SOME PECULIARITIES OF EFFECTIVE HAMILTONIAN REDUCTION FOR THE INTERACTING STATES IN NONRIGID H_2O-TYPE MOLECULES

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Some peculiarities of effective Hamiltonian reduction have been considered for the interacting vibrational states of nonrigid H_2O*-type molecules. It has been demonstrated that reduced forms of* $H_{nm}^{\rm red}$ *operators describing interaction between vibrational states (n) and (m) depend on the degree of excitation of vibrational quantum number* v_2 *associated with the high-amplitude oscillations.*

1. INTRODUCTION

Analyzing the vibration-rotation spectra of nonrigid H_2O-type molecules, we have revealed the following peculiarities: 1) effective rotational Hamiltonian of isolated vibrational state expressed as a series in the angular momentum operators is a divergent series, 2) the factors (spectroscopic parameters) at the powers of operator J_z (z is the axis of a molecule linearization, along which the inertia tensor is minimum) change significantly with the excitation of quantum number v_2 connected with high-amplitude oscillations. Theoretically these peculiarities have already been considered in Refs. 1–3.

It is natural to assume that these peculiarities influence the form of the effective Hamiltonian written for the group of resonating vibration states. Let us consider the example of Fermi resonance when two vibrational states (1) = (1, 0, 0) and (2) = (0, 2, 0) (here (v_1, v_2, v_3) is vibrational state and v_i are vibrational quantum numbers) of the same symmetry type are interacting. The effective Hamiltonian for the pair of the above-written states has the form of the 2×2 matrix

$$H = \begin{bmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{bmatrix}, \tag{1.1}$$

with the diagonal operators H_{nn} of the following form:

$$H_{nn} = H_0^{(n)} + \sum_{p,q,r} h_{pqr}^{(n)} J^{2q} \{J_+^{2p} (J_z+p)^{2r} + (J_z+p)^{2r} J_-^{2p}\}, \tag{1.2}$$

where $p + q + r = 2, 3, \ldots$, and

$$H_0^{(n)} = E_n + A^{(n)} J_z^2 + B^{(n)} J^2 + C^{(n)} (J_+^2 + J_-^2) \tag{1.3}$$

(n = 1, 2)

is the operator of the zero-order approximation. The operator H_{12} that describes the interaction of vibrational states with the accuracy up to J^3 (to the terms containing the third power of angular momentum operators) can be written in the form[4]

$$H_{12} = F_0 + F_{020} J^2 + F_{002} J_z^2 + F_{200} (J_+^2 + J_-^2) + F_{201} \{J_+^2 (J_z + 1) - (J_z + 1) J_-^2\}. \tag{1.4.}$$

Hamiltonian $\tilde{H}$ transformed by rotation contact transformation (CT) has the form

$$\tilde{H} = e^{iS} H e^{-iS} = \begin{bmatrix} \tilde{H}_{11} & \tilde{H}_{12} \\ \tilde{H}_{21} & \tilde{H}_{22} \end{bmatrix}. \tag{1.5}$$

In this formula the generator of the transformation S also has the form of the two-dimensional matrix

$$S = \begin{bmatrix} S_{11} & S_{12} \\ S_{21} & S_{22} \end{bmatrix}. \tag{1.6}$$

Operators $\tilde{H}_{nm}$ entering into Eq.(1.5) satisfy the following relations[4,5,8]:

$$\tilde{H}_{nn} = H_{nn} + [iS_{nn}, H_{nn}] + i(S_{nm} H_{mn} - H_{nm} S_{mn}) + \ldots, \tag{1.7}$$

$$\tilde{H}_{12} = H_{12} + i (S_{11} H_{12} - H_{12} S_{22}) + i (S_{12} H_{22} - H_{11} S_{12}) + \ldots, \tag{1.8}$$

n, m = 1, 2.

Generators of transformation S_{nn} convert H_{nn} to the reduced form $H^{\rm red}$ obtained by Watson[6] for the isolated vibrational state. Operators H_{nm} are called the reduced operators if the parameters of transformation (parameters of S generators) for these operators are chosen in a definite way. For example, the main generator S_{nn} has the form

$$iS_{nn} = \varepsilon_{21}^{(n)} \{J_+^2 (J_z + 1) - (J_z + 1) J_-^2\}, \tag{1.9}$$

with the parameter $\varepsilon_{21}^{(n)}$ being chosen from the condition

$$\tilde{h}_{200}^{(n)} = h_{200}^{(n)} + 2\, \varepsilon_{21}^{(n)} C^{(n)} = 0. \tag{1.10}$$

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This condition permits one to eliminate the summand $\tilde{h}^{(n)}_{200}\,(J^4_+ + J^4_-)$ from operator $\tilde{H}_{nn}$ and to transform $\tilde{H}_{nn}$ expanded up to terms J^4 to the reduced form m^{red}_{nn}, in the basis $|J, K>$ of rotational wave functions of a symmetric top. The reduced operator has matrix elements $<J, K|\,m^{\text{red}}_{nn}\,|\,J, K + \Delta K>$ only with $\Delta K = 0, \pm 2$ (a three-diagonal form of the effective Hamiltonian in the absence of random resonance).

