

A Quantum Theoretical Basis for Some Spectra – Structure Correlations in Crystalline Hydrates

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Starting with the perturbation theory and the Hellmann-Feynmann theorem, an attempt was made to derive a fundamental theoretical basis for some frequency – structure correlations in crystalline hydrates. It was found that within a few reasonable approximations, a satisfactory theoretical background may be found for the $\tilde{\nu}_{\text{OH(OD)}}$ versus $R_{\text{O}\dots\text{O}}$, as well as for the $-2X_{\text{OH(OD)}}$ versus $\tilde{\nu}_{\text{OH(OD)}}$ correlations ($\tilde{\nu}_{\text{OH(OD)}}$ is the spectroscopically measured wavenumber of the OH(OD) stretching vibration, $R_{\text{O}\dots\text{O}}$ is the hydrogen bond distance, and X is the anharmonicity of vibration). The OH(OD) oscillators were treated as mixed cubic – quartic anharmonic systems. The influence of hydrogen bonding on these oscillators was introduced through the changes in the harmonic diagonal force constants (as proposed by Sceats and Rice¹), the other diagonal terms in the potential energy expression being regarded as practically unchanged in the course of the hydrogen bonding. The parameters obtained by empirical correlations, within the proposed model, describe the dependence of the intramolecular potential of the uncoupled OH(OD) species on the hydrogen bond strength.

Key words: Perturbation theory, Hellmann-Feynmann theorem, hydrogen bonding, frequency-structure correlations, anharmonic oscillator, intramolecular water potential

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INTRODUCTION

One of the well-known features of hydrogen bonding is the decrease of the OH (OD) stretching frequency as compared to the value of the free (non-hydrogen bonded) oscillators.²⁻⁴ It has been shown⁵⁻¹⁰ that in hydrogen-bonded crystalline hydrates the wavenumber corresponding to the uncoupled fundamental OH (OD) vibration correlates very well with the proton-donor to proton-acceptor distance, which is one of the crystallographic measures of the hydrogen bond strength. Much work has been done in establishing such empirical correlations in various solid-state systems.¹¹⁻¹³ Hydrogen bonding itself has also been an interesting problem from a purely theoretical viewpoint, and a lot of work has been done to explain various aspects of this specific interaction [Ref. 2 and references therein]. However, regarding the $\tilde{\nu}_{\text{OH(OD)}}$ versus $R_{\text{X...Y}}$ correlations (X being the proton-donor and Y the proton-acceptor atom), to the best of our knowledge, there does not seem to exist a solid theoretical background. One of the first model functions used in these correlations was a linear one,^{14,15} theoretically based on the assumption of predominantly Van der Waals repulsion between the non-bonding orbitals of the X and Y atoms, described by means of the Lennard-Jones (Eqs. (6)–(12)) potential. However, this model function does not have the correct asymptotic behavior, and in the later approaches it was replaced by a new one, which describes correctly the limit of a free OH (OD) oscillator:

$$\tilde{\nu}_{01,\text{OH(OD)}} = \tilde{\nu}_{01,\text{OH(OD)}}^{(0)} + A \cdot \exp(-\alpha R_{\text{X...Y}}) \quad (1)$$

where $\tilde{\nu}_{01,\text{OH(OD)}}^{(0)}$ is the value for a free oscillator (often taken as the gas-phase value, although the correctness of this approach is discussed in Ref. 7), while A and α are constants. Obviously, this function is very suitable for empirical correlations, since it is simple, and mimics the experimentally observed trends in these systems. It is also consistent with intuitive expectations. However, since no solid theoretical basis seems to exist for such an approach, it is fully phenomenological. Further, constants A and α have no exact physical meaning. It is worth mentioning here that the model potential of the Lippincott-Schroeder^{16,17} type allows derivation of the analytical form of functional dependence of the quadratic force constants on the X...Y distance, and within this model, an estimation of the function describing the $\tilde{\nu}_{01,\text{OH(OD)}}$ versus $R_{\text{X...Y}}$ dependence based on the harmonic oscillator expressions is possible. The predicted function¹⁸ is much more complex than the previously used one Eq. (1).

