

Ambiguity in the torsion-rotational Hamiltonian of a CH₃-XH type molecule

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The problem of ambiguity in the torsion-rotational Hamiltonian is considered as applied to a CH₃-XH molecule having a torsion-type oscillation. The parameters of ambiguity are determined on the basis of analysis made by O.N. Ulenikov [*J. Mol. Spectrosc.* **119**, 144-152 (1986)]; the reduction of the effective Hamiltonian is presented.

1. Introduction

For a long time the internal rotations in molecules were of considerable interest for the molecular spectroscopy.^{1,2} Various aspects of this problem, such as the form of a Hamiltonian and wave functions, different approximations and methods for solution of Schrödinger equation, properties of the potential functions and solutions to the Schrödinger equation, problems of symmetry properties, and so on were analyzed and discussed in the spectroscopic literature in detail. However, until now at least one problem is still open, namely, the problem on the ambiguity in the torsion-rotational Hamiltonian. Similar situation for normal molecules has caused numerous problems; it was discussed, for example, in Refs. 1-5. It is interesting to consider the problem of ambiguity as applied to molecules with internal rotation.

Similar situations occurred rather often when studying normal rigid molecules until publication of a series of papers by Watson (Refs. 1-3). These papers analyzed the problem of ambiguity as applied to asymmetric molecules.

For a better understanding of the following estimates, Appendices A and B give some notes to the problems of

(a) derivation of the exact rotational-vibrational Hamiltonian of a molecule;

(b) construction of the effective operator.

2. Effective torsion-rotational Hamiltonian

As shown in the Appendix B, the effective operator (the effective torsion-rotational operator in our case) can be derived in different ways. Nevertheless, all possible effective operators turn out to be related to each other through unitary transformations, namely:

$$\tilde{H}^{\text{ef}} = P^+ H^{\text{ef}} P, \quad (1)$$

where

$$P^+ P = P P^+ = 1. \quad (2)$$

Here the operators \tilde{H}^{ef} , H^{ef} , and P depend on the rotational variables θ , φ , χ , and the torsion variable ρ .

Then the structure of torsion-rotational energy levels can be determined using any effective operator H^{ef} , and any of such effective Hamiltonians can be obtained in the way shown in the Appendix B. On the other hand, the effective Hamiltonian can be derived based only on known symmetry properties of a molecule. (For a CH₃-XH type molecule of the G_6 symmetry group, the table of characters, as well as the properties of the rotational variables θ , φ , χ , and the torsion variable ρ are given in Tables 1 and 2).

Table 1. Table of characters of the $G_6 = C_{3v}$ symmetry group.

Symmetry	e	$2C_3$ (132) (123)	$3\sigma_v$ (13)* (12)* (23)*	Operator	Vibrational functions
A_1	1	1	1	J_y , $\cos(3n\rho)$	$ v_i\rangle$
A_2	1	1	-1	J_x, J_z, J_ρ $\sin(3n\rho)$	$ v_j\rangle$
e	2	-1	0	-	-

Table 2. Transformations of rotational and torsion variables in G_6 .

Symmetry operation	χ	θ	φ	ρ
(123)	χ	θ	φ	$\rho + 2\pi/3$
(23)*	$\pi - \chi$	$\pi - \theta$	$\pi + \varphi$	$-\rho$

Then the effective Hamiltonian can be written in the following form (for an isolated vibrational state):

$$H_v = \sum_{pqrs} \sum_{n \in C} X_{pqrs}^{nC} \{f_{nC}(\rho), J_\rho^s\} + (J_x^p J_y^q J_z^r + J_z^q J_y^r J_x^p), \quad (3)$$

where X_{pqrs}^{nC} are the parameters, which, on the one hand, can be derived from analysis of experimental data, while on the other hand, can be written in the analytical form as functions of fundamental

characteristics of the molecule (see Appendices A and B); $J_x, J_y,$ and J_z are components of the total angular momentum;

$$J_\rho = -i \hbar \frac{\partial}{\partial \rho}; \quad f_{nA_1} = \cos 3n \rho; \quad f_{nA_2} = \sin 3n \rho,$$

where i is an imaginary unit; \hbar is Plank's constant; n is a positive integer; A denotes symmetry.

Having analyzed the derivation of the effective Hamiltonian $H_{(v)}$ with the use of formulas from the Appendices A and B, we can show that the parameters X_{pqrs}^{nC} must have different order of smallness. Actually, assume that λ is Born–Oppenheimer parameter: $\lambda \approx \sqrt[4]{m_e/M}$ or $\lambda \approx \sqrt{B_\alpha/\omega}$, where m_e is the electron mass; M is the average mass of nuclei of a molecule; B_α is the mean value of the rotational constant; ω is the mean harmonic frequency of vibrations. Then, according to formulas from the Appendix A, it turns out that the parameters X_{pqrs}^{0C} ($p + q + r + s = k$) must be on the order of λ^m as compared with the parameters X_{pqrs}^{0C} ($\tilde{p} + \tilde{q} + \tilde{r} + \tilde{s} = 1$); here $m = k/1$.