As stated above, for some nonrigid molecules the considerable change of spectroscopic parameters at the powers of operator J_z is a characteristic feature of excitation of quantum number v_2. As a consequence, $A^{(1)} \neq A^{(2)}$ even in a zero-order approximation (for example, as in the case[7] of H_2O). From this condition it follows that the second summand must be taken into account in the term $m_{22}-m_{11}=(e_2-e_1)+(A^{(2)}-A^{(1)})J_z^2+\ldots$ of Eq. (1.8). By introducing the designation

$$H_0^{(\pm)} = \{H_0^{(1)} \pm H_0^{(2)}\}/2, \tag{1.11}$$

we can write Eq. (1.8) in the form

$$\tilde{H}_{12} = H_{12} + [iS_{12}, H_0^{(+)}] + \{iS_{12}, H_0^{(-)}\} + [iS, H_{12}] + \ldots . \tag{1.12}$$

In this equation it has been considered that $\varepsilon^{(1)}_{12} \cong \varepsilon^{(2)}_{12}$, so that $S_{11} \cong S_{22} \cong S$ (parameters $\varepsilon^{(n)}_{12}$ determined from Eq. (1.10) are expressed through the parameters $h^{(n)}_{200}$ and $C^{(n)}$ which depend weakly on n). Equation (1.12) differs from the analogous one used for semirigid molecules by the presence of anticommutator $\{iS_{12}, H_0^{(-)}\}$ (see, for example, Refs. 4 and 5). The first-order generator of transformation iS_{12} has the form[4]

$$iS_{12} = \gamma_{20}\,(J_+^2 + J_-^2) + \ldots . \tag{1.13}$$

Disregarding in expression for $\tilde{H}_{12}$ the summand $[iS, H_{12}]$ which does not change the form of $\tilde{H}_{12}$ and describes the contribution of higher orders, we find that

$$\begin{aligned}\tilde{H}_{12} &= F_0 + F_{020}J^2 + F_{002}J_z^2 + \tilde{F}_{200}(J_+^2 + J_-^2) + \\ &+ \tilde{F}_{201}\{J_+^2(J_z+1) - (J_z+1)\,J_-^2\} + \\ &+ 2\,\gamma_{20}\,A^{(-)}_{12}\,\{J_+^2\,(J_z+1)^2 + (J_z+1)^2\,J_-^2\} + \ldots .\end{aligned} \tag{1.14}$$

In this expression

$$\tilde{F}_{200} = F_{200} + \{(E_2 - E_1) + 2\,A^{(-)}_{12}\}\,\gamma_{20}, \tag{1.15}$$

$$\tilde{F}_{201} = F_{201} - 4\,A^{(+)}_{12}\,\gamma_{20}, \tag{1.16}$$

and $A^{(\pm)}_{12}$ are defined from the equation

$$A^{(\pm)}_{12} = (A^{(1)} \pm A^{(2)})/2.$$

Choosing the parameter $\gamma_{20} = F_{201}/4\,A^{(+)}_{12}$, we can eliminate the term containing parameter $\tilde{F}_{201}$ from the operator $\tilde{H}_{12}$ and in such a way transform it to the reduced form m^{red}_{12}. However, the summand

$$\Delta H_{12} = 2\,\gamma_{20}\,A^{(-)}_{12}\,\{J_+^2\,(J_z+1)^2 + (J_z+1)^2\,J_-^2\},$$

remains in m^{red}_{12}. This summand is absent in the approximation of such order for the model of semirigid molecules for which it is assumed that $A^{(-)}_{12} = 0$. Let us consider in more detail some peculiarities of accounting for the effects of nonrigidness in the procedure of reduction of the Hamiltonian H given by Eq. (1.1).

2. FERMI PAIRWISE INTERACTION IN NONRIGID H_2O-TYPE MOLECULES

Let us consider again the effective Hamiltonian H given by Eq. (1.1) for the pair of interacting vibrational states $(1) = (1, 0, 0)$ and $(2) = (0, 2, 0)$ having the same symmetry type. The account of strong vibration-rotation interaction is the cause of nonpolynomial character of dependence of zero approximation on operator J_z (see, for example, Refs. 3, 9, and 10)

$$H_n^{(0)} = E_n + h_n(J_z) + B^{(n)}\,J^2 + C^{(n)}\,(J_+^2 + J_-^2). \tag{2.1}$$

Particularly, the operator $h_n(J_z)$ can be expressed in the form[9,10]

$$h_n(J_z) = A^{(n)}\,G_n(J_z), \tag{2.2}$$

where $A^{(n)}$is rotation constant as in Eq. (1.3),

$$G_n(J_z) = 2/\alpha^{(n)}\,(\sqrt{1 + \alpha^{(n)}\,J_z^2} - 1), \tag{2.3}$$

and $\alpha^{(n)}$ is a certain constant dependent on J. Employing the properties of symmetry of a molecule we can write the diagonal operators H_{nn} in the form

$$\begin{aligned}H_{nn} = H_n^{(0)} + \sum_{(p+q+r\,>\,1)} J^{2q}\,\{J_+^{2p}\,(J_z+p)^{2r}\,h^{(n)}_{pqr} + \\ + h^{(n)}_{pqr}\,(J_z+p)^{2r}\,J_-^{2p}\},\end{aligned} \tag{2.4.}$$

where $h^{(n)}_{pqr}$ are some functions dependent on J_z. We can assume[7] that the coefficients $B^{(n)}$ and $q^{(n)}$ in Eq. (2.1) are independent of n, i.e., $B^{(n)} = B$ and $q^{(n)} = q$. According to Refs. 5 and 8 the operator of interaction can be written as

$$\begin{aligned}H_{12} = \sum_{l,k,m} J^{2l}\,\{J_+^{2k}\,(J_z+k)^m\,F_{2k2lm} + \\ + (-1)^m\,F_{2k2lm}\,(J_z+k)^m\,J_-^{2k}\}.\end{aligned} \tag{2.5}$$

