TRANSFORMATION OF THE EFFECTIVE HAMILTONIAN OF NON-RIGID X_2Y MOLECULES IN THE CASE OF A PAIR RESONANCES

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Transformation of the centrifugal distortion Hamiltonian describing a random pair resonance in non-rigid X_2Y molecules to the form having the least number of diagonals in the basis of rotational wavefunctions is considered. An influence of a large-amplitude oscillation upon such transformation is analyzed. The transformation is shown to change significantly the form of the initial Hamiltonian and to be diverging in some cases.

1. INTRODUCTION

Effective centrifugal distortion Hamiltonians H are widely used in analysis of rovibrational molecular spectra. Such Hamiltonians are derived using different versions of the perturbation theory, which give different forms of H. For an isolated vibrational state, the Hamiltonian H is purely rotational. It can be written as a series in operators of angular momentum for semi-rigid molecules. It is shown[1,2] that applying the method of contact transformations to such Hamiltonian for an asymmetric top molecule, one can transform it to the reduced form H_{red}. The reduced Hamiltonian contains only the parameters, which can be unambiguously found from the experiment. What's more, in the basis of rotational symmetric top wavefunctions $|J, K>$ this Hamiltonian has matrix elements $<J, K | H_{red} | J, K + \Delta K>$ only with $\Delta K = 0, \pm 2$.

For non-rigid molecules of the X_2Y type having a large-amplitude oscillation this procedure has some peculiarities. They are in the fact that starting from some rotational quantum number J_{red} the behavior of matrix elements $<J, K | H_{red} | J, K + \Delta K>$ (with $\Delta K = 0, \pm 2$) cannot be described by functions of only one class (for example, using only exponential or linear fractional functions). In Ref. 3 the values of the rotational quantum numbers J_{red} for the ground and (010) vibrational states of m_2n molecule were found from the processing of the experimental data. For the ground vibrational state of m_2n, the non-reduced rotational Hamiltonian H, having matrix elements $<J, K | H | J, K + \Delta K>$ with $\Delta K = 0, \pm 2, \pm 4....$ in the basis of rotational wavefunctions $|J, K>$, is shown to be preferable starting from $J \approx 25$.

Reduction of the centrifugal distortion Hamiltonian H for the case of pair resonance interactions between the states $(V) \equiv 1$ and $(V') \equiv 2$ in semi-rigid asymmetric top molecules is considered in Refs. 4 and 5. The large-amplitude oscillation introduces some peculiarities into the reduction procedure. The aim of this paper is to take them into account (they are partially considered in

Ref. 6). These peculiarities are connected with, first, divergence of polynomial representations of the rotational operators $<n | H | n>$ ($n = 1, 2$) and, second, with abnormally fast change of the series of spectroscopic parameters entering into H.

2. PAIR RESONANCE. GENERAL RELATIONS

For the case of interaction between two rotational energy levels belonging to two different vibrational states $(V) \equiv 1$ and $(V') \equiv 2$, the effective centrifugal distortion Hamiltonian H is written as a 2D operator matrix[4,5]

$$H = \begin{bmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{bmatrix}. \tag{1}$$

Here $(V) \equiv (v_1 v_2 v_3)$, v_i are the vibrational quantum numbers ($i = 1, 2, 3$); $H_{21} = H_{12}^+$ ("+" is for the Hermitian conjugation). The matrix (1) is written in the basis $|V>$, $|V'>$; every H_{nm} ($n, m = 1, 2$) is a rotational operator. In this work the principal attention is paid to the interaction operators H_{12}, therefore the diagonal (in the basis of vibrational wavefunctions) operators H_{nn} are from the outset taken in the reduced form

$$H_{nn} = F^{(n)}(J_z) + \{J_+^2\, \chi^{(n)}(J_z + 1) + \chi^{(n)}(J_z + 1)\, J_-^2\}, \tag{2}$$

where $F^{(n)}(J_z)$ and $\chi^{(n)}(J_z+1)$ are the generating functions for the standard representation of the operators H_{nn} (see, for example, Ref. 7; the effect of contact transformations upon the form of the rotational Hamiltonian $H^{(n)} = H_{nn}$ for an isolated vibrational state will be considered separately). The transformed Hamiltonian $\tilde{H}$ also has the form of 2D matrix

$$\tilde{H} = e^{iS} H\, e^{-iS} = H + [iS, H] + ... = \begin{bmatrix} \tilde{H}_{11} & \tilde{H}_{12} \\ \tilde{H}_{21} & \tilde{H}_{22} \end{bmatrix}, \tag{3}$$

where $[iS, H]$ is the commutator; S is the transformation generator,

$$S = \begin{bmatrix} S_{11} & S_{12} \\ S_{21} & S_{22} \end{bmatrix}, \tag{4}$$

and $S_{21} = S_{12}^{+}$. The transformed operators meet the following relations:

$$\tilde{H}_{nn} = H_{nn}' + i\,(S_{nm}\,H_{mn} - H_{nm}\,S_{mn}) + \ldots,\; m \neq n,$$

$$\tilde{H}_{12} = H_{12} + i\,(S_{12}\,H_{22} - H_{11}\,S_{12}) + \ldots, \tag{5a}$$

where $H_{nn}' = H_{nn} + i\,[S_{nn}, H_{nn}]$. Excitation of the large-amplitude oscillation is expressed as a change of the bending vibrational quantum number v_2; it leads to a great change of the functions $F^{(n)}$ and $\chi^{(n)}$. With allowance made for this fact, Eq. (5a) takes the form

$$\tilde{H}_{12} = H_{12} + [i\,S_{12}, H^{(+)}] + \{i\,S_{12}, H^{(-)}\} + \ldots. \tag{5b}$$

