On the relationship between molecular spectroscopy and statistical mechanics: calculation of partition functions for triatomic molecules undergoing large-amplitude bending vibrations

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Abstract: The evaluation of partition functions for triatomic molecules undergoing large-amplitude bending vibrations is discussed. It was supposed that the needed molecular structure data were obtained by means of *ab initio* calculations. Special attention is paid to the coupling between the bending and stretching modes and the interplay between bending motions and rotations. An appropriate scheme for variational computation of the energy levels is developed.

Keywords: partition functions; triatomic molecules; large-amplitude bending.

INTRODUCTION

The present study was motivated by the need for partition functions of the molecule BC_2, which plays an important role, *e.g.*, in plasma processes that should lead to the synthesis of boron carbide, B_4C. Since it was not possible to find either numerical data for the partition functions or spectroscopically derived molecular structure parameters needed to calculate partition functions by the machinery of statistical mechanics, *ab initio* quantum mechanical calculations on this species were performed.[1] The results of these investigations showed that BC_2 has a very interesting structure. It is characterized by the ground electronic state having $C_{2}v$ (X^2A_1) or slightly distorted $C_{2}v$ (X^2A') symmetry, separated by a barrier of about 2000 cm^{-1} from a local minimum on the potential energy surface, corresponding to the linear molecular geometry ($^2\Sigma^+$). The transition from the one to the other structure occurs in the course of large-amplitude bending vibrations, being strongly coupled to the stretching vibrational modes. Therefore,

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if one wishes to compute reliable partition functions for this molecule, one has to solve a number of specific problems that are normally ignored in textbooks on statistical mechanics. In the present paper, the theoretical background of the problem is dealt with. In the following paper,[2] the results of the calculation of the vibrational–rotational energy levels in the ground electronic state and the corresponding partition functions are given.

The paper is organized as follows. In the second section, an evaluation of the energy levels and partition functions of triatomic molecules with linear and bent equilibrium geometries in the harmonic approximation is reviewed. In the third section, a method for *ab initio* handling of the same problem is presented. An approach for the solution of the Schrödinger equation for large-amplitude bending vibrations is briefly described. The last section presents a short conclusion.

HARMONIC APPROXIMATION

At the beginning, it was found sensible to estimate the relationship between characteristic molecular-energy values and the quantity kT, where k is the Boltzmann constant and T the temperature. In the present study, instead of energy, the wave number, $\tilde{v} = E/hc$, expressed in cm^{-1} (1 J is equivalent to 5.0364×10^{22} cm^{-1}) is often used; in this case, the Boltzmann constant becomes $k = 0.695$ cm^{-1} K^{-1}. In the temperature interval of interest, *i.e.*, 1000–6000 K, the value of kT will be in the range 700–4000 cm^{-1}. The contribution of excited electronic states to the total partition function is neglected. The stretching vibrational wave numbers for molecules such as BC_2, being the subject of our next paper, are around 10^3 cm^{-1}, whereas the bending wave numbers have values of a few hundred cm^{-1}.[1] The rotational constants are of a few cm^{-1}.

First, the partition functions in the harmonic approximation are handled. Triatomic molecules are considered separately in spatially and spin non-degenerate electronic states with linear and non-linear equilibrium geometry. In both cases, the molecular Hamiltonian can be written in the form:

$$\hat{H} = \hat{H}^{\,\mathrm{tr}} + \hat{H}^{\,\mathrm{e}} + \hat{H}^{\,\mathrm{v}} + \hat{H}^{\,\mathrm{r}} \tag{1}$$

where $\hat{H}^{\,\mathrm{tr}}, \hat{H}^{\,\mathrm{e}}, \hat{H}^{\,\mathrm{v}}$ and $\hat{H}^{\,\mathrm{r}}$ represent the translational, electronic, vibrational and rotational parts, respectively. In the following, the translational part of the Hamiltonian, Eq. (1), is ignored and assume the eigenvalues of the electronic part to be included in $\hat{H}^{\,\mathrm{v}}$ as the "potential energy surface", calculated within the framework of the Born–Oppenheimer approximation. Writing Eq. (1), it is implicitly assumed that coupling between vibrational and rotational motions is neglected.

Linear equilibrium geometry

Triatomic molecules with linear equilibrium geometry are traditionally handled as species having two rotational and four vibrational degrees of freedom.

According to such a scheme, the vibrational and rotational parts of the Hamiltonian (1) are written in the forms:

$$\hat{H}^{v} = \hat{H}_{s} + \hat{H}_{b,z} \tag{2}$$

$$\hat{H}^{r} = \hat{H}^{r}_{x,y} \tag{3}$$

The z-axis is chosen to coincide with the molecular axis at linear nuclear arrangements. The vibrational Hamiltonian is separated into a stretching ($\hat{H}_{s}$) and a bending ($\hat{H}_{b,z}$) part. This can be performed because the stretching and bending coordinates are (in the case of linear molecules) not coupled with one another in the harmonic approximation. $\hat{H}^{r}_{x,y}$ is the Hamiltonian for end-over-end rotations.

The stretching part of the vibrational Hamiltonian is in the harmonic approximation represented by:

$$\hat{H}_{s} = -\frac{\hbar^2}{2\mu_r}\frac{\partial^2}{\partial r^2} - \frac{\hbar^2}{2\mu_R}\frac{\partial^2}{\partial R^2} - \frac{\hbar^2}{\mu_{rR}}\frac{\partial^2}{\partial r\partial R} + \frac{1}{2}k_{rr}r^2 + \frac{1}{2}k_{RR}R^2 + k_{rR}rR \tag{4}$$

where r and R are two stretching vibrational coordinates. In the case of linear molecules, ABC, the usual choice is $r = $ A–B and $R = $ B–C, $i.e.$, the stretching coordinates represent the bond lengths (or their changes with respect to the equilibrium values) – Fig. 1. μ_R and μ_r are the corresponding "reduced masses". k_{rr}, k_{RR} and k_{rR} are the quadratic force constants representing the electronic energy as a function of the stretching coordinates. The eigenvalues of the Hamiltonian (4) are:

$$E_{s} = \left(v_{s1} + \frac{1}{2}\right)\hbar\omega_{s1} + \left(v_{s2} + \frac{1}{2}\right)\hbar\omega_{s2} = \left(v_{s1} + \frac{1}{2}\right)hc\tilde{v}_{s1} + \left(v_{s2} + \frac{1}{2}\right)hc\tilde{v}_{s2} \tag{5}$$

where ω is the vibrational frequency (in units s^{-1}) and $\tilde{v}$ the wave number. The energy spectrum is non-degenerated.