In contrast with Refs. 5 and 8, here F_{2k2lm} are some functions of operator J_z. Let us introduce a small parameter $\lambda = 2(\bar{B}/\bar{\omega})^{1/2}$ in the same way as for ordinary molecules ($\bar{B}$ is the mean rotational constant, $\bar{\omega}$ is the mean frequency of harmonic oscillations). For H_2O molecule $\lambda \sim 1/10$. The order of terms Cq^iJ^j in expansion of initial Hamiltonian is determined as λ^{i+j-2} (here C is an arbitrary spectroscopic constant, i is a common power of rotational operators q, and j is a common power of vibrational operators J); therefore, λ^{j+1} is the order of terms in Eq. (2.2) for Fermi resonance formed by operators $C\, q_1\, q_2^2\, J^j$. Such definition is valid for rotation quantum numbers $J \sim 10$. Some exceptions exist in definition of the operator orders because the parameters at operators J_z^{2k} are, as a rule, by an order of magnitude greater than the parameters at operators J^{2k} and $J_\pm^{2k}$. The spectroscopic parameters of the H_2O molecule of the first three orders are presented in Table I. These parameters were calculated from the potential field of a molecule as well as obtained by processing of an experimental spectrum. It is seen from the table that, for example, summands F_0 and $F_{002}\, J_z^2$ are of the same order. The first-order operator of interaction m_{12} has the form

$$H_{12} = F_0 + F_{002}\, J_z^2 + \qquad (\sim\lambda^2)$$

$$+ F_{020}\, J^2 + [J_+^2\, F_{200} + F_{200}\, J_-^2] + \dots\,, \quad (\sim\lambda^3) \qquad (2.6)$$

where $F_0 = F_{000}$.

TABLE I. Values of the effective Hamiltonian parameters of the first three resonating viBrational states of the H_2O *molecule.*

Vibrational centers E_n and rotational constants $A^{(n)}$ (Ref. 7)			
State	(1) = (1, 0, 0)	(2) = (0, 2, 0)	(3) = (0, 0, 1)
E, cm^{-1}	3652.5	3156.2	3755.9
A, cm^{-1}	15.4	23.7	14.9
Calculated parameters of interaction[13] (in cm^{-1})			
$F_0 = 45$		$F_{002} = -0.2$	
$C_{10}^{(1)} = 1$		$C_{11}^{(1)} = 0.3$	
$C_{10}^{(2)} = 0.4$			

Note: The term[13] $< \Psi_n(\rho)|B_1^{zz}(\rho)|\ \Psi_m(\rho) > /\sqrt{2}$ was used to estimate F_{002}.

In the operator $\tilde{H}_{12}$ given by Eq. (1.8) we can disregard the contribution of the commutator $[iS_{nn}, H_{12}]$, which does not change the form of this operator. When calculating $\tilde{H}_{12}$, we use the following properties of the zero-order approximation:

$$H_0^{(n)}\,(J_z \pm k) = H_0^{(n)}(J_z) \pm k\, f^{(n)}(J_z)\,(2\,J_z \pm k); \qquad (2.7)$$

$$[J_+^k,\, h_{nm}^{(+)}] = -\,k\, J_+^k\,(2\,J_z + k)\, f_{nm}^{(+)}, \qquad (2.8)$$

$$\{J_+^k,\, h_{nm}^{(-)}\} = 2\, A_{nm}^{(-)}\, J_+^k\, G\,(J_z + k/2). \qquad (2.9)$$

In these formulas k is an arbitrary integer;

$$f_n(J_z) = A^{(n)}/G_1^{(n)} = A^{(n)}/(1 + \alpha^{(n)}\, J_z^2)^{1/2}, \qquad (2.10)$$

$$f_{nm}^{(\pm)} = A_{nm}^{(\pm)}/G_1,$$

$$A_{nm}^{(\pm)} = (A^{(n)} \pm A^{(m)})/2,\ \alpha_{nm}^{(\pm)} = (\alpha^{(n)} \pm \alpha^{(m)})/2,$$

$$G_1 = (1 + \alpha\, J_z^2)^{1/2}, \quad G = (2/\alpha)\,(G_1 - 1). \qquad (2.11)$$

Consequently $A^{(+)}$ and $\alpha = \alpha^{(+)}$ are some mean values of A and α for two vibrational states. The first-order generators of transformation iS_{12} have the form

$$iS_{12} = (J_+^2\, \gamma_{20} + \gamma_{20}\, J_-^2) + \qquad (\sim\lambda^3)$$

$$+ [J_+^2\,(J_z + 1)\, \gamma_{21} - \gamma_{21}\,(J_z + 1)\, J_-^2] + \qquad (\sim\lambda^4)$$

$$+ (J_+^4 \gamma_{40} + \gamma_{40} J_-^4) + [J_+^2\,(J_z + 1)^2\, \gamma_{22} +$$

$$+ \gamma_{22}\,(J_z + 1)^2\, J_-^2] + \dots \qquad (\sim\lambda^5)$$

$$(2.12)$$

The summands from iS_{12}, which commute with $h_n(J_z)$, are disregarded here. Let us consider the form of the operator ${}^{(k)}m_{12}^{\rm red}$ reduced to λ^{2k}. This operator is obtained from Eq. (1.8) with subsequent fixing of the γ parameter. The operator ${}^{(1)}m_{12}^{\rm red}$ reduced by rotation contact transformation (CT) to λ^2 has the form

$${}^{(1)}H_{12}^{\rm red} = {}^{(1)}\tilde{H}_{12} = F_0 + F_{002}\, J_z^2. \qquad (2.13)$$

The operator reduced to λ^4 is

$${}^{(2)}H_{12}^{\rm red} = F_0 + F_{002}\, J_z^2 + F_{020}\, J^2 + \{J_+^2\, \Psi_2^{(2)}\,(J_z + 1) +$$

$$+ \Psi_2^{(2)}\,(J_z + 1)\, J_-^2\}, \qquad (2.14)$$

where

$$\Psi_2^{(2)}\,(J_z + 1) = \tilde{F}_{200} + 2\, \gamma_{20}\, A_{12}^{(-)}\, G\,(J_z + 1), \qquad (2.15)$$

and parameter $\tilde{F}_{200}$ is defined by relation (1.15). As earlier, the function γ_{20} is chosen to eliminate the summand containing F_{201}, i.e.,

$$\gamma_{20} = F_{201}/4\, f_{12}^{(+)}.$$

The operator ${}^{(3)}m_{12}^{\rm red}$ reduced with the accuracy up to λ^6 can be written as

$${}^{(3)}H_{12}^{\rm red} = {}^{(3)}H_{12,1}^{\rm red} + \Delta^{(3)}H_{12}. \qquad (2.16)$$

