

# Rotational dependence of giant $l$ -type doubling and dipole moments of IR-transitions in Coriolis resonance region for the case of polyatomic molecules

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This article presents analysis of the first order Coriolis resonance between the nondegenerate and degenerate normal modes of the symmetric-top molecules leading to the doubling the sublevels of degenerate mode with the quantum number values of full and vibrational angular momentum projection equal to unity ( $k = l = \pm 1$ ) at strong rotational disturbance. The effective Hamiltonian for “giant  $l$ -type doubling”  $H_{g,d}$  has been constructed based on the theory of coupled schemes for grouping the vibration–rotation interactions. Theory of nonlinear series transformation has been applied to analysis of the series over  $J^2$  obtained in  $H_{g,d}$ . The first diagonal Padé approximant for the vibrational dependence of the giant  $l$ -type doubling is presented in the form:

$$\tilde{H}_{g,d} = \sum \alpha \tau a_s^{-\sigma} a_t^{\sigma\tau} J_\tau \left\{ 1 + \frac{(C_{2,J} J^2)^2}{C_{2,J} J^2 - C_{4,J} J^4} \right\},$$

where  $\alpha$ ,  $C_{2,J}$ ,  $C_{4,J}$  are the coefficients in the  $H_{21}$ ,  $\tilde{H}_{23}$ , and  $\tilde{H}_{25}$  operators in  $H_{g,d}$ . The diagonal Padé approximants of a higher order are presented, in particular the [2/2] one, in terms of the series expansion coefficients for the investigated rotational dependence of the giant  $l$ -type doubling on  $J^2$ . The relationships have been derived for the parameters in Herman–Wallis factors in terms of molecular constants for the case of strong, ( $v_A$ ,  $v_E$ ), Coriolis resonance. Numerical estimates in the Herman–Wallis factors for the  $\text{CH}_4$ ,  $\text{OCS}$ ,  $\text{CO}_2$ , and  $\text{HCN}$  molecules are presented.

## Introduction

The harmonic force field in symmetric-top molecules is such that there exist paired resonances between some degenerate, at the frequency  $\nu_t$ , and nondegenerate, at the frequency  $\nu_s$ , fundamental vibrational modes. Rotational sublevels of these modes are highly disturbed by resonance interaction called the Coriolis random resonance.<sup>1</sup> Resonance interaction of this type leads (in molecules of trigonal symmetry) to doubling of the mode  $\nu_t$  sublevels with the quantum numbers of the projections of full angular momentum  $\mathbf{J}$  and vibrational angular momentum  $\mathbf{L}$  equal to unity:  $k = l = \pm 1$ . The magnitude of the sublevel splitting linearly depends, according to the existing theories,<sup>2,3</sup> on the quantum number of full angular momentum  $\mathbf{J}$ . This effect was many times observed in the IR spectra in some symmetrical molecules  $C_{3v}$  ( $\text{XH}_3$ ,  $\text{YXH}_3$ ) and was called the “giant  $l$ -type doubling.”<sup>3</sup> Theoretical investigations of this effect were limited by consideration of the first extinct contribution to the Coriolis interaction operator, and no question on the sublevel splitting behavior at high rotation energies, say high  $J$  values, was addressed.

The aim of this paper is to present a description of rotational dependence of the giant  $l$ -type doubling effect in symmetrical molecules in the form of

fractional rational functions of the quantum number of the full angular momentum.

The construction is based on the concept of coupled schemes for grouping the vibration–rotation interactions of the effective Hamiltonian of vibration–rotation interactions<sup>4</sup> for the rotational dependence of the Coriolis resonance interaction.

In the dominant approximation, the Coriolis resonance interaction operator, in the series expansion of the initial vibration–rotation Hamiltonian for molecules of  $C_{3v}$  symmetry, can be presented in the following equivalent forms<sup>4–6</sup>:

$$H_{21}(\nu_t, \nu_t) = \frac{iB_x^{(e)} \zeta_{nt_2}^x}{\sqrt{\omega_n \omega_t}} \times \sum_{t=\pm 1} \tau \{ \omega_n p_n(q_{t\tau} J_{-\tau}) + \omega_t q_n(p_{t\tau} J_{-\tau}) J_{-\tau} \}. \quad (1)$$

Formula (1) uses generally accepted designations of the molecular constants:  $B_x^e$  is the equilibrium value of rotational constant;  $\zeta_{nt_2}$  is the Coriolis constant;  $\omega_n$  and  $\omega_t$  are the harmonic frequencies of nondegenerate and degenerate modes.

The Hamiltonian of the zero approximation and the effective rotational Hamiltonian of the excited vibrational state ( $V$ ) can be presented as sums of operators (in the  $H_{mm}$  notation system<sup>3</sup>):

$$H_0 = H_{20} + H_{02}, \quad (2)$$

$$H^{\text{eff}} = H_0^V + H_0^R. \quad (3)$$

The diagonal energy of Coriolis interaction in  $H_{20}$  is determined by the relation

$$\langle H_{21} \rangle = \langle 2\pi_\alpha J_\alpha \rangle, \quad (4)$$

where the bracket  $\langle \rangle$  denotes the extraction superoperator of the diagonal part in  $H_{20}$ ;  $\pi_\alpha$  and  $J_\alpha$  are the components of vibrational and full angular momentums on the molecular-fixed axis  $\alpha$ .