The braces here are used for anticommutator, and

$$H^{(\pm)} = F^{(\pm)}(J_z) + \{J_+^2\,\chi^{(\pm)}(J_z + 1) + \chi^{(\pm)}(J_z + 1)\,J_-^2\}, \tag{6}$$

where

$$F^{(\pm)} = \{F^{(1)} \pm F^{(2)}\}/2;\; \chi^{(\pm)} = \{\chi^{(1)} \pm \chi^{(2)}\}/2. \tag{7}$$

For further consideration, we should estimate the orders of smallness of different functions entering into the above relations. Toward this end, we can use the standard smallness parameter $\lambda = (\bar{B}/\bar{\omega})^{1/2}$ ($\bar{B}$ is the mean value of the rotational constant, $\bar{\omega}$ is the mean frequency of harmonic oscillation) accepted in the molecular spectroscopy.[8] According to such a definition of the parameter λ, the energy of harmonic oscillations in a molecule, as well as the energy of the large-amplitude oscillation and the rotation energy (in the rigid top approximation up to $J \approx 10$), has zero order of smallness. The order of smallness of a function can be estimated from the ratio of a matrix element of this function in the basis of vibrational and rotational wavefunctions (if known) to the energy of harmonic oscillations. If the matrix element is unknown, then the order of function can be estimated by the value of the first coefficient in the Taylor series expansion of this function. For example, $F^{(n)}(K) = \; = \langle J, K\,|\,F^{(n)}(J_z)\,|\,J, K\rangle = E_n + A^{(n)}K^2 - \Delta_K^{(n)}\,K^4 + \ldots,$ $\chi^{(n)}(K + 1) = (B^{(n)} - C^{(n)})/4 - \delta_K^{(n)}\,(K + 1)^2 + \ldots,$ here E_n is the vibrational band center; $A^{(n)}, B^{(n)},$ and $C^{(n)}$ are the rotational constants; $\Delta_K^{(n)}$ and $\delta_K^{(n)} \ldots$ are the centrifugal distortion constants, which are usually known. Using the values of these constants, for example, for m_2n molecule,[9,10] we can find that $F^{(n)} \sim \lambda^0$ and $\chi^{(n)}(K+1) \sim \lambda^3$ for small n and up to $K \sim 10$. Figure 1 demonstrates the calculated behavior of the function $2F^{(-)}(K) = F^{(020)}(K) - F^{(100)}(K)$. The matrix elements $F^{(n)}(K)$ ($n = 1 \equiv (100)$, $n = 2 \equiv (020)$) were determined from the processing of the experimental data for the first triad of interacting states (from Ref. 11, the form of the functions $F^{(n)}$ has been also determined there). It is clearly seen from Fig. 1 that at low values of K $F^{(-)}(K) \sim \lambda$ (determined by purely vibrational

difference), at $K \approx 10$ $F^{(-)}(K) \approx 0$ (random resonance), and at K from 10 to 20 $F^{(-)}(K)$ is again of the order of λ. At $K > 20$, according to the asymptotics, $F^{(-)}(K)$ approaches the energy of harmonic oscillations, that is $F^{(-)}(K) \sim \lambda^0$.
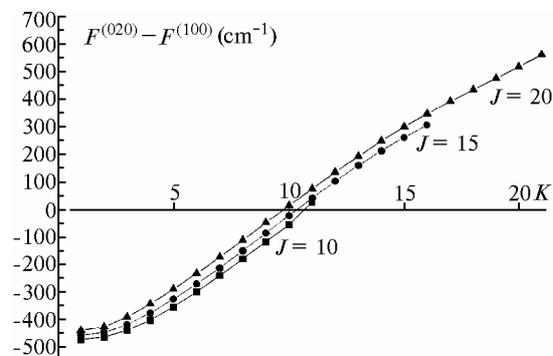

FIG. 1. Behavior of the function $2F^{(-)}(K) = F^{(020)} - F^{(100)}$ at $J = 10$ (■), 15 ( ), and 20 (▲) for the H_2O molecule (from the results of experimental data processing for the first triad of interacting states[11]).