Here

$${}^{(3)}H_{12,1}^{\rm red} = \sum_{i+j=0}^{2} F_{02i2j}\, J^{2i}\, J_z^{2j} + \{J_+^2\, \Psi_2^{(3)}\,(J_z + 1) +$$

$$+ \Psi_2^{(3)}\,(J_z + 1)\, J_-^2\}, \qquad (2.17)$$

$$\Delta^{(3)}H_{12} = 2 A_{12}^{(-)}\, [J_+^4\, \gamma_{40}\, G\,(J_z + 2) + \gamma_{40}\, G\,(J_z + 2)\, J_-^4], \qquad (2.18)$$

$$\Psi_2^{(3)}\,(J_z + 1) = \Psi_2^{(2)}\,(J_z + 1) + \tilde{F}_{202}\,(J_z + 1)^2 +$$

$$+ 2\, A_{12}^{(-)}\, \gamma_{22}\,(J_z + 1)^2\, G\,(J_z + 1), \qquad (2.19)$$

$$\tilde{F}_{202} = F_{202} - 4\, \gamma_{21}\, f_{12}^{(+)} + \gamma_{22}\,(E_2 - E_1).$$

In the generator iS_{12} given by Eq. (2.12) the functions γ_{21}, γ_{40}, and γ_{22} are chosen to eliminate from the transformed operator ${}^{(3)}m_{12}^{\rm red}$ terms containing $\tilde{F}_{400}$,

$\widetilde{F}_{401}$, and $\widetilde{F}_{203}$. This process can be continued up to higher orders of λ^{2k}. In any case, the operator ${}^{(k)}m_{12}^{\mathrm{red}}$ can be reduced to the form

$$ {}^{(k)}H_{12}^{\mathrm{red}} = {}^{(k)}H_{12,1}^{\mathrm{red}} + \Delta^{(k)}H_{12}, \tag{2.20}$$

where

$$ {}^{(k)}H_{12,1}^{\mathrm{red}} = \sum_{i+j=0} \widetilde{F}_{02i2j}\, J^{2i} J^{2j} + \{J_+^2\, \Psi_2^{(k)}\, (J_z + 1) + $$
$$ + \Psi_2^{(k)}\, (J_z + 1)\, J_-^2\}, \tag{2.21}$$

and the concrete form of operators $\Psi_2^{(k)}$ and $\Delta^{(k)}m_{12}$ depends on the value of k. It is evident however that beginning from $k = 3$ (i.e., from λ^6) the operator ${}^{(k)}m_{12}^{\mathrm{red}}$ contains the terms $\Delta^{(k)}m_{12}$. These terms in the basis of rotational wave functions $|J, K>$ have matrix elements with $\Delta j = \pm 4, \pm 6, \ldots$ and are absent in the case of semirigid molecules. If $A_{12}^{(-)} = 0$, the results coincide with that presented in Refs. 4 and 8, i.e., for any order of the perturbation theory m_{12}^{red} can be reduced to the form that in the basis $|J, K>$ has matrix elements only with $\Delta j = 0, \pm 2$.

3. PAIRWISE INTERACTION IN NONRIGID H_2O-TYPE MOLECULES IN THE CASE OF CORIOLIS RESONANCE

Let us consider now the interaction of states (1) = (1, 0, 0) or (2) = (0, 2, 0) and 3 = (0, 0, 1) that have different types of symmetry. In the case of pairwise interaction, effective Hamiltonian H of a molecule still has the form given by Eq. (1.1). The operators m_{nn} are set by Eq. (2.4) and operators of interaction m_{n3} ($n = 1, 2$) are set by the equation[5,8,11]

$$ H_{n3} = \sum_{k,j,l} \{J_+^{2k+1}\, J^{2l}\, C_{2k+1jl}^{(n)}\, (2\, J_z + 2k + 1)^{j} + $$
$$ + (-1)^{j+1}\, \mathrm{HC}\}, \tag{3.1}$$

where HC means Hermitian conjugate part. When only first orders of expansion of operator m_{n3} in a small parameter λ are considered, this operator can be written in the form

$$ H_{n3} = (J_+\, C_{10}^{(n)} - C_{10}^{(n)}\, J_-) + \{J_+\, (2\, J_z + 1)\, C_{11}^{(n)} + $$
$$ + C_{11}^{(n)}\, (2\, J_z + 1)\, J_-\} + \ldots . \qquad (\sim\lambda) \text{ or } (\sim\lambda^2) \tag{3.2}$$

The designation $q_{ij}^{(n)} = q_{ijl=0}^{(n)}$ is introduced in Eq. (3.2). Parameters $q_{2k+1jl}^{(n)}$ are some functions of the operator J_z. It is seen from the table that the first two terms of m_{n3} are of the same order and we will keep this order for $n = 1, 2$. Operator m_{n3} written up to orders λ^2 contains two summands, up to λ^3 - four, up to λ^4 - eight, etc. Similarly to the case of Fermi interaction considered in the previous section, let us consider the operator of interaction $\widetilde{H}_{n3}$ only, disregarding the contribution of the last summand in the transformed operator

$$ \widetilde{H}_{n3} = H_{n3} + [iS_{n3}, H_0^{(+)}] + \{iS_{n3}, H_0^{(-)}\} + [iS_{nn}, H_{n3}] + \ldots \tag{3.3}$$

assuming that this summand does not change the form of $\widetilde{H}_{n3}$. Starting from Eq. (3.1), we can obtain the generator of rotation contact interaction iS_{n3} in the general form[8,11]

$$ iS_{n3} = \sum_{k,l,j} \{J_+^{2k+1}\, J^{2l}\, \beta_{2k+1jl}^{(n)}\, (2J_z + 2k + 1)^{j} + $$
$$ + (-1)^{j+1}\mathrm{HC}\}. \tag{3.4}$$

