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Published online: 16 Jun 2014.

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# RESEARCH ARTICLE

# On the 'expanded local mode' approach applied to the methane molecule: isotopic substitutions CH₃D ←CH₄ and CHD₃ ←CH₄

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Operator perturbation theory and the symmetry properties of the axially symmetric XYZ₃ ($C_{3v}$) type molecules are used for the determination of the spectroscopic parameters in the form of functions of structural parameters and parameters of the intramolecular potential function. Several relations between sets of spectroscopic parameters of these molecules are obtained. The 'expanded local mode' model and the general isotopic substitution theory are used to estimate the relations between spectroscopic parameters of CH₃D and CHD₃, on one hand, and with the $T_d$ symmetric isotopic species, CH₄, on the other hand. Test calculations with the isotopic relations show that even without including prior information about the CH₃D and CHD₃ species, numerical results of calculations are in a good agreement both with experimental data and with results of *ab initio* calculations.

**Keywords:** methane; isotope effects; effective Hamiltonians; energy levels; infrared spectra

## 1. Introduction

For many years high-resolution rotational–vibrational (ro-vibrational) spectroscopy has been and still continues to be the source of the most precise and accurate information about the structure and dynamics of molecules [1]. Information that may be extracted from highly accurate experiments in the microwave, infrared, and visible regions can then be used in numerous ways to solve problems of pure and applied science in the areas of physical chemistry, astrophysics and planetology, in the study of the Earth's atmosphere, and in dealing with environmental problems. Extracting physical information from high-resolution spectra is based on the treatment of two closely connected problems: the mathematical modelling of intramolecular interactions, first of all in terms of the intramolecular potential energy hypersurface (PES), and second, the methods of assignments of spectral lines in experimentally recorded spectra. The assignment of spectral lines often is a very complicated problem, especially for highly excited vibrational states with the presence of numerous interactions.

As an illustration we may mention the methane molecule and its different deuterated isotopomers. The spectra of methane have been the subject of spectroscopic study for about 150 years with an early mentioning of the methane spectrum in 1862 [2]. High-resolution spectra of methane and its isotopomers have also been analysed over a period of more than 70 years, the recent publications

[3–8] being a guide to the extensive literature. It should be mentioned here that, in spite of an extensive effort undertaken during this time, only the region below 6000 cm⁻¹ has been analysed in detail so far. Until recently, only some restricted small wavenumber regions above 6000 cm⁻¹ have been analysed with high resolution in [5,9,10] for the CH₄ molecule, and the CH-infrared-chromophore bands of the CHD₃ and CH₃D isotopomers were partially analysed in [11–18], particularly also in view of the strong CH stretching–bending Fermi resonance in CHD₃ [19]. More recently some systematic investigations of the high-resolution spectra in the region above 6000 cm⁻¹ of both methane, CH₄, and its three deuterated isotopomers have begun [4,6,20–28] (see also earlier papers [29,30]). The most important difficulty in the study of methane spectra in the shorter wavelength region resides in the assignment of the numerous observable transitions and the further theoretical analysis of the very complicated ro-vibrational structure of all of the methane isotopomers. In order to solve this problem, one needs a prediction of line positions in the short-wavelength region on the basis of spectroscopic parameters: rotational parameters, vibrational frequencies and anharmonic coefficients, and different kinds of Coriolis- and Fermi-type interaction coefficients.

It would be very helpful in such analyses to be able to derive spectroscopic parameters for different isotopomers of a molecule (say, CH₃D and CHD₃), if the parameters of

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one isotopomer are known (say, $CH_4$ or of either $CH_3D$ or $CHD_3$). This is in principle possible in the framework of the adiabatic or Born–Oppenheimer approximation. The usual approach consists of deriving a potential hypersurface for the molecule on the basis of spectroscopic parameters of one isotopomer. This implies solving the 'inverse spectroscopic problem' which is possible, even if some additional constraints or approximations are necessary. One such constraint might be a predicted analytical structure of the potential hypersurface with a sufficiently small number of parameters [31,32]. These are derived from the spectroscopy of the main species (say, $CH_4$), and then with the aid of that potential hypersurface, the spectra of other species (say, $CH_3D$) can be calculated, best by variational methods. However, such a procedure is very difficult and costly as well and at present hardly feasible for five-atom species such as methane. Therefore, an alternative approach would be to derive directly spectroscopic or effective Hamiltonian parameters of an isotopomer, given the spectroscopic parameters of another isotopomer. This can be achieved by 'isotopic substitution theory'. The basic hypotheses and assumptions of this approach are as follows:

(1) An intramolecular potential hupersurface being written in terms of the 'natural', $\Delta r_i/\Delta \alpha_{ij}$, or symmetrised, $S_m$, vibrational coordinates has exactly the same form for every isotopomer of a molecule in the framework of the Born–Oppenheimer approximation.

(2) To express the spectroscopic parameters of a molecule in analytical form as functions of force field parameters, it is necessary, first of all, to make a transformation from vibrational coordinates $\Delta r_i/\Delta \alpha_{ij}$, or $S_m$ to normal-mode coordinates, $Q_\lambda$ (in other words, to make a transformation from the $F_{i...j}$, or $f_{l...m}$ parameters to a set of $k_{\lambda...\mu}$). In this case, both the normal-mode coordinates and sets of parameters $k_{\lambda...\mu}$ will be different for different isotopomers. The problem is how to connect the parameters $k_{\lambda...\mu}$ of different isotopomers with each other.

(3) This problem was solved in [33,34] where it was shown that a solution strongly depends on the relations between so-called transformation coefficients, $l_{N\alpha\lambda}$ (the index $N$ enumerates the nuclei of a molecule, $\alpha = x, y, z$, and the index $\lambda$ enumerates the vibrational modes), of the pairs of isotopomers considered.

In the recent publications [35,36], we proposed the use of the 'expanded local mode' approach [37–39] and isotopic substitution theory (see, e.g. [34]) for the determination of isotopic relations that allow one to predict with satisfactory accuracy values of different spectroscopic parameters of $CH_2D_2$ on the basis of information about values of spec-

troscopic parameters of $CH_4$ only. In the present work, we present analogous isotopic substitution results for the $C_{3v}$-symmetric deuterated methane species, $CH_3D$ and $CHD_3$. In this case, because of the $C_{3v}$ symmetry of $CH_3D$ and $CHD_3$, we use for analysis theorems and statements of the theory of irreducible tensorial sets [40–42] (see also [43]).

The present paper is organised as follows. Section 2 presents briefly the necessary information about symmetrised wavefunctions and operators which is essential for further analysis. The effective rotational operator matrix that can be used for the analysis of different polyads of interacting vibrational states in the $XYZ_3$ ($C_{3v}$) molecules is derived in Section 3. Section 4 presents general formulae of operator perturbation theory which are used in Section 5. In Section 5, we present general formulae that allow one to calculate the most important spectroscopic parameters of the effective rotational Hamiltonian in the form of analytical functions of the structural parameters and parameters of the intramolecular potential energy surface of the $XYZ_3$ molecule. It should be mentioned that the equations derived here give us the possibility to determine numerous relations between different spectroscopic parameters of the $XYZ_3$ molecule. Sections 6 and 7 present the 'expanded local mode' information about the $CH_4$ molecule and some extraction from the isotopic substitution theory, respectively, which are then used in Section 8 for the determination of isotopic relations in the substitutions $CH_3D$ $\leftarrow CH_4$ and $CHD_3 \leftarrow CH_4$. Figure 1 shows the structure of $CH_4$, $CH_3D$, and $CHD_3$, and the axis definitions used in the present work.