In those estimates, it was assumed that the "main" parameters X_{0002}^{0q} (corresponding to the parameter F in standard designations) and $X_{2000}^{0q}, X_{0200}^{0q},$ and X_{0020}^{0q} (corresponding to the rotational parameters $A, B,$ and q) have the same order of smallness.

In the general case, the effective operator $H_{(i)}$ must satisfy some requirements, namely⁵:

- 1) it must be Hermitian, that is

$$H_{(v)}^\dagger = H_{(v)} \quad (4)$$

or

$$\sum_{pqrs} \sum_{nC} (X_{pqrs}^{nC})^* \sum_{pqrsnC} X_{pqrs}^{nC} \{f_{nC}(\rho), J_\rho^s\}_+ (J_x^p J_y^q J_z^r + J_z^r J_y^q J_x^p) = \sum_{pqrs} \sum_{nC} X_{pqrs}^{nC} \{f_{nC}(\rho), J_\rho^s\}_+ (J_x^p J_y^q J_z^r + J_z^r J_y^q J_x^p). \quad (5)$$

In Eq. (5) it is taken into account that $J_x, J_y, J_z, J_\rho, f_{nC}(\rho)$ are Hermitian and every of $J_x, J_y,$ and J_z commutes with J_ρ and f_{nq} . It follows from Eq. (5) that the parameters X_{pqrs}^{nC} must be real;

2) $H_{(v)}$ must be transformed by the fully symmetric representation A_1 under the symmetry operations of the group G_6 , that is, $X_{pqrs}^{nA_1} \neq 0$ only for even values of the sums $(p + r + s)$ and $X_{pqrs}^{nA_2} \neq 0$ for the odd sums $(p + r + s)$;

3) The Hamiltonian $H_{(v)}$ must be invariant to the inversion of time:

$$\sum_{pqrsnC} X_{pqrs}^{nC} \{f_{nC}(\rho), J_\rho^s\}_+ (J_x^p J_y^q J_z^r + J_z^r J_y^q J_x^p) = (-1)^{p+q+r+s} \sum_{pqrsnC} X_{pqrs}^{nC} \{f_{nC}(\rho), J_\rho^s\}_+ (J_x^p J_y^q J_z^r + J_z^r J_y^q J_x^p), \quad (6)$$

that is, the parameters $X_{pqrs}^{nA_1}$ and $X_{pqrs}^{nA_2}$ are nonzero only for odd sums $(p + r + s)$. The largest of the parameters

X_{pqrs}^{nC} are given in Table 3. The corresponding orders of the parameters in terms of λ^m are also given in Table 3.

Table 3. Symmetry-allowed parameters X_{pqrs}^{1C} ($p + q + r + s = 2$) of the effective Hamiltonian H_2 .

X_{pqrs}^{nC}						X^l
P	Q	R	S	C	$n = 1, 2, 3$	l
2	0	0	0	A_1	n	$2n$
0	2	0	0	A_1	n	$2n$
0	0	2	0	A_1	n	$2n$
1	0	1	0	A_1	n	$2n$
1	0	0	1	A_1	n	$2n$
0	0	1	1	A_1	n	$2n$
0	0	0	2	A_1	n	$2n$
1	1	0	0	A_2	n	$2n$
0	1	1	0	A_2	n	$2n$
0	1	0	1	A_2	n	$2n$

P	Q	R	S	C	$n^* = 0, 1, 2$	$l^* = 4$
					$n^* \geq 3$	$l^* = 2n^*$
4	0	0	0	A_1	n^*	l^*
0	4	0	0	A_1	n^*	l^*
0	0	4	0	A_1	n^*	l^*
0	0	0	4	A_1	n^*	l^*
2	2	0	0	A_1	n^*	l^*
2	0	2	0	A_1	n^*	l^*
2	0	0	2	A_1	n^*	l^*
0	2	2	0	A_1	n^*	l^*
0	2	0	2	A_1	n^*	l^*
0	0	2	2	A_1	n^*	l^*
3	0	1	0	A_1	n^*	l^*
3	0	0	1	A_1	n^*	l^*
1	0	3	0	A_1	n^*	l^*
0	0	3	1	A_1	n^*	l^*
1	0	0	3	A_1	n^*	l^*
0	0	1	3	A_1	n^*	l^*
2	0	1	1	A_1	n^*	l^*
1	2	1	0	A_1	n^*	l^*
1	2	0	1	A_1	n^*	l^*
0	2	1	1	A_1	n^*	l^*
1	0	2	1	A_1	n^*	l^*
1	0	1	2	A_1	n^*	l^*
3	1	0	0	A_2	n^*	l^*
1	3	0	0	A_2	n^*	l^*
0	3	1	0	A_2	n^*	l^*
0	3	0	1	A_2	n^*	l^*
0	1	3	0	A_2	n^*	l^*
0	1	0	3	A_2	n^*	l^*
2	1	1	0	A_2	n^*	l^*
2	1	0	1	A_2	n^*	l^*
1	1	2	0	A_2	n^*	l^*
0	1	2	1	A_2	n^*	l^*
0	1	1	2	A_2	n^*	l^*
1	1	0	2	A_2	n^*	l^*
1	1	1	1	A_2	n^*	l^*