In the first-order approximation formula (3.4) has the form

$$ iS_{n3} = (J_+\, \beta_{10}^{(n)} - \beta_{10}^{(n)}\, J_-) + \qquad (\sim\lambda) $$
$$ + [J_+\, (2\, J_z + 1)\, \beta_{11}^{(n)} - \beta_{11}^{(n)}\, (2\, J_z + 1)\, J_-] + \ldots\ (\sim\lambda^2). \tag{3.5}$$

Designation $\beta_{ij}^{(n)} = \beta_{ijl=0}^{(n)}$ is introduced here. Let us consider the form of the operator ${}^{(k)}m_{n3}$ transformed up to orders λ^{2k}. The operator ${}^{(1)}m_{n3}$ transformed up to orders λ^2 ($k = 1$) has the form

$$ {}^{(1)}\widetilde{H}_{n3} = {}^{(1)}\widetilde{H}_{n3,1} + \Delta\, {}^{(1)}H_{n3}\ , \tag{3.6}$$

where

$$ {}^{(1)}\widetilde{H}_{n3,1} = (J_+\, \widetilde{C}_{10}^{(n)} - \widetilde{C}_{10}^{(n)}\, J_-) + [J_+\, (2\, J_z + 1)\, \widetilde{C}_{11}^{(n)} + $$
$$ + \widetilde{C}_{11}^{(n)}\, (2\, J_z + 1)\, J_-], \tag{3.7}$$

$$ \Delta\, {}^{(1)}H_{n3} = 2\, A_{n3}^{(-)}\, [J_+\, G\, (J_z + 1/2)\, \beta_{10}^{(n)} - $$
$$ - \beta_{10}^{(n)}\, G\, (J_z + 1/2)\, J_-]. \tag{3.8}$$

Parameters $\widetilde{C}_{10}^{(n)}$ and $\widetilde{C}_{11}^{(n)}$ are set by formulas

$$ \widetilde{C}_{10}^{(n)} = C_{10}^{(n)} + \beta_{10}^{(n)}\, (E_3 - E_n), \tag{3.9}$$
$$ \widetilde{C}_{11}^{(n)} = C_{10}^{(n)} + \beta_{10}^{(n)}\, (2\, C - f_{n3}^{(+)}). \tag{3.10}$$

The independent parameters of ${}^{(1)}\widetilde{H}_{n3}$ for $n = 1$ and $n = 2$ can be chosen in different ways, because when $n = 1$ the term $\Delta^{(1)}m_{13}$ can be neglected. In this case the parameter $\beta_{10}^{(1)}$ can be chosen so that the term $\widetilde{C}_{10}^{(n)}$ vanishes, i.e.,

$$ \beta_{10}^{(1)} = C_{10}^{(1)} / (E_1 - E_3), \tag{3.11}$$

then

$$ {}^{(1)}H_{13}^{\mathrm{red}} = [J_+ (2J_z + 1)\, \widetilde{C}_{11}^{(n)} + \widetilde{C}_{11}^{(n)}\, (2\, J_z + 1)\, J_-]. \tag{3.12}$$

Such choice is not obligatory for the operator ${}^{(1)}m_{23}$ and the parameter $\beta_{10}^{(2)}$ can be chosen in different ways, i.e., unambiguously, because its choice depends on the value of detuning $A_{23}^{(-)}$. For example, it can be chosen to eliminate the higher-order term $\tilde{C}_{12}^{(2)}$, where

$$\tilde{C}_{12}^{(2)} = C_{12} - \beta_{10}^{(2)} A_{23}^{(-)}/2. \tag{3.13}$$

(Here we used the expansion of G function entering into Eq. (3.8) in a series in $(J_z + 1/2)$.) In this case

$$ {}^{(1)}H_{23}^{\mathrm{red}} = (J_+ \tilde{C}_{10}^{(2)} - \tilde{C}_{10}^{(2)} J_-) + \{J_+ (2J_z + 1)\, \tilde{C}_{11}^{(2)} + $$

$$ + \tilde{C}_{11}^{(2)} (2J_z + 1) J_-\}. \tag{3.14}$$

However, it should be noted that such method is not unique. Let us consider the transformation up to terms λ^4. In the same manner as in the case of ${}^{(1)}\tilde{H}_{n3}$ let us represent the operator ${}^{(2)}\tilde{H}_{n3}$ in the form given by Eq. (3.6), i.e.,

$$ {}^{(2)}\tilde{H}_{n3} = {}^{(2)}\tilde{H}_{n3,1} + \Delta\, {}^{(2)}\tilde{H}_{n3}\ . \tag{3.15}$$

In this representation ${}^{(2)}\tilde{H}_{n3}$ is given by Eq. (3.2) and includes eight summands whose parameters $C^{(n)}$ are connected with five parameters of the generator $\beta^{(n)}$ of transformation (3.5).