3. ANHARMONIC RESONANCES

According to the symmetry properties, the operator H_{12} describing interaction between the vibrational states of the same type of symmetry in X_2Y molecules can be presented as

$$H_{12} = \Psi_0(J_z) + \{J_+^2\,\Psi_2^{(+)}(J_z + 1) + \Psi_2^{(-)}(J_z + 1)\,J_-^2\} +$$
$$+ \{J_+^4\,\Psi_4^{(+)}(J_z + 2) + \Psi_4^{(-)}(J_z + 2)\,J_-^4\} + \ldots, \tag{8}$$

where $\Psi_0(J_z)$, $\Psi_k^{(\pm)}(J_z + k)$, $k = 1, 2$, are some functions of the operators $\mathbf{J}^2$, J_z ($\mathbf{J}$ is the total angular momentum operator). The functions $\Psi_{2k}^{(\pm)}(J_z + k)$, $k = 1, 2$, can be presented in the form:

$$\Psi_{2k}^{(\pm)}(J_z + k) = \Psi_{2k}^{(e)}(J_z + k) \pm \Psi_{2k}^{(o)}(J_z + k), \tag{9}$$

in which the superscripts e and o denote even or odd character of a function with respect to its argument. Most important among anharmonic resonances are the Fermi resonances between the vibrational states $(V) = (v_1\,v_2\,v_3)$ and $(V') = (v_1 - 1\,v_2 + 2\,v_3)$ with the different quantum number v_2. In standard approximation for semi-rigid molecules[12]:

$$\Psi_0(J_z) = 1/2\,[v_1\,(v_2 + 1)\,(v_2 + 2)/2]^{1/2} \times$$

$$\times [F_0^{VV'} + F_K^{VV'}\,J_z^2 + F_J^{VV'}\,\mathbf{J}^2 + \ldots], \tag{10}$$

where $F_0^{VV'}$, $F_K^{VV'}$, and $F_J^{VV'}$ are the resonance parameters. For the m_2n molecule $F_0^{VV'} \approx 100\text{ cm}^{-1}$ (Ref. 12), therefore we can believe that the operator $H_{12} \sim \lambda$. For $J \sim \lambda^{-1}$ the function $\Psi_{2k}^{(\pm)}(K)$ can be estimated as $\Psi_{2k}^{(\pm)}(K) \sim \lambda^{2k+2}$. According to the symmetry properties, the operators S_{12} from Eq. (5a) can be written as

$$iS_{12} = g_0(J_z) + \{J_+^2 \, g_2^{(+)}(J_z + 1) + g_2^{(-)}(J_z + 1) \, J_-^2\} +$$

$$+ \{J_+^4 \, g_4^{(+)}(J_z + 2) + g_4^{(-)}(J_z + 2) \, J_-^4\} + \dots , \qquad (11)$$

where $g_{2k}^{(\pm)} = g_{2k}^{(e)} \pm g_{2k}^{(o)}$ $(k = 1, 2)$, and $g_{2k}^{(e)}$ and $g_{2k}^{(o)}$ are even and odd functions of their arguments. The operator S_{12} is of the order of λ (what is necessary for the contact transformations convergence), consequently, for $J \sim \lambda^{-1}$ $g_0(J_z) \sim \lambda$, $g_2(J_z + 1) \sim \lambda^3$, ... that is $g_{2k}(J_z + k) \sim \lambda^{1+2k}$. The substitution of Eqs. (2) and (11) into Eq. (5a) gives the following expressions for the transformed operators $\tilde{H}_{nm}$:

$$\tilde{H}_{11} = H_{11}' + \Delta H_F, \ \tilde{H}_{22} = H_{22}' - \Delta H_F, \qquad (12)$$

$$\tilde{H}_{12} = \tilde{\Psi}_0(J_z) + \{J_+^2 \, \tilde{\Psi}_2^{(+)}(J_z + 1) + \tilde{\Psi}_2^{(-)}(J_z + 1) \, J_-^2\} +$$

$$+ \{J_+^4 \, \tilde{\Psi}_4^{(+)}(J_z + 2) + \tilde{\Psi}_4^{(-)}(J_z + 2) \, J_-^4\} + \dots . \qquad (13)$$

Here

$$\Delta H_F = J_+^2 \, \Delta \chi(J_z + 1) + \Delta \chi(J_z + 1) \, J_-^2\}; \qquad (14)$$

$$\Delta \chi(J_z + 1) = [g_0(J_z + 2) + g_0(J_z)] \, \Psi_2^e(J_z + 1) +$$

$$+ [g_0(J_z) - g_0(J_z + 2)] \, \Psi_2^o(J_z + 1). \qquad (15)$$

The transformed functions $\tilde{\Psi}_{2k}(J_z + k)$ are defined by the relations:

$$\tilde{\Psi}_0(J_z) = \Psi_0(J_z) + \underline{2g_0(J_z) \, F^{(-)}(J_z)} \, , \qquad (16\text{=})$$

$$\tilde{\Psi}_2^e(x) = \Psi_2^e(x) + g_2^o(x) \Delta F^{(+)}(0,2) + \underline{g_2^e(x) \Delta F^{(-)}(2,0)} \, , (16\text{b})$$

$$\tilde{\Psi}_2^o(x) = \Psi_2^o(x) + g_2^e(x) \Delta F^{(+)}(0,2) + \underline{g_2^o(x) \Delta F^{(-)}(2,0)} \, +$$

$$+ \chi(x) \, [g_0(x + 1) - g_0(x - 1)]; \qquad (16\text{c})$$

$$\tilde{\Psi}_4^\sigma(y) = \Psi_4^\sigma(y) + g_2^{\sigma'}(y) \Delta F^{(+)}(0,4) + \underline{g_4^\sigma(y) \Delta F^{(-)}(4,0)} \, +$$

$$+ \chi(x) \, g_2^{\sigma'}(x + 2) - \chi(x + 2) \, g_2^{\sigma'}(x). \qquad (16\text{d})$$

In these expressions $\sigma, \sigma' = e$ or o $(\sigma \neq \sigma')$, $x = J_z + 1$, $y = x + 1$, $\chi = \chi^{(+)}$, and $\Delta F^{(\pm)}(k, r) \equiv \Delta F^{(\pm)}(J_z + k, J_z + r) = F^{(\pm)}(J_z + k) - F^{(\pm)}(J_z + r)$.