It is possible to include all the  $\tilde{H}_{mn}$  operators having the magnitude of the order of rotational constants in  $H_0^R$ ;  $\sim \chi^2 \omega_{\text{vib}} \sim \chi^4 \omega_e$  ( $\chi$  is the Born–Oppenheimer parameter), i.e.,  $H_0^R$  can be presented as a sum of the following operators:

$$H_0^R = H_{02} + \langle H_{21} \rangle + \langle \tilde{H}_{40} \rangle. \quad (5)$$

For the symmetric-top molecule,  $H_0^R$  can be presented as:

$$H_0^R = B_x J^2 + (B_x - B_z - \sum_t \tilde{\zeta}_t) J_z^2 + \sum_t (\tilde{\zeta}_t + \kappa_{l_t l_t}) \hat{l}_t^2 + \sum_t \tilde{\zeta}_t G_t^2, \quad (6)$$

where  $\tilde{\zeta}_t = 2B_z \zeta_{t^2}^z$ ;  $\kappa_{l_t l_t}$  are the constants in the  $\tilde{H}_{40}$  operator and the  $G_t = J_z - \hat{l}_z$  operator has been introduced, while the operator of the vibration mode momentum projection on the symmetry axis is written in terms of the ladder operators  $a_t^{\sigma\tau}$  (see Appendix) in the following way<sup>7</sup>:

$$l_{t_z} = \frac{1}{8} \sum_{\sigma\tau=\pm 1} \sigma\tau a_t^{\sigma\tau} a_t^{-\sigma,-\tau}. \quad (7)$$

In passing from  $l_t$  operator to a zero operator  $\hat{l}_t \rightarrow 0 \cdot \hat{l}_t$ , that corresponds to realization of nondegenerate vibrational state, the operator  $G$  transforms to the operator  $J_z$ :  $\hat{G} \rightarrow J_z$ . Owing to the obvious conditions for the commutators

$$[J_z, l_{t_z}] = [J_z, G] = [l_{t_z}, G_t] = 0 \quad (8)$$

the following commutativity should hold

$$[J_z, H_{20}] = [\hat{l}_t, H_{20}] = [G_t, H_{20}] = 0. \quad (9)$$

Therefore, for the case of symmetric-top molecules harmonic Hamiltonian  $H_{20}$  and operators of the projection of the angular momentum of  $\hat{l}(l_a, l_b, l_c)$  mode on the symmetry axis  $l_c$  have common spectrum of eigenvalues. In addition to the principal quantum number  $v_t$ , the vibration–rotation states of the degenerate mode  $v_t$  can be determined

by the  $k$ ,  $l_t$ , and  $G$  quantum numbers, i.e., the  $G_t$  quantum number is a good quantum number. At high  $J$ , i.e., when  $J \gg \chi^{-1}$ , the first term  $H_{21}$  in  $H_0^R$  becomes dominating. Reference 8 presents the relations of purely vibrational and Coriolis energy at high  $J$  values. In this paper, the model is proposed for description of rotational dependence of the giant  $l$ -type doubling in both polynomial and nonpolynomial forms.

## 1. Effective Hamiltonian for the giant $l$ -type doubling

Coriolis interaction in symmetric-top molecules between the nondegenerate  $v_s$  and doubly degenerate  $v_t$  modes of the series expansion of the initial Hamiltonian in the dominant approximation is described by the operator, which in contrast to expression (1), is written in terms of the ladder operators:

$$H_{21}(v_s, v_t) = \frac{1}{4} \frac{B_x^{(e)} \zeta_{st}^x}{\sqrt{\omega_s \omega_t}} \sum_{\tau, \sigma, \sigma' = \pm 1} \tau (\sigma \omega_s - \sigma' \omega_t) a_s^\sigma a_t^{\sigma'\tau} J_{-\tau}. \quad (10)$$

In the case of a resonance at the harmonic frequency  $\omega_s \approx \omega_t$ , it is possible to analyze  $H_{21}$  from Eq. (10) using perturbation theory only for the nonresonance part:

$$H_{21}^{(*)} = \frac{1}{4} \frac{B_x^{(*)} \zeta_{st}^x}{\sqrt{\omega_s \omega_t}} \sum_{\sigma\tau} \sigma\tau (\omega_s - \omega_t) a_s^\sigma a_t^{\sigma\tau} J_{-\tau}. \quad (11)$$

The  $S$ -function of the contact transformation method corresponding to the  $H_{21}$  operator (Eq. (11)) is determined by the relation

$$S_{21}^{(*)} = -\frac{i}{4} \frac{B_x^{(*)} \zeta_{st}^x}{\sqrt{\omega_s \omega_t}} \sum_{\sigma\tau} \tau \frac{\omega_s - \omega_t}{\omega_s + \omega_t} a_s^\sigma a_t^{\sigma\tau} J_{-\tau}. \quad (12)$$

Resonance part of the  $H_{21}(v_s, v_t)$  operator, according to the definition by Eq. (10), has the following form

$$\tilde{H}_{21}(v_s, v_t) = \alpha \sum_{\sigma\tau} \sigma\tau a_s^\sigma a_t^{-\sigma\tau} J_{-\tau}, \quad (13)$$

where

$$\alpha = \frac{1}{4} \frac{B_x^{(*)} \zeta_{st}^x (\omega_s + \omega_t)}{\sqrt{\omega_s \omega_t}}. \quad (14)$$

In analyzing accidental resonances in molecules, one should use the operator  $S_{mm}^{(*)}$  instead of the full generator of contact transformations  $S_{mm}$ .

