

APPROXIMATION FORMULAS FOR SPECTROSCOPIC PARAMETERS OF SLIGHTLY ASYMMETRIC MOLECULES WITH INTERNAL ROTATION

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Expressions for spectroscopic parameters $a_m(K)$ determining rotational energy of a molecule have been derived for slightly asymmetric molecules with internal rotation. These expressions depend on a solution of the Schrödinger equation that takes into account the periodicity of the potential function and strong interaction between internal and external rotation. It has been suggested that the solution of this equation for its eigenvalues be sought as a ratio of the Fourier series in the rotational quantum number K . The expressions for $a_m(K)$ have been applied to the CH_3OH molecule with triad rotational axis.

INTRODUCTION

Molecules with internal rotation form a sufficiently large group of nonrigid molecules. Torsional vibration of large amplitude can be manifested even in simple tetratomic molecules such as H_2S_2 , N_2H_2 , H_2O_2 , ... In polyatomic molecules (CH_3NH_2 , CH_3OH , ...) it is usually related to rotation of group of atoms (tops) about a certain axis. It is of interest to study such molecules to solve complicated problems that arise in interpretation of spectra of these molecules. Moreover, some of them (e.g., the H_2O_2 molecule) are constituents of the Earth's atmosphere. The other molecules (e.g., the CH_3OH molecule) represent a rich and efficient medium for molecular lasers.

As of the present time, it is possible to identify two basic approaches used in theoretical description of spectra of the molecules under study. The first approach is based on calculus of variations with the potential function $V_0(\gamma)$ being modeled by the Fourier series¹⁻⁵

$$V_0(\gamma) = \sum_l V_{lN} / 2 (1 - \cos(Nl\gamma)) \quad (1)$$

in the variable γ describing the torsion in molecule with N -fold rotational axis. The second approach, widely used in particular for the methanol molecule, is based on an empirical formula for rotational energy⁶⁻⁸

$$E(K, q, J) = \sum_m a_m(K, q) [J(J+1)]^m + 1/2 + \frac{(J+K)!}{(J-K)!} [S(K, q) + J(J+1)T(K, q)]. \quad (2)$$

In this expression, J is the principal rotational quantum number; K is the projection of J onto the rotational axis of the top; and, q is a set of the remaining quantum numbers. The second term in Eq. (2) describes splitting of energy levels due to molecular asymmetry. The procedure of identifying the spectrum based on Eq. (2) is simple and efficient; however, the number of adjustable parameters $a_m(K, q)$ determined for each K and q is sufficiently large.⁸ Expansion of $a_m(K, q)$ in a power series in the quantum number K is divergent even for small K , and there are no other presently available representations for $a_m(K, q)$.

In this paper, the analytical dependence of the spectroscopic parameters $a_m(K, q)$ on the rotational quantum number K has been derived. The analytical expressions for $a_m(K, q)$ are primarily determined by the solution of the Schrödinger equation that takes into account periodicity of the potential function and strong torsion-rotation interaction in the molecule.

ANALYTICAL REPRESENTATION FOR THE DEPENDENCE OF TORSIONAL ENERGIES ON THE ROTATIONAL QUANTUM NUMBER K

Let us consider the particular case of molecule with triad internal rotation axis, i.e., assume $N = 3$ in Eq. (1) and take account of only the first term in this expansion. Then the Schrödinger equation describing torsion takes the form

$$H_0^{\text{tor}} \phi_{n\sigma}(\gamma) = \left\{ -F \frac{\partial^2}{\partial \gamma^2} + V_3/2 (1 - \cos 3\gamma) \right\} \phi_{n\sigma}(\gamma) = E_{n\sigma} \phi_{n\sigma}(\gamma). \quad (3)$$