A theoretical explanation for the observed $\tilde{\nu}_{01,\text{OH}} / \tilde{\nu}_{01,\text{OD}}$ versus $\tilde{\nu}_{01,\text{OH}}$ correlations in solid hydrates was given by Wójcik *et al.*¹⁹, by solving the variational one-dimensional problem with a simple cubic-quartic potential.

In their work, the influence of variations in the O–H (D) distance was also considered.

On the other hand, it has also been shown that the anharmonicity constants ($-2X$) of the uncoupled OH (OD) oscillators in crystalline hydrates (either obtained experimentally or by some of the theoretical methods^{1,20–21}) correlate well with the $\tilde{\nu}_{01,\text{OH(OD)}}$ values.^{21–24} Several purely phenomenological model functions are currently in use for such correlations,^{21–24} none of which is based on a solid theoretical background.

The main scope of this paper is to propose a possible theoretical basis for the above problem regarding both the $\tilde{\nu}_{\text{OH(OD)}}$ versus $R_{\text{X...Y}}$ and ($-2X$) versus $\tilde{\nu}_{01,\text{OH(OD)}}$ correlations, based on the stationary perturbation theory (and the Hellmann-Feynmann theorem), as well as to establish a new semiempirical method for determining the dependence of water intramolecular potential on the hydrogen bond strength in a series of crystalline hydrates. Within this model, the empirically obtained constants reveal an exact physical meaning.

THEORETICAL MODEL

Many experimental data have shown that the non-hydrogen bonded X-H oscillators are highly anharmonic systems. The Hamiltonian of such a system can be written in the form:

$$\hat{H}^{(0)} = \frac{\hat{p}^2}{2\mu} + \frac{1}{2}k_{qq}^{(0)}q^2 + k_{qqq}^{(0)}q^3 + k_{qqq}^{(0)}q^4 \quad (2)$$

where the superscripts (0) refer to a free (not perturbed by hydrogen bonding) oscillator, and μ is its reduced mass. Quantity q is defined as $r - r_0$, r being the distance between the atoms in the X–H oscillator, while r_0 is the corresponding equilibrium distance. When the oscillator is perturbed by atom Y, the Hamiltonian in Eq. (2) takes the following form:

$$\hat{H}^{(0)} = \frac{\hat{p}^2}{2\mu} + \frac{1}{2}k_{qq}q^2 + k_{qqq}^{(0)}q^3 + k_{qqq}^{(0)}q^4. \quad (3)$$

Namely, it is widely accepted that the cubic and quartic force constants do not change in the course of hydrogen bonding¹ and the whole increase in the anharmonicity of the X–H mode is due to an increased amplitude of the hydrogen atom motion. Let us now consider the relationship between the quadratic force constants k_{qq} and $k_{qq}^{(0)}$. Obviously, when the hydrogen bond distance (R) is large, the k_{qq} should practically be equal to $k_{qq}^{(0)}$, while with

the decrease in R , the force constant k_{qq} should diminish. A function of the type:

$$k_{qq} = k_{qq}^{(0)} \{1 - \exp[-\alpha(R - R_0)]\} \quad (4)$$

where α and R_0 are constants, correctly describes the mentioned features. Complications occur for the values of R that are fairly close to R_0 . However, since this model is perturbationally based, only weak and hydrogen bonds of intermediate strength are considered, and thus this function gives a satisfactory description of the variation of k_{qq} with R within the considered range of its values.

If only linear, or practically linear hydrogen bonds are considered within the model, the parameter R will suffice to describe the dependence of k_{qq} on the hydrogen bond strength for a given X and Y pair. For a different choice of a proton donor and proton acceptor, the hydrogen bond strength will be influenced also by other factors, such as the effective atomic charge of the acceptor atom Y. Constant R_0 may be regarded as the closest possible distance between the proton acceptor Y and the proton donor X. Combining Eqs. (4) and (3), the Hamiltonian of the oscillator perturbed by hydrogen bonding takes the form:

$$\hat{H} = \hat{H}^{(0)} - \frac{1}{2} k_{qq}^{(0)} \cdot \exp[-\alpha(R - R_0)] \cdot q^2 . \quad (5)$$