In the harmonic approximation, the bending part of the vibrational Hamiltonian has the form:

$$\hat{H}_{b,z} = -\frac{\hbar^2}{2\mu_b}\left(\frac{\partial^2}{\partial\theta^2} + \frac{1}{\theta}\frac{\partial}{\partial\theta} + \frac{1}{\theta^2}\frac{\partial^2}{\partial\varphi^2}\right) + \frac{1}{2}k_{\theta}\theta^2 \tag{6}$$

if the volume element $dV = \theta d\theta d\varphi$ is assumed. For molecules with linear equilibrium geometry, the bending coordinate is usually chosen to be the supplement of the bond angle, $i.e.$, $\theta = \pi - \angle$ A–B–C, expressed in length units. Equation (6) represents the Hamiltonian of an isotropic two-dimensional harmonic oscillator, the eigenvalues of which are:

$$E_{b,z} = \left(v_b + 1\right)\hbar\omega_b = \left(v_b + 1\right)hc\tilde{v}_b \tag{7}$$

Each energy level is $v_b + 1$ degenerated, because for every $v_b = 0,1,2,\dots$ there are sublevels of the same energy corresponding to the value of the vibrational angular quantum number $l = -v_b,-v_b+2,\dots,v_b$. Beyond the harmonic approximation, this degeneracy is lifted and the energy depends on both v_b and the absolute value of l – for this reason, l is usually considered as an unsigned quantity. Each $E_{v_b,|l|}$ level is in the case of anharmonicity twofold degenerate for $|l| \neq 0$.

The rotational Hamiltonian is usually written as:

$$\hat{H}^r_{x,y} = \frac{\hat{J}^2_x}{2I_B} + \frac{\hat{J}^2_y}{2I_B} = \frac{\hat{J}^2}{2I_B} \tag{8}$$

since the z-component of the nuclear angular momentum equals zero and thus:

$$\hat{J}^2 \equiv \hat{J}^2_x + \hat{J}^2_y + \hat{J}^2_z = \hat{J}^2_x + \hat{J}^2_y \tag{9}$$

where I_B is the moment of inertia along the axes perpendicular to the molecular axis. The energy levels corresponding to the Hamiltonian (8) are:

$$E^r_{x,y} = \frac{J(J+1)\hbar^2}{2I_B} \equiv BhcJ(J+1), \tag{10}$$

where

$$B \equiv \frac{h}{8\pi^2 c I_B} = \frac{\hbar}{4\pi c I_B} \tag{11}$$

is the rotational constant, usually expressed in cm^{-1}. Each J-level is $(2J+1)$-degenerated because the wave functions for a given J are also characterized by the quantum number M ($M = -J,-J+1,\dots,J$), denoting the projection of the angular momentum along a space-fixed (Z) coordinate axis.

If the above scheme is assumed, the total molecular partition function for the degrees of freedom considered is such as given in the majority of textbooks:[3]

$$Z = Z_{s1}Z_{s2}Z_{b,z}Z^r_{x,y} \tag{12}$$

with:

$$Z_{s1} = \left(1 - e^{-\frac{\hbar\omega_{s1}}{kT}}\right)^{-1}, \quad Z_{s2} = \left(1 - e^{-\frac{\hbar\omega_{s2}}{kT}}\right)^{-1} \tag{13}$$

$$Z_{b,z} = \left(1 - e^{-\frac{\hbar\omega_b}{kT}}\right)^{-2} \tag{14}$$

$$Z^r_{x,y} = \frac{kT}{\sigma hcB} = \frac{kT}{\sigma 2\pi\hbar cB} \tag{15}$$

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In all formulae (13–15), the Boltzmann constant is assumed to have its "normal" value, $k = 1.380 \times 10^{-23}$ J K^{-1}. The "symmetry number" in the present case (asymmetric ABC molecules) is $\sigma = 1$. In the following formulae, it will be omitted. It is assumed that the zeroth vibrational–rotational level is taken to be zero on the energy scale. The rotational partition function is derived in the "high-temperature approximation" by replacing the sum with the corresponding integral:

$$Z^{\mathrm{r}}_{x,y} = \sum_{J=0}^{\infty} (2J+1)e^{-\frac{BhcJ(J+1)}{kT}} \cong \int_{J=0}^{\infty} (2J+1)e^{-\frac{BhcJ(J+1)}{kT}} \, \mathrm{d}J = \frac{kT}{hcB} \quad (16)$$

However, when Eq. (9) is written, the fact is ignored that triatomic molecules have a non-vanishing component of the total angular momentum along the molecular axis. This arises from the vibrational angular momentum, and relation (9) has to be replaced by the correct one:

$$\hat{J}^2 \equiv \hat{J}_x^2 + \hat{J}_y^2 + \hat{l}^2 \quad (17)$$

The origin of the vibrational angular momentum becomes clear when the rotational Hamiltonian is formally written in the general form of a prolate symmetric top:

$$\hat{H}^{\mathrm{r}}_{x,y} = \frac{\hat{J}_x^2}{2I_{\mathrm{B}}} + \frac{\hat{J}_y^2}{2I_{\mathrm{B}}} + \frac{\hat{J}_z^2}{2I_{\mathrm{A}}} \quad (18)$$

where I_{A} is the moment of inertia along the z-axis. Since $I_{\mathrm{A}} = 0$ for linear geometry, one prefers to incorporate the last term on the right-hand side in the bending Hamiltonian – it appears in it (Eq. (6)) in the form of:

$$\frac{\hat{J}_z^2}{2I_{\mathrm{A}}} = \frac{\left(-i\hbar \frac{\partial}{\partial \varphi}\right)^2}{2I_{\mathrm{A}}} = -\frac{\hbar^2}{2\mu_{\mathrm{b}}\theta^2}\frac{\partial^2}{\partial \varphi^2} \quad (19)$$