Besides, the terms of the same order are left in these expressions (apart from the underlined ones). The order of the underlined terms significantly depends on the rotational quantum number K. Let us consider the conditions, under which some parameters can be removed from the interaction operator $\tilde{H}_{12}$ due to proper choice of the functions $g_{2k}(J_z + k)$ and transformation of the operator to the reduced form H_{12}^{red}. Let us start from the approximation, in which the interaction operator H_{12} in Eq. (8) includes only the functions $\Psi_0(J_z)$ and $\tilde{\Psi}_2^{(\pm)}(J_z + 1)$, and the transformation generator S includes only the function $g_0(J_z)$. There are two equations (16a) and (16c) for determination of this function. The function $g_0(J_z)$

cannot be determined from the condition $\tilde{\Psi}_0(J_z) = 0$, that is $g_0(J_z) = -\Psi_0(J_z)/(2F^{(-)}(J_z))$, because at some values K_r of the rotational quantum number K the function $F^{(-)}(K_r) \approx 0$. The function $g_0(J_z)$ can be found from the condition $\tilde{\Psi}_2^o(J_z) = 0$ (Eq. (16c), where $g_2^e = g_2^o = 0$), which leads to the following equation:

$$-\tilde{\Psi}_2^o(x) = \chi(x) \, [g_0(x + 1) - g_0(x - 1)]. \qquad (17)$$

This equation is the difference equation for the discrete variable x. If the difference operator Δ is defined as

$$\Delta g_0(x) = \{g_0(x + 1) - g_0(x - 1)\}/2, \qquad (18)$$

then Eq. (17) takes the form

$$\Delta g_0(x) = -\Psi_2^o(x)/[2\chi(x)]. \qquad (19)$$

Let us now pass on to the continuous variable x. Then the difference equation (19) for the discrete variable will be transformed into the differential equation $g_0' = -\Psi_2^o(x)/[2\chi(x)]$ for the continuous variable (prime denotes differentiation with respect to x), which has the solution

$$g_0(x) = -1/2 \int \Psi_2^o(x) \, dx / \chi(x) + c, \qquad (20)$$

where c is the integration constant. Thus, in the considered approximation, the reduced operator H_{12}^{red} has the form

$$H_{12}^{\text{red}} = \tilde{\Psi}_0(J_z) + \{J_+^2 \, \tilde{\Psi}_2^e(J_z + 1) + \tilde{\Psi}_2^e(J_z + 1) \, J_-^2\}, \quad (21)$$

in which the functions $\tilde{\Psi}_0(J_z)$ and $\tilde{\Psi}_2^e(J_z + 1)$ are determined by Eqs. (16a), (16b), and (20) (in this approximation $\tilde{\Psi}_2^e(J_z + 1) = \Psi_2^e(J_z + 1)$; the operator H_{12}^{red} is referred to as a reduced one by analogy with the semi-rigid model of a molecule). In the particular case of the Taylor expansion, the function $\Psi_2^o(x) = f_{12} \, x + \dots$ (and similarly for the function $\chi(x)$)

$$g_0(x) = -f_{12}/4 \int dt / [C_0 - \delta_K \, t +$$

$$+ h_K \, t^2 + l_K \, t^3 + \dots] + c, \qquad (22)$$

where $t = x^2$; $C_0 = (B - C)/4$, and $B, C, \delta_K, \dots$ are the rotational and centrifugal constants averaged over two vibrational states. The form of the function $g_0(x)$ is completely determined by roots of the equation $\chi(x) = 0$. In the particular case, when centrifugal effects in a molecule are negligible, that is when $\chi(x) = C_0$ (in Eq. (22) we should take $\delta_K = h_K = l_K = \dots = 0$), $g_0(x) = c - f_{12} \, x^2/(4C_0)$ (i.e. the function $g_0(x)$ has the polynomial form). In the approximation, when $\delta_K \neq 0$, $h_K = l_K = \dots = 0$,

$$g_0(x) = f_{12}/[4 \, \delta_K] \ln |C_0 - \delta_K \, x^2| + c. \qquad (23)$$

In the approximation, when $\delta_K \neq 0$, $h_K \neq 0$, $l_K = \dots = 0$,

$$g_0(x) = -f_{12}/(2\sqrt{D})\, \arctan[(2h_K\, x^2 - \delta_K)/\sqrt{D}] + c, \tag{24}$$

where $D = 4C_0\, h_K - \delta_K^2$ (for $D > 0$). These expressions demonstrate that if centrifugal distortion in a molecule cannot be neglected, then the function $g_0(x)$ and, consequently, the function $\widetilde{\Psi}_0(J_z)$ from the operator H_{12}^{red} have a non-polynomial form, even if the initial functions $\Psi_0(J_z)$ and $\Psi_2^o(x)$ were polynomial.