If the second term in Eq. (5) is small enough, it may be regarded as a (small) perturbation to the non-hydrogen-bonded oscillator. This condition is fulfilled when $\exp[-\alpha(R - R_0)] \ll 1$. This is true of weak hydrogen bonds as well as those of intermediate strength. Substituting Q for $R - R_0$, the Hamiltonian in Eq. (5) becomes:

$$\hat{H} = \hat{H}^{(0)} - \frac{1}{2} k_{qq}^{(0)} \cdot \exp[-\alpha Q] \cdot q^2 . \quad (6)$$

Considering only those cases where the condition $\exp[-\alpha(R - R_0)] \ll 1$ is fulfilled, the stationary perturbation theory is applicable to this problem, with the perturbation operator:

$$\hat{V} = -\frac{1}{2} k_{qq}^{(0)} \cdot \exp[-\alpha Q] \cdot q^2 . \quad (7)$$

The energy of the n -th level of the hydrogen-bonded oscillator can be represented by the perturbation series:

$$E_n = E_n^{(0)} + E_n^{(1)} + E_n^{(2)} + \dots \quad (8)$$

By calculating the matrix elements of the type:

$$V_{mn} = \langle \Psi_m^{(0)} | \hat{V} | \Psi_n^{(0)} \rangle \quad (9)$$

in the basis of the eigenfunctions of the non-perturbed by hydrogen bonding anharmonic oscillator they read:

$$V_{mn} = -\frac{1}{2} k_{qq}^{(0)} \cdot \exp[-aQ] \cdot \langle \Psi_m^{(0)} | \hat{q}^2 | \Psi_n^{(0)} \rangle \quad (10)$$

and the corrections of various orders are easily obtained. The corresponding expressions are:

$$E_n^{(1)} = \exp[-aQ] \cdot \left[-\frac{1}{2} k_{qq}^{(0)} \cdot \langle \Psi_m^{(0)} | \hat{q}^2 | \Psi_n^{(0)} \rangle \right] \quad (11)$$

$$E_n^{(1)} = \exp[-aQ] \cdot \left[-\frac{1}{4} k_{qq}^{(0)} \cdot \sum_{m \neq n} \frac{\left| \langle \Psi_m^{(0)} | \hat{q}^2 | \Psi_n^{(0)} \rangle \right|^2}{\hbar \omega_{nm}} \right] \quad (12)$$

$$E_n^{(3)} = \exp[-3aQ] \cdot \left[-\frac{1}{8} \left(k_{qq}^{(0)} \right)^3 \cdot \sum_{k \neq n} \sum_{m \neq n} \frac{\langle \Psi_n^{(0)} | \hat{q}^2 | \Psi_m^{(0)} \rangle \cdot \langle \Psi_m^{(0)} | \hat{q}^2 | \Psi_k^{(0)} \rangle \cdot \langle \Psi_k^{(0)} | \hat{q}^2 | \Psi_n^{(0)} \rangle}{\hbar^2 \omega_{mn} \omega_{kn}} + \frac{1}{8} \left(k_{qq}^{(0)} \right)^3 \cdot \langle \Psi_n^{(0)} | \hat{q}^2 | \Psi_m^{(0)} \rangle \sum_{m \neq n} \frac{\left| \langle \Psi_n^{(0)} | \hat{q}^2 | \Psi_m^{(0)} \rangle \right|^2}{\hbar^2 \omega_{mn}^2} \right] \quad (13)$$

The energy expression, thus, takes the form:

$$E_n = E_n^{(0)} + \exp[-aQ] \cdot f_n^{(1)} + \exp[-2aQ] \cdot f_n^{(2)} + \exp[-3aQ] \cdot f_n^{(3)} + \dots \quad (14)$$

where:

$$f_n^{(1)} = -\frac{1}{2} k_{qq}^{(0)} \cdot \langle \Psi_n^{(0)} | \hat{q}^2 | \Psi_n^{(0)} \rangle \quad (15)$$

$$f_n^{(2)} = -\frac{1}{4} \left(k_{qq}^{(0)} \right)^2 \cdot \sum_{m \neq n} \frac{\left| \langle \Psi_m^{(0)} | \hat{q}^2 | \Psi_n^{(0)} \rangle \right|^2}{\hbar \omega_{nm}} \quad (16)$$