In this expression the coefficient $F = h/8\pi^2 c I_\gamma$ (I_γ is the tensor of inertia about the axis of internal rotation¹); V_3 describes the height of a potential barrier for this rotation; n is the principal torsional quantum number; and, the subscript σ describes symmetry (periodicity) of the wave function and for $N = 3$ takes the three values: 0, ± 1 . Equation (3) is the Mathieu equation,⁹ which can be solved by numerical methods. Let us also consider the term $W = 2pFKJ_\gamma$ (Refs. 1 and 3) from the initial molecular Hamiltonian, which describes interaction between the torsion (operator $J_\gamma = -i\partial/\partial\gamma$) and total rotation (quantum number K). In the expression for W , the parameter $p = I_\gamma/I_z$ determines the relation between the inertia tensors I_γ and I_z about the principal rotational axis z . If the term W is considered as perturbation to Eq. (3), then in the perturbation theory it generates the series

$$E_n(K) = E_n + \sum_m \kappa_m (2pFK)^m, \quad (4)$$

where $\kappa_1 = V_{nm}$, $\kappa_2 = -\sum_{i=1}^n V_{ni} V_{in} / (E_i - E_n)$, ... (expressions for κ_3 and κ_4 can be found, e.g., in Ref. 10).

Here the subscript σ is omitted for brevity, $V_{ni} = \langle n\sigma | J_y | i\sigma' \rangle$, and for $\sigma = 0$ all $\kappa_{2m+1} = 0$. Using the maximum matrix element $V_{nm\pm 1}$, one can estimate (tentatively) the convergence radius $R_k = K_{\max}$ of series (4) from the expression

$$|V_{n\ n\pm 1} / (E_n - E_{n\pm 1})| 2 p F K_{\max} = 1,$$

which reduces to the formula

$$R_K = | (E_n - E_{n\pm 1}) / V_{n\ n\pm 1} | (2 F p)^{-1}. \quad (5)$$

By the method of continued fractions,¹ using the values of the parameters F and V_3 , we can assess the first Fourier coefficients for the wave functions $\phi_{n\sigma=0}$ and hence the radius R_k . If the convergence radius is sufficiently large, then the dependence of torsional energies on the quantum number K can be expressed by series formula (4). For small radius R_k , the perturbation theory cannot be used, and the term W should be considered in zero approximation in combination with H_0^{tor} . Such a situation appears, e.g., for the methanol molecule. The estimate of the convergence radius R_k for this molecule reveals that $R_k \cong 5$ for the ground state ($n=0$, $\sigma=0$) and $R_k \cong 0.5$ for $n=1$, $\sigma=0$ as well as for the state $cn=2$, $\sigma=0$. For such molecules the dependence of torsional energies $E_{n\sigma}(K)$ on the quantum number K has to be found from the equation

$$\{ F J_\gamma^2 + 2 F p K J_\gamma + V_3 / 2(1 - \cos(3\gamma)) \} \psi_{n\sigma}(\gamma; K) = E_{n\sigma}(K) \psi_{n\sigma}(\gamma; K), \quad (6)$$

which is also the Mathieu equation.⁹ To determine the form of $E_{n\sigma}(K)$, the property of periodicity of the potential function $V_0(\gamma)$ can be used, as was done in Refs. 2 and 11. The wave function $\psi_{n\sigma}(\gamma; K)$ can be written as^{5,11}

$$\psi_{n\sigma}(\gamma; K) = \exp [i (\sigma + K p) \gamma] \sum_m b_m^{nK} \exp (i 3 m \gamma). \quad (7)$$

It is seen from this formula that any change of the value

$$\sigma(K) = \sigma + p K$$

by a factor multiple of three does not change the solution for the wave function. This fact can be used for searching $E_{n\sigma}(K)$ as a periodic function of the parameter $\theta = a'K$ ($a' = 2\pi p/3$). In Refs. 2 and 11, it has been suggested that the expansion in the Fourier series be used for internal energy $E_{n\sigma}$. For the molecule with the triad rotational axis, it assumes the form

$$E_{n\sigma}(K) = \sum_l w_l \cos l(\theta + \theta_0). \quad (8)$$

In this expression, $\theta_0 = -(2\pi/3)\sigma$, and w_l are the parameters independent of σ .