The next functions $g_2(x)$ from the expansion (11) in some cases can be found from the condition $\widetilde{\Psi}_4^\sigma(x+1) = 0$, which significantly simplifies the form of the interaction operator. With terms containing the functions $g_4^\sigma(y)$ $(\sigma = e, o)$ omitted in Eq. (16d), the following difference equation

$$\Delta g_2^\sigma(x)\,\chi(x) - \Delta\chi(x)\, g_2^\sigma(x) = -\Psi_4^{\sigma\prime}(x+1)/2,\ \sigma \neq \sigma', \tag{25}$$

can be obtained. In this equation, the difference operator Δ for the functions $\{g_2^\sigma(x),\ \chi(x)\} \equiv \varphi(x)$ is introduced by the expression $2\Delta\varphi(x) = \varphi(x+2) - \varphi(x)$. The corresponding differential equation

$$[g_2^\sigma(x)]' - \chi'(x)/\chi(x)\, g_2^\sigma(x) = -\Psi_4^{\sigma\prime}(x+1)/[2\,\chi(x)]$$

has the solution

$$g_2^\sigma(x) = \{-1/2 \int \Psi_4^{\sigma\prime}(x+1)/\chi^2(x) + c\}\,\chi(x) \tag{26}$$

provided that $\chi(x) \neq 0$ and the functions $\chi'(x)$ and $\Psi_4^\sigma(x+1)$ are bounded. The function $g_0(x)$ is determined from the condition $\widetilde{\Psi}_2^o(J_z) = 0$ as before; it has the form

$$g_0(x) = -1/2 \int [\Psi_2^o(x) + g_2^e(x)\Delta F^{(+)}(x-1,\, x+1) +$$

$$+ g_2^o(x)\Delta F^{(-)}(x+1,\, x-1)]\, \mathrm{d}x/\chi(x) + c. \tag{27}$$

The reduced interaction operator H_{12}^{red} is again reduced to the form (21). In the basis of rotational wavefunctions $|J, K\rangle$ it has the matrix elements $\langle J, K \mid H_{12}^{\mathrm{red}} \mid J, K + \Delta K\rangle$ only with $\Delta K = 0, \pm 2$. The more general solution for the functions $g_2^\sigma(x)$, following from the requirement $\widetilde{\Psi}_4^\sigma(x+1) = 0$, can be formally written, according to Eq. (16d), in the form

$$g_2^\sigma(x) = \{-1/2 \int {}'\Psi_4^{\sigma\prime}(x+1)\mathrm{d}x/\chi^2(x) + c\}\,\chi(x), \tag{28}$$

in which

$${}'\Psi_4^\sigma(y) = \Psi_4^\sigma(y) + g_4^{\sigma\prime}(y)\,\Delta F^{(+)}(0,4) +$$

$$+ g_4^\sigma(y)\,\Delta F^{(-)}(4,0)\quad (y = x+1).$$

The functions $\Psi_4^\sigma(y)$ are of the order of λ^6; $g_4^\sigma(y) \sim \lambda^5$; $\Delta F^{(+)} \sim \lambda$; and the function $\Delta F^{(-)}$, as was noted above, is of the order of λ for small values of the quantum number K; $\Delta F^{(-)}(K_r) \approx 0$ for $K \approx K_r$ and for some highly excited rotational states $\Delta F^{(-)} \sim \lambda^0$. In the latter case, the term containing the operator $\Delta F^{(-)}$ is an order of magnitude greater than all other terms. So it should be omitted in Eq. (28), otherwise the

convergence of contact transformations breaks down. The terms underlined in Eqs. (16) cannot be removed by unitary transformations, and therefore the reduced interaction operator H_{12}^{red} takes the form

$$H_{12}^{\mathrm{red}} = \widetilde{\Psi}_0(J_z) + \{J_+^2\, \widetilde{\Psi}_2^e(J_z + 1) +$$

$$+ \widetilde{\Psi}_2^e(J_z + 1)\, J_-^2\} + \Delta H_{12}^{\mathrm{red}}. \tag{29}$$

The functions $\widetilde{\Psi}_0(J_z)$ and $\widetilde{\Psi}_2^e(J_z + 1)$ are determined by Eqs. (16a) and (16b), while the operator $\Delta H_{12}^{\mathrm{red}}$ (appearing for those rotational states, for which $\Delta F^{(-)}$ is comparable with the energy of harmonic oscillations) has the form

$$\Delta H_{12}^{\mathrm{red}} = \{J_+^2\, \Delta\widetilde{\Psi}_2^o(J_z + 1) - \Delta\widetilde{\Psi}_2^o(J_z + 1)\, J_-^2\} +$$

$$+ \{J_+^4\, \Delta\widetilde{\Psi}_2^e(J_z + 2) + \Delta\widetilde{\Psi}_2^e(J_z + 2)\, J_-^4\} + \dots , \tag{30}$$

where

$$\Delta\widetilde{\Psi}_2^o(J_z + 1) = \Delta F^{(-)}(2,0)\, g_2^o(J_z + 1);$$

$$\Delta\widetilde{\Psi}_2^e(J_z + 2) = \Delta F^{(-)}(4,0)\, g_2^e(J_z + 2). \tag{31}$$

In this case, the interaction operator H_{12}^{red} in the basis of rotational wavefunctions $|J, K\rangle$ has the matrix elements $\langle J, K \mid H_{12}^{\mathrm{red}} \mid J, K + \Delta K\rangle$ with $\Delta K = 0, \pm 2, \pm 4, \dots$.