The effective Hamiltonian (EH) taking into account the accidental Coriolis resonances and essential resonance interactions in polyatomic molecules and radicals can most simply be constructed, within the frameworks of the problem under study, in the limiting group (W) proposed by Watson.<sup>8</sup> The concept of ordering vibration–rotation

interactions in quasi-rigid molecules has been developed in Ref. 9 and presented in the Table below.

**Table. Determination of orders of magnitude of vibrational and rotational operators and commutators in different schemes of grouping**

| Parameter               | W                         | AN                    | BOO          | M                          |
|-------------------------|---------------------------|-----------------------|--------------|----------------------------|
| $r$                     | 1                         | 1                     | 1            | $\chi^{-1+\varepsilon}$    |
| $J$                     | $\chi^{-2+\varepsilon}$   | $\chi^{-1}$           | 1            | 1                          |
| $[p, q]_v$              | $-i$                      | $-i$                  | $-i$         | $-i\chi^{-2+2\varepsilon}$ |
| $[J_\alpha, J_\beta]_R$ | $-i\chi^{-2+\varepsilon}$ | $-iJ_\gamma\chi^{-1}$ | $-iJ_\gamma$ | $-iJ_\gamma$               |

The Table uses the following designations and abbreviations:  $q$  and  $p$  are the normal coordinates and the related momentums;  $J_\alpha$  are the components of full angular momentum;  $i$  is the imaginary unit;  $\varepsilon$  is the parameter of smallness,  $\varepsilon \rightarrow 0$ ; W denotes the abbreviated name for the Watson scheme of ordering (grouping) the vibration–rotation perturbations and then following this principle: AN is for Amat–Nielsen; BOO for Born–Oppenheimer–Oka; M for Mikhailov schemes.

We shall briefly discuss two ordering schemes, namely W and M, which are called the limiting ordering schemes.<sup>4,9,11</sup>

The *W ordering scheme*. According to the Table, this scheme takes the following orders of magnitude for the operators:

$$H_{20} \sim \chi^2 E_e, \quad (15)$$

$$H_{02} \sim \chi^\varepsilon E_e \sim \chi^A \chi^{-4+\varepsilon} E_e, \quad \varepsilon \rightarrow 0. \quad (16)$$

The *M ordering scheme*. In this scheme, the following orders of magnitude for the operators are taken in accordance with the table:

$$H_{20} \sim \chi^\varepsilon E_e \sim \chi^2 \chi^{-2+2\varepsilon} E_e, \quad \varepsilon \rightarrow 0, \quad (17)$$

$$H_{02} \sim \chi^A E_e \sim \chi^2 \omega_{\text{vib}}. \quad (18)$$

The form of EH in different groupings of the vibration–rotation interactions can be related to different types of tables.<sup>10</sup> In the Amat–Nielsen ordering scheme, the EH can be presented by a square ordering array

$$H^{\text{eff}} = \left\| \overrightarrow{H}_{mm}^m \right\| \downarrow, \quad m = n. \quad (19)$$

In the ordering schemes of W or M types, the EH can be presented by the limiting cases of table degeneracy into the column or row:

$$\begin{array}{ll} \text{W type,} & \text{M type,} \\ |H_{mn}| \quad m \ll n & \overline{H}_{mn} \quad m \gg n, \quad (20) \\ \text{row} & \text{column} \end{array}$$

The EH describing rotational dependence of the  $l$ -type doubling effects including the “giant  $l$ -type doubling,” can be introduced into the W group by the following series:

$$H_d^{\text{eff}} = H_{\text{cent}} + \sum \{ \tilde{H}_{2,2n+1} + \tilde{H}_{2,2n} \} = H_{\text{cent}} + (H_{20} + \tilde{H}_{22} + \tilde{H}_{24} + \dots) + (\tilde{H}_{21} + \tilde{H}_{23} + \tilde{H}_{25} + \dots). \quad (21)$$

The EH reduction for the case of paired intermode resonance interaction was investigated in Ref. 11. It should be noted that the general form of EH reduction for the molecules of  $C_{3v}$  symmetry in the doubly degenerate states has been discussed in the review 12. Reference 13 presents the detailed relationships for the spectroscopic and molecular constants. Reference 8 discusses the rotational dependence of the first order Coriolis interaction in its nonreduced form and in the approximation of an isolated vibrational state while in this paper we develop spectroscopic models for the reduced EH describing the “giant  $l$ -type doubling” in symmetrical molecules.