The singularity caused by the term $\hat{J}_z^2 / (2I_{\mathrm{A}})$ is then exactly cancelled by the singularities caused by the remaining two terms in the Hamiltonian (6). The eigenvalues of the operator $\hat{J}_z^2 = -\hbar^2 \partial^2 / \partial \varphi^2$ are $\hat{l}^2 \hbar^2$. Consequently, Eqs. (8) and (10) are replaced, respectively, by:

$$\hat{H}^{\mathrm{r}}_{x,y} = \frac{\hat{J}_x^2}{2I_{\mathrm{B}}} + \frac{\hat{J}_y^2}{2I_{\mathrm{B}}} = \frac{\hat{J}^2 - \hat{J}_z^2}{2I_{\mathrm{B}}} \quad (20)$$

and

$$E^{\mathrm{r}}_{x,y} = \frac{\left[J(J+1) - l^2\right]\hbar^2}{2I_{\mathrm{B}}} \equiv Bhc\left[J(J+1) - l^2\right] \quad (21)$$

The quantum numbers J and l are connected with each other by the relation $J \geq l$. We write now the energy values corresponding to the operator $\hat{H}_{b,z} + \hat{H}^r_{x,y}$ as:

$$E_{b,z} = (v_b + 1)\hbar\omega_b + Bhc\left[J(J+1) - l^2\right] = (2n + l + 1)\hbar\omega_b + \\ + Bhc\left[J(J+1) - l^2\right]$$ (22)

where the integer n takes the values 0,1,2,... Taking into account that the degeneracy of each J-level is $(2J + 1)$ and that $l = 0$ levels are non-degenerated, whereas for $l \neq 0$, there are two sublevels corresponding to $l = \pm|l|$, one obtains for the corresponding partition function:[4]

$$Z^{b,r} = \sum_{l=0}^{\infty} \sum_{n=0}^{\infty} \sum_{J=l}^{\infty} g_l(2J+1)e^{-\frac{(2n+l)\hbar\omega_b + Bhc\left[J(J+1)-l^2\right]}{kT}} \cong$$
$$\cong \sum_{l=0}^{\infty} g_l e^{-\frac{l\hbar\omega_b - l^2 Bhc}{kT}} \sum_{n=0}^{\infty} e^{-\frac{2n\hbar\omega_b}{kT}} \int_{J=l}^{\infty} (2J+1)e^{-\frac{BhcJ(J+1)}{kT}} \mathrm{d}J =$$ (23)
$$= \frac{kT}{Bhc} \frac{\left(1 + e^{-\frac{\hbar\omega_b + Bhc}{kT}}\right)}{\left(1 - e^{-\frac{2\hbar\omega_b}{kT}}\right)\left(1 - e^{-\frac{\hbar\omega_b + Bhc}{kT}}\right)}$$

Since $\hbar\omega_b \gg Bhc$, it follows from Eq. (23):

$$Z^{b,r} \cong \frac{kT}{Bhc} \frac{1}{\left(1 - e^{-\frac{\hbar\omega_b}{kT}}\right)^2}$$ (24)

In this approximation, the same result is obtained as the product of $Z_{b,z}$, Eq. (14) and $Z^r_{x,y}$, Eq. (15). Therefore, in spite of the fact that the neglect of the relationship between the quantum numbers J and l, representing the heart of the approximation/misconception, Eq. (9), leads to an unreliable energy level scheme, it does not causes serious errors in the partition function.

Nonlinear equilibrium geometry

Triatomic molecules with nonlinear equilibrium geometry have three rotational and three vibrational degrees of freedom. Several sets of internal coordinates can be applied to describe the molecular vibrations. One possibility is to use the same "valence type" coordinates as for triatomic molecules. However, in the case of nonlinear molecules, they loose somewhat their convenience because their employment leads to terms in the Hamiltonian that couple the stretching and

bending vibrational motions. When dealing with large-amplitude bending vib-rations and particularly when one atom migrates around a more or less compact skeleton of the other two (as *e.g.*, the H-atom around the N–C moiety in course of the HNC→HCN isomerisation process,[5,6] or the B-atom around the C–C diato-mic rest in the BC_2 molecule), it is more convenient to use the "Jacobi coordi-nates", R, r and θ, where R is the distance between the nuclei building the diatomic part, r the distance between the migrating atom and the midpoint of the diatomic part, and θ is defined as the angle between the vectors $\vec{r}$ and $\vec{R}$ (Fig. 1). An advantage of these coordinates is that there is no coupling between the three vibrational modes through the kinetic energy part of the vibrational Hamil-tonian, and the coupling terms in the potential energy part are generally dimi-nished.
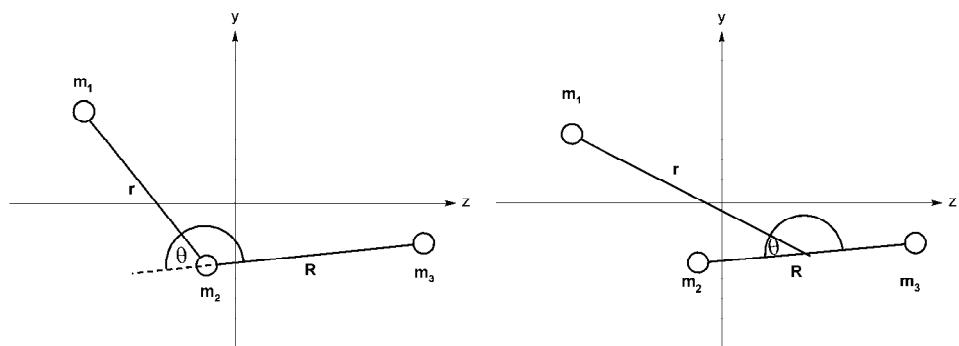

Fig. 1. Vibrational coordinates employed in the present study. Left-hand side: valence coordinates; right-hand side: Jacobi coordinates.

Although the stretching and bending vibrations are mutually coupled in triatomic molecules with nonlinear equilibrium geometry, this coupling is neg-lected in this subsection, because here the primarily interest lies in bookkeeping concerning the evaluation of the partition functions. The emphasis lies on the consequences of the gradual transformation of the twofold degenerate bending vibration in linear molecules to the one-dimensional bending plus the rotation around the z-axis in bent nuclear arrangements. Thus, the vibrational Hamiltonian in the form:

$$\hat{H}^{v} = \hat{H}_{s} + \hat{H}_{b} \tag{25}$$

is assumed, where the stretching part has the form given by Eq. (4), and the bending part is:

$$\hat{H}_{b} = -\frac{\hbar^2}{2\mu_b} \frac{\partial^2}{\partial\theta^2} + \frac{1}{2} k_{\theta} \left(\theta - \theta_e\right)^2 \tag{26}$$

The equilibrium value of the coordinate θ is denoted by θ_e. When handling one-dimensional bending vibrations, it is sensible to assume the volume (integration) element $dV = d\theta$. The bending energy corresponding to the operator (26) is:

$$E_b = \left(v_b + \frac{1}{2}\right)\hbar\omega_b \tag{27}$$

and the spectrum is non-degenerated.