## 2. Symmetrised operators and wavefunctions of the $XYZ_3$ ($C_{3v}$) molecule using irreducible tensorial sets

The $XYZ_3$ ($C_{3v}$) molecule is a symmetric top, and its nine vibrational modes have the symmetries $A_1$ or $E$. In this case, we have three non-degenerate modes $q_j$ ($j = 1, 2, 3$) $\in A_1$ and three doubly degenerate modes $q_{\lambda_1}$ and $q_{\lambda_2}$ ($\lambda = 4, 5, 6$) $\in E$. The presence of degenerate modes in a symmetric top molecule leads to a complicated picture of their ro-vibrational spectra, especially in excited overtone and combination bands. Therefore, the most suitable approach to study such molecules uses their symmetry properties on the basis of theorems and results of the theory of irreducible tensorial sets.

### 2.1. *Rotational irreducible operators*

(1) *Irreducible rotational operators of the SO*(3) *group*. In accordance with general statements of the theory of irreducible tensorial sets (see [40–42,44]), the basic first-rank irreducible rotational operators $R_m^{\Omega(K)}$ ($m = 0, \pm 1, \ldots, \pm K$)
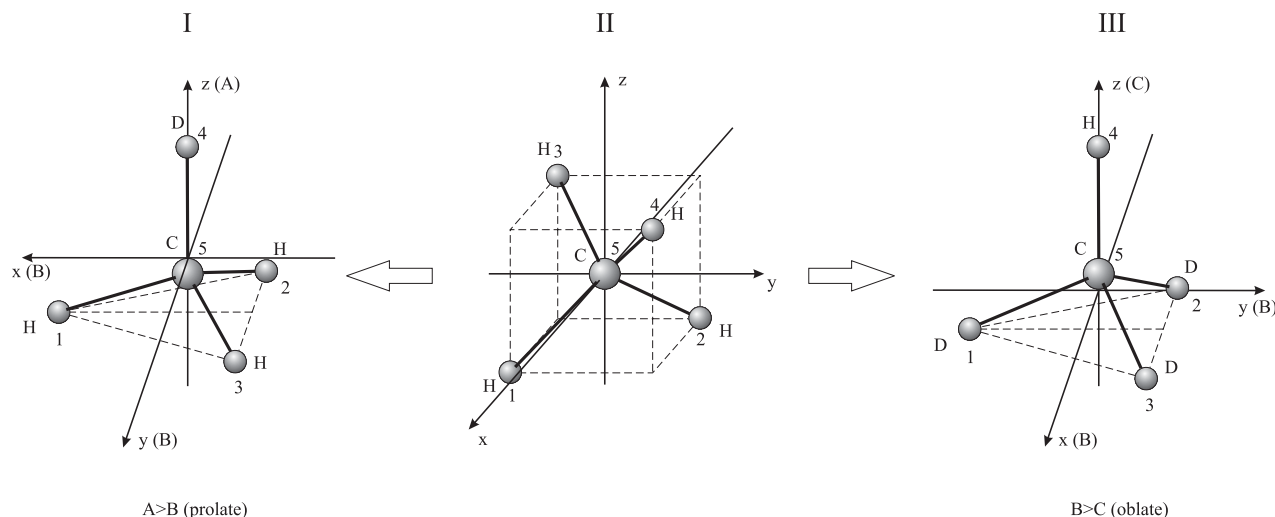
Figure 1. Equilibrium structures of the $CH_4$ (II), $CH_3D$ (I), and $CHD_3$ (III) molecules and axis definitions used in the present work. The symbols $x$, $y$, and $z$ refer to the axis definitions for the $T_d$ (II) and $C_{3v}$ (I and III) symmetry groups used in the classification of the states. The symbols in parentheses refer to the Cartesian axis definitions of the prolate and oblate symmetric top molecules. The figures are to scale.

can be chosen to be of the following form:

$$R_1^{1(1)} = -\frac{1}{\sqrt{2}}(J_x - i J_y) \equiv -J_+,$$

$$R_{-1}^{1(1)} = \frac{1}{\sqrt{2}}(J_x + i J_y) \equiv J_-,$$

$$R_0^{1(1)} = J_z \equiv J_0. \tag{1}$$

In the operators $R_m^{\Omega(K)}$, the following notations are used: $\Omega$ is the total degree of rotational operators $J_\alpha$, $\alpha = x, y, z$ (for example, for $\Omega = 1$, $R_{...}^{1(...)} \sim J_\alpha$; for $\Omega = 2$, $R_{...}^{2(...)} \sim J_\alpha J_\beta$; etc.); the indices $K$ and $m$ indicate the irreducible representation $D^{(K)}$ of the $SO(3)$ symmetry group and its $m$th line. Irreducible rotational operators $R_{\widetilde{m}}^{\Omega+1(K+1)}$ can be constructed from the corresponding irreducible rotational operators $R_m^{\Omega(K)}$ ($m = 0, \pm 1, \ldots, \pm K$) and $R_l^{1(1)}$ ($l = 0, \pm 1$) of lower degree and rank in accordance with the general rule [44],

$$R_{\widetilde{m}}^{\Omega+1(K+1)} = \sum_{l=-1,0,1} C_{K\,\widetilde{m}-l,1\,l}^{K+1\,\widetilde{m}} R_{\widetilde{m}-l}^{\Omega(K)} R_l^{1(1)}, \tag{2}$$

where the $C_{K\,\widetilde{m}-l,1\,l}^{K+1\,\widetilde{m}}$ are Clebsch–Gordan coefficients [42]. Irreducible rotational operators $R_m^{\Omega(K)}$ with $K < \Omega$ (in this case, the parity of $\Omega$ and $K$ must be the same; as was shown in [44], operators $R_m^{\Omega(K)}$ with different parities of the values of $\Omega$ and $K$ are reduced to operators $R_m^{\widetilde{\Omega}(K)} = R_m^{\Omega-1(K)}$, where the parities of the numbers $\widetilde{\Omega}$ and $K$ are the same) are constructed as

$$R_m^{\Omega(K)} = R_m^{K(K)}(R^{2(0)})^{(\Omega-K)/2}, \tag{3}$$

where

$$R^{2(0)} = -\frac{1}{\sqrt{3}}\left\{J_0^2 + \frac{1}{2}(J_+J_- + J_-J_+)\right\}$$

$$= -\frac{1}{\sqrt{3}}(J_x^2 + J_y^2 + J_z^2). \tag{4}$$

(2) *Irreducible rotational operators of the $C_{3v}$ group*. Different rotational operators, $R_\sigma^{\Omega(K,n\Gamma)}$, which are symmetries in accordance with the irreducible representations, $\Gamma$, of the $C_{3v}$ symmetry group, can be easily constructed from the operators $R_m^{\Omega(K)}$ by using the following general relations [44,45]:

$$R_\sigma^{\Omega(K,n\Gamma)} = \sum_m {}^{(K)}G_{n\Gamma\sigma}^m R_m^{\Omega(K)}. \tag{5}$$