It is convenient to represent the operator $\Delta^{(2)}\tilde{H}_{n3}$ as a sum of two terms

$$\Delta\, {}^{(2)}\tilde{H}_{n3} = \Delta\, {}^{(2)}H_{n3,1} + \Delta\, {}^{(2)}H_{n3,2}\ , \tag{3.16}$$

where

$$\Delta\, {}^{(2)}H_{n3,1} = -\,2\, A_{3n}^{(-)} \{[J_+ \beta_{10}^{(n)}\, G\, (J_z + 1/2) - \mathrm{HC}] + $$

$$ + [J_+ \beta_{11}^{(n)}\, G\, (J_z + 1/2)\, (2J_z + 1) + \mathrm{HC}], \tag{3.17}$$

$$\Delta\, {}^{(2)}H_{n3,2} = -2A_{3n}^{(-)} \{[J_+ \beta_{12}^{(n)}\, G(J_z + 1/2)\, (2J_z + 1)^2 - $$

$$ - \mathrm{HC}] + J^2\, [J_+ \beta_{102}^{(n)}\, G\, (J_z + 1/2) - \mathrm{HC}] + $$

$$ + [J_+^3\, \beta_{30}^{(n)}\, G\, (J_z + 3/2) - \mathrm{HC}]\}. \tag{3.18}$$

Such representation is convenient because the first terms of the summand $\Delta^{(2)}\tilde{H}_{n3,1}$ in the expansion of G function in a Taylor series in powers $(J_z + 1/2)$ allow us to convert the operator ${}^{(2)}\tilde{H}_{n3}$ to the form

$$ {}^{(2)}\tilde{H}_{n3} = {}^{(2)}\tilde{H}'_{n3,1} + \Delta\, {}^{(2)}H_{n3,2}\ , \tag{3.19}$$

with the operator ${}^{(2)}\tilde{H}'_{n3}$ still keeping the form given by Eq. (3.1). The connection of operator $\tilde{q}^{(n)}$ parameters with parameters $\beta^{(n)}$ is considered in the next section. Reduced forms ${}^{(2)}m_{n3}^{\mathrm{red}}$ depend on $A_{n3}^{(-)}$. When operator $\Delta^{(2)}m_{n3,2}$ given by Eq. (3.18) can be neglected, the eight parameters of ${}^{(2)}\tilde{H}_{n3}$ will be related to five independent parameters $\beta^{(n)}$ entering into Eq. (3.5). As in the case of semirigid molecules, these parameters can be chosen so that in the basis $|J, K>$ the number of diagonals of ${}^{(2)}m_{n3}^{\mathrm{red}}$ be minimum, i.e., matrix elements $<J, K\ |\ {}^{(2)}m_{n3}^{\mathrm{red}}\ |J, K + \Delta K>$ be nonzero only when $\Delta K = \pm 1$. As in the case of ${}^{(1)}m_{n3}^{\mathrm{red}}$ operator, among the terms that include matrix elements with $\Delta K = \pm 1$ it is expedient to keep summands with powers J_z. Thus, one of the possible forms of the reduced operator ${}^{(2)}m_{n3}^{\mathrm{red}}$ written up to λ^4, for which $A_{n3}^{(-)} = 0$, is

$$ {}^{(2)}H_{n3}^{\mathrm{red}} = \{J_+ (2J_z + 1)\, \tilde{C}_{11}^{(n)} + \mathrm{HC}\} + $$

$$ + \{J_+ (2J_z + 1)^2\, \tilde{C}_{12}^{(n)} - \mathrm{HC}\} + J^2 \{J_+ (2J_z + 1)\, \tilde{C}_{112}^{(n)} + \mathrm{HC}\}. \tag{3.20}$$

If we cannot neglect the operator $\Delta^{(2)}m_{n3,2}^{\mathrm{red}}$ (for example, for the H_2O molecule when $n = 2$), the reduced operator ${}^{(2)}m_{n3}^{\mathrm{red}}$ includes matrix elements with $\Delta K = \pm 1, \pm 3$ and many forms of ${}^{(2)}m_{n3}^{\mathrm{red}}$ are acceptable. Let us consider now the transformation up to λ^6. According to Ref. 11, the initial operator H_{n3} given by Eq. (3.1) and written up to λ^6 includes 18 summands and in the generator of transformation iS_{n3} the summands up to λ^5 should be considered. There are 12 such summands. The transformed operator ${}^{(3)}H_{n3,}$ can be written in the form given by Eq. (3.19), i.e.,

$$ {}^{(3)}\tilde{H}_{n3} = {}^{(3)}\tilde{H}'_{n3} + \Delta\, {}^{(3)}H_{n3,2}\ , \tag{3.21}$$

where ${}^{(3)}H'_{n3}$ has the form of the initial operator given by Eq. (3.1) and the operator $\Delta^{(3)}H_{n3,2}$ has the form

$$\Delta\, {}^{(3)}H_{n3,2} = 1/2\, A_{n3}^{(-)} \{[J_+ (\beta_{14}^{(n)} - \alpha^{(n)}\, \beta_{12}^{(n)}/4) \times $$

$$ \times (2J_z + 1)^6 - \mathrm{HC}] + J^2\, [J_+ (2J_z + 1)^4 \times $$

$$ \times (\beta_{122}^{(n)} - \alpha^{(n)}\, \beta_{102}^{(n)}/4) - \mathrm{HC}] + [J_+^3 (2J_z + 3)^4 \times $$

$$ \times (\beta_{32}^{(n)} - \alpha^{(n)} \beta_{30}^{(n)}/4) - \mathrm{HC}] + [J_+^5 (2J_z + 5)\, \beta_{50}^{(n)} - \mathrm{HC}]\}. \tag{3.22}$$

with the accuracy up to the first terms of expansion of G functions. If the operator $\Delta^{(3)}m_{n3,2}$ can be neglected, the operator ${}^{(3)}\tilde{H}_{n3}$ still can be reduced to the form ${}^{(3)}m_{n3}^{\mathrm{red}}$ which has matrix elements $<J, K|\, {}^{(3)}m_{n3}^{\mathrm{red}}\, |J, K + \Delta K>$ only with $\Delta K = \pm 1$. It is obvious that ${}^{(3)}m_{n3}^{\mathrm{red}}$ includes six summands [the first three can be defined, for example, by Eq. (3.20)]. If the operator $\Delta^{(3)}m_{n3,2}$ cannot be neglected, then the reduced operator ${}^{(3)}m_{n3}^{\mathrm{red}}$ includes summands that have matrix elements with $\Delta K = \pm 1, \pm 3, \pm 5$.