Triatomics with bent equilibrium geometry are asymmetric top molecules and thus the corresponding rotational Schrödinger equation cannot be solved analytically. In this subsection, they are handled as if they were symmetric tops, because the primary interest lies in the qualitative features of the partition functions. The rotational Hamiltonian of a symmetric top is given by:

$$\hat{H}^r = \frac{\hat{J}_x^2}{2I_B} + \frac{\hat{J}_y^2}{2I_B} + \frac{\hat{J}_z^2}{2I_A} = \frac{\hat{J}^2 - \hat{J}_z^2}{2I_B} + \frac{\hat{J}_z^2}{2I_A} = \frac{\hat{J}^2}{2I_B} + \frac{\hat{J}_z^2}{2}\left(\frac{1}{I_A} - \frac{1}{I_B}\right) \tag{28}$$

and the corresponding energy is:

$$E^r = Bhc\left[J(J+1) - K^2\right] + AhcK^2 = BhcJ(J+1) + (A-B)hcK^2 \tag{29}$$

$$A \equiv \hbar^2/4\pi c I_A$$

For a given J, the quantum numbers K and M (not appearing in the energy expression, Eq. (29)) take the values $K,M = -J,-J+1,\ldots,J$; since the energy does not depend on the sign of K, the energy levels for a particular combination of J and K are $g_K(2J+1)$-degenerated, with $g_K = 1$ for $K = 0$, and $g_K = 2$ at $K \neq 0$. The quantum number K, determining the projection of the angular momentum on the z-axis of the coordinate system fixed at the molecule, is fully equivalent to the quantum number l defined for linear molecules and, in order to emphasize this equivalence, the symbol l will be used instead of K in this subsection.

The complete vibrational–rotational molecular partition function of a triatomic molecule with non-linear equilibrium geometry is given by:

$$Z = Z_{s1}Z_{s2}Z_bZ^r \tag{30}$$

where the stretching partition functions are of the same forms as those for linear molecules (Eq. (13)). The remaining part of the partition functions can be handled in several different ways:

Case a. The partition function for the (one-dimensional) bending vibrations is:

$$Z_b = \sum_{v_b=0}^{\infty} e^{-\frac{v_b\hbar\omega_b}{kT}} = \left(1 - e^{-\frac{\hbar\omega_b}{kT}}\right)^{-1} \tag{31}$$

The partition function corresponding to the rotational energy expression, Eq. (29), is:

$$Z^r = \sum_{J=0}^{\infty} \sum_{l=-J}^{J} g_l \left(2J+1\right) e^{-\frac{BhcJ\left(J+1\right)+(A-B)hcl^2}{kT}} \cong \left(\frac{kT}{hc}\right)^{3/2} \frac{\sqrt{\pi}}{\sqrt{AB}} \quad (32)$$

The final expression is derived in the high-temperature approximation, taking into account the fact that the term Bl can be neglected in the expression $\exp\left[-(Al^2 + Bl)hc / kT\right]$ and that:

$$\sum_{l=0}^{\infty} g_l e^{-\frac{Ahcl^2}{kT}} = \sum_{l=-\infty}^{\infty} e^{-\frac{Ahcl^2}{kT}} \quad (33)$$

If B is replaced in Eq. (32) by $\sqrt{BC}$, the expression for the rotational partition function of molecules with three unequal moments of inertia (asymmetric tops), as quoted in textbooks, (*e.g.*, Ref. 3), is obtained.

The correlation of the energy levels for bending vibrations plus rotations in a linear and a bent molecule are shown in Fig. 2.
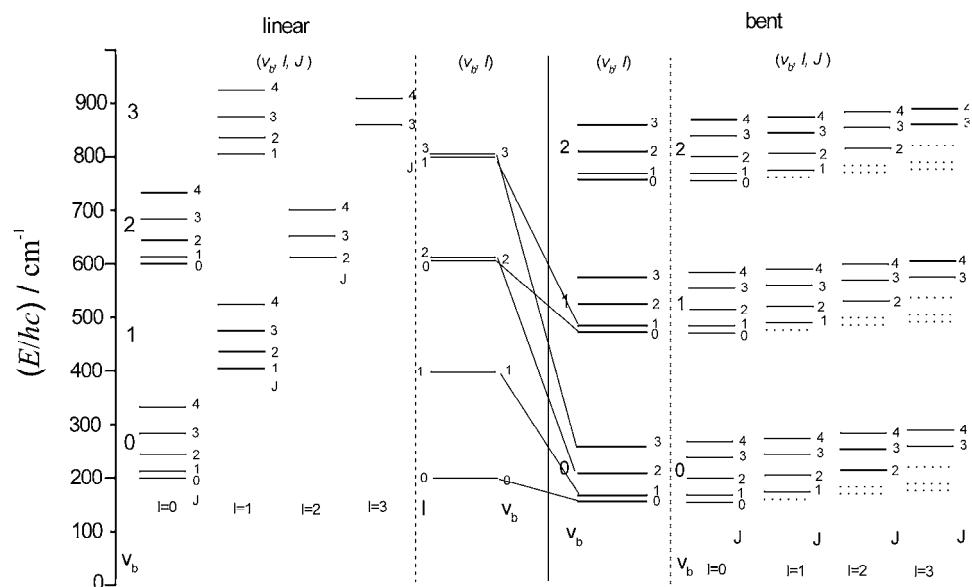

Fig. 2. Correlation between bending vibrational and rotational energy levels of a linear (left-hand side) and a bent (right-hand side) molecule. The levels with the inscription (v_b, l) do not involve a contribution of end-over-end (x,y) rotations. They are computed by means of Eq. (7) for a linear molecule and Eq. (41) for a bent molecule. The levels with the inscription (v_b, l, J) also involve a contribution of x, y rotations (Eqs. (21) and (43)). The values of $\tilde{\nu}_b = 200$ cm^{-1}, $B = 5$ cm^{-1} for linear molecule and $\tilde{\nu}_b = 300$ cm^{-1}, $A = 10$ cm^{-1}, $B = 5$ cm^{-1} for bent molecule are used.