The so-called reduction matrix elements, ${}^{(K)}G_{n\Gamma\sigma}^m$, which are presented in Equation (5), are determined by the point group considered. In particular, for the $C_{3v}$ group, these elements, taken from [44], are presented in the Appendix A. If one takes into account Equations (1)–(5) and the data from the Appendix, then one can easily construct all possible irreducible rotational operators of the $C_{3v}$ symmetry group. For illustration, the first of them (for both the $SO(3)$ and the $C_{3v}$ symmetry groups) are presented in Appendix B. The qualitative level structure and the nomenclature of the rotational states are summarised in Figure 2 (see also Appendix A).
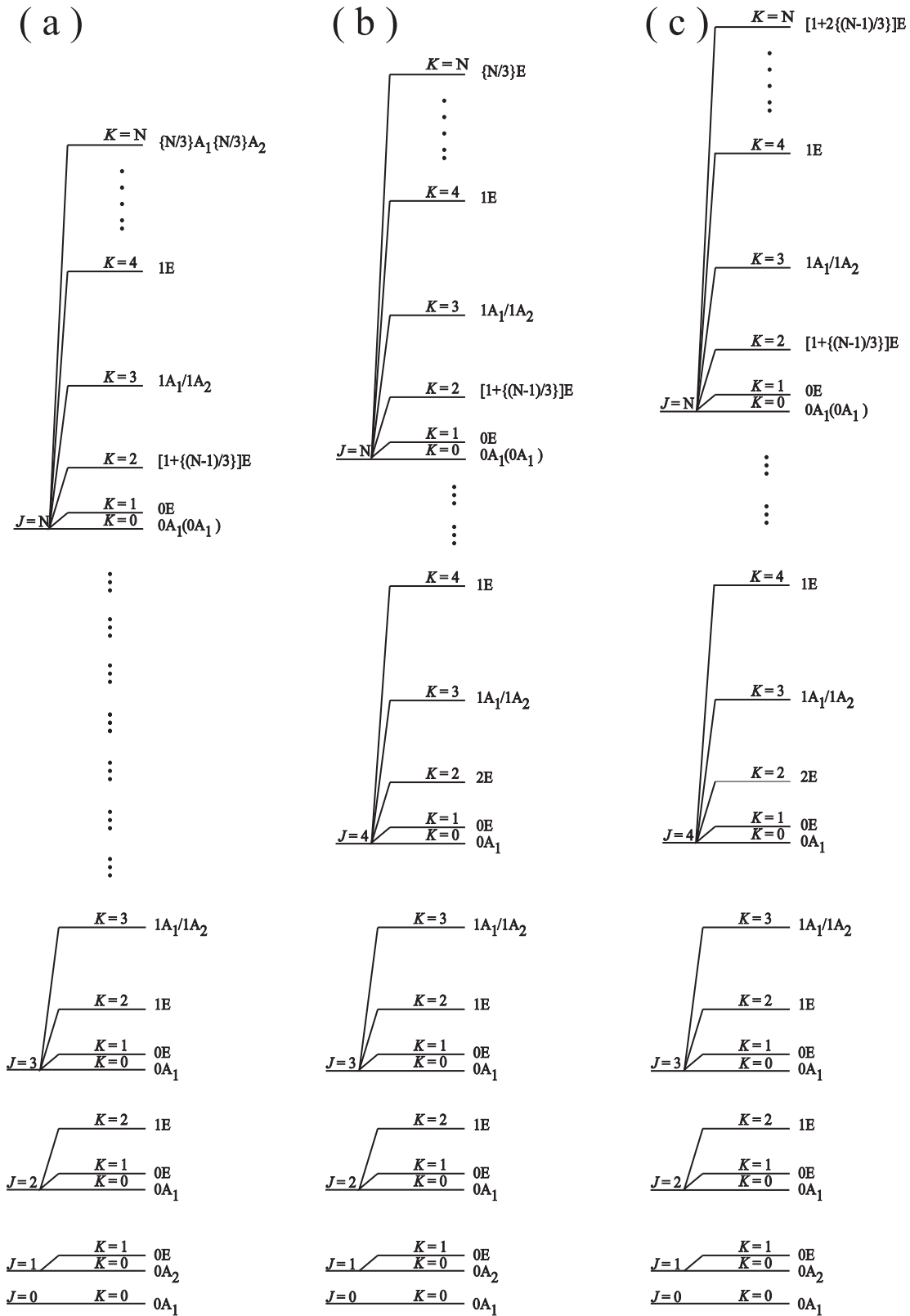
Figure 2. Nomenclature of states of different species for a given value of quantum number $J$: (a) $J$ is divisible by 3; (b) $J-1$ is divisible by 3; (c) $J+1$ is divisible by 3. It should be noted that the indices $n\Gamma$ determine uniquely the index $K$ and vice versa; for $nA$ the indices are $K = 3n$ at $0 \leq n \leq \left\{\frac{J}{3}\right\}$; for $nE$ the indices are $K = 3n+1$ at $0 \leq n \leq \left\{\frac{(J-1)}{3}\right\}$, or $K = 3(n - \frac{(J-1)}{3}) - 1$ at $n \geq 1 + \left\{\frac{(J-1)}{3}\right\}$. The symbol $\{B\}$ denotes the integer part of the number $B$.

### 2.2. Symmetrised vibrational operators

Because both the coordinates, $q_j$, and conjugate momentum operators, $p_j = -i\hbar\partial/\partial q_j$ ($j = 1, 2, 3$), are non-degenerate and thus belong to the totally symmetric irreducible representation $A_1$, we discuss here only doubly degenerate vibrations $q_{\lambda_s}$ ($\lambda = 4, 5, 6$ and $s = 1, 2$) and their conjugate momenta $p_{\lambda_s}$. In this case, taking into account the properties of these operators (see, e.g. [44,46]), it is possible to construct pairs of coordinates, $q_{\lambda,E_1} = q_{\lambda_1} = \frac{1}{2}(q_\lambda^- + q_\lambda^+)$ and $q_{\lambda,E_2} = -q_{\lambda_2} = \frac{i}{2}(q_\lambda^+ - q_\lambda^-)$ ($\lambda = 4, 5, 6$), that are transformed in accordance with the first and second lines of the irreducible representation $E$ of the $C_{3v}$ group, respectively. Similarly, pairs of momentum operators, $p_{\lambda,E_1} = p_{\lambda_1} = \frac{1}{2}(p_\lambda^- + p_\lambda^+)$ and $p_{\lambda,E_2} = -p_{\lambda_2} = \frac{i}{2}(p_\lambda^+ - p_\lambda^-)$, also belong to the irreducible representation $E$. Here the operators $q_\lambda^+/p_\lambda^+$ and $q_\lambda^-/p_\lambda^-$ are the creation and annihilation operators that increase, or decrease, the value of the quantum number $l$ in the vibrational functions, where the $|v\ l\rangle$ are eigenfunctions of a doubly degenerate harmonic oscillator:

$$\langle v+1\ l\pm 1|q^\pm|v\ l\rangle = \mp\left(\frac{v\pm l+2}{2}\right)^{1/2}, \qquad (6)$$

$$\langle v-1\ l\pm 1|q^\pm|v\ l\rangle = \pm\left(\frac{v\mp l}{2}\right)^{1/2}, \qquad (7)$$

and

$$\langle v+1\ l\pm 1|p^\pm|v\ l\rangle = \mp i\hbar\left(\frac{v\pm l+2}{2}\right)^{1/2}, \qquad (8)$$

$$\langle v-1\ l\pm 1|p^\pm|v\ l\rangle = \mp i\hbar\left(\frac{v\mp l}{2}\right)^{1/2}. \qquad (9)$$