4. CORIOLIS INTERACTION

The operator H_{12} describing the interaction between vibrational states of different types of symmetry in X_2Y molecules, according to the symmetry properties, can be written in the form

$$H_{12} = \{J_+\, C_1^{(+)}(2\,J_z + 1) - C_1^{(-)}(2\,J_z + 1)\, J_-\} +$$

$$+ \{J_+^3\, C_3^{(+)}(2J_z + 3) - C_3^{(-)}(2J_z + 3)\, J_-^3\} + \dots , \tag{32}$$

where $C_{2k+1}(2J_z + 2k + 1)$ $(k = 0, 1)$ are some functions of the operators $\mathbf{J}^2$ and J_z. They can be presented as $C_{2k+1}^{(\pm)} = C_{2k+1}^e \pm C_{2k+1}^o$, where the superscripts e and o denote even or odd character of the function with respect to its argument. In semi-rigid molecules, for interacting states $(V) = (v_1\, v_2\, v_3)$ and $(V') = (v_1 - 1\ v_2\ v_3 + 1)$ (with the same v_2)

$$C_1^e(2J_z + 1) = g_{VV'}/2\, C_{01}^{VV'} + \dots ,$$

$$C_1^o(2J_z + 1) = g_{VV'}/2\, C_{11}^{VV'}(2J_z + 1) + \dots , \tag{33}$$

where $g_{VV'} = [v_1\,(v_3 + 1)]^{1/2}/2$. This is so-called Coriolis resonance of the first type. The Coriolis resonance of the second type involves vibrational states $(V) = (v_1\, v_2\, v_3)$ and $(V') = (v_1\ v_2 - 2\ v_3 + 1)$ with different values of the quantum number v_2. In the standard approximation, Eqs. (33) are used for them, where $g_{VV'} = 1/2\,[(v_2\,(v_2 - 1)\,(v_3 + 1)/2]^{1/2}$. For the

m_2n molecule[12] $|C_{01}^{VV'}| \sim 2\,\mathrm{cm}^{-1}$, $|C_{11}^{VV'}| \sim 0.3\,\mathrm{cm}^{-1}$. Consequently, one can think that for $J \sim \lambda^{-1}$ $C_1^{(\pm)}(2J_z + 1) \sim \lambda^3$ and $C_{2k+1}^{(\pm)}(2J_z + 1) \sim \lambda^{3+2k}$.

According to the symmetry properties, the operator S_{12} from Eq. (4) can be written in the form

$$iS_{12} = \{J_+\,\theta_1^{(+)}(2\,J_z + 1) - \theta_1^{(-)}(2\,J_z + 1)\,J_-\} +$$

$$+ \{J_+^3\,\theta_3^{(+)}(2J_z + 3) - \theta_3^{(-)}(2J_z + 3)\,J_-^3\} + \dots\,, \qquad (34)$$

where $\theta_{2k+1}^{(\pm)} = \theta_{2k+1}^e \pm \theta_{2k+1}^o$ and superscripts e and o are again for the even and odd character of the function with respect to its argument. The operator S_{12} is of the order of λ and, consequently, for $J \sim \lambda^{-1}\ \theta_{2k+1}^{(\pm)} \sim \lambda^{2+2k}$. Substitution of Eq. (34) into Eqs. (5a) gives the following expressions for the transformed operators $\tilde{H}_{nm}$:

$$\tilde{H}_{11} = H_{11}' + \Delta H_C, \quad \tilde{H}_{22} = H_{22}' - \Delta H_C, \qquad (35)$$

$$\tilde{H}_{12} = H_{12} + \{J_+\,\tilde{C}_1^{(+)}(y) - \tilde{C}_1^{(-)}(y)\,J_-\} +$$

$$+ \{J_+^3\,\tilde{C}_3^{(+)}(z) - \tilde{C}_3^{(-)}(z)\,J_-^3\} + \dots\,. \qquad (36)$$

Here

$$\Delta H_C = \Delta F_C + \{J_+^2\,\Delta\chi(x) + \Delta\chi(x)\,J_-^2\}; \qquad (37)$$

$$\Delta F_C = 2\,(\mathbf{J}^2 - J_z^2)\,\delta F^{(+)} - 2J_z\,\delta F^{(-)}; \qquad (38)$$

$$- \Delta\chi(x) = \theta_1^{(+)}(z)\,C_1^{(-)}(y) + \theta_1^{(+)}(y)\,C_1^{(+)}(z); \qquad (39)$$

$$\delta F^{(\pm)} = \theta_1^{(-)}(y)\,C_1^{(-)}(y) \pm \theta_1^{(+)}(y-2)\,C_1^{(+)}(y-2),$$

and $x = J_z + 1$, $y = 2J_z + 1$, $z = 2J_z + 3$. For the functions $\tilde{C}_1^e$, $\tilde{C}_1^o$, and $\tilde{C}_3^\sigma$ ($\sigma = e, o$) we have the following expressions:

$$\tilde{C}_1^e(y) = C_1^e(y) + \theta_1^o(y)\,\Delta F^{(+)}\,(0,1) +$$

$$+ \underline{\theta_1^e(y)\,\Delta F^{(-)}\,(0,1)} + \Delta C_1^e(y); \qquad (40)$$

$$\tilde{C}_1^o(y) = C_1^o(y) + \theta_1^e(y)\,\Delta F^{(+)}\,(0,1) +$$

$$+ \underline{\theta_1^o(y)\,\Delta F^{(-)}\,(0,1)} - \Delta C_1^o(y); \qquad (41)$$

$$\tilde{C}_3^\sigma(z) = C_3^\sigma(z) + \theta_1^{\sigma'}(z+2)\,\chi(x) - \chi(x+1)\,\theta_1^{\sigma'}(y) +$$

$$+ \theta_3^{\sigma'}(z)\,\Delta F^{(+)}\,(0,3) + \underline{\theta_3^\sigma(z)\,\Delta F^{(-)}\,(0,3)}\,. \qquad (42)$$

In Eq. (40)

$$\Delta C_1^\sigma(y) = \theta_1^{\sigma'}(y+2)\,\chi(x)\,\phi(x) -$$

$$- \theta_1^{\sigma'}(y-2)\,\chi(x-1)\,\phi(x-2), \qquad (43)$$

and $\phi(J_z - 1) = J_+ J_- = \mathbf{J}^2 - J_z\,(J_z - 1)$. Let us consider the conditions, under which the interaction operator $\tilde{H}_{12}$ can be reduced to a simpler form by proper choice of the functions θ entering into the transformation generator. In the first approximation,

two functions $\tilde{C}_1^e(y)$ and $\tilde{C}_1^o(y)$ are related by the function $\theta_1^e(y)$. The analysis of the first two equations (40) and (41), in which $\theta_1^o = \theta_3^e = \theta_3^o = 0$, depends on the order of the operator $\Delta F^{(-)}$ and, consequently, on the type of resonance interaction. For the Coriolis resonance of the first type, the bending quantum number v_2 is the same for both interacting states (V) and (V'). In this case, $\Delta F^{(-)} \sim \lambda$ for any K. For the Coriolis resonance of the second type, the quantum number v_2 is different for the states (V) and (V'). The order of the operator $\Delta F^{(-)}$ is determined by the value of the quantum number K, arising in the processing. Figures 2 and 3 show the behavior of the matrix elements $\Delta F^{(n)}(K)$ for three vibrational states of the m_2n molecule (from the results of Ref. 11), which determine the behavior of the function $\Delta F^{(-)}(K) = \{F^{(V)}(K) - F^{(V')}(K)\}/2$ (for $J = 15$).
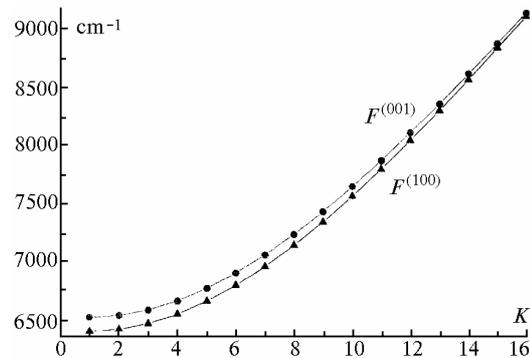

FIG. 2. Behavior of the functions $F^{(100)}(K)$ and $F^{(001)}(K)$ (for $J = 15$) involved into the Coriolis resonance of the first type in the H_2O molecule (from the results of Ref. 11).
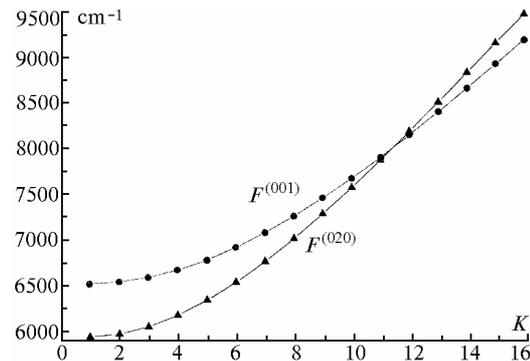

FIG. 3. Behavior of the functions $F^{(020)}(K)$ and $F^{(001)}(K)$ (for $J = 15$) involved in the Coriolis resonance of the second type in the H_2O molecule (from the results of Ref. 11).

It is seen from Fig. 3 that for the Coriolis resonance of the second type the behavior of the function $\Delta F^{(-)}(K)$ is similar to that of the function $\Delta F^{(-)}(K)$ for the Fermi resonance (see Fig. 1); and in

asymptotics $\Delta F^{(-)}(K)$ can have zero order of the parameter of smallness. For the Coriolis resonance of the first type, the function $\theta_1^e(y)$ can be found from the condition $\tilde{C}_1^e(y) = 0$, that is

$$\theta_1^e(y) = - C_1^e(y) / \Delta F^{(-)}(0,1). \quad (44)$$

The reduced interaction operator takes the form:

$$\tilde{H}_{12}^{red} = \{J_+ \tilde{C}_1^o (2J_z + 1) + \tilde{C}_1^o (2J_z + 1) J_-\}. \quad (45)$$

