The Vibrational Stark Effect on the Doubly Degenerate ν₁₉ Modes of the Benzene Guest Molecules in Hofmann Type Clathrates

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An alternative mechanism is proposed for the observed splitting of the ν_{19} γ(CH) mode of the benzene guest molecules in Hofmann type clathrates to the one presented previously.[1] According to the proposed model, the splitting is due to the vibrational Stark effect. A simple quantum theoretical model for this effect is derived, based on the degenerate-case stationary perturbation theory, both with and without explicit inclusion of the vibrational angular momentum. The model allows estimation of the relative field strengths at the enclathration sites of the guest molecules in a series of structurally similar clathrates. The derived equations may be used for calculation of the local field strength as well, if particular anharmonic coupling constants for enclathrated species are available. The predictions of the proposed method are fully in line with the observed room temperature–low temperature trends for a particular clathrate, as well as with the trends in the series of isostructural clathrate compounds for which experimental data are available.

Key words: vibrational Stark effect, Hofmann clathrates, host-guest interactions, electrostatic field induced degenerate mode splitting, perturbation theory.

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INTRODUCTION

Hofmann clathrates constitute one of the most thoroughly studied families of inclusion compounds. Their general formula is $M(NH_3)_2M'(CN)_4 \cdot 2G$, where $M \in \{Mn, Fe, Co, Ni, Cu, Zn, Cd\}$, $M' \in \{Ni, Pd, Pt\}$, while G denotes the guest molecule, which may be benzene, pyrrole, thiophene, dioxane, aniline or biphenyl. These inclusion compounds have attracted significant attention because of their structural peculiarities, such as orientation of particular guest molecules, nature of the host-guest interactions, differences in the enclathration energies, *etc*.[2–20]

Of particular interest to the present study are the various aspects of the problem of host-guest interactions in compounds of this type. These interactions are, generally speaking, weak. It has been found that it is the hydrogen bonding between the host fragments and guest molecules that plays the key role in determining the relative stability of the members in a particular series of the Hofmann clathrates.[2–4] The probability of modulating the stability of these compounds by varying the substituents of the guest molecules has been outlined as well.[7] For the above reasons, these compounds are very convenient model systems for both experimental and theoretical studies of weak interactions as a general problem.

Quantitative studies of the host-guest interactions in Hofmann type clathrates have been carried out at various levels of theory. Extended Hückel tight binding formalism has been successfully applied to explain the orientation of aniline and pyrolle as guest molecules in $Ni(NH_3)_2Ni(CN)_4 \cdot 2G$ type clathrates.[5,6] In these two studies, the crystal orbital displacement (COD) and integrated crystal orbital displacement functions (ICOD) have been used to predict the nature of the interacting orbitals and the relative roles of different building blocks of the host lattices in the host-guest interactions. Also, *ab initio* HF and MP2 studies of these interacions in the $Ni(NH_3)_2Ni(CN)_4$ host with benzene, aniline, pyrolle and toluene as guest molecules have been carried out.[7] Attempts to evaluate the interaction energy in the Hofmann clathrates with benzene as a guest molecule have been also made using the semiempirical INDO method.[8] The problem of orientation of benzene guest molecules in the Hofmann and related types of clathrates has been treated by molecular mechanics calculations as well.[3] Of particular importance for a study of the host-guest interactions in these compounds is the solid state ^2H and ^1H NMR study of guest and host motions in the Hofmann type and related benzene clathrates,[9] and the study of the effects of NH_3 free rotation on the INS spectrum of $Ni(NH_3)_2Ni(CN)_4 \cdot 2C_6D_6$ at low temperatures.[10–15]

Previous studies of several Hofmann and Hofmann-T_d clathrates with benzene guest molecules have shown that the only IR manifestation of the

host-guest interaction in compounds of this type is the shift of the $\gamma\,(CH)$ modes of the benzene molecules, as compared to the gaseous benzene.[16–19] We have recently proposed a quantum theoretical model that qualitatively explains the observed shifts, allowing estimation of the relative importance of the anharmonicity and the local field effects upon these vibrational modes of the guest molecules.[20] Another interesting feature, which is the central point in the present study, is the low-temperature splitting of the ν_{19} mode of the guest molecules.[1,17] This splitting has been explained in terms of the tunnel effect, a quasi-classical model proposed for a semi-quantitative study of the splitting.[1] However, the proposed model has several weak points. Namely, the local electrostatic field due to the host lattice has not been explicitly included in this model, and the double degeneracy of the mentioned normal mode has not been accounted for. In this work, we propose an alternative me　chanism for the observed splitting. According to the proposed model, the splitting is due to the vibrational Stark effect.[21–24] The presented model allows derivation of conclusions regarding the local field strengths in the series of structurally similar compounds and is, we believe, more acceptable from the physical point of view and more intuitively based.