In the present paper, the following expression for the torsional energy levels is used:

$$E_{n\sigma}(K) = \sum_l b_l \cos l(\theta + \theta_0) / (1 + \sum_l z_l \cos l(\theta + \theta_0)), \quad (9)$$

which is also a periodic function of the parameter θ and allows one, as is shown for the CH_3OH molecule, to improve

substantially the convergence of Eq. (9) as compared to Eq. (8). The expression (9) can be derived in approximation similar to the approximation of "strong bond" widely used in the quantum theory of solid body when considering the motion of electron with a given momentum in a periodic field of crystal lattice (see, e.g., Refs. 12 and 13). In this case, the approximation is valid for torsional energy levels lying below the top of a potential barrier. In the approximation under study, the potential function $V_0(\gamma)$ is represented as a sum of one-dimensional potentials spaced at $a = 2\pi/3$

$$V_0(\gamma) \cong \sum_m W_m(\gamma - a m),$$

and the wave function is represented as a sum of wave functions

$$\psi_n(\gamma; K) \cong \sum_m \exp[i \sigma(K) m a] \phi_n(\gamma - a m), \quad (10)$$

localized above individual potentials. Substitution of Eq. (10) into the formula for the energy

$$E_n(K) = \langle \psi_n | H_0^{\text{tor}} | \psi_n \rangle / \langle \psi_n | \psi_n \rangle,$$

where H_0^{tor} can be found from Eq. (3), leads to expression (9) in which the denominator appears due to overlap of the wave functions $\phi_n(\gamma - am)$ and $\phi_n(\gamma - al)$. The internal energy $E_n(K)$ is the smooth function of the quantum number K for fixed torsional quantum numbers n and τ . For given n , the quantum number τ takes the three values: 1, 2, or 3 and is related to σ by the following relations⁵: $K + \tau = 3N + 1$ for $\sigma = 0$, $K + \tau = 3N$ for $\sigma = 1$, and $K + \tau = 3N + 2$ for $\sigma = -1$, where N is an integer. By introducing the parameter $\alpha = (2\pi/3)(1 - p)$ into Eq. (9), expression for $E_{n\tau}(K)$ can be written in the form:

$$E_{n\tau}(K) = \sum_l \alpha_l \cos l(aK - \theta_0') / \left(1 + \left(\sum_l z_l \cos l(\alpha K - \theta_0') \right) \right),$$

where $\theta_0' = 0$ for $\tau = 1$, $\theta_0' = 2\pi/3$ for $\tau = 2$, and $\theta_0' = -2\pi/3$ for $\tau = 3$. From this formula, one can obtain a convenient expression for combinations of torsional energies

$$\begin{aligned} E_n^{(-)}(K) &= \{ E_{n\tau=2} - E_{n\tau=3}(K) \} / 2 = \\ &= \sum_l a_l' \sin(\alpha K l) / (1 + \sum_l z_l' \cos(\alpha K l) + \dots) = \\ &= \sum_l a_l \sin(\alpha K l) / (1 + \sum_l z_l K^{2l} + \dots). \end{aligned} \quad (11)$$

ANALYTICAL REPRESENTATION FOR THE SPECTROSCOPIC PARAMETERS $a_m(K)$

The expression obtained for torsional energy levels enables one to find easily the analytical form for the spectroscopic parameters $a_m(K)$. For slightly asymmetric molecules with internal rotation, the corrections for the energy levels caused by molecular asymmetry can be taken into account according to the perturbation theory. In this case, the matrix of molecular Hamiltonian, which is nondiagonal on the basis of torsion-rotation wave functions, is reduced to a diagonal form. The form of the matrix elements coincides with expression (2). For $m = 0$, the parameter $a_0(K)$ determines the rotational energy (for a hypothetical level with $J = 0$), i.e.,

$$a_0(K) = E_{n\tau}(K) + E_{\text{rot}}(K), \quad (12)$$

where the second term describes rotation of the entire molecule and can be conventionally represented as

$$E_{\text{rot}}(K) = A K^2 - D_K K^4 + H_K K^6 + \dots$$

For torsional states with $\tau = 2, 3$, it is convenient to convert to the combinations

$$a_0^{(\pm)}(K) = \{a_0(K, \tau = 2) \pm a_0(K, \tau = 3)\} / 2 \tag{13}$$

and to make use of relation (11). When the matrix is diagonalized using the perturbation theory (PT), there appear the dominators $a_0(K, \tau) - a_0(K', \tau')$ in the formulas for spectroscopic constants $a_m(K)$. They are assumed to be "sufficiently large" and allow the use of PT (without random resonances). Otherwise, the matrix of Hamiltonian should be diagonalized numerically. Here, we omit the detailed derivation of the parameters $a_m(K)$ and consider final expressions for the first coefficients $a_1(K)$ and $a_2(K)$ that were obtained using either representation (9) for torsional energies or power–law representation for these energies. Thus, the rotational "constant" $a_1(K)$ has the form