The EH for the “giant  $l$ -type doubling” can be presented by the following series

$$\tilde{H}_{g,d} = P_{11} \left( \sum_n H_{2,2n+1} \right) P_{1-1}, \quad (22)$$

where  $P_{11} = P_{|l=\pm 1, |k=1|}$  is the operator of projection onto the state shell with the projection values of the pseudovibrational and full angular momentums on the axis of symmetry equal to unity. The operator sequence (22) for the  $A$ – $E$  resonance in molecules of axial and trigonal symmetry can be presented by a product of a tensor operator for the investigated resonance and a scalar operator as a function of full angular momentum  $\mathbf{J}$  and its projection  $J_z$ . This statement is easily proved based on the symmetry properties of vibrational and rotational operators presented above:

$$\begin{aligned} \tilde{H}_d = & \sum_\tau \tau a_s^\sigma a_t^{-\sigma\tau} J_{-\tau} \alpha \{ 1 + C_{2J} J^2 + \\ & + C_{2K} J_z^2 + C_{4J} J^4 + C_{4JK} J^2 J_z^2 + \dots \}, \quad (23) \end{aligned}$$

where  $C_{n,J(K)} = (\tilde{b}_{2,n}) / \alpha$ ,  $\tilde{b}_{2,n}$  are the coefficients in the  $\tilde{H}_{2,n}$  operators (resonance). Allowing for the action of the projection operator  $P_{11}$  in  $\tilde{H}_{g,d}$ , we obtain the following definition of the effective Hamiltonian for rotational dependence of the giant  $l$ -type doubling:

$$\begin{aligned} \tilde{H}_{g,d} = & P_{11} \sum \tau a_s^\sigma a_t^{-\sigma\tau} J_{-\tau} \alpha \left\{ 1 + \sum_n C_{2n,J} J^{2n} \right\} P_{1-1} = \\ = & P_{11} \sum \tau a_s^\sigma a_t^{-\sigma\tau} J_{-\tau} P_{1-1} f(J^2). \quad (24) \end{aligned}$$

It is difficult to apply the methods improving the series convergence to the sequence in braces, i.e., the so-called nonlinear sequence transformations, having in mind by this the assumption that  $[J^2, H_0^R] = 0$  and substitution  $J^2 \rightarrow J(J+1)$ . The diagonal Padé approximant for  $f(J^2)$ , which can be employed in handling the spectra at the lowest stage,

modifies the EH for the giant *l*-type doubling to the following form:

$$\tilde{H}_{g,d} = P_{11} \sum \tau a_s^\sigma a_t^{-\sigma} J_{-\tau} \alpha P_{1-1} \left\{ 1 + \frac{(C_{2J})^2}{C_{2J} - C_{4J} J^2} J^2 \right\}, \quad (25)$$

where  $\alpha$ ,  $C_{2J}$ , and  $C_{4J}$  are the coefficients in resonance operators  $H_{21}$ ,  $\tilde{H}_{23}$ , and  $H_{25}$ , respectively.

There are two limiting cases for  $H_{g,d}$ . In the one ( $C_{4J} \ll C_{2J}$ ) it appears in a polynomial form; in the other ( $C_{2J} \sim \varepsilon C_{4J}$ ) it determines the characteristic properties of the analytical function  $f(J^2)$  (simple poles, bifurcation points, etc.). In  $J$  units, the distance to the first pole  $C_{2J} - C_{4J} \sim 0$  can be estimated by the following formula:

$$\langle J^2 \rangle \sim C_{2J} / C_{4J}, \quad (26)$$

$$J_{\text{critical}} \sim \text{modul} \sqrt{\langle J^2 \rangle_{\text{critical}}} \sim \text{modul} \sqrt{C_{2J} / C_{4J}}. \quad (27)$$

The definitions of different ordering schemes of vibration–rotation interactions presented in the Table, give an opportunity of constructing the empirical model in order to describe the considered effect in terms of the expansion parameter  $\lambda$ , which is the function of the Born–Oppenheimer parameter,  $\lambda \sim \chi^{a/b}$  (see Ref. 9), and of the full angular momentum. Summation of the series like  $\sum \lambda^m J^n$  that appear in using such an approach can be carried out by the methods described in Refs. 14–16. Let us show two sequences and corresponding Padé approximants as an example.

Let us write a simplified model of  $\tilde{H}_{g,d}$ :

$$\tilde{H}_{g,d} = \sum (\alpha a_s^\sigma a_t^{-\sigma} J_{-\tau}) \left\{ 1 + \lambda J^2 + \sum_{n=3}^{\infty} \lambda^{2n-1} (J^2)^n \right\}, \quad (28)$$

where  $\lambda \sim \chi^{1/2}$ , summation by the Padé method yields the same expression for all Padé approximants, except for the trivial one:

$$\tilde{H}_{g,d} = \sum P_{11} (\alpha a_s^\sigma a_t^{-\sigma} J_{-\tau}) P_{11} \times \left\{ \frac{1 + (-\lambda^2 + \lambda) J^2 + (\lambda^3 + \lambda^2) J^4}{-\lambda^2 J^2 + 1} \right\}. \quad (29)$$

On the other hand, a series for  $f(J^2)$  with the sum  $\sum_{n=3}^{\infty} (-1)^{n+1} \lambda^{2n-1} (J^2)^n$  in braces gives the same effect, as the change of  $J^2$  sign in formula (28).

This expression was obtained for the considered series over  $J^2$  by means of the Padé approximants up to the sixth order inclusive. This formula can be used for calculation of rotational contributions to the giant *l*-type doubling for the symmetric-top molecules.