THEORETICAL MODEL

Perturbation Theoretic Approach without Inclusion of the Vibrational Angular Momentum

We consider the guest benzene molecule in the electrostatic field generated by the host lattice within the effective local homogeneous field approximation.[20] The potential of a polyatomic molecule in a uniform electrostatic field may be written in the form:

$$\hat{V}=V_0 + \frac{1}{2}\sum_i m_i \omega_{0i}^2 \, \hat{q}_i^2 + \sum_{i\leq j\leq k} k_{ijk}\, \hat{q}_i\, \hat{q}_j\, \hat{q}_k \; + \sum_{i\leq j\leq k\leq l} k_{ijkl}\, \hat{q}_i\, \hat{q}_j\, \hat{q}_k\, \hat{q}_l - \hat{\boldsymbol{\mu}}\boldsymbol{E} \qquad (1)$$

where $\hat{\boldsymbol{\mu}}$ is the dipole moment vector function, $\boldsymbol{E}$ is the electrostatic field vector, $\hat{q}_i$ denotes the i-th normal coordinate with a reduced mass m_i and harmonic frequency ω_{0i}, while k_{ijk} and k_{ijkl} are the cubic and quartic force constants, respectively. Expanding $\hat{\boldsymbol{\mu}}$ in power series with respect to the normal coordinates:

$$\hat{\boldsymbol{\mu}} = \boldsymbol{\mu}_0 + \sum_i \left(\frac{\partial \boldsymbol{\mu}}{\partial q_i}\right)_0 \cdot \hat{q}_i + \frac{1}{2}\sum_i \sum_j \left(\frac{\partial^2 \boldsymbol{\mu}}{\partial q_i \partial q_j}\right)_0 \cdot \hat{q}_i\, \hat{q}_j + \cdots \qquad (2)$$

and including the first–order terms in q_i only, the dot product $\hat{\mu} \bullet E$ takes the form:

$$\begin{bmatrix} \mu_x \mu_y \mu_z \end{bmatrix} \cdot \begin{bmatrix} E_x \\ E_y \\ E_z \end{bmatrix} = \begin{bmatrix} \mu_{x,0} \mu_{y,0} \mu_{z,0} \end{bmatrix} \cdot \begin{bmatrix} E_x \\ E_y \\ E_z \end{bmatrix} +$$

$$+ \sum_i \begin{bmatrix} \partial\mu_x/\partial q_i \ \partial\mu_y/\partial q_i \ \partial\mu_z/\partial q_i \end{bmatrix} \cdot q_i \cdot \begin{bmatrix} E_x \\ E_y \\ E_z \end{bmatrix}.$$

Since the dipole moment of the unperturbed (free) benzene molecule is zero, assuming that the electrostatic field is oriented along the *z*-axis of the laboratory coordinate system, within the electrical harmonic approximation, the potential takes the form:

$$\hat{V} = V_0' + \sum_i \left[\frac{1}{2} m_i \omega_{0i}^2 \hat{q}_i^2 - \left(\frac{\partial\mu_z}{\partial q_i} \right) \hat{q}_i E_z \right] + \sum_{i \leq j \leq k} k_{ijk} \hat{q}_i \hat{q}_j \hat{q}_k + \sum_{i \leq j \leq k \leq l} k_{ijkl} \hat{q}_i \hat{q}_j \hat{q}_k \hat{q}_l. \quad (3)$$

Treating the last two sums in the previous expression as a perturbation, the unperturbed total molecular Hamiltonian becomes diagonal, and the field-dependent vibrational wavefunction may be factorized:

$$\left| \Psi_{\{n\}}(\{q\}, E_z) \right\rangle = \prod_i \left| \Psi_{ni}(q_i, E_z) \right\rangle \quad (4)$$

where $\{q\} = \{q_1, q_2, ..., q_N\}$, and $\{n\} = \{n_1, n_2, ..., n_N\}$.