$$\begin{aligned}
 f_n^{(3)} = & -\frac{1}{8} \left(k_{qq}^{(0)}\right)^3 \cdot \sum_{k \neq n} \sum_{m \neq n} \frac{\langle \Psi_n^{(0)} | \hat{q}^2 | \Psi_m^{(0)} \rangle \cdot \langle \Psi_m^{(0)} | \hat{q}^2 | \Psi_k^{(0)} \rangle \cdot \langle \Psi_k^{(0)} | \hat{q}^2 | \Psi_n^{(0)} \rangle}{\hbar^2 \omega_{mn} \omega_{kn}} + \\
 & + \frac{1}{8} \left(k_{qq}^{(0)}\right)^3 \cdot \langle \Psi_n^{(0)} | \hat{q}^2 | \Psi_n^{(0)} \rangle \cdot \sum_{m \neq n} \frac{\left| \langle \Psi_n^{(0)} | \hat{q}^2 | \Psi_m^{(0)} \rangle \right|^2}{\hbar^2 \omega_{mn}^2}. \quad (17)
 \end{aligned}$$

Since only small perturbation was considered (*i.e.*, weak hydrogen bonding), the terms that contain $2aQ$, $3aQ$ *etc.* in Eq. (14) may be neglected, and the energy expression reduces to:

$$E_n = E_n^{(0)} + \exp[-aQ] \cdot f_n^{(1)}. \quad (18)$$

The energy difference between the ground and the first excited state, on the basis of Eq. (18) is, thus:

$$\begin{aligned}
 E_1 - E_0 = & E_1^{(0)} - E_0^{(0)} - \\
 & - \frac{k_{qq}^{(0)}}{2} \cdot \left[\langle \Psi_1^{(0)}(q) | \hat{q}^2 | \Psi_1^{(0)}(q) \rangle - \langle \Psi_0^{(0)}(q) | \hat{q}^2 | \Psi_0^{(0)}(q) \rangle \right] \cdot \exp(-aQ) \quad (19)
 \end{aligned}$$

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

$$\begin{aligned}
 \tilde{\nu}_{01} = & \tilde{\nu}_{01}^{(0)} - \frac{k_{qq}^{(0)}}{2hc} \cdot \left[\langle \Psi_1^{(0)}(q) | \hat{q}^2 | \Psi_1^{(0)}(q) \rangle - \langle \Psi_0^{(0)}(q) | \hat{q}^2 | \Psi_0^{(0)}(q) \rangle \right] \cdot \\
 & \cdot \exp(-aR_0) \cdot \exp(-aR). \quad (20)
 \end{aligned}$$

By comparing the perturbation theorem-based equation (20) with the empirically obtained correlation equations of the type:

$$\tilde{\nu}_{01} = \tilde{\nu}_{01,g} - A \cdot \exp(-aR) \quad (21)$$

where the quantity $\tilde{\nu}_{01,g}$ refers to the gas phase, the physical meaning of empirical constants becomes obvious. Thus, Eqs. (20) and (21) enable an experimental determination of constant a that describes the dependence of the quadratic force constant k_{qq} on the hydrogen bond strength ($R_{X...Y}$). Further, constant A is equal to the quantity:

$$-\frac{k_{qq}^{(0)}}{2hc} \cdot \left[\langle \Psi_1^{(0)}(q) | \hat{q}^2 | \Psi_1^{(0)}(q) \rangle - \langle \Psi_0^{(0)}(q) | \hat{q}^2 | \Psi_0^{(0)}(q) \rangle \right] \cdot \exp(-aR_0). \quad (22)$$

Since all quantities in Eq. (22) except for the expression in parentheses are known, an experimental determination of the difference $\langle \Psi_1^{(0)}(q) | \hat{q}^2 | \Psi_1^{(0)}(q) \rangle - \langle \Psi_0^{(0)}(q) | \hat{q}^2 | \Psi_0^{(0)}(q) \rangle$ is possible. On the other hand, if one calculates this difference using the eigenfunctions of the Morse-type oscillator (assuming that the so calculated value is close to the one in this case), parameter R_0 may be estimated from experimental data.