The symmetry properties of the elementary (first-degree) vibrational operators allow one to construct the symmetrised second degree, third degree, etc., of vibrational operators. For the construction of such operators, one can use the general relation from Refs. [40,41,44]:

$$(A^\Gamma \otimes B^{\Gamma'})_\sigma^\gamma = \sqrt{[\gamma]}\sum_{ss'}\begin{pmatrix}\gamma & \Gamma & \Gamma' \\ \sigma & s & s'\end{pmatrix} A_s^\Gamma B_{s'}^{\Gamma'}. \quad (10)$$

Here $[\gamma]$ is the dimension of the irreducible representation $\gamma$ (for the $C_{3v}$ group, $[A_1] = [A_2] = 1$, and $[E] = 2$). The values $\begin{pmatrix}\gamma & \Gamma & \Gamma' \\ \sigma & s & s'\end{pmatrix}$ are the so-called $3\Gamma$ symbols of a point symmetry group (see, for more details, Refs. [40,44]) which satisfy the conditions

$$\begin{pmatrix}\gamma & \Gamma & \Gamma' \\ \sigma & s & s'\end{pmatrix} = \begin{pmatrix}\Gamma & \Gamma' & \gamma \\ s & s' & \sigma\end{pmatrix} = \begin{pmatrix}\Gamma' & \gamma & \Gamma \\ s' & \sigma & s\end{pmatrix}$$

$$= (-1)^{\gamma+\Gamma+\Gamma'}\begin{pmatrix}\Gamma & \gamma & \Gamma' \\ s & \sigma & s'\end{pmatrix}$$

$$= (-1)^{\gamma+\Gamma+\Gamma'}\begin{pmatrix}\gamma & \Gamma' & \Gamma \\ \sigma & s' & s\end{pmatrix}$$

$$= (-1)^{\gamma+\Gamma+\Gamma'}\begin{pmatrix}\Gamma' & \Gamma & \gamma \\ s' & s & \sigma\end{pmatrix}. \qquad (11)$$

Here the indices $s$, $s'$, and $\sigma$ denote lines of the corresponding irreducible representations (the indication of lines is omitted for the one-dimensional irreducible representations $A_1$ and $A_2$); $(-1)^{A_1} = (-1)^E = -(-1)^{A_2} = 1$; the symbol $\otimes$ denotes the tensorial product. In this case, for the $C_{3v}$ group, the non-zero $3\Gamma$ symbols are

$$\begin{pmatrix}A_1 & A_1 & A_1\end{pmatrix} = \begin{pmatrix}A_1 & A_2 & A_2\end{pmatrix} = 1, \qquad (12)$$

$$\begin{pmatrix}A_1 & E & E \\ & 1 & 1\end{pmatrix} = \begin{pmatrix}A_1 & E & E \\ & 2 & 2\end{pmatrix} = \begin{pmatrix}A_2 & E & E \\ & 1 & 2\end{pmatrix}$$

$$= -\begin{pmatrix}A_2 & E & E \\ & 2 & 1\end{pmatrix} = \frac{1}{\sqrt{2}}, \qquad (13)$$

$$\begin{pmatrix}E & E & E \\ 1 & 2 & 2\end{pmatrix} = -\begin{pmatrix}E & E & E \\ 1 & 1 & 1\end{pmatrix} = \frac{1}{2}. \qquad (14)$$

This allows one to construct any vibrational operator belonging to one of the irreducible representations of the $C_{3v}$ symmetry group.

### 2.3. Vibration–rotation Hamiltonian in a symmetrised form

The information from the previous subsections allows us to derive the vibration–rotation Hamiltonian of a molecule in a form that will be adapted to the symmetry properties of a molecule. Before presenting the Hamiltonian in this form, we point out that in agreement with general rovibrational theory (see, e.g. Refs. [46–48]), the Hamiltonian of a molecule can be presented in the following form, Equations (15)–(22), being valid for nonlinear polyatomic molecules without large amplitude motions:

$$H^{\text{vib–rot}}/hc = \frac{1}{2}\sum_a \omega_b\left(p_a^2 + q_a^2\right)$$

$$+ \frac{1}{2}\sum_{\alpha\beta}\mu_{\alpha\beta}(J_\alpha - G_\alpha)(J_\beta - G_\beta)$$

$$+ \sum_{abc}k_{abc}q_aq_bq_c + \sum_{abcd}k_{abcd}q_aq_bq_cq_d + \cdots.$$

$$(15)$$

The operators $G_\alpha$ and $\mu_{\alpha\beta}$ in Equation (15) have the following form:

$$G_\alpha = \sum_{a,b>a}\zeta_{ab}^\alpha\left[\left(\frac{\omega_b}{\omega_a}\right)^{1/2}q_ap_b - \left(\frac{\omega_a}{\omega_b}\right)^{1/2}q_bp_a\right] \quad (16)$$

and

$$\frac{1}{2}\mu_{\alpha\beta} = \frac{1}{2}\left(\mu_{\alpha\beta}^e + \sum_a \mu_{\alpha\beta}^a q_a + \sum_{ab}\mu_{\alpha\beta}^{ab}q_a q_b + \cdots\right)$$

$$= B_\alpha^e \delta_{\alpha\beta} - \sqrt{2}\sum_a \left(\frac{B_\alpha^e B_\beta^e}{\omega_a^{1/2}}\right)\widetilde{a}_a^{\alpha\beta}q_a$$

$$+ \frac{3}{2}\sum_{\gamma ab}\left(\frac{B_\alpha^e B_\beta^e B_\gamma^e}{\omega_a^{1/2}\omega_b^{1/2}}\right)\widetilde{a}_a^{\alpha\gamma}\widetilde{a}_b^{\gamma\beta}q_a q_b + \cdots, \quad (17)$$

where

$$\zeta_{ab}^\alpha = \sum_N \sum_{\beta\gamma}\epsilon_{\alpha\beta\gamma}l_{N\beta a}l_{N\gamma b} \qquad (18)$$