The order of smallness of the parameters X_{pqrs}^{nC} was estimated using the Hamiltonian (A.1) from Appendix A and general formulas for the effective Hamiltonian (see Appendix B). In this case, the effective Hamiltonian can be presented in the following form:

$$H^{\text{ef}} = \lambda^0 H_0 + \lambda^2 H_2 + \lambda^4 H_4 + \dots,$$

where H_n is the operator of the order of λ^n as compared with the zero order of smallness of the operator H_0 .

3. Ambiguity in torsion-rotational Hamiltonian

Let us consider the unitary transformation of the effective operator (1) in a more detail. Obviously, the form of the operator H^{ef} does not change at a random unitary transformation, that is, H^{ef} and \tilde{H}^{ef} must have the same structure (3), but different values of the parameters X_{pqrs}^{nC} and \tilde{X}_{pqrs}^{nC} . In this situation it is important to address the following questions:

a) A set of what parameters obtained from analysis of the spectrum (X_{pqrs}^{nC} and \tilde{X}_{pqrs}^{nC}) should be used for determination of really fundamental characteristics of the molecule?

b) How many and which parameters are independent?

To answer these questions, let us take into account that the unitary operator P in Eq. (1) depends on the same operators, as the operators H^{ef} and \tilde{H}^{ef} do. Furthermore:

a) Because the operator P is unitary by definition, it can be presented in the exponential form

$$P = \exp(iS), \quad (7)$$

where $S = S^+$ is the Hermitian operator;

b) Because the Hamiltonian H^{ef} in Eq. (1) is a set of operators of different orders of smallness, it is reasonable to believe that the operator S in Eq. (7) is also a series expansion into operators of different orders of smallness:

$$S = \sum_l S_l; \quad (8)$$

c) In the general case any of the S_l operators can be presented in the form

$$S_l = \sum_{pqrsnC} {}^l S_{pqrs}^{nC} \{f_{nC}(\rho), J_\rho^s\}_+ (J_x^p J_y^q J_z^r + J_z^r J_y^q J_x^p); \quad (9)$$

d) The operators S_l must be transformed by the irreducible representation A_1 of the symmetry group of a molecule and must alternate the sign at the inversion of time. The latter circumstance means that the parameters ${}^l S_{pqrs}^{nC}$ must be real and nonzero for odd values of the sum $(p + q + r + s)$. Moreover, ${}^l S_{pqrs}^{nA_1} = 0$ for odd values of the sum $(p + r + s)$ and ${}^l S_{pqrs}^{nA_2} = 0$ for the even sum $(p + r + s)$. The nonzero parameters ${}^l S_{pqrs}^{nC}$, which satisfy these conditions, are presented in the Table 4.

Table 4. Symmetry-allowed parameters of the ambiguity S_{pqrs}^{nC} ($p + q + r + s = 1, 3$).

P	Q	R	S	n	C
0	1	0	0	n	A_1
1	0	0	0	n	A_2
0	0	1	0	n	A_2
0	0	0	1	n	A_2
2	1	0	0	n	A_1
0	1	2	0	n	A_1
0	1	0	2	n	A_1
0	3	0	0	n	A_1
1	1	1	0	n	A_1
1	1	0	1	n	A_1
0	1	1	1	n	A_1
3	0	0	0	n	A_2
0	0	3	0	n	A_2
0	0	0	3	n	A_2
2	0	1	0	n	A_2
2	0	0	1	n	A_2
0	0	2	1	n	A_2
1	0	2	1	n	A_2
0	0	1	2	n	A_2
1	0	0	2	n	A_2
1	0	1	1	n	A_2
1	2	0	0	n	A_2
0	2	1	0	n	A_2
0	2	0	1	n	A_2

Assume that (as is usually believed in the rotational-vibrational theory) the operator $\exp(iS)$ in Eq. (7) performs the small transformation of the initial Hamiltonian H^{ef} (that is, summation in Eq. (8) for $M \hat{E} 1$). In this case the exponential operator $\exp(iS)$ can be presented as a series expansion

$$\exp(iS) = 1 + \sum_l iS_l + \frac{1}{2!} (\sum_l iS_l)^2 + \dots, \quad (10)$$

and the transformed effective Hamiltonian can be derived in the following form:

$$\begin{aligned} \tilde{H}^{\text{ef}} &= \tilde{H}_0^{\text{ef}} + \tilde{H}_1^{\text{ef}} + \dots = \\ &= \sum_{pqrsnC} \tilde{X}_{pqrs}^{nC} \{f_{nC}(\rho), J_\rho^s\}_+ (J_x^p J_y^q J_z^r + J_z^r J_y^q J_x^p) = \\ &= H^{\text{ef}} + \sum_l [iS_l, H^{\text{ef}}] + \frac{1}{2!} \sum_{ml} [iS_m, [iS_l, H^{\text{ef}}]] + \dots \end{aligned} \quad (11)$$