Let us consider the energy matrix for this problem in the basis of symmetric functions<sup>7,8</sup>:

$$|v_t^l; J, K, S\rangle = \frac{e^{i\pi S}}{\sqrt{2}} \{ |v_t^l JK\rangle + (-1)^S |v_t^{-l} J - K\rangle \}, \quad (30)$$

$S = 0, 1.$

Classification of vibration–rotation functions for the molecules of  $C_{3v}$  symmetry in the subspace with  $k = l_t = \pm 1$  yields the following result<sup>7</sup>:

$$|v_t^l; J, 1, S\rangle \begin{cases} J_{\text{even}} & J_{\text{odd}} \\ |+\rangle A_2 & A_1 \\ |-\rangle A_1 & A_2. \end{cases} \quad (31)$$

Vibration–rotation functions for the nondegenerate mode can be classified in the following way:

$$|10^0 J 0\rangle \begin{cases} J_{\text{even}} & J_{\text{odd}} \\ A_1 & A_2. \end{cases} \quad (32)$$

The energy matrix of  $\tilde{H}_{g,d}$  Hamiltonian in a symmetrized basis  $|v_t, l_t, J, K, S\rangle$  has the following form<sup>7,15</sup>:

$$\begin{array}{ccc|ccc} & J_{\text{even}} & & J_{\text{odd}} & & \\ \tau_1 & \tau_2 & \tau_3 & \tau_1 & \tau_2 & \tau_3 \\ \hline E_{11} & 0 & 0 & E_{11} & b & 0 \\ 0 & E_{22} & a & b & E_{22} & 0 \\ 0 & a & E_{33} & 0 & 0 & E_{33}, \end{array} \quad (33)$$

where

$$|\tau_1\rangle = |+\rangle, \quad |\tau_2\rangle, \quad |\tau_3\rangle = |-\rangle, \quad a = \langle - | \tilde{H}_{g,d} | \tau_2 \rangle, \\ b = \langle + | \tilde{H}_{g,d} | \tau_2 \rangle.$$

The expression for rotational energy of the degenerate mode  $v_t$  can be presented, according to Refs. 3 and 10 as follows:

$$E_{JKl_t G_t} = B_x^{[v_t]} J(J+1) + B_x - B_z + \tilde{\zeta}_t^{[v_t]} k^2 + \\ + (\tilde{\zeta}_t + \chi_{ll_t})^{[v_t]} l_t^2 - \zeta_t^{[v_t]} G_t^2, \quad (34)$$

where  $\tilde{\zeta}_t^{[v_t]} = 2B_z^{[v_t]} \zeta_{t_1 t_2}^{[v_t]}$ ;  $\chi_{ll_t}$  are the anharmonicity constants in the operator  $\tilde{H}_{40}$ ;  $G_t = J_z - l_{t_2}$ . The two-dimensional determinant chosen from the corresponding levels for  $J_{\text{even}}$  and  $J_{\text{odd}}$  in the basis  $|\tau_i\rangle$ , can be diagonalized in the following way<sup>5</sup>:

$$\begin{bmatrix} x & \sigma y \\ -\sigma y & x \end{bmatrix} \times \begin{bmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{bmatrix} \times \begin{bmatrix} x & -\sigma y \\ \sigma y & x \end{bmatrix} = \begin{bmatrix} E^+ & 0 \\ 0 & E^- \end{bmatrix}, \quad (35)$$

where  $H_{21} = H_{12}$  are real and

$$E^\pm = \frac{1}{2}(H_{11} + H_{22}) \pm \frac{1}{2}\Delta, \quad (36)$$

where  $\Delta = [\delta + 4H_{12}]^{1/2}$  and  $\delta = H_{11} - H_{22}$ . Square root was taken positive so that the relation  $E^+ \geq E^-$

always holds. The eigenvectors are given by the following relations:

$$x = [(\Delta + \delta)/2\Delta]^{\frac{1}{2}}; \quad y = [(\Delta - \delta)/2\Delta]^{\frac{1}{2}}. \quad (37)$$

The square root was also chosen positive, so that  $x$  and  $y$  are both positive, and  $x > y$  at  $\delta > 0$  and  $x < y$  at  $\delta < 0$ . Sign symbol  $\sigma = +1$ , when  $H_{12}$  ( $H_{12} = a$  and  $b$ ) is positive, and  $\sigma = -1$ , when  $H_{12}$  is negative.

Therefore, the degenerate levels with  $k = l = \pm 1$  of the  $v_l$  mode are split into two components:  $\tau_+$  and  $\tau_-$ . The sublevel  $\tau_-$  interacts with the level  $k = 0$  of the  $v_s$  mode while the  $\tau_+$  sublevel remains unperturbed. For odd  $J$ , the  $\tau_+$  symmetry is  $A_1$ , the  $\tau_-$  symmetry is  $A_2$ , whereas for even  $J$  the contrary is valid. The giant  $l$ -type doubling of the levels with  $k = l = \pm 1$  is by one, two or three orders of magnitude greater than ordinary  $l$ -type doubling in the  $H_{22}$  operator. Nevertheless, when the resonance is not so strong and the doubling coefficients in expression (36) become of the same order of magnitude as the constant  $\alpha$  (see Eq. (14)), the width of splitting is proportional to  $J(J + 1)$  (see Refs. 15 and 17).