Inclusion of higher-order perturbation terms in Eqs. (18) and (19) leads to the following function:

$$\tilde{v}_{01} = \tilde{v}_{01,g} - A \cdot \exp(-aR) + B \cdot \exp(-2aR) + C \cdot \exp(-3aR) + \dots \quad (23)$$

where constants B and C are given by:

$$B = \frac{1}{4} (k_{qq}^{(0)})^2 \cdot \left[\sum_{m \neq 1} \frac{|\langle \Psi_m^{(0)} | \hat{q}^2 | \Psi_1^{(0)} \rangle|^2}{\hbar^2 \omega_{1m}} - \sum_{m \neq 0} \frac{|\langle \Psi_m^{(0)} | \hat{q}^2 | \Psi_0^{(0)} \rangle|^2}{\hbar^2 \omega_{0m}} \right] \quad (24)$$

$$C = -\frac{1}{8} (k_{qq}^{(0)})^3 \cdot \left[\sum_{k \neq 0} \sum_{m \neq 0} \frac{\langle \Psi_0^{(0)} | \hat{q}^2 | \Psi_m^{(0)} \rangle \cdot \langle \Psi_m^{(0)} | \hat{q}^2 | \Psi_k^{(0)} \rangle \cdot \langle \Psi_k^{(0)} | \hat{q}^2 | \Psi_0^{(0)} \rangle}{\hbar^2 \omega_{m0} \omega_{k0}} - \langle \Psi_1^{(0)} | \hat{q}^2 | \Psi_1^{(0)} \rangle \cdot \sum_{m \neq 1} \frac{|\langle \Psi_1^{(0)} | \hat{q}^2 | \Psi_m^{(0)} \rangle|^2}{\hbar^2 \omega_{m1}^2} - \sum_{k \neq 0} \sum_{m \neq 0} \frac{\langle \Psi_0^{(0)} | \hat{q}^2 | \Psi_m^{(0)} \rangle \cdot \langle \Psi_m^{(0)} | \hat{q}^2 | \Psi_k^{(0)} \rangle \cdot \langle \Psi_k^{(0)} | \hat{q}^2 | \Psi_0^{(0)} \rangle}{\hbar^2 \omega_{m0} \omega_{k0}} + \langle \Psi_0^{(0)} | \hat{q}^2 | \Psi_0^{(0)} \rangle \cdot \sum_{m \neq 0} \frac{|\langle \Psi_0^{(0)} | \hat{q}^2 | \Psi_m^{(0)} \rangle|^2}{\hbar^2 \omega_{m0}^2} \right] \quad (25)$$

It should be mentioned once again that previous derivations are valid for systems in which the stationary perturbation theory is applicable (*i.e.*, for hydrogen bonds of low and medium strength). The experimental results⁶⁻⁸ have shown that $\tilde{v}_{\text{OH(OD)}}$ and $R_{\text{X...Y}}$ values correlate very well for weak and moderately strong hydrogen bonds, while the correlation is poorer for strong bonds. Note that, at least partially, this poorer correlation may be

attributed to the more complicated assignment of the $\nu(\text{OH}, \text{OD})$ modes in the case of strong hydrogen bonds, due to the broadness and structure of the corresponding spectral bands.^{6-8,10} The elaborated model, however, suggests that there is a more fundamental reason for it. Also, all of the empirical correlations of this type include not only linear hydrogen bonds, which further complicates the situation. In the case of non-linear hydrogen bonds, the distance between the proton-donor and the proton-acceptor is not the only factor governing the hydrogen bond strength, so the observed scattering of experimental points in regression analyses is expected.

As mentioned above, quantities $\tilde{\nu}_{01,g}$ used in empirical correlations refer to the gas phase values of the wavenumbers for $\nu(\text{OH}, \text{OD})$ modes. It has been discussed whether this approach is valid, mainly because the gas phase values are not the same as those for non-hydrogen bonded OH (OD) oscillators in solid state. Since the choice of the value of $\tilde{\nu}_{01}$ for a non-hydrogen bonded oscillator present in a crystal lattice depends on the electrostatic crystal field of a particular structure, it is not unique. By using the gas phase value, the approach is significantly simplified. Within this model, this »limiting« value is related to the differences of the energies of the unperturbed system in Eq. (20). The empirically obtained constant a is the value that determines the dependence of the quadratic force constant on the proton donor to proton acceptor distance in Eq. (4).