The right-hand side of Eq. (11) is the sum of the operators the left-hand side of it is dependent on, that is, the parameters \tilde{X}_{pqrs}^{nC} of the transformed effective Hamiltonian are functions of not only the parameters \tilde{X}_{pqrs}^{nC} of the initial effective operator but also of the parameters ${}^l S_{pqrs}^{nC}$ entering into Eq. (8). This means that not all the X_{pqrs}^{nC} parameters of the effective Hamiltonian are independent. The dependence between the parameters can be excluded by the corresponding choice of the variables ${}^l S_{pqrs}^{nC}$. At the same time, studying the dependence of the parameters \tilde{X}_{pqrs}^{nC} on X_{pqrs}^{nC} and ${}^l S_{pqrs}^{nC}$ favors better understanding and explanation of some discrepancies following from the results of theoretical analysis of different experimental data.

Consider Eq. (11) in a more detail. As seen from the data presented in Tables 3 and 4 the zeroth approximation gives the following results:

$$\tilde{H}_0 = H_0 \quad \text{or} \quad \tilde{X}_{pqrs}^{0A_1} = X_{pqrs}^{0A_1} \quad (12)$$

for the following combinations of the subscripts $p, q, r,$ and s : 2000, 0200, 0020, 0002, 1001, 0011, 1010.

We have omitted the expressions corresponding to the contribution to the rotational potential function because there were no problems with the ambiguity in the potential function.

The next approximation in Eq. (1) gives

$$\tilde{H}_2 = H_2 + [iS_2, H_0]. \quad (13)$$

With the appearance of the operator of the order of λ^1 in the effective Hamiltonian, we have neglected the contribution from the operators S_1 of the first order in Eq. (8). In other words, the operator $S_1 = S_{0100}^{0A_1} J_y$ can be included into S from Eq. (8). However, this gives only small corrections to the parameters $X_{pqrs}^{0A_1}$.

As seen from Table 3, in this case seven parameters of the type $X_{pqrs}^{1A_1}$ and three parameters of the type $X_{pqrs}^{1A_2}$ will become allowed from the viewpoint of symmetry (in both cases $p + q + r + s = 2$). At the same time, according to Table 4, four parameters of the type S_2 are allowed in Eq. (3), namely, ${}^{(2)}S_{0100}^{1A_1}$, ${}^{(2)}S_{1000}^{1A_2}$, ${}^{(2)}S_{0010}^{1A_2}$, ${}^{(2)}S_{0001}^{1A_2}$, i.e., ten symmetry allowed spectroscopic parameters of the type X_{pqrs}^{1C} ($p + q + r + s = 2$) are related to each other with four additional relations. Consequently, only six parameters X_{pqrs}^{1C} ($p + q + r + s = 2$) can be considered independent; just these parameters can be found from analysis of the experimental data.

Analysis of Eq. (13) based on the data from Tables 3 and 4 gives the relations between the parameters \tilde{X}_{pqrs}^{1C} ($p + q + r + s = 2$). These relations are given in Table 5 in the following form:

$$\begin{aligned} (\tilde{X}_{pqrs}^{1C} - X_{pqrs}^{1C})/\hbar = \Delta_{pqrs} = & \alpha_1^{(2)} S_{1000} + \alpha_2^{(2)} S_{0100} + \\ & + \alpha_3^{(2)} S_{0010} + \alpha_4^{(2)} S_{0001}. \end{aligned} \quad (14)$$

As seen from Table 5, the parameter $X_{0200}^{1A_1}$, that is, the difference $(F_v - q_2)$ in the standard designations (see Table 6 for correspondence between the standard designations and those used in this paper) remains unchanged after unitary transformation (1). At the same time, any of the rest nine parameters can be changed.