Case b. In order to enable direct comparison of the results for partition functions obtained in the harmonic approximation with their counterparts evaluated beyond that approximation, the rotational partition function is now computed in another way. It will be shown that the partition function of a symmetric top can be replaced in a good approximation by the product of the partition functions of a one-dimensional and a two-dimensional rotator with the quantum numbers being independent of one another.[4] It is thus assumed the rotational Hamiltonian in the form:

$$\hat{H}^{\mathrm{r}} = \hat{H}_1^{\mathrm{r}} + \hat{H}_2^{\mathrm{r}} = \hat{H}_z^{\mathrm{r}} + \hat{H}_{\mathrm{x,y}}^{\mathrm{r}} \tag{34}$$

with

$$\hat{H}_1^{\mathrm{r}} = \frac{\hat{J}_z^2}{2I_{\mathrm{A}}}, \quad \hat{H}_2^{\mathrm{r}} = \frac{\hat{J}_x^2 + \hat{J}_y^2}{2I_{\mathrm{B}}} \tag{35}$$

The corresponding energy levels are:

$$E_1^{\mathrm{r}} = Ahcl^2, \quad l = 0,1,2,..., , \; g_1 = 1\,(l = 0); 2\,(l \neq 0) \tag{36}$$

$$E_2^{\mathrm{r}} = Bhc \cdot j\,(j+1), \quad j = 0,1,2,..., \quad g_{\mathrm{j}} = 2j+1 \tag{37}$$

Note that the quantum number j appearing in Eq. (37) does not have the same sense as the quantum number J for the magnitude of the total angular momentum. The partition functions are now

$$Z_1^{\mathrm{r}} = \sum_{l=0}^{\infty} g_{\mathrm{K}} \mathrm{e}^{-\frac{Ahcl^2}{kT}} \cong \int_{-\infty}^{\infty} \mathrm{e}^{-\frac{Ahcl^2}{kT}} \, \mathrm{d}l = \sqrt{\frac{\pi kT}{Ahc}} \tag{38}$$

$$Z_2^{\mathrm{r}} = \sum_{j=0}^{\infty} (2j+1)\mathrm{e}^{-\frac{BhcJ(J+1)}{kT}} \cong \int_0^{\infty} (2j+1)\mathrm{e}^{-\frac{Bhcj(j+1)}{kT}} \, \mathrm{d}j = \frac{kT}{Bhc} \tag{39}$$

Multiplying Eq. (38) with Eq. (39), the result of Eq. (32) is indeed obtained. Comparison of the rotational-energy levels of the symmetric top and the sum of the corresponding one-dimensional and two-dimensional rotators is presented in Fig. 3.

Case c. According to the last statement above, when evaluating the partition functions, the term $\hat{J}_z^2 / (2I_{\mathrm{A}})$ from the last but one expression for the rotational Hamiltonian, Eq. (28), can be extracted and put together with the bending Hamiltonian, Eq. (26), into the operator $\hat{H}_{\mathrm{b,z}}$:

$$\begin{aligned}
\hat{H}_{\mathrm{b,z}} &= -\frac{\hbar^2}{2\mu_{\mathrm{b}}} \frac{\partial^2}{\partial \theta^2} + \frac{1}{2} k_\theta (\theta - \theta_0)^2 + \frac{\hat{J}_z^2}{2I_{\mathrm{a}}} = \\
&= -\frac{\hbar^2}{2\mu_{\mathrm{b}}} \frac{\partial^2}{\partial \theta^2} + \frac{l^2 \hbar^2}{2I_{\mathrm{a}}} + \frac{1}{2} k_\theta (\theta - \theta_0)^2
\end{aligned} \tag{40}$$
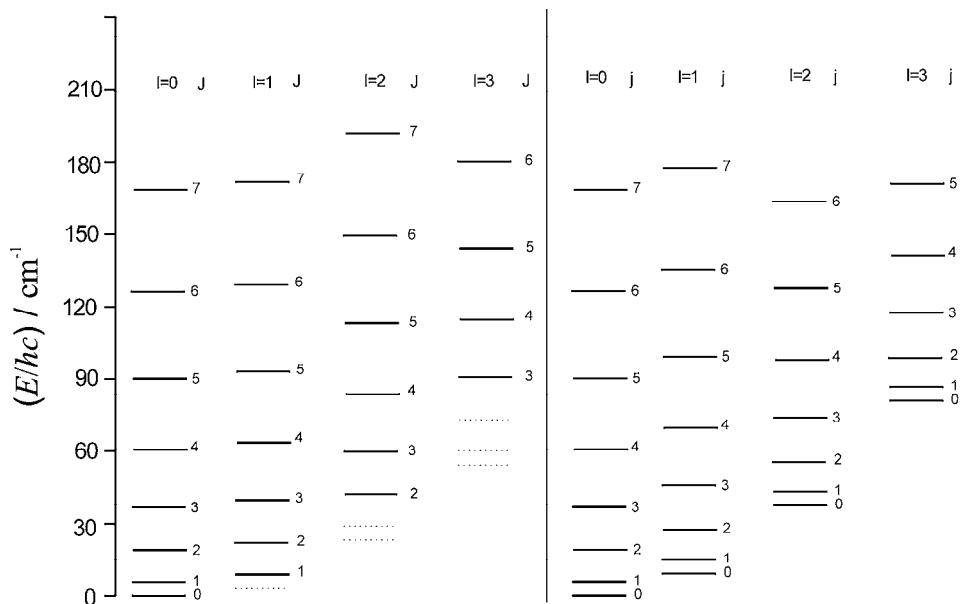
Fig. 3. Correlation between the rotational states of a symmetric top (left-hand side), and the sum of a one-dimensional and a two-dimensional rotator (right-hand side). The values of $A = 3$ cm^{-1} and $B = 1$ cm^{-1} are used.