It should be mentioned that Eq. (20) may also be derived using the Hellmann-Feynman theorem:

$$\frac{dE_n}{dQ} = \left\langle \frac{\partial \hat{H}}{\partial Q} \right\rangle = \left\langle \Psi_n(q, Q) \left| \frac{\partial \hat{H}}{\partial Q} \right| \Psi_n(q, Q) \right\rangle \quad (26)$$

with:

$$\frac{\partial \hat{H}}{\partial Q} = \frac{a}{2} k_{qq}^{(0)} \cdot \exp[-aQ] \cdot q^2. \quad (27)$$

$\Psi_n(q, Q)$ is the wavefunction of the hydrogen bonded oscillator, represented by the perturbation series:

$$\Psi_n(q, Q) = \Psi_n^{(0)}(q) + \Psi_n^{(1)}(q, Q) + \Psi_n^{(2)}(q, Q) + \dots \quad (28)$$

where $\Psi_n^{(0)}(q)$ is the eigenfunction of the (anharmonic) non-hydrogen bonded X–Y oscillator. Corrections to the zeroth-order wavefunction are readily obtained by using the matrix elements given by Eq. (10) (Appendix 1). Considering again only small perturbations and neglecting the terms proportional to higher degrees in $\left\langle \Psi_m^{(0)} \left| \hat{q}^2 \right| \Psi_n^{(0)} \right\rangle$, the following expression is obtained upon the integration of the Hellmann-Feynman expression:

$$E_n = C_n - \frac{k_{qq}^{(0)}}{2} \cdot \langle \Psi_n^{(0)}(q) | \hat{q}^2 | \Psi_n^{(0)}(q) \rangle \cdot \exp(-aQ) \quad (29)$$

where C_n is the integration constant. The energy difference corresponding to the fundamental transition thus reduces to the form of Eq. (19), expressed through wavenumbers. The integration constant in Eq. (29) thus has an obvious physical meaning.

On the other hand, calculating the difference $E_2 - E_0$ from Eq. (18) and expressing its value through the corresponding wavenumber $\tilde{\nu}_{02, \text{OH(OD)}}$, one obtains, on the basis of Eq. (20), the following expression for the anharmonicity constant ($-2X = 2\tilde{\nu}_{01} - \tilde{\nu}_{02}$):

$$-2X = -2X^{(0)} + \left[1 - \frac{\langle \Psi_2^{(0)} | \hat{q}^2 | \Psi_2^{(0)} \rangle - \langle \Psi_1^{(0)} | \hat{q}^2 | \Psi_1^{(0)} \rangle}{\langle \Psi_1^{(0)} | \hat{q}^2 | \Psi_1^{(0)} \rangle - \langle \Psi_0^{(0)} | \hat{q}^2 | \Psi_0^{(0)} \rangle} \right] \cdot (\tilde{\nu}_{01}^{(0)} - \tilde{\nu}_{02}^{(0)}) \quad (30)$$

where the superscript (0) denotes the value corresponding to the free (non-hydrogen bonded oscillator). Thus, a linear dependence of the anharmonicity constant on the wavenumber of the fundamental transitions is predicted in cases where perturbation theory is applicable. As it may be also concluded from the experimental data,²¹⁻²⁴ for weak hydrogen bonds, the dependence of the anharmonicity constant on the wavenumber of the corresponding fundamental transition may be considered as nearly linear, which is again in agreement with the general predictions of this model.

Further study regarding the theoretical basis of these correlations, based on several model potentials including those of the Lippincott-Schroeder type, is in progress.

Appendix 1

Perturbation corrections to the zeroth-order wavefunction in Eq. (28) are readily obtained using the matrix elements represented by Eq. (10). The expressions obtained are:

$$\Psi_n^{(1)}(q, Q) = \exp(-aQ) \cdot \left[-\frac{1}{2} k_{qq}^{(0)} \sum_{m \neq n} \frac{\langle \Psi_m^{(0)} | \hat{q}^2 | \Psi_n^{(0)} \rangle}{\hbar \omega_{nm}} \Psi_m^{(0)}(q) \right] \quad (31)$$

i.e.:

$$\Psi_n^{(1)}(q, Q) = \exp(-aQ) \cdot \varphi_n^{(1)}(q) \quad (32)$$

where:

$$\varphi_n^{(1)}(q) = -\frac{1}{2} k_{qq}^{(0)} \sum_{m \neq n} \frac{\langle \Psi_m^{(0)} | \hat{q}^2 | \Psi_n^{(0)} \rangle}{\hbar \omega_{nm}} \Psi_m^{(0)}(q). \quad (33)$$

