}\frac{|\langle\Psi_1^{(0)}|\Delta r^2|\Psi_m^{(0)}\rangle|^2}{\hbar^2\omega_{m1}^2}\right.$$

$$-\sum_{k\neq 0}\sum_{m\neq 0}\frac{\langle\Psi_0^{(0)}|\Delta r^2|\Psi_m^{(0)}\rangle\langle\Psi_m^{(0)}|\Delta r^2|\Psi_k^{(0)}\rangle\langle\Psi_k^{(0)}|\Delta r^2|\Psi_0^{(0)}\rangle}{\hbar^2\omega_{m0}\omega_{k0}}$$

$$+\langle\Psi_0^{(0)}|\Delta r^2|\Psi_0^{(0)}\rangle\sum_{m\neq 0}\frac{|\langle\Psi_0^{(0)}|\Delta r^2|\Psi_m^{(0)}\rangle|^2}{\hbar^2\omega_{m0}^2}\Bigg]. \tag{27}$$

It is important to recall at this point that the outlined model is based on Rayleigh–Schrödinger perturbation theory (RSPT), using the non-hydrogen-bonded (cubic–quartic) *anharmonic* XH(D) oscillator as an unperturbed eigenvalue problem. In fact, great attention has been paid to the general problem of anharmonic oscillators in the literature [1,3,4,6–14,17,19–21,23,26,31,35,36,40,43–45,47,48,50,53,54]. This is mainly due to both fundamental significance of the problem, and its applicability to real physico-chemical systems. It has been firmly elaborated that the RSPT is not the most efficient computational technique for treatment of the anharmonic oscillators [4,44]. Obviously, the obtained expressions beyond the second order become somewhat cumbersome. A lot of theoretical work has been devoted to overcome the shortcomings of the RSPT [1,3,6–14,17,19–21,23,26,31,35,36,40,43,45,47,48,50,53,54], and methods like Hill determinant approach [9,17], inner product perturbation technique [50], hypervirial relations [3,23,40], operator method [11–13], Hsue–Chern approach [36], Van Vleck perturbation theory [43], as well as the quantum Monte-Carlo methodologies have been developed [7]. However, for the present approach the RSPT model is sufficient as it allows a straightforward derivation of *analytical* expressions relating experimentally observable parameters. Furthermore, it allows an assignment of an exact physical significance to the parameters obtained statistically.

As it has been pointed out several times, the present model is applicable for weak hydrogen bonds as well as for those of intermediate strength. In such cases, the inclusion of the first order corrections to the energy should be sufficient to obtain the mentioned relationships. This is so since both the constants B and C that appear in (25) and the corresponding $f^2(R)$ and $f^3(R)$ terms are at least an order of magnitude smaller than the constant A and $f(R)$. On the other hand, according to the experimental results [33], the $\widetilde{\nu}_{XH(D)}$ and $R_{X\cdots Y}$ values correlate very well for weak and moderately strong hydrogen bonds, while the correlation becomes significantly poorer for strong ones. At least partially, this poorer correlation may be attributed to complications connected with the assignment of the $\nu(XH(D))$ modes in the case of strong hydrogen bonds, due to broadness and structure of the corresponding spectral bands [25,33]. It is, however, suggested by the elaborated model that there is a more fundamental reason for it. It should also be mentioned at this point that not all of the empirical correlations of this type include only linear hydrogen bonds, which further complicates the situation. In the case of nonlinear hydrogen bonds, the distance between the proton donor and the proton acceptor is not the only factor governing the hydrogen bond strength for a given combination of proton donor and proton acceptor. The observed scatter of experimental points in regression analyses of the mentioned types is, thus, somehow expected.

The most reliable experimental parameter characterizing the hydrogen bond strength is the spectroscopically determined wavenumber of the $1 \leftarrow 0$ transition of an isotopically isolated X–H(D) oscillator – $\widetilde{\nu}_{01}$, involved in the hydrogen bonding interaction. Although the value of the last parameter depends on other factors as well [15,16,34], such as the local crystalline field strength (long-range interactions), the magnitude of short-range forces, etc., it still allows a much better characterization of the hydrogen-bonded system than the structural parameters, such as proton donor–proton acceptor distance $R_{\mathrm{X\cdots Y}}$. Strictly speaking, the above presented model is applicable for a series of *linear* hydrogen bonds, and a particular proton donor–proton acceptor pair. A question arises as to how is the nonlinearity of the H-bonds reflected on the X–H potential dependence on the hydrogen bond strength within this model, or, in other words, can equation (25) coupled with the experimental $\widetilde{\nu}_{01}$ data serve as a test for nonlinearity of hydrogen bonds? If a given X–H . . . Y system is nonlinear, the *measured* $\widetilde{\nu}_{01}$ value is expected to be significantly higher than the value predicted on the basis of correlation equations of the form (25), derived using the $(\widetilde{\nu}_{01}, R_{\mathrm{X\cdots Y}})$ data for a series of structurally similar compounds, characterized by *linear* (or almost linear) H-bonds in the structure. It is, thus, expected that the largest discrepancy between theoretical predictions and experimental findings should appear for such a case. Thus, for a series of structurally similar compounds (preferably isomorphous), and a particular proton donor–proton acceptor pair, equations of the form (25) coupled with the experimental $(\widetilde{\nu}_{01}, R_{\mathrm{X\cdots Y}})$ data may indicate nonlinearity for a particular member of the series.

However, if data for a large number (variety of hydrogen bond strengths) of systems with linear (or *almost linear*) hydrogen bonds are available, than the presented model is a basis for a choice of the best model function for the empirical correlations. Namely, inclusion of some function in (25) would allow the best fit of experimental data within a wide range of R values. That function would be also the best physically based one, and it would allow most accurate determination of the coefficients in (25) derived by the perturbation-theoretical expansion.

3. Conclusions

Within the assumption of Sceats and Rice, a perturbation theoretical method was derived that enables determination of the analytical form of the function $k_{rr} = f(R_{\mathrm{X\cdots Y}})$ on the basis of experimentally obtained $\widetilde{\nu}_{01,\mathrm{XH(D)}}$ versus $R_{\mathrm{X\cdots Y}}$ correlations. The experimental data show that this function is often of the form $k_{rr} = k_{rr}^{(0)}[1 - \exp(-aR_{\mathrm{X\cdots Y}})]$. The other parameters obtained by empirical correlations have also an exact physical meaning within the framework of the proposed model.

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