The data of Table 5 allow one:

a) to select six of the ten parameters X_{pqrs}^{1C} , which should be used as independent variables in analysis of the experimental data. The rest of four parameters can be found by setting the parameters $\tilde{X}_{0101}^{1A_2}$, $\tilde{X}_{0110}^{1A_2}$, $\tilde{X}_{1100}^{1A_2}$, and $\tilde{X}_{1100}^{1A_2}$ zero in Eq. (4). At the same time, assuming that the parameters X_{pqrs}^{1q} in Eq. (14) are found from the fundamental characteristics of the torsion-rotational-

vibrational Hamiltonian (A.1) using the formulas from the Appendices A and B, we can determine the unique correct relations between the parameters obtained from analysis and from the fundamental characteristics;

b) to determine the relations between the set of parameters obtained in analysis of the same experimental data. In the latter case, we can write the following relations (using the relations between the parameters from Table 6):

$$\tilde{F}_v - \tilde{C}_2 = F_v - C_2. \quad (15)$$

That is, the difference $(F_v - q_2)$ must be invariant at any set of the parameters obtained from analysis of the same experimental data:

$$\begin{aligned} \frac{2\rho}{F} (\tilde{X}_{1001}^{1A_1} - X_{1001}^{1A_1}) + \frac{\tilde{d}_{ab} - d_{ab}}{2} + \\ + \frac{\tilde{F}_v - F_v + \tilde{C}_2 - C_2}{4D_{ab}} [B - A + \rho^2/4F] = 0; \end{aligned} \quad (16)$$

$$\begin{aligned} \frac{2D_{ab}}{F} (\tilde{X}_{1001}^{1A_1} - X_{1001}^{1A_1}) + \rho(\tilde{F}_v - F_v + \tilde{C}_2 - C_2)/4F + \\ + (B - C)(2\tilde{F}_v - 2F_v + \tilde{C}_2 - C_2 + \tilde{k}_5 - k_5)/\rho + \\ + 3(\tilde{D}_{bc} - D_{bc}) = 0; \end{aligned} \quad (17)$$

$$\begin{aligned} [(2F/\rho) - (\rho/2F)](\tilde{F}_v - F_v + \tilde{k}_5 - k_5) + \\ + 2F(\tilde{F}_v - F_v + \tilde{C}_2 - C_2)/\rho - 2(\tilde{k}_6 - k_6) = 0; \end{aligned} \quad (18)$$

$$\begin{aligned} \frac{2(C - A)}{F} (\tilde{X}_{1001}^{1A_1} - X_{1001}^{1A_1}) + \\ + \left(\frac{C - A}{F} + 9\right) \frac{\rho}{D_{ab}} \frac{\tilde{F}_v - F_v + \tilde{C}_2 - C_2}{4} + 3(\tilde{D}_{ac} - D_{ac}) - \\ - \frac{D_{ab}}{\rho}(2\tilde{F}_v + \tilde{C}_2 + \tilde{k}_5 - 2F_v - C_2 - k_5) = 0; \end{aligned} \quad (19)$$

$$\begin{aligned} \left(\frac{18F}{D_{ab}} - \frac{\rho^2}{2FD_{ab}}\right) (\tilde{F}_v - F_v + \tilde{C}_2 - C_2) + \\ + 24(\tilde{X}_{0101}^{1A_1} - X_{0101}^{1A_1}) - \frac{4\rho}{F} (\tilde{X}_{0101}^{1A_1} - X_{0101}^{1A_1}) = 0. \end{aligned} \quad (20)$$

A similar approach to the next approximation in the Eq. (11) allows analysis of the centrifugal distortions X_{pqrs}^{0q} ($p + q + r + s = 4$). In this case, as seen from Tables 3 and 4, 20 parameters of ambiguity ${}^{(4)}S_{pqrs}^{0q}$ ($p + q + r + s = 3$) (7 ${}^{(4)}S_{pqrs}^{0A_1}$ and 13 ${}^{(4)}S_{pqrs}^{0A_2}$) can exclude 20 of 35 parameters X_{pqrs}^{0q} ($p + q + r + s = 4$). That is, only 15 parameters X_{pqrs}^{0q} can be considered independent and used in analysis of the experimental data.

Table 5. Relations between the parameters \tilde{X}_{pqrs}^{1C} and X_{pqrs}^{1C} ($p + q + r + s = 2$) of the effective Hamiltonians \tilde{H}_2 and H_2 .

C_{pqrs}	α_1	α_2	α_3	α_4
A_12000	$-12X_{1001}$	$4X_{1010}$	—	—
A_10200	—	—	—	—
A_10020	—	$-4X_{1010}$	$-12X_{0011}$	—
A_10002	—	—	—	$-24X_{0002}$
A_11010	$-12X_{0011}$	$8(X_{0020} - X_{2000})$	$-12X_{1001}$	—
A_11001	$-24X_{0002}$	$4X_{0011}$	—	$-12X_{1001}$
A_10011	—	$-4X_{1001}$	$-24X_{0002}$	$-12X_{0011}$
A_11100	$-4X_{1010}$	$12X_{1001}$	$8(X_{2000} - X_{0200})$	—
A_10110	$8(X_{0200} - X_{0020})$	$12X_{0011}$	$4X_{1010}$	—
A_10101	$-4X_{0011}$	$24X_{0002}$	$4X_{1001}$	—

Note. For brevity $X_{pqrs} \equiv X_{pqrs}^{0A1}$.

Table 6. Relations between the parameters X_{pqrs}^{nC} used in the literature and in this paper.