Similarly,:

$$\Psi_n^{(2)}(q, Q) = \exp(-2\alpha Q) \cdot \varphi_n^{(2)}(q) \quad (34)$$

where:

$$\begin{aligned} \varphi_n^{(2)}(q) = & \frac{(k_{qq}^{(0)})^2}{4} \left[\sum_{m \neq n} \sum_{k \neq n} \frac{\langle \Psi_m^{(0)} | \hat{q}^2 | \Psi_k^{(0)} \rangle \langle \Psi_k^{(0)} | \hat{q}^2 | \Psi_n^{(0)} \rangle}{\hbar^2 \omega_{nk} \omega_{nm}} \Psi_m^{(0)}(q) - \right. \\ & \left. - \sum_{m \neq n} \frac{\langle \Psi_n^{(0)} | \hat{q}^2 | \Psi_n^{(0)} \rangle \langle \Psi_m^{(0)} | \hat{q}^2 | \Psi_k^{(0)} \rangle}{\hbar^2 \omega_{nm}^2} \Psi_m^{(0)}(q) + \frac{1}{2} \Psi_n^{(0)}(q) \sum_{m \neq n} \frac{\langle \Psi_m^{(0)} | \hat{q}^2 | \Psi_n^{(0)} \rangle^2}{\hbar^2 \omega_{nm}^2} \right] \quad (35) \end{aligned}$$

and:

$$\Psi_n^{(3)}(q, Q) = \exp(-3\alpha Q) \cdot \varphi_n^{(3)}(q) \quad (36)$$

and so on.

By combining the Hellmann-Feynmann theorem (26) with (27), and after performing several algebraic transformations, one arrives at the following expression:

$$\begin{aligned} \frac{dE_n}{dQ} = & \exp(-\alpha Q) \cdot \frac{ak_{qq}^{(0)}}{2} \cdot \langle \Psi_n^{(0)}(q) | \hat{q}^2 | \Psi_n^{(0)}(q) \rangle + \exp(-2\alpha Q) \cdot \frac{ak_{qq}^{(0)}}{2} \cdot \\ & \cdot \left[\langle \Psi_n^{(0)}(q) | \hat{q}^2 | \varphi_n^{(0)}(q) \rangle + \langle \varphi_n^{(1)}(q) | \hat{q}^2 | \Psi_n^{(0)}(q) \rangle \right] + \exp(-3\alpha Q) \cdot \frac{ak_{qq}^{(0)}}{2} \cdot \\ & \cdot \left[\langle \Psi_n^{(0)}(q) | \hat{q}^2 | \varphi_n^{(0)}(q) \rangle + \langle \varphi_n^{(1)}(q) | \hat{q}^2 | \varphi_n^{(1)}(q) \rangle + \langle \varphi_n^{(2)}(q) | \hat{q}^2 | \Psi_n^{(0)}(q) \rangle \right] + \dots \quad (37) \end{aligned}$$

Considering only small perturbations, the energy derivative with respect to Q reduces to the following expression:

$$\frac{dE_n}{dQ} = \exp(-\alpha Q) \cdot \frac{ak_{qq}^{(0)}}{2} \cdot \langle \Psi_n^{(0)}(q) | \hat{q}^2 | \Psi_n^{(0)}(q) \rangle. \quad (38)$$

Upon integration, Eq. (38) gives Eq. (29).

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SAŽETAK

**Kvantno-teorijski temelj nekih korelacija spektar-struktura
u kristalnim hidratima**

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Uporabom perturbacijske teorije i Hellmann-Feynmannova teorema izveden je teorijski temelj nekih korelacija između frekvencije i strukture u kristalnim hidratima. Unutar prihvatljivih aproksimacija nađena je zadovoljavajuća teorijska podloga za korelacije $\nu_{\text{OH(OD)}}$ i $R_{\text{O...O}}$ i $-2X_{\text{OH(OD)}}$ i $\nu_{\text{OH(OD)}}$; $\nu_{\text{OH(OD)}}$ je spektroskopski određen valni broj OH(OD) vibracije istezanja, $R_{\text{O...O}}$ je duljina vodikove veze, a X anharmoničnost vibracije OH (OD).