Since we are particularly interested in the doubly degenerate (E_{2u}) ν_{19} mode of the guest benzene molecule, a more convenient way to write the wavefunction is:

$$\left| \Psi_{\{n\}}(\{q\}, E_z) \right\rangle = \left[\prod_i \left| \Psi_{ni}(q_i, E_z) \right\rangle \right] \cdot \left| \Psi_a(q_a, E_z) \right\rangle \cdot \left| \Psi_b(q_b, E_z) \right\rangle \quad (5)$$

where $\left| \Psi_a(q_a, E_z) \right\rangle$ and $\left| \Psi_b(q_b, E_z) \right\rangle$ are the wavefunctions corresponding to the ν_{19} mode components. Applying the stationary perturbation theory with the perturbation operator:

$$\hat{H}^{(1)} = \sum_{i \leq j \leq k} k_{ijk}\, \hat{q}_i\, \hat{q}_j\, \hat{q}_k + \sum_{i \leq j \leq k \leq l} k_{ijkl}\, \hat{q}_i\, \hat{q}_j\, \hat{q}_k\, \hat{q}_l \tag{6}$$

the first-order energy corrections $E_{1(a,b)}^{(1)}$ to the degenerate states

$$\left|\Psi_0(q_1,E_z)\right\rangle\left|\Psi_0(q_2,E_z)\right\rangle...\left|\Psi_1(q_a,E_z)\right\rangle\left|\Psi_0(q_b,E_z)\right\rangle$$

$$\left|\Psi_0(q_1,E_z)\right\rangle\left|\Psi_0(q_2,E_z)\right\rangle...\left|\Psi_0(q_a,E_z)\right\rangle\left|\Psi_1(q_b,E_z)\right\rangle \tag{7}$$

are obtained by solving the secular equation:[25]

$$\begin{vmatrix} H_{(10;10)}^{(1)} - E_1^{(1)} & H_{(01;10)}^{(1)} \\ H_{(10;01)}^{(1)} & H_{(01;01)}^{(1)} - E_1^{(1)} \end{vmatrix} = 0 \tag{8}$$

where:

$$H_{(10;10)}^{(1)} = \left\langle \Psi_0^{(0)}(q_1,E_z)\right|...\left\langle \Psi_1^{(0)}(q_a,E_z)\right|\left\langle \Psi_0^{(0)}(q_b,E_z)\right|\hat{H}^{(1)}\left|\Psi_0^{(0)}(q_1,E_z)\right\rangle...$$
$$\left|\Psi_1^{(0)}(q_a,E_z)\right\rangle\left|\Psi_0^{(0)}(q_b,E_z)\right\rangle$$

$$H_{(01;01)}^{(1)} = \left\langle \Psi_0^{(0)}(q_1,E_z)\right|...\left\langle \Psi_0^{(0)}(q_a,E_z)\right|\left\langle \Psi_1^{(0)}(q_b,E_z)\right|\hat{H}^{(1)}\left|\Psi_0^{(0)}(q_1,E_z)\right\rangle...$$
$$\left|\Psi_0^{(0)}(q_a,E_z)\right\rangle\left|\Psi_1^{(0)}(q_b,E_z)\right\rangle$$

$$H_{(01;10)}^{(1)} = \left\langle \Psi_0^{(0)}(q_1,E_z)\right|...\left\langle \Psi_0^{(0)}(q_a,E_z)\right|\left\langle \Psi_1^{(0)}(q_b,E_z)\right|\hat{H}^{(1)}\left|\Psi_0^{(0)}(q_1,E_z)\right\rangle...$$
$$\left|\Psi_1^{(0)}(q_a,E_z)\right\rangle\left|\Psi_0^{(0)}(q_b,E_z)\right\rangle$$

$$H_{(10;01)}^{(1)} = \left\langle \Psi_0^{(0)}(q_1,E_z)\right|...\left\langle \Psi_1^{(0)}(q_a,E_z)\right|\left\langle \Psi_0^{(0)}(q_b,E_z)\right|\hat{H}^{(1)}\left|\Psi_0^{(0)}(q_1,E_z)\right\rangle...$$
$$\left|\Psi_0^{(0)}(q_a,E_z)\right\rangle\left|\Psi_1^{(0)}(q_b,E_z)\right\rangle. \tag{9}$$

Note that $H_{(10;10)}^{(1)} = H_{(01;01)}^{(1)}\, (=A)$ and $H_{(01;10)}^{(1)} = H_{(10;01)}^{(1)}\, (=B)$.
The secular equation thus becomes:

$$\begin{vmatrix} A - E_1^{(1)} & B \\ B & A - E_1^{(1)} \end{vmatrix} = 0\,. \tag{10}$$