$$a_1(K) = \frac{\sum_i a_i K^i}{1 + \sum_i z_i \cos l(a K + \theta_0) + \sum_i \tilde{z}_i \sin l(a K + \theta_0)}$$

or

$$a_1(K) = \frac{\sum_i a_i K^i}{1 + \sum_i z_i K^i} \tag{14}$$

It should be noted that in the numerators the series expansion of trigonometric functions in the parameter K was used, for these functions no to be confused with polynomial ones. The formula for the quadratic constant $a_2(K)$ has the form

$$a_2(K) = \frac{\sum_i a_i K^i}{1 - K^2 + \sum_i z_i K^i} \tag{15}$$

In the aforegigen formulas, $a_i, z_i,$ and \tilde{z}_i are the adjustable parameters that should be determined from the experimental values for $a_m(K)$.

APPLICATION TO THE METHANOL MOLECULE

As of the present time, a large number of experimental values of the parameters $a_m(K)$ are known for the methanol molecule that were obtained by experimental data processing. These values can be used to check the analytical expressions for the parameters under study. The results of this check are listed in Tables I–III. In the first column of the tables, there are analytical formulas for $a_m(K)$; in the second column, there is the number of adjustable parameters; in the third column, there is a maximum error in fitting the experimental results; and finally in the last column, there are the quantum numbers K for which the experimental parameters $a_m(K)$ were used (at random resonances formula (2) is inapplicable; therefore, some of the parameters $a_m(K)$ cannot be used to solve the inverse problem). In the tables, a comparison with the polynomial representation of these parameters is made. In particular, as is seen from Tables I and III, polynomial representation cannot be used for combinations of torsional energies $a_0^{(-)}(K)$ and quadratic constants $a_2(K)$. Moreover, an analysis reveals that the increased number of adjustable parameters does not ensure the acceptable accuracy of approximation of the experimental data (such accuracy can be ensured when the number of adjustable parameters approaches the number of experimental data). Fitting by new models seems to be sufficiently good.

TABLE I. Quality of fitting the parameters $a_0(K)$ (see Ref. 8) for the ground state of the CH₃OH molecule.

Model	L	$a_0^{\text{max}} \times 10^4 \text{ cm}^{-1}$	K
$a_0 + \frac{P(8)}{1 + z_4 K^4 + z_6 K^6}$ $P(8)$ $\sum_{i=1}^5 a_i K^{2i}$	7	26.35	$K \leq 14$ $K \neq 9, K \neq 12$
	7	2.6	
$a_0 + \frac{P(8)}{1 + z_1 K + z_2 K^2 + z_3 K^3}$ $P(8)$ $a_1 K + a_2 K^2 + a_4 K^4 + a_6 K^6 + a_8 K^8$	8	33.4	$K \leq 14$
	8	4.4	
$\frac{P(5)}{1 + z_1 K^2}$ $P(5)$ $a_1 \sin(a K) + a_2 \sin(2a K) + a_4 \sin(4a K)$	5	13100	$K \leq 10$
	5	7.1	$K \leq 10$
	7	4.4	$K \leq 14$ $K \neq 13$
$\frac{\sum_{i=1}^4 a_i \sin(a i K)}{1 + z_1 K^2 + z_2 K^4}$	7	4.4	$K \leq 14$ $K \neq 13$

Note: $a_0^{\text{max}} = \max |a_0^{\text{cal}} - a_0^{\text{exp}}|$; L is the number of adjustable parameters $a_i, z_i, \alpha,$ and $P(N) = \sum_{i=0}^N a_i K^{2i}$. The value 0.3970871 was found for the parameter α . The value of the parameter a_0 was borrowed from Ref. 8.

TABLE II. Quality of fitting the parameters $a_1(K)$ (see Ref. 8) for the ground state of the CH₃OH molecule.