($\epsilon_{\alpha\beta\gamma}$ being a completely antisymmetric tensor, $\epsilon_{xyz} = \epsilon_{yzx} = \epsilon_{zxy} = \epsilon_{yxz} = -\epsilon_{xzy} = -\epsilon_{zyx} = 1$ and zero otherwise):

$$\widetilde{a}_b^{\alpha\beta} = a_b^{\alpha\beta}\left(\frac{4\pi c}{\hbar}\right)^{1/2}, \qquad (19)$$

and

$$a_b^{\alpha\alpha} = 2\sum_{\beta\gamma}\left(\delta_{\beta\gamma} - \delta_{\alpha\beta}\delta_{\alpha\gamma}\right)\sum_N m_N^{1/2}r_{N\beta}^e l_{N\gamma b}, \quad (20)$$

$$a_b^{\alpha\beta} = -2\sum_N m_N^{1/2}l_{N\alpha b}r_{N\beta}^e, \quad \alpha \neq \beta, \qquad (21)$$

$$B_\alpha^e = \frac{\hbar}{4\pi c I_{\alpha\alpha}^e} = \frac{\hbar}{4\pi c}\left\{\sum_N m_N\left[\left(r_{N\beta}^e{}^2\right) + \left(r_{N\gamma}^e{}^2\right)\right]\right\}^{-1}. \qquad (22)$$

In Equation (22) the indices $\alpha$, $\beta$, and $\gamma$ are all different. The transformation coefficients, $l_{N\beta b}$, in Equations (18), (20), and (21) are defined in vibration–rotation theory (see, e.g. Refs. [46–48]) as coefficients which connect the Cartesian coordinates of a nucleus in a molecule with mass-dependent normal vibrational coordinates, $Q_b$, as

$$r_{N\beta} = r_{N\beta}^e + \sum_b m_N^{-1/2}l_{N\beta b}Q_b.$$

In this case, the values $r_{N\alpha}^e$ are equilibrium Cartesian coordinates of a nucleus. One can show that the Hamiltonian, Equation (15), being transformed to the symmetrised form in agreement with the discussion above, will have the following form:

$$H^{\text{vib--rot}}/(hc) = \frac{\sqrt{[\Gamma_a]}}{2}\sum_a \omega_a\left\{(p_a \otimes p_a)^{A_1} + (q_a \otimes q_a)^{A_1}\right\}$$

$$+ \frac{1}{2}\sum_{nm}\sum_{\gamma\gamma'\widetilde{\gamma}}\{\mu^{n,\gamma}(q) \otimes [(J^{\gamma'} - G^{\gamma'}) \otimes (J^{\widetilde{\gamma}} - G^{\widetilde{\gamma}})]^{m,\gamma}\}^{A_1} + V_{\text{anh}}.$$

$$(23)$$

The anharmonic part of the intramolecular potential energy surface, $V_{\text{anh}}$, for the $XYZ_3$ molecule is presented in Appendix C.

### 2.4. Symmetrised vibrational functions

Following the principles of the theory of irreducible tensorial sets, a general vibrational wavefunction, $|v\gamma_v\sigma\rangle$, for the $ZXY_3(C_{3v})$ molecule can be constructed as

$$|v\gamma_v\sigma\rangle = |v_1\ v_2\ v_3\rangle\{[|v_4\ l_4\ \gamma_4\rangle$$
$$\otimes|v_5\ l_5\ \gamma_5\rangle]^{\gamma_{45}} \otimes |v_6\ l_6\ \gamma_6\rangle\}_\sigma^\gamma. \qquad (24)$$

Here $|v_1\ v_2\ v_3\rangle$ represents a wavefunction of the non-degenerate vibrational modes $q_1$, $q_2$, and $q_3$. Wavefunctions that depend on the doubly degenerate vibrational modes $q_{4\sigma}$, $q_{5\sigma}$, or $q_{6\sigma}$ ($\sigma = 1, 2$) are the tensorial products of symmetrised elementary vibrational functions of the separate degenerate modes, $|v_4\ l_4\gamma_4\rangle$, $|v_5\ l_5\gamma_5\rangle$, or $|v_6\ l_6\gamma_6\rangle$ (the elementary symmetrised vibrational functions, $|v_\lambda\ l_\lambda\ \gamma_\lambda\rangle$, $\lambda = 4, 5, 6$, are presented in Appendix D). Using the general formula, Equation (10), it is possible to show that the symmetrised functions, Equation (24), can be presented in the form of one of the following four combinations:

$$|v, \text{I}_\pm\rangle = \frac{(-i^\phi)}{\sqrt{2}}|v_1\ v_2\ v_3\rangle(|v_\lambda l_\lambda\rangle|v_\mu l_\mu\rangle|v_\nu l_\nu\rangle$$
$$\pm |v_\lambda - l_\lambda\rangle|v_\mu - l_\mu\rangle|v_\nu - l_\nu\rangle), \qquad (25)$$

$$|v, \text{II}_\pm\rangle = \frac{(-i^\varphi)}{\sqrt{2}}|v_1\ v_2\ v_3\rangle(|v_\lambda - l_\lambda\rangle|v_\mu l_\mu\rangle|v_\nu l_\nu\rangle$$
$$\pm |v_\lambda l_\lambda\rangle|v_\mu - l_\mu\rangle|v_\nu - l_\nu\rangle), \qquad (26)$$

$$|v, \text{III}_\pm\rangle = \frac{(-i^\chi)}{\sqrt{2}}|v_1\ v_2\ v_3\rangle(|v_\lambda l_\lambda\rangle|v_\mu - l_\mu\rangle|v_\nu l_\nu\rangle$$
$$\pm |v_\lambda - l_\lambda\rangle|v_\mu l_\mu\rangle|v_\nu - l_\nu\rangle), \qquad (27)$$

$$|v, \text{IV}_\pm\rangle = \frac{(-i^\psi)}{\sqrt{2}}|v_1\ v_2\ v_3\rangle(|v_\lambda l_\lambda\rangle|v_\mu l_\mu\rangle|v_\nu - l_\nu\rangle$$
$$\pm |v_\lambda - l_\lambda\rangle|v_\mu - l_\mu\rangle|v_\nu l_\nu\rangle). \qquad (28)$$

Here the phases can be equal to $\pm i$, or $\pm 1$; pairs of functions ($\ldots \pm \ldots$) where the signs $\pm$ inside the parentheses are related to the functions as transforming in accordance with the $E$ irreducible representation of the $C_{3v}$ group, or belong to the $A_1/A_2$ irreducible representations, the relations being not simply one to one.

### 3. Effective rotational Hamiltonian matrix: symmetry properties

Following general vibration–rotation theory [44,46,47], the Hamiltonian of a molecule can be reduced to a set of so-called effective Hamiltonians, or, more generally, to a set

of effective operator matrices of the form

$$H^{\text{vib--rot}} = \sum_{a,b} |a\rangle\langle b|H^{a,b}. \qquad (29)$$

Here $|a\rangle$ and $\langle b|$ are the vibrational basis functions; the operators $H^{a,b}$ depend on rotational operators, $J_\alpha$, only, and the summation is carried out over all degenerate and interacting vibrational states. In our case, because an $XYZ_3$ molecule has $C_{3v}$ symmetry, both the rotational operators, $H^{a,b}$, and the vibrational functions, $|a\rangle$ and $\langle b|$, in Equation (29) have to possess properties of irreducible tensorial sets belonging to the $C_{3v}$ group. Thus, they have to be wavefunctions and operators as discussed in the previous section, and the effective operator, Equation (29), has to be rewritten in the form that takes into account the symmetry properties of rotational operators and vibrational functions:

$$H^{\text{vib--rot}} = \sum_{vl\gamma,v'l'\gamma'} \sum_{n\Gamma} [(|v\ l\ \gamma\rangle \otimes \langle v'l'\ \gamma'|)^{n\Gamma} \otimes H^{n\Gamma}_{vl\gamma,v'l'\gamma'}]^{A_1},$$

$$(30)$$

where, in agreement with the presence of three different irreducible representations of the $C_{3v}$ group, the indices $\gamma$, $\gamma'$, and $\Gamma$ can take the values $A_1, A_2$, or $E$. In this case, different combinations of the indices $\gamma$, $\gamma'$, and $\Gamma$ in Equation (30) lead to different forms of rotational operators $H^{n\Gamma}_{vl\gamma,v'l'\gamma'}$.