Such a partitioning of the Hamiltonian is performed in order to enable a correlation of the results obtained in the harmonic approximation with those generated by employing the *ab initio* approach described below. The eigenvalues of the Hamiltonian, Eq. (40), are:

$$E_{b,z} = \left(v_b + \frac{1}{2} \right) \hbar \omega_b + Ahcl^2 \tag{41}$$

and the partition function is:

$$Z_{b,z} = \sum_{v_b=0}^{\infty} \sum_{l=0}^{\infty} g_l e^{-\frac{v_b \hbar \omega_b + Ahcl^2}{kT}} \cong \sum_{v_b=0}^{\infty} e^{-\frac{v_b \hbar \omega_b}{kT}} \int_{-\infty}^{\infty} e^{-\frac{Ahcl^2}{kT}} \, dl =$$
$$= \left(1 - e^{-\frac{\hbar \omega_b}{kT}} \right)^{-1} \sqrt{\frac{kT\pi}{Ahc}} \tag{42}$$

The eigenvalues of the remaining part of the rotational Hamiltonian, $\left(\hat{J}^2 - \hat{J}_z^2 \right) / \left(2I_B \right)$, are:

$$E_{x,y}^r = Bhc \left[J(J+1) - l^2 \right] \tag{43}$$

where $l \leq J$. However, when the partition function corresponding to this part of the Hamiltonian is independently evaluated, one has to put $l = 0$ and to sum over all J-values (from 0 to ∞), as was done in Eq. (19). The total bending–rotational partition function is then the product of Eqs. (42) and (19).

The complete bending–rotational energy is the sum of Eqs. (41) and (43):

$$E_{\text{b,r}} = \left(v_{\text{b}} + \frac{1}{2} \right) \hbar \omega_{\text{b}} + Ahcl^2 + Bhc \left[J \left(J + 1 \right) - l^2 \right] \tag{44}$$

and equals, of course, the sum of E_{b} (Eq. (27)) and E_{b} (Eq. (29)) ($l = K$). The partition function corresponding to the energy expression, Eq. (44), equals the product of the partition functions, Eqs. (31) and (32) (case a), as well as the product of Eqs. (31), (38) and (39) (case b). However, recall that the energy spectra are different for the cases a and c on the one hand, and b on the other. In the first case, the energy levels are given by Eq. (44) with the condition $l \leq J$; for a given combination of J and l the energy level is $g_l(2J+1)$-fold degenerated ($g_l = 1$ for $l = 0$ and $g_l = 2$ for $l \neq 0$). In case b, the energy is:

$$E_{\text{b,z}} = \left(v_{\text{b}} + \frac{1}{2} \right) \hbar \omega_{\text{b}} + Ahcl^2 + Bhcj \left(j + 1 \right) \tag{45}$$

where the quantum numbers $l = 0,1,2,\ldots$ and $j = 0,1,2\ldots$ are independent from each other. The energy level for a given combination of j and l is $g_l(2j+1)$-degenerated (Fig. 3).

In this subsection, the triatomic molecules were handled as symmetric tops. In a treatment beyond this approximation, the $g_l = 2$ degeneracy of the rotation levels with $l \neq 0$ would be lifted.

AN *AB INITIO* APPROACH TO TRIATOMIC MOLECULES UNDERGOING LARGE-AMPLITUDE BENDING VIBRATIONS

The complete vibration–rotation Hamiltonian for a triatomic molecule, expressed in terms of the Jacobi coordinates r, R, and θ (Fig. 1) and the Euler angles α, β and φ, which determine the orientation of the instantaneous molecular principal axes of inertia (*ipia*) with respect to a space-fixed coordinate system, was derived in a previous study.[5] Its kinetic energy part can be written as the sum of the vibrational, rotational and vibration–rotational (coupling) terms:

$$\hat{T} = \hat{T}_{\text{v}} + \hat{T}_{\text{vr}} + \hat{T}_{\text{r}} \tag{46}$$

with

$$\hat{T}_v = -\frac{\hbar^2}{2}\frac{1}{\mu_r}\frac{\partial^2}{\partial r^2} - \frac{\hbar^2}{2}\frac{1}{\mu_R}\frac{\partial^2}{\partial R^2} - \frac{\hbar^2}{2}\left(\frac{1}{\mu_r r^2} + \frac{1}{\mu_R R^2}\right)\left(\frac{\partial^2}{\partial \theta^2} + \cot\theta\frac{\partial}{\partial \theta}\right)$$

$$\hat{T}_{vr} = -\frac{2\hbar\sin\theta}{I_{xx}^2}(-\mu_R r R^2\cos\theta\frac{\partial}{\partial r} + \mu_r r^2 R\cos\theta\frac{\partial}{\partial R} +$$

$$+ \left(\mu_R R^2 - \mu_r r^2\right)\left(\sin\theta\frac{\partial}{\partial \theta} + \cos\theta\right)i\hat{J}_x$$

$$\hat{T}_r = \frac{\hat{I}_{xx}}{2\left(I_{yy} - I_{zz}\right)^2}\hat{J}_x^2 + \frac{1}{2I_{yy}}\hat{J}_y^2 + \frac{1}{2I_{zz}}\hat{J}_z^2$$

(47)

where μ_r and μ_R are the "reduced masses":

$$\mu_r = \frac{m_3\left(m_1+m_2\right)}{M}, \mu_R = \frac{m_1 m_2}{m_1 + m_2}$$

(48)

and

$$I_{xx} = \mu_r r^2 + \mu_R R^2 = I_{yy} + I_{zz}$$

$$I_{yy} = \frac{1}{2}\left[\left(\mu_r r^2 + \mu_R R^2\right) + \sqrt{\mu_r^2 r^4 + \mu_R^2 R^4 + 2\mu_r\mu_R r^2 R^2\cos(2\theta)}\right]$$

$$I_{zz} = \frac{1}{2}\left[\left(\mu_r r^2 + \mu_R R^2\right) - \sqrt{\mu_r^2 r^4 + \mu_R^2 R^4 + 2\mu_r\mu_R r^2 R^2\cos(2\theta)}\right]$$

(49)

are the instantaneous principal moments of inertia. $\hat{J}_x$, $\hat{J}_y$ and $\hat{J}_z$ are the components of the molecular angular momentum along the axes of the coordinate system bound to the molecule (*ipia* -system):[7]

$$\hat{J}_x = -i\hbar\left(-\frac{\cos\varphi}{\sin\beta}\frac{\partial}{\partial \alpha} + \sin\varphi\frac{\partial}{\partial \beta} + \cot\beta\cos\varphi\frac{\partial}{\partial \varphi}\right)$$

$$\hat{J}_y = -i\hbar\left(\frac{\sin\varphi}{\sin\beta}\frac{\partial}{\partial \alpha} + \cos\varphi\frac{\partial}{\partial \beta} - \cot\beta\sin\varphi\frac{\partial}{\partial \varphi}\right)$$

$$\hat{J}_z = -i\hbar\frac{\partial}{\partial \varphi}$$

(50)

The integration element is assumed in the form $dV = \sin\beta\sin\theta\prod dq_i$ (q_i represent the vibrational and rotational coordinates). The potential energy corresponding to the kinetic energy operator, Eq. (47), represents the electronic energy computed within the framework of the Born–Oppenheimer approximation for a set of relevant values of the coordinates r, R and θ.