Let us consider the expressions for EH describing the rotational dependence for the giant  $l$ -type doubling in molecules of trigonal symmetry, in the diagonal [2/2] Padé approximant approach from Ref. 14, written in terms of  $C$ -coefficients of the initial EH (26):

$$\{C_{2J}J^2[C_{4J}J^2 - (C_{2J}J^2)^2] - C_{6J}J^6 - C_{4J}J^8\} / \{C_{4J}J^4 - [C_{2J}J^2]^2 + C_{4J}J^4C_{2J}J^2 - C_{6J}J^6 + C_{2J}J^2C_{6J}J^6\}. \quad (38)$$

Relations for the EH parameters presented in this section in the Padé form involving molecular constants applicable to analysis of some molecular system of astrophysical interest: for the analysis of the ( $E - F_2$ )-resonance in the methane, of the ( $A - E$ )-resonance in ammonia, as well as in other symmetrical molecules.

## 2. First order Herman–Wallis factors in the case of strong Coriolis resonance ( $v_A, v_E$ ), ( $v_E, v_{F_2}$ )

The effective operator of the dipole moment of a vibrational transition in the W grouping can be presented as the following series<sup>11</sup>:

$$\tilde{M}(\Delta V = 1) = M_{11} + \tilde{M}_{12} + \tilde{M}_{13} + \dots \quad (39)$$

The theory of intensity of the vibration–rotation transitions that uses the limiting schemes of ordering, admits the use of methods improving the rate of series convergence. Let us introduce the specific Padé approximant<sup>10,14</sup> for rotational operators in the series (39):

$$\tilde{M}(\Delta V = 1) = M_{11} + \frac{\tilde{M}_{12}^2}{\tilde{M}_{12} - \tilde{M}_{13}} + \dots \quad (40)$$

This series better describes the behavior of line intensities at high rotational quantum numbers.<sup>9,10</sup> In this paper, we shall restrict ourselves to consideration of the Herman–Wallis factors for the accidental ( $v_A, v_E$ ) Coriolis resonances. The first order Herman–Wallis factors are determined by the  $\tilde{M}_{12}$  operator in  $\tilde{M}(\Delta V = 1)$ . In the general form, the expression for  $\tilde{M}_{12}$  operator is as follows

$$\tilde{M}_{12} = \frac{1}{2} \sum_{k,\alpha\beta} \Theta_k^{\alpha,\beta} p_k [J_\alpha, \lambda_{A\beta}]_{\pm}, \quad (41)$$

where  $p_k = -i\partial/\partial q_k$  is the nondimensional normal momentum;  $\lambda_{A\beta}$  are the direction cosines. Relations for the nonzero parameters in the  $C_{3v}$  symmetry group are the following:

|                                    |  |
|------------------------------------|--|
| parallel band                      | perpendicular band   |
| $\Theta_n^{y,x} = -\Theta_n^{x,y}$ | $\Theta_{t_1}^{y,z} = -\Theta_{t_2}^{x,z},$  |
|                                    | $\Theta_{t_1}^{z,y} = -\Theta_{t_2}^{z,x},$  |
|                                    | $\Theta_{t_1}^{x,y} = \Theta_{t_1}^{y,x} = \Theta_{t_2}^{x,x} = \Theta_{t_2}^{y,y}.$ |

(42)

In case of strong accidental Coriolis resonance  $H_{21}(v_m, v_{m'})$ , the parametric tensor in the  $\tilde{M}_{12}$ -operator has the following modified form

$$\tilde{M}_{12}^{(*)} = \frac{1}{2} \sum_{\alpha\beta} \{^{(*)}\Theta_m^{\alpha,\beta} p_m + ^{(*)}\Theta_{m'}^{\alpha,\beta} p_{m'} + \sum_{k \neq m, m'} \Theta_k^{\alpha,\beta} p_k\} [J_\alpha, \lambda_{A\beta}]_{\pm}. \quad (43)$$

Expressions for the parameters marked with asterisk have the following form:

$$^{(*)}\Theta_m^{\alpha,\beta} = \gamma_m^\alpha \left\{ \zeta_{mm'}^\alpha \mu_{m'}^\beta \frac{1}{2} \sqrt{\frac{\omega_m}{\omega_{m'}}} \frac{(\omega_{m'} - \omega_m)}{(\omega_{m'} + \omega_m)} - \sum_{\gamma\delta} e_{\beta\gamma\delta} \left( \frac{B_m^{\alpha\gamma}}{B_\alpha^{(\delta)}} \right) \mu_e^\delta + 2 \sum_{k \neq m'} \zeta_{mk}^\alpha \mu_k^\beta \frac{\sqrt{\omega_k/\omega_{m'}}}{1 - (\omega_k/\omega_{m'})^2} \right\}. \quad (44)$$

In the case with no resonance the first term in Eq. (44) has the following form<sup>3</sup>:

$$\zeta_{mm'}^\alpha \mu_{m'}^\beta \frac{\sqrt{\omega_m \omega_{m'}}}{\omega_m - \omega_{m'}}. \quad (45)$$

Analysis of parameters  $\Theta_k^{\alpha,\beta}$ , made with the allowance for the symmetry properties of molecular constants  $\zeta_{mk}^\alpha$  and  $\mu_k^\beta$  in the  $C_{3v}$  symmetry group, yields the following equations relating the parameters in  $\tilde{M}_{12}$  marked with asterisk,  $^{(*)}\Theta_k^{\alpha,\beta}$ , and full  $\Theta_k^{\alpha,\beta}$  ones

$$\begin{aligned}
^{(*)}\Theta_S^{y,x} \neq \Theta_S^{y,x} \quad ^{(*)}\Theta_{I_1}^{y,z} \neq \Theta_{I_1}^{y,z}, \\
^{(*)}\Theta_{I_1}^{z,y} = \Theta_{I_1}^{z,y}, \\
^{(*)}\Theta_{I_1}^{x,y} = \Theta_{I_1}^{x,y}.
\end{aligned} \quad (46)$$