NC_{pqrs}	Parameters used in the literature
$0A_10002$	$F/4$
$0A_10011$	$\rho/4$
$0A_10020$	$A/4$
$0A_12000$	$B/4$
$0A_10200$	$C/4$
$0A_11010$	$D_{ab}/2$
$0A_10004$	$K_4/4$
$1A_10002$	$-K_7/2$
$0A_10013$	$K_3/4$
$1A_10011$	$-K_6/2$
$0A_10022$	$(G_v + K_2)/4$
$0A_10202$	$(G_v - 2C_1)/4$
$0A_12002$	$(G_v + 2C_1)/4$
$0A_11012$	$\Delta_{ab}/2$
$1A_20110$	$D_{ac}/2$
$1A_12000$	$-(F_v + C_2)/4$
$1A_10200$	$-(F_v - C_2)/4$
$1A_10020$	$-(F_v + K_3)/4$
$1A_11010$	$-D_{ab}/2$
$0A_10031$	$(K_1 + L_v)/4$
$0A_10211$	$(L_v - 2C_4)/4$
$0A_12011$	$(L_v + 2C_4)/4$
$0A_11021$	$\delta_{ab}/2$
$0A_14000$	$(-\Delta_j - 2\delta_j - \delta_{jk})/4$
$0A_10400$	$(-\Delta_j + 2\delta_j - \delta_{jk})/4$
$0A_10040$	$(-\Delta_j - \Delta_k - \Delta_{jk})/4$
$0A_12200$	$(-\Delta_j + \delta_{jk})/2$
$0A_12020$	$(-\Delta_j - 0.5\Delta_{jk} - \delta_k - \delta_j)/2$
$0A_10220$	$(-\Delta_j - 0.5\Delta_{jk} + \delta_k + \delta_j)/2$
$0A_11210$	$(D_{abj} - 2D_{abjk})/2$
$0A_13010$	$(D_{abj} + 2D_{abjk})/2$
$0A_11030$	$(D_{abk} + D_{abj})/2$
$1A_21030$	$D_{ba}/2$

Note. D_{abjk} denotes the parameters at $[(J_x J_z + J_z J_x), J_x^2 - J_y^2]_+$, and $(-\delta_{jk})$ is the parameter at $(J_b^2 - J_c^2)^2$, that is, the contribution is $[-\delta_{jk}(J_b^2 - J_c^2)^2]$.

Table 7 gives the relations between the fourth-order parameters of the transformed and initial torsion-rotational Hamiltonians as functions of the parameters of ambiguity $({}^4)S_{pqrs}^{0q}$ ($p + q + r + s = 3$).

Table 7. Relations between the parameters \tilde{X}_{pqrs}^{nC} and X_{pqrs}^{nC} ($p + q + r + s = 4$) of the effective Hamiltonians \tilde{H}_4 and H_4 .