4. APPLICATION TO THE FIRST TRIAD OF THE H_2O MOLECULE

Let us consider the application of the technique developed to the first triad of resonating vibrational states of the m$_2$n molecule. Three vibrational states $(1) = (1, 0, 0)$, $(2) = (0, 2, 0)$, and $(3) = (0, 0, 1)$ form this group of states. Effective Hamiltonian of the first triad has the form of a matrix

$$H = \begin{bmatrix} H_{11} & H_{12} & H_{13} \\ & H_{22} & H_{23} \\ \mathrm{HC} & & H_{33} \end{bmatrix} . \tag{4.1}$$

The operators m_{nm} $(n, m = 1, 2, 3)$ are defined by formulas (2.4), (2.5), and (3.1).

The generator of transformation S entering into formula (1.5) also has the form of a matrix

$$S = \begin{bmatrix} S_{11} & S_{12} & S_{13} \\ & S_{22} & S_{23} \\ \mathrm{HC} & & S_{33} \end{bmatrix} , \tag{4.2}$$

In this matrix S_{nm} are defined by relations (1.9), (2.12), and (3.5) (to define S_{nm}, only the main generator is used). When $n = m$, transformed operators $\tilde{H}_{nm}$ can be written in the form

$$\tilde{H}_{nn} = H_{nn} + i \sum_{m=1}^{3} (S_{nm} H_{mn} - H_{nm} S_{mn}) + \ldots \tag{4.3}$$

and when $m \neq n$,

$$\tilde{H}_{nm} = H_{nm} + [iS, H_{nm}] + [iS, H_{nm}^{(+)}] + \{iS_{nm}, H_{nm}^{(-)}\} + \ldots . \tag{4.4}$$

Here $iS = iS_{nn}$ and $n, m = 1, 2, 3$. Thus, main distinctions of the proposed calculation technique from analogous one used for semirigid molecules are the following: 1) the zero-order approximation $\overset{0}{m}_n$ given by Eq. (2.1) has essentially nonpolynomial form, 2) due to the considerable difference between the values of rotational constants the anticommutator enters into formula (4.4) for operators of interaction. Let us consider the form of transformed (or reduced) operators of interaction ${}^{(k)}H_{nm}^{\mathrm{red}}$ obtained for different orders of a small parameter λ.

Transformation up to λ^2. Operators ${}^{(1)}\tilde{H}_{12} = {}^{(1)}m_{12}^{\mathrm{red}}$ and ${}^{(1)}\tilde{H}_{n3}$ $(n = 1, 2)$ are defined by formulas (2.13) and (3.6), respectively. Formulas (3.12) and (3.14) can be taken as examples of reduced forms of ${}^{(1)}m_{13}^{\mathrm{red}}$ and ${}^{(1)}m_{23}^{\mathrm{red}}$. With the exception of the zero-order approximation, reduced diagonal operators have the form[6]

$$\begin{aligned} H_{nn}^{\mathrm{red}} = {} & H_n^{(0)} + \tilde{h}_{020}^{(n)} J^4 + \tilde{h}_{002}^{(n)} J_z^4 + \tilde{h}_{011}^{(n)} J^2 J_z^2 + \\ & + J^2 (J_+^2 \tilde{h}_{110}^{(n)} + \tilde{h}_{110}^{(n)} J_-^2) + [J_+^2 (J_z + 1)^2 \tilde{h}_{101}^{(n)} + \\ & + \tilde{h}_{101}^{(n)} (J_z + 1)^2 J_-^2]. \end{aligned} \tag{4.5}$$

In this formula, parameters $\tilde{h}^{(n)}$ are connected with the parameter $\varepsilon_{21}^{(n)}$ by the same relations as in the case of semirigid molecules, with the exception of the parameter

$$\tilde{h}_{101}^{(n)} = h_{101}^{(n)} - 4\, \varepsilon_{21}^{(n)} f_n(J_z). \tag{4.6}$$

It can be shown (see, for example, Ref. 12) that for an isolated vibrational state in the basis of rotational functions of symmetric top the effective vibrational Hamiltonian always can be reduced to the three-diagonal symmetric form. This means that operators m_{nm}^{red} of any order can be reduced to the form m_{nm}^{red}. In the basis $|J, K>$ of the wave functions, this form has the matrix elements $<J, K | m_{nn}^{\mathrm{red}} | J, K + \Delta K>$ only with $\Delta K = 0$ or $\Delta K = \pm 2$. After formal substitution $J_z^2 \Rightarrow G + \alpha G^2/4$ performed in this operator, operators m_{nn}^{red} can be written as

$$\begin{aligned} H_{nn}^{\mathrm{red}} = {} & \sum_{i,j} g_{ij}^{(n)} J^{2i} G_n^j + \\ & + \sum_{i,j} u_{ij}^{(n)} J^{2i} [J_+^2 G_n^j (J_z + 1) + G_n^j (J_z + 1) J_-^2], \end{aligned} \tag{4.7}$$

where, for example, $g_{00}^{(n)} = E_n$, $g_{01}^{(n)} = A^{(n)}$, … . The connection of parameters α, g_{ij}, and u_{ij} with initial parameters was considered by Tyuterev and Starikov.[9,10] In what follows we consider only the form of operators that describe the resonance interaction.