Let us consider methane molecule as an example. The harmonic force field in the methane molecules is such that it causes the occurrence of resonances at the frequencies of the valence and deformation vibrations. In particular, there is a dyad of states ( $v_2, v_4$ ) already in the lower energy range. In the upper energy range, there is a dyad of states ( $v_1, v_3$ ). Let us present numerical estimates<sup>18</sup> of  $\Theta$ -parameters in the operator  $M_{12}$  for the lower states ( $v_2, v_4$ ). Using Gray–Robiette force field<sup>18</sup> and electrooptical parameters calculated *ab initio* in Ref. 11, we obtain the following values of  $\Theta$ -parameters in  $M_{12}$  operator of the methane molecule:

$$\begin{aligned}
\Theta_{3y}^{z,x} &= -2.833 \cdot 10^{-4} D, \\
\Theta_{4y}^{x,z} &= -3.113 \cdot 10^{-4} D, \\
^*\Theta_{2b}^{z,z} &= 3.96 \cdot 10^{-3} D.
\end{aligned} \quad (47)$$

As follows from the above analysis and transformation symmetry properties of normal coordinates and angular momentum components<sup>6</sup> for the tetrahedral molecules the  $\Theta$ -parameters of the  $v_4$  band in the region of ( $v_2, v_4$ ) states do not change, while  $\Theta$ -parameter of the  $v_2$  band changes according to Eq. (44). This conclusion is confirmed by the numerical calculations presented.

The mixing coefficients in the line intensity are obtained from wave functions presented in this section and using the expressions (44) for the  $^{(*)}\Theta$ -parameters in  $\tilde{M}_{12}$  as well as the corresponding matrix elements of the operator of the dipole moment of the transitions.

Ignoring the effect of intermode resonance interaction ( $A-E$ ) considered in the paper for symmetrical molecules, the  $F$ -factors for parallel and perpendicular bands of linear molecules are presented in Ref. 4. Let us present here the generalized formula from Ref. 4 for the  $F$ -factors:

$$F_{\sigma,\tau,\rho}^{(n)} = [1 - \sigma(\gamma_n \Theta_n)(f_\rho(J) + f_{\rho\tau}(k))]^2, \quad (48)$$

where

$$\begin{aligned}
f_\rho(J) &= \frac{\rho}{2}(2J + \rho + 1), \\
f_{\rho\tau}(k) &= \delta_{J,J+\rho} \tau \left( k + \frac{\tau}{2} \right), \quad \gamma_n = \frac{2B_v}{\omega_n}.
\end{aligned}$$

For the parallel bands  $n = S$  and the factor  $F^{(0)} = F_{\sigma,0,\rho}^{(S)}$ , while for the perpendicular bands  $n = t$  and  $F_{\sigma,\tau,\rho}^{(\perp)} = F_{\sigma,\tau,\rho}^{(t)}$ . As follows from the above-mentioned relations, the vibration–rotation transition

with  $\Delta N = 1$  is characterized by the quantum numbers of the initial state ( $v_s, J$ ) or ( $v_t^h, J, k$ ) and by three numbers ( $\sigma, \rho, \tau$ ), which are defined by known expressions:

$$\begin{aligned}
\sigma &= +1(-1) \text{ is the absorption (emission);} \\
\rho &= 1, 0, -1 \text{ denote the } R, Q, \text{ and } P \text{ branches;} \\
\tau &= +1, 0, -1 \text{ denote the } r, q, \text{ and } p \text{ subbranches.}
\end{aligned}$$

These relations are valid not only for linear molecules but also for the molecules with equilibrium configuration referring to the point groups of middle symmetry.

Dependence of the  $F$ -factor on the quantum number  $J$  for lines due to transitions in the region of the giant  $l$ -type doubling is the same as in Eqs. (47) and (48) ( $v = 1$ ), but the  $\Theta_n$  coefficients in Eqs. (47) and (48) are replaced by the  $\Theta$ -coefficients (44).

Calculation of  $\Theta$ -parameters for the OCS molecule gives the following values<sup>4</sup>:

$$\begin{aligned}
\Theta_1 &= 1.035, \\
\Theta_2 &= -1.635, \\
\Theta_3 &= 0.310.
\end{aligned} \quad (49)$$

For a comparison, we present below the  $\Theta_n$  values for HCN, DCN and CO<sub>2</sub> molecules determined from the measured intensity ratios of the lines with the same  $J$  in  $P$  and  $R$  branches<sup>19</sup>:

$$\begin{aligned}
\Theta_1(\text{DCN}) &= 3.10, \\
\Theta_3(\text{DCN}) &= 0.38, \\
\Theta_3(\text{HCN}) &= 2.55, \\
\Theta_2(\text{CO}_2) &= 1.50.
\end{aligned} \quad (50)$$

## Conclusion

In this paper, we have applied, for the first time, the concept of coupled schemes for grouping the vibration–rotation interactions to analysis of accidental resonances in spectra of quasi-rigid molecules. The Padé approximant method has been used as a basis for studying the rotational dependence of the paired resonance interactions in molecules. Two Padé approximants have been proposed for rotational dependence of the giant  $l$ -type doubling in symmetrical molecules. The relations have been derived that relate the parameters of the Herman–Wallis factor with the molecular constants for the case of Coriolis resonances in the energy spectrum of molecules. Numerical estimates for methane confirm the fact that parameters in the Herman–Wallis factor, estimated ignoring the accidental resonances, can yield values that are overestimated by orders of magnitude. Numerical estimates for the parameters in the  $F$ -factor are presented for a number of linear triatomic molecules, for which accidental first order Coriolis resonance is not essential.