$\Delta X_{004} = 0$
$\Delta X_{102} = 24S_{111}X_{002}$
$\Delta X_{200} = -6S_{111}X_{100}$
$\Delta X^{004} = 4S^{012}X^{101}$
$\Delta X^{022} = 8S^{111}X^{002} - 8S^{111}X^{101} + 12S^{030}X^{101}$
$\Delta X^{040} = 0$
$\Delta X^{103} = -8S^{012}X^{002} + 4S^{111}X^{101} + 8S^{012}X^{200}$
$\Delta X^{121} = -24S^{030}X^{002} + 16S^{210}X^{002} + 16S^{012}X^{020}\Delta X^{103} - 16S^{210}X^{020} - 16S^{012}X^{200} + 24S^{030}X^{200}$
$\Delta X^{202} = 8S^{111}(X^{200} - X^{002}) + 4(-S^{012} + S^{210})X^{101}$
$\Delta X^{220} = 8S^{111}(X^{002} - X^{200}) - 12S^{030}X^{101} + 8S^{210}X^{101}$
$\Delta X^{301} = 8S^{210}(X^{200} - X^{002}) - 4S^{111}X^{101}$
$\Delta X^{400} = -4S^{210}X^{101}$
$\Delta X_{001}^{003} = 4S_{001}^{011}X^{101} + 4S_{001}^{012}X_{001}^{100}$
$\Delta X_{001}^{021} = -4S_{001}^{011}X^{101} + 8S_{001}^{110}(X^{002} - X^{020}) + 4S^{111}X_{001}^{001} - 8S_{001}^{012}X_{001}^{100} + 12S_{001}^{030}X_{001}^{100}$
$\Delta X_{001}^{102} = 4S_{001}^{110}X^{010} + 8S_{001}^{011}(X^{200} - X^{002}) - 4S_{001}^{012}X_{001}^{001} + 4S_{001}^{111}X_{001}^{100}$
$\Delta X_{001}^{120} = 4S_{001}^{110}X^{101} + 8S_{001}^{011}(X^{020} - X^{200}) - 12S_{001}^{030}X_{001}^{001} - 8S_{001}^{210}X_{001}^{001} - 4S_{001}^{111}X_{001}^{100}$
$\Delta X_{001}^{201} = -4S_{001}^{011}X^{101} + 8S_{001}^{110}(X^{200} - X^{002}) - 4S_{001}^{111}X_{001}^{001} + 4S_{001}^{210}X_{001}^{100}$
$\Delta X_{001}^{300} = -4S_{001}^{110}X^{101} - 4S_{001}^{210}X_{001}^{001}$
$\Delta X_{002}^{002} = 4S_{002}^{010}X^{101} + 4S_{001}^{011}X_{001}^{100}$
$\Delta X_{002}^{020} = 4S_{001}^{110}X_{001}^{001} - 4S_{001}^{011}X_{001}^{100}$
$\Delta X_{002}^{101} = -4S_{001}^{011}X_{001}^{001} + 8S_{002}^{010}(X^{200} - X^{002}) + 4S_{001}^{110}X_{001}^{100} - 4S_{001}^{111}X_{001}^{100}$
$\Delta X_{002}^{200} = -4S_{002}^{010}X^{101} - 4S_{001}^{110}X_{001}^{001}$
$\Delta X_{003}^{001} = 4S_{002}^{010}X_{001}^{100}$
$\Delta X_{003}^{100} = -4S_{002}^{010}X_{001}^{001}$
$\Delta X_{100}^{002} = 4S_{100}^{010}X^{101} + 12S_{110}^{001}X_{001}^{001}$
$\Delta X_{100}^{020} = 0$
$\Delta X_{100}^{200} = -4S_{100}^{010}X^{101} + 12S_{110}^{100}X_{001}^{100}$
$\Delta X_{101}^{001} = 24S_{110}^{001}X_{002} + 12S_{111}X_{001}^{001} + 4S_{100}^{010}X_{001}^{100}$
$\Delta X_{101}^{100} = 24S_{110}^{100}X_{002} - 4S_{100}^{010}X_{001}^{001} + 12S_{111}X_{001}^{100}$
$\Delta X_{110}^{011} = 12S_{001}^{011}X_{100} + 8S_{110}^{100}(X^{002} - X^{020}) - 4S_{110}^{001} - 12S_{100}^{010}X_{001}^{001}$
$\Delta X_{110}^{110} = 12S_{001}^{110}X_{100} + 8S_{110}^{001}(X^{020} - X^{200}) + 4S_{110}^{100} - 12S_{100}^{010}X_{001}^{001}$
$\Delta X_{111}^{010} = 24S_{002}^{010}X_{100} - 24S_{100}^{010}X_{002} + 4S_{110}^{100}X_{001}^{001} - 4S_{110}^{001}X_{001}^{100}$

Note. Here $\Delta X_{nC_s}^{pqr} = \tilde{X}_{nC_s}^{pqr} - X_{nC_s}^{pqr}$.

Appendix A

It can be shown that the main part of the torsion-rotational Hamiltonian (dependent on the operators $J_x, J_y, J_z,$ and J_ρ) for a molecule having a large-amplitude motion can be written in the following form:

$$H = \frac{1}{2} \sum_{\lambda} P_{\lambda}^2 + \frac{1}{2} \sum_{ij} \mu_{ij}(q_{\lambda}, \rho)(J_i - G_i)(J_j - G_j) + V(q_{\lambda}, \rho), \tag{A.1}$$

where $i, j = x, y, z, \rho;$ $G_i = \sum_{\lambda \vartheta} \zeta_{\lambda \vartheta}^i q_{\lambda} p_{\vartheta}$ (subscripts $\alpha = x, y, z, \lambda, \nu$ denote different small-amplitude oscillations); $\zeta_{\lambda \vartheta}^{\alpha} = \sum_{N\beta\gamma} \varepsilon_{\alpha\beta\gamma} M_{\beta\lambda} M_{\gamma\vartheta};$ $\zeta_{\lambda\nu}^{\rho} = -\zeta_{\vartheta\lambda}^{\rho} = \sum_{N\alpha} M_{\alpha\vartheta} \frac{dM_{\alpha\lambda}}{d\rho};$ parameters $M_{\alpha\nu}$ depend on the torsion angle $\rho;$

$$\mu_{ij}(q, \rho) = \mu_{ij}^0 + \sum_{\lambda} \mu_{ij}^{\lambda}(\rho) q_{\lambda} + \sum_{\lambda \vartheta} \mu_{ij}^{\lambda \vartheta}(\rho) q_{\lambda} q_{\vartheta} + \dots, \tag{A.2}$$

μ_{ij} in (A.2) are parameters of different order of smallness; μ_{ij}^0 are independent of ρ and are of the order of λ^2 in relative to the main part (harmonic vibrations) of the Hamiltonian (A.1); μ_{ij}^{λ} are parameters of the order of $\lambda^3;$ they can be divided into two parts: (a) those that depend on $\sin 3\rho$ and $\cos 3\rho$ and (b) independent of the torsion parameter $\rho;$ $\mu_{ij}^{\lambda \vartheta}(\rho)$ are the parameters of the order of $\lambda^4,$ dependent on $\sin^2 3\rho, \cos^2 3\rho,$ and $\sin\rho \cos\rho$ (or, in other words, on $\sin 6\rho$ and $\cos 6\rho$), etc.