### 3.1. Diagonal blocks of $A_1$ and/or $A_2$ symmetry

General symmetry properties of the $ZXY_3$ ($C_{3v}$) molecule allow one to obtain operators of diagonal blocks of $A_1$ or $A_2$ symmetry in the following form:

$$\begin{aligned}
H_{vA_\lambda,vA_\lambda} = |vA_\lambda\rangle\langle vA_\lambda|\Big\{ &E^{vA_\lambda} + A^{vA_\lambda}\big(J_x^2 + J_y^2\big) \\
&+ B^{vA_\lambda}J_z^2 - D_J^{vA_\lambda}J^4 - D_{JK}^{vA_\lambda}J^2J_z^2 - D_K^{vA_\lambda}J_z^4 \\
&+ H_J^{vA_\lambda}J^6 + H_{JK}^{vA_\lambda}J^4J_z^2 + H_{KJ}^{vA_\lambda}J^2J_z^4 \\
&+ H_K^{vA_\lambda}J_z^6 + L_J^{vA_\lambda}J^8 + \cdots \\
&+ \Big\{\Big[\Big(\tfrac{1}{2}\epsilon^{vA_\lambda} + \tfrac{1}{2}\epsilon_J^{vA_\lambda}J^2 + \epsilon_K^{vA_\lambda}J_z^2 + \cdots\Big), \\
&\quad (J_+^3 - J_-^3)\Big]_+ + \big[(\epsilon'^{vA_\lambda}J_z + \epsilon_J'^{vA_\lambda}J_zJ^2 \\
&\quad + \epsilon_K'^{vA_\lambda}J_z^3 + \cdots), (J_+^3 + J_-^3)\big]_+ \\
&+ h'^{vA_\lambda}\big(J_+^6 + J_-^6\big) + \cdots\Big\}. \qquad (31)
\end{aligned}$$

Here $B^{vA_\lambda}$, $C^{vA_\lambda}$, $D_J^{vA_\lambda}$, $D_{JK}^{vA_\lambda}$, $D_K^{vA_\lambda}$, $H_J^{vA_\lambda}$, $H_{JK}^{vA_\lambda}$, $H_{KJ}^{vA_\lambda}$, $H_K^{vA_\lambda}$, $L_J^{vA_\lambda}$, ... are the rotational and centrifugal distortion parameters. The operators $(J_+^3 + J_-^3)$ connect the rotational states $|Jk\rangle$ and $|Jk'\rangle$ $(-J \le k, k' \le J)$ with different values of the quantum numbers $k$, namely $\Delta k = k - k' = \pm$

3 (the corresponding operators $J_+$, $J_-$, and $J_0$ are given in Equation (1)). They account, in particular, for the $a_1/a_2$ splittings of $K = 3$ ($K = |k|$) levels. The parameters $\epsilon_J^{A_\lambda}/\epsilon_J'^{A_\lambda}$, $\epsilon_K^{A_\lambda}/\epsilon_K'^{A_\lambda}$, ...describe the $J$ and $K$ dependencies of the main $\epsilon^{A_\lambda}/\epsilon'^{A_\lambda}$ parameter. The expression $[\ldots,\ldots]_+$ denotes an anticommutator.

### 3.2. Diagonal blocks of E symmetry

For doubly degenerate vibrational states, the $H^{vE,vE}$ operator is

$$H_{vE,vE} = H_{vE,vE}^{(1)} + H_{vE,vE}^{(2)} + H_{vE,vE}^{(3)}, \qquad (32)$$

where

$$\begin{aligned}
H_{vE,vE}^{(1)} = (&|vE_1\rangle\langle vE_1| + |vE_2\rangle\langle vE_2|)\Big\{E^{vE} \\
&+ A^{vE}\big(J_x^2 + J_y^2\big) + B^{vE}J_z^2 - D_J^{vE}J^4 \\
&- D_{JK}^{vE}J^2J_z^2 - D_K^{vE}J_z^4 + H_J^{vE}J^6 + H_{JK}^{vE}J^4J_z^2 \\
&+ H_{KJ}^{vE}J^2J_z^4 + H_K^{vE}J_z^6 + L_J^{vE}J^8 + \cdots \\
&+ \Big\{\Big[\Big(\tfrac{1}{2}\epsilon^{vE} + \tfrac{1}{2}\epsilon_J^{vE}J^2 + \epsilon_K^{vE}J_z^2 + \cdots\Big), \\
&\quad (J_+^3 - J_-^3)\Big]_+ + \big[(\epsilon'^{vE}J_z + \epsilon_J'^{vE}J_zJ^2 \\
&\quad + \epsilon_K'^{vE}J_z^3 + \cdots), \big(J_+^3 + J_-^3\big)\big]_+\Big\}, \qquad (33)
\end{aligned}$$

$$\begin{aligned}
H_{vE,vE}^{(2)} = (&|vE_1\rangle\langle vE_2| - |vE_2\rangle\langle vE_1|)\Big\{\eta^{vE}J_z + \eta_J^{vE}J_zJ^2 \\
&+ \eta_K^{vE}J_z^3 + \eta_{JJ}^{vE}J_zJ^4 + \eta_{JK}^{vE}J_z^3J^2 + \eta_{KK}^{vE}J_z^5 \\
&+ \eta_{JJJ}^{vE}J_zJ^6 + \eta_{JJK}^{vE}J_z^3J^4 + \eta_{JKK}^{vE}J_z^5J^2 \\
&+ \eta_{KKK}^{vE}J_z^7 + \cdots\Big\}, \qquad (34)
\end{aligned}$$

and

$$\begin{aligned}
H_{vE,vE}^{(3)} = (&|vE_2\rangle\langle vE_2| - |vE_1\rangle\langle vE_1|)\Big\{\big[iA^{vE}, (J_+ - J_-)\big]_+ \\
&+ \big[B^{vE}, (J_+ + J_-)\big]_+ + \big[C^{vE}, (J_+^2 + J_-^2)\big]_+ \\
&+ \big[iD^{vE}, (J_-^2 - J_+^2)\big]_+ + \big[F^{vE}, (J_+^4 + J_-^4)\big]_+ \\
&+ \big[iG^{vE}, (J_-^4 - J_+^4)\big]_+\Big\} + (|vE_1\rangle\langle vE_2| \\
&+ |vE_2\rangle\langle vE_1|)\Big\{\big[A^{vE}, (J_+ + J_-)\big]_+ \\
&+ \big[iB^{vE}, (J_- - J_+)\big]_+ + \big[iC^{vE}, (J_+^2 - J_-^2)\big]_+ \\
&+ \big[D^{vE}, (J_+^2 + J_-^2)\big]_+ + \big[iF^{vE}, (J_+^4 - J_-^4)\big]_+ \\
&+ \big[G^{vE}, (J_+^4 + J_-^4)\big]_+\Big\}, \qquad (35)
\end{aligned}$$