For the Coriolis resonance of the second type, the function $\theta_1^e(y)$ cannot be found from the condition $\tilde{C}_1^e(y) = 0$, that is by Eq. (44), because for some $K = K_r$, $\Delta F^{(-)}(0,1) \approx 0$. This function can be determined from the condition $\tilde{C}_1^o(y)$. The approximate analytical expression

$$\theta_1^e(y) = - \tilde{C}_1^o(y) / [\Delta F^{(+)}(0,1) + 2C_0 y] \quad (46)$$

for this function can be derived, if the approximate expression $\Delta \tilde{C}_1^o(y) = 2 \theta_1^e(y) C_0 y$ is used in Eq. (43). The reduced interaction operator in this case has the form

$$\tilde{H}_{12}^{red} = \{J_+ \tilde{C}_1^e (2J_z + 1) - \tilde{C}_1^e (2J_z + 1) J_-\}. \quad (47)$$

The following two functions $\theta_1^o(y)$ and $\theta_3^e(y)$ (entering into the transformation generator S_{12}) for the Coriolis resonance of the first type can be found from the conditions $\tilde{C}_3^\sigma(z) = 0$ ($\sigma = e, o$), which result in the equations

$$- C_3^e(z) = \theta_1^o(z + 2) \chi(x) - \chi(x + 1) \theta_1^o(y) +$$
$$+ \underline{\theta_3^e(z) \Delta F^{(-)}(0,3)} \; ; \quad (48)$$

$$- C_3^o(z) = \theta_1^e(z + 2) \chi(x) - \chi(x + 1) \theta_1^e(y) +$$
$$+ \theta_3^e(z) \Delta F^{(+)}(0,3). \quad (49)$$

For the presented difference equations, the corresponding differential equations can be found, from which the solutions for $\theta_1^o(y)$ and $\theta_3^e(y)$ can be determined. The analytical expressions for these solutions are not presented here; it is important that at $\chi(x) \neq 0$ these solutions exist. Thus, for the Coriolis resonance of the first type the reduced operator H_{12}^{red} can be again transformed into the form (45), which has the matrix elements $<J, K | H_{12}^{red} | J, K + \Delta K>$ with $\Delta K = \pm 1$ in the basis of rotational wavefunctions $| J, K>$.

For the Coriolis resonance of the second type, this procedure is valid for such quantum numbers K, for which $\Delta F^{(-)}(K) \sim \lambda$ (or $\Delta F^{(-)}(K) \approx 0$). For the values of K, at which $\Delta F^{(-)}(K) \sim \lambda^0$, the terms

underlined in Eqs. (40) − (42) and (48) cannot be removed, because this breaks down the convergence of the contact transformations. In this case, the reduced operator H_{12}^{red} takes the form

$$\tilde{H}_{12}^{red} = \{J_+ \tilde{C}_1^e (2J_z + 1) - \tilde{C}_1^e (2J_z + 1) J_-\} + \Delta H_{12}^{red}, \quad (50)$$

in which the operator ΔH_{12}^{red} should be taken into account for those rotational quantum numbers, for which $\Delta F^{(-)}(K) \sim \lambda^0$. It has the form

$$\Delta H_{12}^{red} = \{J_+ \Delta \tilde{C}_1^o (2J_z + 1) + \Delta \tilde{C}_1^o (2J_z + 1) J_-\} +$$
$$+ \{J_+^3 \Delta C_3^e (2J_z + 3) - \Delta C_3^e (2J_z + 3) J_-^3\} + \dots , \quad (51)$$

where

$$\Delta \tilde{C}_1^o (2J_z + 1) = \theta_1^o (2J_z + 1) \Delta F^{(-)} (J_z, J_z + 1),$$
$$\Delta C_3^e (2J_z + 3) = \theta_3^e (2J_z + 3) \Delta F^{(-)} (J_z, J_z + 3). \quad (52)$$

In the basis of rotational wavefunctions $| J, K>$ of a symmetric top, the operator H_{12}^{red} has the matrix elements $<J, K | H_{12}^{red} | J, K + \Delta K>$ with $\Delta K = \pm 1, \pm 3$. The matrix elements with $\Delta K = \pm 3$ should be taken into account in analysis of resonance interactions in high-excited states.

5. DISCUSSION

The large-amplitude oscillation in non-rigid molecules of the X_2Y type introduces some peculiarities in the procedure of Hamiltonian transformation to the reduced form, having the least number of rotational diagonals in the basis of symmetric top rotational wavefunctions. For the case of resonance interactions (particularly, when the vibrational states with different values of the bending quantum number v_2 are involved in the resonance), this oscillation results in the following. The matrix elements of the interaction operator (starting from some value J_{kr} of the rotational quantum number J) cannot generally be described by functions of the same class (for example, only polynomial functions with respect to rotational quantum numbers). This means that the procedure of the Hamiltonian transformation to the reduced form is ill-defined (diverging) starting from J_{kr}. In this case, the matrix elements with $\Delta K = \pm 4, \dots$ for Fermi resonances and $\Delta K = \pm 3, \dots$ for Coriolis resonances should be included in consideration. The values of the quantum number J_{kr}, starting from which these effects manifest themselves, can be determined from the processing of the experimental data for a particular molecule.

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