The potential function $V(q, \rho)$ can be presented as

$$V(q, \rho) = \sum_{\lambda} \omega_{\lambda} q_{\lambda}^2 + \sum_{\lambda\mu\nu} k_{\lambda\mu\nu}(\rho) q_{\lambda} q_{\mu} q_{\nu} + (1 - \cos 3\rho) + \sum_{\lambda\mu\nu\xi} k_{\lambda\mu\nu\xi}(\rho) q_{\lambda} q_{\mu} q_{\nu} q_{\xi} + \dots$$

The second term here is of the order of λ^1 relative to the main part, the next two terms are of the order of $\lambda^2,$ etc.

Appendix B

If the operator theory of perturbations is presented in the matrix form, then the effective torsion-rotational Hamiltonian of the isolated vibrational state $|v\rangle$ can be written in the general case as

$$H_{(v)}^{ef} = \langle v | \sum_{mklpq=1} \frac{1}{m!} [iS_k, [iS_l, \dots [iS_p, H_0 + \sum_{q=1} H_q] \dots]] | v \rangle. \tag{B.1}$$

Here the subscript m is the number of the commutator in the considered term; the subscripts k and q in S_k and H_q show the orders of smallness of the corresponding operators; H_0 and $|v\rangle$ are the zero-order

operator and its wave functions. It is important that the effective operator $H_{(v)}^{ef}$ can only be considered determined if all the matrix elements $\langle \tilde{v} | iS_k | \tilde{v} \rangle$ are determined in Eq. (B.1). At the same time it can be shown¹⁰ that any effective operator, for which:

- 1) the matrix elements $\langle v | iS_k | \tilde{v} \rangle$ and $\langle \tilde{v} | iS_k | v \rangle$ ($\tilde{v} \neq v$) are calculated as

$$\langle v | iS_n | \tilde{v} \rangle = \frac{1}{\langle \tilde{v} | H_0 | \tilde{v} \rangle - \langle v | H_0 | v \rangle} \times \langle v | \sum_{mklpq} \frac{1}{m!} [iS_k, [iS_l, \dots [iS_p, H_0 + \sum_q H_q] \dots]] | v \rangle \tag{B.2}$$

(in Eq. (B.1) only the terms for which $(m + k + \mu + p + q = n)$ are summed);

- 2) any other matrix elements $\langle v | iS_k | v \rangle$ and $\langle \tilde{v} | iS_k | \tilde{v} \rangle$ ($\tilde{v} \neq v$) are not determined by Eq. (B.2) and can be considered as random operators. This means that:

a) for the vibrational state considered we can obtain an unlimited set of Hamiltonians, every of which is correct;

b) the simplest method to obtain the effective Hamiltonian is to set the matrix elements $\langle v | iS_k | v \rangle$ and $\langle \tilde{v} | iS_k | \tilde{v} \rangle$ ($\tilde{v}, \tilde{v} \neq v$) equal to zero.

At the same time it can be shown¹⁰ that the ambiguity arising in the effective Hamiltonians of the type of Eq. (B.1) is none other than the unitary equivalence of different effective operators, that is,

$$\tilde{H}^{ef} = P^+ H^{ef} P,$$

where \tilde{H}^{ef} and H^{ef} are two different effective operators for the same vibrational state; these operators are constructed in accordance with Eq. (B.1); P is the unitary operator depending on the torsion and rotational parameters.

Analysis we have done above favors understanding of some differences in the results of analysis of torsion-rotational spectra.⁶⁻⁹

The Hamiltonian H^{ef} , which has been analyzed in this paper, differs by the term $X_{1001}^{0A_1} J_x J_\rho$ from the Hamiltonian used in Refs. 6-9. Nevertheless, the unitary transformation of the form $\exp(-2\pi C J_y / h) H^{ef} \exp(-2\pi C J_y / h),$ where $q = \frac{X_{1001}^{0A_1}}{X_{0011}^{0A_1}},$

can exclude the term $X_{1001}^{0A_1} J_x J_\rho.$ In this case all the above results and conclusions are correct.

In particular, in Ref. 8 devoted to global analysis of $v_t = 0, 1, 2$ torsion states, 17 quartic centrifugal distortion parameters corresponding to X_{pqrs}^{0q} ($p + q + r + s = 4$) were used as independent. At the same time, from the above analysis it follows that only 15 parameters are really independent. Naturally, the use of dependent parameters may give an unpredictable result. In particular, the parameters may differ widely as in Refs. 8 and 6, 7, and 9.

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