The vibrational Stark splitting of the ν_{19} mode components expressed through wavenumbers, on the basis of (10) – see Appendix 1, is thus:

$$\Delta \widetilde{v}_{a,b} = \frac{k_{aabb}^2}{\pi c m^3 \omega_0^5} \left(\frac{\partial \mu_z}{\partial q} \right)_0 E^2.$$ (11)

It follows from the last expression that the ratio of the $\Delta \widetilde{v}_{a,b}$ values for two structurally similar clathrates is equal to the square of the ratio of the effective local electrostatic fields at particular enclathration sites. Further, it follows that the vibrational Stark splitting of the v_{19} mode components increases with the square of the field strength, as it is intuitively expected. This is what has been really experimentally observed.[16–19] Namely, as the previous experimental observations have shown, the splitting of this mode increases with the decrease of the temperature, *i.e.* with the decrease of the unit-cell volume for a particular clathrate. On the other hand, for a series of isostructural Hoffman type clathrates, the splitting increases with the decrease of the unit cell volume, as well. A good correlation between the observed v_{19} mode splitting and the unit cell volume of the members of the mentioned series of compounds has been found.[17] Since the local field is expected to increase in both of the mentioned cases, the presented model is in line with the experimental observations.

Note that the dipole polarizability has not been explicitly included in the model. Inclusion of this quantity would add an additional term in potential (3) within the electrical harmonic approximation of the form:

$$-\alpha_{zz,0} E_z^2 - \sum_i \left(\frac{\partial \mu_{zz}}{\partial q_i} \right)_0 \hat{q}_i E_z^2$$

where α_{zz} denotes the corresponding component of the polarizability tensor. The explicit inclusion of this parameter contributes to the linear in q_i term in the single mode field dependent Hamiltonian and the effective charge of the oscillator placed in the electric field will be:

$$\left(\frac{\partial \mu_z}{\partial q_i} \right)_0 + \left(\frac{\partial \mu_{zz}}{\partial q_i} \right)_0 E_z$$

instead of:

$$\left(\frac{\partial \mu_z}{\partial q_i} \right)_0.$$

Thus, the same equations as the previously obtained ones will hold, with the new expression for the effective charge instead of the field-independent one.

It is important to note at this point that the treatment of the benzene guest molecule within some effective local homogeneous electrostatic field neglects the other contributions to the total interaction energy with the host lattice (for example, the short-range exchange repulsive forces). Such an approximation is valid in the present case, since the short-range forces decrease exponentially, and the host-lattice cavities for the studied systems are sufficiently large.

Perturbation Theoretic Approach Including the Vibrational Angular Momentum

The wavefunctions Eq. (7) allow an adequate description of the system in question, so the results obtained with the matrix elements calculated it the basis spanned by them may be regarded as appropriate. However, in the case of degenerate vibrations, in general, the atoms do not move along straight lines. Their motions are along elliptical trajectories. Therefore, a vibrational angular momentum arises due to such curvilinear motions. This angular momentum is not explicitly quantized by the choice of the basis Eq. (7). In order to obtain an adequate description of the system that explicitly includes the vibrational angular momentum, we apply, following basically the approach used for the field-independent cases,[26] the following coordinate transformations:

$$\tilde{z}_a = \rho \cos\varphi \tag{12}$$

$$\tilde{z}_b = \rho \sin\varphi \tag{13}$$

where:

$$\tilde{z}_a = \tilde{q}_a - \left(\frac{\partial \mu_z}{\partial q_a}\right)_0 \frac{E}{m_a q_0 \omega_0^2} \quad, \tag{14}$$

$$\tilde{z}_b = \tilde{q}_b - \left(\frac{\partial \mu_z}{\partial q_b}\right)_0 \frac{E}{m_b q_0 \omega_0^2} \quad \text{and} \tag{15}$$

$$\tilde{q}_i = q_i/q_0; \qquad q_0 = \sqrt{\frac{\hbar}{m_0 \omega_o}} \tag{16}$$

while ρ and φ are the polar coordinates in the configurational space spanned by $\tilde{z}_a$ and $\tilde{z}_b$. Within the new representation, the part of the total Hamiltonian that refers to the doubly degenerate motion takes the form:

$$\hat{H}_a + \hat{H}_b = -\frac{1}{2}\hbar\omega_{0i}\left[\frac{1}{\rho}\frac{\partial}{\partial\rho}\left(\rho\frac{\partial}{\partial\rho}\right) + \frac{1}{\rho^2}\frac{\partial^2}{\partial\varphi^2} - \rho^2\right].$$ (17)

The complete eigenfunctions of (25) have the form:

$$\left|\Psi_{n,l}(\rho,\varphi)\right\rangle = N_{n,l}\exp(-\rho^2/2)\,\rho^{|l|}L_n^{|l|}\,(\rho^2)\exp\left(il\varphi\right)$$ (18)

where the normalization factor $N_{n,l}$ is given by:

$$N_{n,l} = \frac{1}{\sqrt{\pi}}\frac{\left[(n-|l|)2!\right]^{1/2}}{\left[(n+|l|)2!\right]^{1/2}}$$ (19)

and $L_n^{|l|}$ are the associated Laguerre polynomials.