Transformation up to λ^4. The operator ${}^{(2)}m_{12}^{\mathrm{red}}$ which describes the Fermi resonance has the form of Eq.(2.14), i.e.,

$$\begin{aligned} {}^{(2)}H_{12}^{\mathrm{red}} = {} & F_0 + F_{002} J_z^2 + \tilde{F}_{020} J^2 + \\ & + \{J_+^2 \Psi_2^{(2)} (J_z + 1) + \Psi_2^{(2)} (J_z + 1) J_-^2\}, \end{aligned}$$

where

$$\tilde{F}_{020} = F_{020} - \beta_{10}^{(1)} C_{10}^{(2)} - \beta_{10}^{(2)} C_{10}^{(1)},$$

$$\Psi_2^{(2)} (J_z + 1) = \tilde{F}_{200} + 2\, \gamma_{20} A_{12}^{(-)} G (J_z + 1) -$$

$$- 2\, \varepsilon_{21} F_{002} (J_z + 1)^2,$$

$$\begin{aligned} \tilde{F}_{200} = {} & F_{200} - \beta_{10}^{(1)} (C_{10}^{(2)} + C_{11}^{(2)}) + \beta_{10}^{(2)} (C_{10}^{(1)} + C_{11}^{(1)}) + \\ & + \{(E_2 - E_1) + 2 A_{12}^{(-)}\} \gamma_{20} . \end{aligned} \tag{4.8}$$

Parameter γ_{20} is chosen so that $\tilde{F}_{201} = 0$, where

$$\tilde{F}_{201} = F_{201} - 4\, \gamma_{20} f_{12}^{(+)} - 2\, [\beta_{10}^{(1)} C_{11}^{(2)} + \beta_{10}^{(2)} C_{11}^{(1)}] . \tag{4.9}$$

Let us represent the operators ${}^{(2)}m_{n3}$ in the form given by Eq. (3.19). Parameters q_{ijl} of the operator ${}^{(2)}m'_{n3,1}$ and initial parameters are related by the following expressions:

$$
\begin{aligned}
&\tilde{C}_{10}^{(n)} = C_{10}^{(n)} + \beta_{10}^{(n)} (E_3 - E_n) - \beta_{10}^{(n')} F_0 ,\\
&\tilde{C}_{11}^{(n)} = C_{11}^{(n)} - \beta_{10}^{(n')} F_{002} + \beta_{10}^{(n)} (2C - f_{n3}^{(+)}) + \beta_{11}^{(n)} (E_3 - E_n),\\
&\tilde{C}_{30}^{(n)} = C_{30}^{(n)} + \varepsilon_{21} C_{10}^{(n)} + \gamma_{20} C_{10}^{(n')} + 4\beta_{11}^{(n)} C + \beta_{30}^{(n)} (E_3 - E_n),\\
&\tilde{C}_{12}^{(n)} = C_{12}^{(n)} - 5\varepsilon_{21}/4 C_{10}^{(n)} + [\gamma_{20} C_{10}^{(n')} - 2\beta_{10}^{(n')} F_{002}]/8 +\\
&+ \beta_{11}^{(n)} (3C - f_{n3}^{(+)}) + \beta_{12}^{(n)} (E_3 - E_n) - 1/2\, \beta_{10}^{(n)} A_{3n}^{(-)},\\
&\tilde{C}_{31}^{(n)} = C_{31}^{(n)} - 3\beta_{30}^{(n)} f_{n3}^{(+)} + 4\beta_{12}^{(n)} C,\\
&\tilde{C}_{13}^{(n)} = C_{13}^{(n)} - \beta_{12}^{(n)} f_{n3}^{(+)} - 1/2\, \beta_{11}^{(n)} A_{3n}^{(-)},\\
&\tilde{C}_{102}^{(n)} = C_{102}^{(n)} - \beta_{10}^{(n')} F_{020} + \varepsilon_{21} C_{10}^{(n)} + \beta_{102}^{(n)} (E_3 - E_n) + 4\beta_{11}^{(n)} C,\\
&\tilde{C}_{112}^{(n)} = C_{112}^{(n)} + \beta_{102} (2C - f_{n3}^{(+)}).
\end{aligned}
\tag{4.10}
$$

Here n', $n = 1, 2$ and $n' \neq n$. The possible reduced forms of ${}^{(2)}m_{n3}^{\text{red}}$ operators have been considered in the previous section. In operators ${}^{(2)}m_{23}^{\text{red}}$ there appear the summands with $\Delta K = \pm 3$. According to Section 3, the summands that in the basis $|J, K>$ have matrix elements with $\Delta K = \pm 4$ appear in Fermi blocks of the Hamiltonian reduced up to λ^6 and they have elements with $\Delta K = \pm 3, \pm 5$ in m_{23}^{red} blocks. It should be noted that additional purely vibrational transformation can be applied to operator H to eliminate one more parameter from m_{12}^{red} block.[4]

5. CONCLUSION

In the present article it has been shown that the reduced forms of interaction operators m_{nm}^{red} $(n \neq m)$ depend on multiplicity of excitation of vibration quantum number v_2 in states (n) and (m). This quantum number is associated with high-amplitude oscillations. Due to large difference between the degrees of excitation of this quantum number in (n) and (m) states, operators m_{nm}^{red} in the basis $|J, K>$ of rotational wave functions have matrix elements $<J, K|m_{nm}^{\text{red}}|J, K + \Delta K>$ with $\Delta K = 0, \pm 2, \pm 4, \ldots$ in blocks describing Fermi interaction, and matrix elements with $\Delta K = \pm 1, \pm 3, \pm 5, \ldots$ in blocks describing the interaction of Coriolis type. The results of application of concrete models of effective Hamiltonian to interpretation of experimental data on the H_2O molecule will be presented in the next paper.

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