To find approximate solutions of the corresponding Schrödinger equation, a procedure resembling the Born–Oppenheimer approximation (normally used for the separation of electronic and nuclear motions) was applied to the stretching––bending problem. Since the stretching vibrations in the species under consideration are characterized by much larger energies ($\tilde{\nu}_s \approx 1000\,\text{cm}^{-1}$) than those for

the other nuclear degrees of freedom (in the case of BC_2, the bending wave number is as small as $\tilde{\nu}_b \approx 200$ cm^{-1}), the stretching Schrödinger equation was first solved with the Hamiltonian:

$$\hat{H}_s = -\frac{\hbar^2}{2\mu_r}\frac{\partial^2}{\partial r^2} - \frac{\hbar^2}{2\mu_R}\frac{\partial^2}{\partial R^2} + \frac{1}{2}k_{rr}(\theta)r^2 +$$
$$+\frac{1}{2}k_{RR}(\theta)R^2 + k_{rR}(\theta)rR + ... \tag{51}$$

The force constants $k_{rr}(\theta), k_{RR}(\theta), k_{rR}(\theta),...$ represent the stretching potential surface. One calculates them separately for a number of values of the bending coordinate, handled as a parameter in the same sense as the nuclear coordinates when the electronic Schrödinger equation is solved in the usual Born–Oppenheimer approximation. Since the stretching vibrations are normally small-amplitude ones, the calculations are restricted to the quadratic field only. The solutions of Eq. (51) are then:

$$E_s(\theta) = \left(v_{s1} + \frac{1}{2}\right)\hbar\omega_{s1}(\theta) + \left(v_{s2} + \frac{1}{2}\right)\hbar\omega_{s2}(\theta) \tag{52}$$

From the above kinetic energy operator are now extracted the terms of central importance when dealing with large-amplitude bending vibrations, namely those describing the bending vibrations and rotations around the z-axis, coinciding for linear geometries with the molecular axis:

$$\hat{T}_{b,z} = -\frac{\hbar^2}{2}\left(\frac{1}{\mu_r r^2} + \frac{1}{\mu_R R^2}\right)\left(\frac{\partial^2}{\partial\theta^2} + \cot\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{2I_{zz}}\hat{J}_z^2 \tag{53}$$

Were the coupling between the bending and stretching vibrations negligible, the stretching coordinates r and R could be replaced in Eq. (53) by their equilibrium values, r_e and R_e, respectively. Since this is not the case, it is assumed the stretching coordinates are certain functions of θ, $r_e(\theta) \equiv r(\theta)$, $R_e(\theta) \equiv R(\theta)$. However, r and R cannot be directly replaced by $r(\theta)$ and $R(\theta)$ in Eq. (53), as written in Eq. (17) of Ref. 5, because such a Hamiltonian would not be hermitian. Instead, the symmetrised form thereof must be used:

$$\hat{T}_{b,z} = -\frac{\hbar^2}{4}\left\{\left(\frac{1}{\mu_r r_{(\theta)}^2} + \frac{1}{\mu_R R_{(\theta)}^2}\right)\left(\frac{\partial^2}{\partial\theta^2} + \text{ctg}\,\theta\frac{\partial}{\partial\theta}\right) + \right.$$
$$\left. + \left(\frac{\partial^2}{\partial\theta^2} + \text{ctg}\,\theta\frac{\partial}{\partial\theta}\right)\left(\frac{1}{\mu_r r_{(\theta)}^2} + \frac{1}{\mu_R R_{(\theta)}^2}\right)\right\} - \frac{\hbar^2}{2I_{zz}(\theta)}\frac{\partial^2}{\partial\varphi^2} \tag{54}$$

This operator can be alternatively written as:

$$T = -\frac{\hbar^2}{2}\left[T_1(\theta)\frac{\partial^2}{\partial\theta^2} + T_2(\theta)\frac{\partial}{\partial\theta} - l^2 T_3(\theta) + T_4(\theta)\right] \tag{55}$$

where

$$T_1(\theta) = \frac{1}{\mu_r r_{(\theta)}^2} + \frac{1}{\mu_R R_{(\theta)}^2}$$

$$T_2(\theta) = \left[\frac{1}{\mu_r r_{(\theta)}^2} + \frac{1}{\mu_R R_{(\theta)}^2}\right]\cot\theta - 2\left[\frac{1}{\mu_r r_{(\theta)}^3}\frac{\mathrm{d}r_{(\theta)}}{\mathrm{d}\theta} + \frac{1}{\mu_R R_{(\theta)}^3}\frac{\mathrm{d}R_{(\theta)}}{\mathrm{d}\theta}\right]$$

$$T_3(\theta) = \frac{1}{I_{zz}(\theta)}$$

$$\begin{aligned}
T_4(\theta) = &-\left[\frac{1}{\mu_r r_{(\theta)}^3}\frac{\mathrm{d}r_{(\theta)}}{\mathrm{d}\theta} + \frac{1}{\mu_R R_{(\theta)}^3}\frac{\mathrm{d}R_{(\theta)}}{\mathrm{d}\theta}\right]\cot\theta + \\
&+3\left\{\frac{1}{\mu_r r_{(\theta)}^4}\left[\frac{\mathrm{d}r_{(\theta)}}{\mathrm{d}\theta}\right]^2 + \frac{1}{\mu_R R_{(\theta)}^4}\left[\frac{\mathrm{d}R_{(\theta)}}{\mathrm{d}\theta}\right]^2\right\} - \\
&-\frac{1}{\mu_r r_{(\theta)}^3}\frac{\mathrm{d}^2 r_{(\theta)}}{\mathrm{d}\theta^2} - \frac{1}{\mu_R R_{(\theta)}^3}\frac{\mathrm{d}^2 R_{(\theta)}}{\mathrm{d}\theta^2}
\end{aligned} \tag{56}$$