The matrix elements (9) calculated in this basis, explicitly including the vibrational angular momentum, have the form:

$$B = \frac{k_{aabb}}{m\pi c\hbar^2\omega_0^3}\left(\frac{\partial\mu_z}{\partial q}\right)_0^2 E^2$$ (20)

leading to the following value for the $\Delta\tilde{v}_{a,b}$:

$$\Delta\tilde{v}_{a,b} = \frac{2k_{aabb}}{m\pi c\hbar^2\omega_0^3}\left(\frac{\partial\mu_z}{\partial q}\right)_0^2 E^2.$$ (21)

Obviously, the field dependence of the splitting is essentially the same within this representation. The explicit inclusion of the vibrational angular momentum in the model, however, causes a stronger dependence of the v_{19} mode splitting on the effective charge of the mode $(\partial\mu/\partial q_i)_0$.

The measured low-temperature splittings of the v_{19} mode in a series of structurally similar Hofmann type clathrates are presented in Table I, together with the relative field strengths at the enclathration sites estimated by the presented model (both representations lead to the same values). The benzene guest molecules may thus serve as a probe for »measuring« the local field strengths in this series of inclusion compounds.

TABLE I

The measured splittings of the ν_{19} mode components, the corresponding unit-cell volumes, and the estimated relative field strengths (with respect to the member with the smallest measured splitting)

Compound[a]	$\Delta\tilde{\nu}_{a,b}/cm^{-1}$ [b]	V/nm^3	Rel. field[b]
Ni–Ni–Bz	5.3	0.434	1.3292
Mg–Ni–Bz	4.5	0.444	1.2247
Fe–Ni–Bz	4.0	0.448	1.1547
Co–Ni–Bz	4.3	0.449	1.1972
Zn–Ni–Bz	4.1	0.453	1.1690
Mn–Ni–Bz	3.0	0.460	1.0000
Cd–Ni–Bz	0.0	0.488	–
Ni–Pd–Bz	4.0	0.464	1.5811
Co–Pd–Bz	3.5	0.471	1.4790
Zn–Pd–Bz	3.0	0.478	1.3693
Mn–Pd–Bz	1.6	0.490	1.0000
Cd–Pd–Bz	0.0	0.506	–
Ni–Pt–Bz	4.3	0.456	1.1972
Zn–Pt–Bz	3.0	0.476	1.0000
Cd–Pt–Bz	0.0	0.502	–

[a] M–M'–Bz $\equiv$ M(NH$_3$)$_2$M'(CN)$_4 \cdot$2C$_6$H$_6$.
[b] Values measured at the boiling temperature of the liquid nitrogen (LNT).

CONCLUSIONS

A quantum mechanical model is proposed, according to which the splitting of the doubly degenerate ν_{19} mode of the benzene guest molecule in Hofmann type clathrates is due to the vibrational Stark effect. The model is capable of explaining the experimentally observed trends in a series of structurally similar compounds of this type. The increased splitting of the ν_{19} mode components with the decrease of the unit-cell volume is due to the increase of the local electrostatic field strength. Analytical expressions are derived on the basis of the degenerate stationary perturbation theory, relating the observed splitting to the anharmonic force constant and the local field strength. Regardless of whether the vibrational angular momentum is explicitly included in the model or not, the same qualitative field dependence of the splitting is obtained. On the basis of the available experimental data, within the proposed methodology, the relative field strengths at the enclathration sites of the benzene guest molecules in a series of isostructural Hofmann type clathrates were estimated.