### Appendix

Vibrational and rotational ladder operators and phase factors for matrix elements have the same form as in Refs. 3 to 6:

$$\begin{aligned} q_{t_\tau} &= q_{t_a} + \tau q_{t_b}, & q_{t_\tau} &= -i \frac{\partial}{\partial q_{t_\tau}}, \\ a_t^{\sigma\tau} &= q_{t_\tau} - i\sigma p_{t_\tau}, & J_\tau &= J_x = -i\tau J_y, \\ a_S^\sigma &= q_S - i\sigma p_S, \end{aligned} \quad (\text{A1})$$

$$\begin{aligned} a_t^{\sigma\tau} |V_t, l_t\rangle &= [2(V_t + 1 + \sigma + \sigma\tau l_t)]^{\frac{1}{2}} |V_t + \sigma, l_t + \tau\rangle, \\ a_S^\sigma |V_S\rangle &= [2V_S + 1 + \sigma]^{\frac{1}{2}} |V_S + \sigma\rangle, \\ J_\tau |J, k\rangle &= [J(J+1) - k(k-\tau)]^{\frac{1}{2}} |J, k-\tau\rangle. \end{aligned} \quad (\text{A2})$$

With the operators introduced by Shaffer and Lawk,<sup>20</sup> the  $a_t^{\sigma\tau}$  operators of two-dimensional oscillator are related by the following expression<sup>4</sup>:

$$a^{++} = -i\xi, \quad a^{+-} = -i\eta^+, \quad a^{-+} = i\eta, \quad a^{--} = i\xi^+.$$

Relations (A1) and (A2) are used at formation of energy matrix (see Section 1) and in calculating the transitions strengths (see Section 2) of this paper for investigations of accidental Coriolis resonances in symmetrical molecules.

### References

1. J.S. Garing, H.H. Nielsen, and K.N. Rao, *J. Mol. Spectrosc.* **3**, Is. 1–6, 496–527 (1959).
2. G. Amat, H.H. Nielsen, and G. Tarrago, *Vibration–Rotation of Molecules* (Marcell-Dekker, New York, 1971), 370 pp.
3. D. Papousek and M.R. Aliev, *Molecular Vibration–Rotation Spectra* (Elsevier, Amsterdam, 1982), 323 pp.
4. V.M. Mikhailov, in: *Microwave Spectroscopy and Its Applications* (Nauka, Moscow, 1985), pp. 235–238.
5. G. DiLauro and I.M. Mills, *J. Mol. Spectrosc.* **21**, Is. 1–4, 383–413 (1966).
6. J.K.G. Watson, in: *Vibrational Spectra and Structure*, ed. by J.R. Durig (Elsevier, Amsterdam, 1977), pp. 2–89.
7. W.E. Blass, *J. Mol. Spectrosc.* **31**, Is. 1–13, 196–207 (1969).
8. M.R. Aliev and J.K.G. Watson, *J. Mol. Spectrosc.* **75**, Is. 1, 150–160 (1979).
9. V.M. Mikhailov, *Atmos. Oceanic Opt.* **14**, No. 1, 15–28 (2001).
10. V.M. Mikhailov and M.A. Smirnov, *Proc. SPIE* **3583**, 60–68 (1998).
11. S.P. Gavva and V.M. Mikhailov, in: *High Resolution Spectroscopy of Small Molecules* (Nauka, Moscow, 1987), pp. 148–195.
12. M.R. Aliev and J.K.G. Watson, in: *Molecular Spectroscopy: Modern Research*, ed. by K.N. Rao (Acad. Press, New York, 1985), Vol. 3, pp. 2–67.
13. E.I. Lobodenko, O.N. Sulakshina, V.I. Perevalov, et al., *J. Mol. Spectrosc.* **126**, Is. 1, 159–170 (1987).
14. J. Beiker and P. Grave-Morris, *Padé Approximants* [Russian translation] (Mir, Moscow, 1986), 502 pp.
15. V.M. Mikhailov and M.A. Smirnov, *Proc. SPIE* **4063**, 90–96 (2000).
16. E.A. Weniger, *Comput. Phys. Rep.* **10**, 189–371 (1989).
17. J.K.G. Watson, C. Gerke, M. Hander, et al., *J. Mol. Spectrosc.* **187**, 131–141 (1998).
18. D.L. Gray and A.G. Robiette, *Mol. Phys.* **37**, No. 6, 1901–1920 (1979).
19. N. Jacobbe and J.F. Jaffe, *J. Mol. Spectrosc.* **10**, Is. 1–6, 1–11 (1963).
20. R.C. Louck and W.H. Shaffer, *J. Mol. Spectrosc.* **4**, Is. 1–6, 285–297 (1960).