The operator $\hat{J}_z^2 = -\hbar^2\left(\partial^2/\partial\varphi^2\right)$ was replaced by $l^2\hbar^2$, because we assume the bending functions in the form:

$$\psi(\theta,\varphi) = \frac{1}{\sqrt{2\pi}}e^{il\varphi}\Theta(\theta) \tag{57}$$

The potential energy part of the bending–z-rotation Hamiltonian $\hat{H}_{b,z}$ is assumed in the form:

$$V(\theta) = V_{r,R}(\theta) + E_s(\theta) = V(\theta) + \left(v_{s1} + \frac{1}{2}\right)\hbar\omega_{s1}(\theta) + \left(v_{s2} + \frac{1}{2}\right)\hbar\omega_{s2}(\theta) \tag{58}$$

where $V_{r,R}(\theta)$ is the bending potential corresponding to the bond lengths optimized at each particular value of the coordinate θ. In the language of reaction kinetics, $V_{r,R}(\theta)$ represents the "minimum-energy path" along the "reaction coordinate" θ. The second and the third term on the right-hand side of Eq. (58) are the stretching energies. The bending Schrödinger equation has to be solved separately for each combination of the bending quantum numbers v_{s1} and v_{s2}. Thus, by solving the Schrödinger equation with the Hamiltonians, Eqs. (55) and (58), the stretching–bending–z-rotational energy levels are obtained with the stretch––bend coupling incorporated through the parametric dependence of r_e, R_e, ω_{s1}

and ω_{s2} on θ. In Eq. (58), the stretching energy contribution is written in the harmonic approximation. A generalization involving anharmonicity of the stretching vibrations is straightforward.

Finally, the contribution of the x,y-rotations to the total energy can be calculated at different levels of sophistication – the choice depends on the concrete numerical values of the parameters in question. In the case of a HBC molecule, when the hydrogen atom migrates around the relatively heavy BC fragment, $I_{xx} \cong I_{yy} >> I_{zz}$ (Eq. (49)), and I_{xx} and I_{yy} do not dramatically vary with a change of θ. This was the situation in previous works on HNC→HCN isomerisation.[5,6] The x,y-rotational contribution to the total energy can then be calculated by means of Formula (21). If the above conditions are not fulfilled, the average values of the rotational constants can first be calculated over the bending wave functions and after that the rotational spectrum. When the molecular shape if far from a symmetric top, it might be better not to include the z-rotational part in the bending Hamiltonian and calculate the energy levels of the asymmetric top separately, using the averaged rotational constants. Of course, the computation of the partition functions must be performed numerically when the energy levels are calculated beyond the harmonic approximation.

In the next study of this series,[2] the molecular Schrödinger equation is solved employing the variational approach introduced in Ref. 5. The key points thereof are repeated here.

The Hamiltonian of Eqs. (55) and (58) has two features that distinguish it from the usual forms of the vibrational Hamiltonian. It is periodical in θ with the period π and has singularities at $\theta = 0, \pi$. The periodicity is taken into account if all terms in the kinetic and potential energy operator are expanded into Fourier series in θ. The singularities are caused by the presence of the terms T_2 and T_3 with the asymptotic behaviour $\lim_{\theta \to 0, \pi} T_2 \propto \sin^{-1}\theta$, and $\lim_{\theta \to 0, \pi} T_3 \propto \sin^{-2}\theta$. Since the volume element $dV = \sin\theta d\theta d\varphi$ is used, the first singularity disappears in computations of the matrix elements. The second singularity also vanishes when $l = 0$, but remains for $l \neq 0$. In the first case, one employs for representation of the Hamiltonian, the basis functions:

$$\varphi_n = \cos(n\theta) \qquad (59)$$

For $l \neq 0$, the basis consists of the functions:

$$\varphi_n = \sqrt{\sin\theta}\cos(n\theta) \qquad (60)$$

One cannot use the same basis (particularly Eq. (60)) for both the cases $l = 0$ and $l \neq 0$ because the $l = 0$ wave functions must have non-vanishing values at $\theta = 0, \pi$. Due to the presence of the weight factors $\sin\theta$ (appearing in the volume element) and $\sqrt{\sin\theta}$ (in the basis functions of Eq. (60)), one has to compute matrix elements of the type:

$$\int_0^\pi \cos(m\theta)\left[T_i / V \sin\theta\right]\cos/\sin n\theta \mathrm{d}\theta$$

$$\int_0^\pi \cos(m\theta)\left[T_i / V \sin^2\theta\right]\sin/\cos(n\theta)\mathrm{d}\theta \qquad (61)$$

$$\int_0^\pi \cos(m\theta)\left[T_i / V \sin\theta\cos\theta\right]\sin/\cos(n\theta)\mathrm{d}\theta$$

They can be easily calculated when the functions in the square brackets are fitted by $\sin(k\theta)$ or $\cos(k\theta)$ series.

CONCLUSIONS

In the present study, an evaluation of partition functions for linear and bent triatomic molecules in the harmonic approximation was reviewed and a scheme was presented for *ab initio* variational calculation of the vibration–rotational energy levels in triatomics undergoing large-amplitude bending vibrations. The harmonic formulae and the variational approach will be employed in the second paper of this series to obtain the energy levels and the partition functions in the ground electronic state of the BC_2 molecule.

ИЗВОД

ВЕЗА ИЗМЕЂУ МОЛЕКУЛСКЕ СПЕКТРОСКОПИЈЕ И СТАТИСТИЧКЕ МЕХАНИКЕ: РАЧУНАЊЕ ПАРТИЦИОНИХ ФУНКЦИЈА ТРОАТОМСКИХ МОЛЕКУЛА КОЈИ ВРШЕ САВИЈАЈУЋЕ ВИБРАЦИЈЕ ВЕЛИКИХ АМПЛИТУДА

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Разматрано је одређивање партиционих функција троатомских молекула који врше савијајуће вибрације великих амплитуда. Претпостављено је да се сви потребни подаци добијају помоћу *ab initio* рачунања. Посебна пажња посвећена је спрези савијајућих и истежућих вибрационих степена слободе, као и интеракцији савијајућих вибрација и ротација. Развијена је погодна схема за варијационо рачунање енергијских нивоа.

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