$$\begin{aligned}
A^{vE} = &\tfrac{1}{2}\alpha^v + \tfrac{1}{2}\alpha_J^v J^2 + \alpha_K^v J_z^2 + \tfrac{1}{2}\alpha_{JJ}^v J^4 + \alpha_{JK}^v J^2 J_z^2 \\
&+ \alpha_{KK}^v J_z^4 + \cdots + \alpha_{JJK}^v J^4 J_z^2 \\
&+ \cdots + \alpha_{JKK}^v J^2 J_z^4 + \cdots,
\end{aligned}$$

$$
\begin{aligned}
B^{vE} &= \beta^v J_z + \beta_J^v J_z J^2 + \beta_K^v J_z^3 + \beta_{JJ}^v J^4 J_z \\
&\quad + \beta_{JK}^v J^2 J_z^3 + \cdots, \\
C^{vE} &= \frac{1}{2}\gamma^v + \frac{1}{2}\gamma_J^v J^2 + \gamma_K^v J_z^2 + \frac{1}{2}\gamma_{JJ}^v J^4 \\
&\quad + \gamma_{JK}^v J^2 J_z^2 + \cdots + \gamma_{JJK}^v J^4 J_z^2 + \cdots, \\
D^{vE} &= \delta^v J_z + \delta_J^v J_z J^2 + \delta_K^v J_z^3 + \delta_{JJ}^v J_z J^4 \\
&\quad + \delta_{JK}^v J^2 J_z^3 + \cdots, \\
F^{vE} &= \frac{1}{2}\kappa^v + \frac{1}{2}\kappa_J^v J_z^2 + \kappa_K^v J_z^2 + \frac{1}{2}\kappa_{JJ}^v J^4 \\
&\quad + \kappa_{JK}^v J^2 J_z^2 + \cdots, \\
G^{vE} &= \theta^v J_z + \theta_J^v J_z J^2 + \theta_K^v J_z^3 + \theta_{JJ}^v J_z J^4 \\
&\quad + \theta_{JK}^v J^2 J_z^3 + \cdots.
\end{aligned} \tag{36}
$$

In Equation (33), the $E^{vE}$, $A^{vE}$, ..., $\epsilon_{\cdot\cdot}^{\prime vE}$ parameters have the same meaning as the corresponding ones in Equation (31) with one exception: although the operators $(J_+^3 + J_-^3)$ connect the rotational states $|Jk\rangle$ and $|Jk'\rangle$ with $\Delta k = k - k' = \pm 3$, they do not split $a_1/a_2$ levels. The operator $H_{vE,vE}^{(2)}$ describes the $k$–$l$ splittings. Different operators, $(J_+^n \pm J_-^n)$, in $H_{vE,vE}^{(3)}$ connect the rotational states $|Jk\rangle$ and $|Jk'\rangle$ where $\Delta k = k - k' = \pm n$. Here, the operators with $n = 2m$ provide the $a_1/a_2$ splittings of energy levels with $K = m$.

### 3.3. Coriolis interaction blocks of the $A_1$–$E$, or $A_2$–$E$, type

Coriolis interaction operators which connect vibrational states of the $A_1/A_2$ symmetry, on one hand, and of the $E$ symmetry, on the other hand, have the following form:

$$
\begin{aligned}
H_{vA_1,v'E} &= |vA_1\rangle\langle v'E_1|\{[iA^{vA_1,v'E}, (J_+ - J_-)]_+ \\
&\quad + [B^{vA_1,v'E}, (J_+ + J_-)]_+ + [C^{vA_1,v'E}, (J_+^2 + J_-^2)]_+ \\
&\quad + [iD^{vA_1,v'E}, (J_-^2 - J_+^2)]_+ + [F^{vA_1,v'E}, (J_+^4 + J_-^4)]_+ \\
&\quad + [iG^{vA_1,v'E}, (J_-^4 - J_+^4)]_+\} + |vA_1\rangle\langle v'E_2|\{[A^{vA_1,v'E}, \\
&\quad (J_+ + J_-)]_+ + [iB^{vA_1,v'E}, (J_- - J_+)]_+ + [iC^{vA_1,v'E}, \\
&\quad (J_+^2 - J_-^2)]_+ + [D^{vA_1,v'E}, (J_+^2 + J_-^2)]_+ + [iF^{vA_1,v'E}, \\
&\quad (J_+^4 - J_-^4)]_+ + [G^{vA_1,v'E}, (J_+^4 + J_-^4)]_+\}
\end{aligned} \tag{37}
$$

and

$$
\begin{aligned}
H_{vA_2,v'E} &= -|vA_2\rangle\langle v'E_2|\{[iA^{vA_2,v'E}, (J_+ - J_-)]_+ \\
&\quad + [B^{vA_2,v'E}, (J_+ + J_-)]_+ + [C^{vA_2,v'E}, (J_+^2 + J_-^2)]_+ \\
&\quad + [iD^{vA_2,v'E}, (J_-^2 - J_+^2)]_+ + [F^{vA_2,v'E}, (J_+^4 + J_-^4)]_+ \\
&\quad + [iG^{vA_2,v'E}, (J_-^4 - J_+^4)]_+\} + |vA_2\rangle\langle v'E_1|\{[A^{vA_2,v'E}, \\
&\quad (J_+ + J_-)]_+ + [iB^{vA_2,v'E}, (J_- - J_+)]_+ + [iC^{vA_2,v'E},
\end{aligned}
$$

$$
\begin{aligned}
&(J_+^2 - J_-^2)]_+ + [D^{vA_2,v'E}, (J_+^2 + J_-^2)]_+ \\
&+ [iF^{vA_2,v'E}, (J_+^4 - J_-^4)]_+ + [G^{vA_2,v'E}, (J_+^4 + J_-^4)]_+\}.
\end{aligned} \tag{38}
$$

The operators $A^{vA_iv'E}$, $B^{vA_iv'E}$, ..., etc., can be derived from Equation (36) by replacement of parameters $\alpha^v$, $\beta^v$, ... with $\alpha^{va_i,v'e}$, $\beta^{va_i,v'e}$, ..., etc. ($i = 1, 2$).