Appendix 1

The first-order energy corrections, on the basis of the secular equation (10), are:

$$E^{(1)}_{1(a,b)} = A \pm B \tag{A1}$$

leading to an energy splitting between the two components of the magnitude:

$$\Delta E^{(1)}_{1(a,b)} = 2B. \tag{A2}$$

In order to calculate the matrix elements B, the wavefunctions $\left| \Psi^{(0)}_{ni}(q_i, E) \right\rangle$ are required. These are eigenfunctions of the single-mode zeroth-order field-dependent Hamiltonian:

$$\hat{H}_i = \frac{\hat{p}_i^2}{2m_i} + \frac{1}{2} m_i \omega_{0i}^2 \, \hat{q}_i^2 - \left(\frac{\partial \mu_z}{\partial q_i} \right)_0 \hat{q}_i E \tag{A3}$$

and may be written in the form:

$$\left| \Psi^{(0)}_{ni}(q_1, E) \right\rangle = \left(\frac{m_i \omega_{0i}}{\pi \hbar} \right)^{1/4} \frac{1}{\sqrt{2^n \, n!}} \exp\left[-\frac{m_i \omega_{0i}}{2\hbar} \left(q_i - \left(\frac{\partial \mu_z}{\partial q_i} \right)_0 \frac{E}{m_i \omega_{0i}^2} \right)^2 \right] \cdot$$

$$\cdot H_n \left[\sqrt{\frac{m_i \omega_{0i}}{\hbar}} \left(q_i - \left(\frac{\partial \mu_z}{\partial q_i} \right)_0 \frac{E}{m_i \omega_{0i}^2} \right) \right] \tag{A4}$$

where H_n is the n-th degree Hermite polynomial.

For symmetry reasons, only the terms of the form:

$$k_{aabb} \, \hat{q}_a^2 \, \hat{q}_b^2, \; k_{aaaa} \, \hat{q}_a^4 \; and \; k_{bbbb} \, \hat{q}_b^4$$

would yield non-zero values of the matrix elements $H^{(1)}_{(01;10)}$ and $H^{(1)}_{(10;01)}$. Note that it is the term $k_{aabb} \, \hat{q}_a^2 \, \hat{q}_b^2$ in the potential that leads to removal of the degeneracy, but only in the presence of the field, *i.e.* only if the matrix elements are calculated in the basis of the field-dependent harmonic oscillator wavefunctions. Having in mind that the coordinates q_a and q_b are in fact equivalent and the wavefunctions $\left| \Psi^{(0)}_{ni}(q_1, E) \right\rangle$ are real, the constant B takes the form:

$$B = k_{aabb}^2 \left(\int \Psi_0^{(0)}(q,E) \hat{q}^2 \, \Psi_1^{(0)}(q,E) \mathrm{d}q \right)^2. \qquad (A5)$$

Introducing a new variable:

$$z_i = \sqrt{\frac{m_i \omega_{0i}}{\hbar}} \left[q_i - \left(\frac{\partial \mu_z}{\partial q_i} \right)_0 \frac{E}{m_i \omega_{0i}^2} \right] \qquad (A6)$$

one obtains:

$$B = \frac{k_{aabb}^2}{2\pi} \left\{ \int H_0(z) H_1(z) \left[\sqrt{\frac{\hbar}{m\omega_0}} z + \left(\frac{\partial \mu_z}{\partial q} \right)_0 \frac{E}{m\omega_0^2} \right]^2 \exp(-z^2) \mathrm{d}z \right\}^2 \qquad (A7)$$

and finally:

$$B = 2 k_{aabb}^2 \, \frac{\hbar}{m^3 \omega_0^5} \left(\frac{\partial \mu_z}{\partial q} \right)_0 E^2. \qquad (A8)$$

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SAŽETAK

Utjecaj vibracijskog Starkova efekta na dvostruko degenerirani mod ν_{19} molekula benzena uklopljenih u klatrate Hofmannova tipa

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Predložen je alternativni mehanizam opaženog cijepanja moda ν_{19} γ (CH) molekula benzena uklopljenih u klatrate Hofmannova tipa, prema kojem do cijepanja dolazi djelovanjem vibracijskog Starkova efekta. Efekt je objašnjen jednostavnim kvantno-teorijskim modelom, temeljenim na stacionarnoj teoriji smetnje za degenerirana stanja, s uključenim ili neuključenim vibracijskom kutnom količinom gibanja. Model omogućuje procjenu relativne jačine polja na mjestima uklapanja molekule-gosta u nizu strukturno sličnih klatrata. Kada su poznate anharmoničke konstante sprezanja za uklopljenu vrstu izvedene jednadžbe također se mogu upotrijebiti za računanje jačine lokalnog polja. Predviđanja predložene metode u skladu su s trendovima opaženim pri sobnoj i nižim temperaturama, kako za pojedinačne tipove klatrata tako i za nizove izostrukturnih klatratnih spojeva.