Model	L	$a_1^{\max} \times 10^6 \text{ cm}^{-1}$	K
$P(3)$ $a_0 + \frac{a_2 K^2 + a_4 K^4}{1 + z_2 K^2 + z_4 K^4}$	3	10.7	
	4	7.9	$K \leq 14$ $K \neq 8, K \neq 9$ $K \neq 13$
	3	5.8	
$a_0 + \frac{a_2 K^2 + a_4 K^4}{1 + z_1 \sin(\alpha K)}$ $P(4)$ $a_0 + \frac{a_2 K^2 + a_4 K^4}{1 + z_1 K + z_2 K^2}$	4	12	
	4	11.5	$K \leq 14$ $K \neq 1, K \neq 7$
	3	12	
$a_0 + \frac{a_2 K^2 + a_4 K^4}{1 + z_1 \sin(\alpha K - \theta_0)}$ $P(4)$ $a_0 + \frac{a_1 K + a_2 K^2}{1 + z_1 K^2 + z_2 K^4}$	4	42.1	
	4	8.7	$K \leq 14$ $K \neq 1$ $K \neq 13$
	4	10.9	

Note: $\alpha = 0.3970871$ and $\theta_0 = 2\pi/3$.

TABLE III. Quality of fitting the parameters $a_2(K)$ (see Ref. 8) for the ground state of the CH₃OH molecule.

Model	L	$a_2^{\max} \times 10^8 \text{ cm}^{-1}$	K
$a_0 + \frac{a_1 K + a_2 K^2 + a_4 K^4 + a_6 K^6}{1 + z_1 K - K^2}$	5	8.3	$K \leq 14$ $K \neq 1, K \neq 9$
	4	11	$K \leq 14$ $K \neq 1$
$a_0 + \frac{a_1 K + a_2 K^2 + a_4 K^4 + a_6 K^6}{1 - K^2}$	4	11	$K \leq 14$ $K \neq 1$
	4	5.9	$K \leq 14$ $K \neq 1$
$P(5)$	5	1104.8	

TABLE IV. Quality of predicting the parameters $a_0(K)$ for the ground state of the CH₃OH molecule with the adjustable parameters found by fitting with $K \leq 10$.

	$a_0(\tau = 1)$	$a_0^{(+)}$	$a_0^{(-)}$
L	5	6	5
$\Delta a_0^{\max} \times 10^4 \text{ cm}^{-1}, K \leq 10$	8	3.7	7.21
$K = 11$ exp. ⁸	552.33	549.50	- 9.72
pred.	552.33	549.50	- 9.73
$K = 12$ exp. ⁸	628.92	629.74	- 10.54
pred.	628.96	629.75	- 10.57
$K = 13$ exp. ⁸	712.55	716.69	- 9.49
pred.	712.70	716.67	- 9.75
$K = 14$ exp. ⁸	803.49	810.19	- 7.21
pred.	803.83	809.93	- 7.28

Note: In the prediction, the following models were used:

Table IV shows the quality of prediction of torsional energies $a_0(K)$ for the ground molecular state. At the first stage of fitting, the experimental data were processed using the obtained relations for $a_0(K)$ with $K \leq 10$, and at the second stage the obtained adjustable parameters were used for calculating $a_0(K)$ for $10 < K \leq 14$, and the results were compared to the experimental constants. And finally Table V represents the calculated parameters $a_m(K)$ ($m = 0, 1, 2$) with $K = 15$ that can be used for searching new absorption lines in the spectrum of the molecule.

$$a_0(\tau = 1) = a_0 + \sum_{i=1}^3 a_i K^{2i} / (1 + z_1 K + z_4 K^4);$$

$$a_0^{(+)} = a_0 + \sum_{i=1}^3 a_i K^{2i} / (1 + \sum_{i=1}^3 z_i K^{2i});$$

$$a_0^{(-)} = [a_1 \sin(\alpha K) + a_2 \sin(2\alpha K) + a_4 \sin(4\alpha K)] / (1 + z_2 K^2).$$

TABLE V. Calculated values of the parameters $a_m(K)$ for the ground state of the CH_3OH molecule with $K = 15$.

Parameter	$\tau = 1$	$\tau = 2$	$\tau = 3$
a_0, cm^{-1}	901.95	908.5	912.00
a_1, cm^{-1}	0.804962	0.80480	0.80468
$a_2 \times 10^{-6}, \text{cm}^{-1}$	- 2.6	- 1.75	- 1.6

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