### 3.4. Coriolis interaction blocks of the $A_1$–$A_2$ type

The operator of the $A_1$–$A_2$ Coriolis type interactions has the following form:

$$
\begin{aligned}
H_{vA_1,v'A_2} &= |vA_1\rangle\langle v'A_2|\{\eta^{vA_1,v'A_2} J_z + \eta_J^{vA_1,v'A_2} J_z J^2 \\
&\quad + \eta_K^{vA_1,v'A_2} J_z^3 + \eta_{JJ}^{vA_1,v'A_2} J_z J^4 + \eta_{JK}^{vA_1,v'A_2} J_z^3 J^2 \\
&\quad + \eta_{KK}^{vA_1,v'A_2} J_z^5 + \eta_{JJJ}^{vA_1,v'A_2} J_z J^6 + \eta_{JJK}^{vA_1,v'A_2} J_z^3 J^4 \\
&\quad + \eta_{JKK}^{vA_1,v'A_2} J_z^5 J^2 + \eta_{KKK}^{vA_1,v'A_2} J_z^7 + \cdots\}.
\end{aligned} \tag{39}
$$

### 3.5. Fermi interactions of the $A_1$–$A_1$, $A_2$–$A_2$, or $E$–$E$ type

In agreement with the general symmetry properties, operators of the Fermi-type interactions have exactly the same form, as the diagonal operators, Equations (31)–(36), from Sections 3.1 and 3.2. Of course, all the spectroscopic parameters, such as $E^{v\gamma}$, $A^{v\gamma}$, ..., $\eta^{vE}$, ..., $\alpha^v$, ..., etc. should be replaced by the corresponding interaction parameters, such as $F^{v\gamma,v'\gamma}$, ..., $\eta^{vE,v'E}$, ..., $\alpha^{v,v'}$, ..., etc.:

$$
\begin{aligned}
H_{vA_\lambda,v'A_\lambda} &= |vA_\lambda\rangle\langle v'A_\lambda|\{F^{vA_\lambda,v'A_\lambda} \\
&\quad + F_A^{vA_\lambda,v'A_\lambda}(J_x^2 + J_y^2) + F_B^{vA_\lambda,v'A_\lambda} J_z^2 - F_{D_J}^{vA_\lambda,v'A_\lambda} J^4 \\
&\quad - F_{D_{JK}}^{vA_\lambda,v'A_\lambda} J^2 J_z^2 - F_{D_K}^{vA_\lambda,v'A_\lambda} J_z^4 + F_{H_J}^{vA_\lambda,v'A_\lambda} J^6 \\
&\quad + F_{H_{JK}}^{vA_\lambda,v'A_\lambda} J^4 J_z^2 + F_{H_{KJ}}^{vA_\lambda,v'A_\lambda} J^2 J_z^4 \\
&\quad + F_{H_K}^{vA_\lambda,v'A_\lambda} J_z^6 + F_{L_J}^{vA_\lambda,v'A_\lambda} J^8 + \cdots + [(F_{\epsilon'}^{vA_\lambda,v'A_\lambda} J_z \\
&\quad + F_{\epsilon_j'}^{vA_\lambda,v'A_\lambda} J_z J^2 + F_{\epsilon_k'}^{vA_\lambda,v'A_\lambda} J_z^3 + \cdots), (J_+^3 + J_-^3)]_+ \\
&\quad + F_{h'}^{vA_\lambda,v'A_\lambda}(J_+^6 + J_-^6) + \cdots\},
\end{aligned} \tag{40}
$$

where $\lambda = 1$ or $2$ and

$$
H_{vE,v'E} = H_{vE,v'E}^{(1)} + H_{vE,v'E}^{(2)} + H_{vE,v'E}^{(3)}, \tag{41}
$$

where

$$
\begin{aligned}
H_{vE,v'E}^{(1)} &= (|vE_1\rangle\langle v'E_1| + |vE_2\rangle\langle v'E_2|)\{F^{vE,v'E} + F_J^{vE,v'E} \\
&\quad (J_x^2 + J_y^2) + F_K^{vE,v'E} J_z^2 - F_{JJ}^{vE,v'E} J^4 - F_{JK}^{vE,v'E} J^2 J_z^2 \\
&\quad - F_{KK}^{vE,v'E} J_z^4 + F_{JJJ}^{vE,v'E} J^6 + F_{JJK}^{vE,v'E} J^4 J_z^2 \\
&\quad + F_{JKK}^{vE,v'E} J^2 J_z^4 + F_{KKK}^{vE,v'E} J_z^6 + \cdots + [(F_{\epsilon'}{}^{vE,v'E} J_z \\
&\quad + F_{\epsilon_J'}{}^{vE,v'E} J_z J^2 + F_{\epsilon_K'}{}^{vE,v'E} J_z^3 + \cdots), (J_+^3 + J_-^3)]_+ \cdots\},
\end{aligned} \tag{42}
$$

$$
\begin{aligned}
H_{vE,v'E}^{(2)} = (|vE_1\rangle\langle v'E_2| - |vE_2\rangle\langle v'E_1|)\big\{ & \eta^{vE,v'E} J_z \\
& + \eta_J^{vE,v'E} J_z J^2 + \eta_K^{vE,v'E} J_z^3 + \eta_{JJ}^{vE,v'E} J_z J^4 \\
& + \eta_{JK}^{vE,v'E} J_z^3 J^2 + \eta_{KK}^{vE,v'E} J_z^5 + \eta_{JJJ}^{vE,v'E} J_z J^6 \\
& + \eta_{JJK}^{vE,v'E} J_z^3 J^4 + \eta_{JKK}^{vE,v'E} J_z^5 J^2 \\
& + \eta_{KKK}^{vE,v'E} J_z^7 + \cdots \big\},
\end{aligned}
\tag{43}
$$

and

$$
\begin{aligned}
H_{vE,v'E}^{(3)} = & (|vE_2\rangle\langle v'E_2| - |vE_1\rangle\langle v'E_1|)\{[iA^{vE,v'E}, \\
& (J_+ - J_-)]_+ + [B^{vE,v'E}, (J_+ + J_-)]_+ + [C^{vE,v'E}, \\
& (J_+^2 + J_-^2)]_+ + [iD^{vE,v'E}, (J_-^2 - J_+^2)]_+ + [F^{vE,v'E}, \\
& (J_+^4 + J_-^4)]_+ + [iG^{vE,v'E}, (J_-^4 - J_+^4)]_+\} \\
& + (|vE_1\rangle\langle v'E_2| + |vE_2\rangle\langle v'E_1|)\{[A^{vE,v'E}, (J_+ + J_-)]_+ \\
& + [iB^{vE,v'E}, (J_- - J_+)]_+ + [iC^{vE,v'E}, (J_+^2 - J_-^2)]_+ \\
& + [D^{vE,v'E}, (J_+^2 + J_-^2)]_+ + [iF^{vE,v'E}, (J_+^4 - J_-^4)]_+ \\
& + [G^{vE,v'E}, (J_+^4 + J_-^4)]_+\}\},
\end{aligned}
\tag{44}
$$

$$
\begin{aligned}
A^{vE,v'E} = & \frac{1}{2}\alpha^{vv'} + \frac{1}{2}\alpha_J^{vv'} J^2 + \alpha_K^{vv'} J_z^2 + \frac{1}{2}\alpha_{JJ}^{vv'} J^4 \\
& + \alpha_{JK}^{vv'} J^2 J_z^2 + \alpha_{KK}^{vv'} J_z^4 + \cdots + \alpha_{JJK}^{vv'} J^4 J_z^2 + \\
& + \alpha_{JKK}^{vv'} J^2 J_z^4 + \cdots, \\
B^{vE,v'E} = & \beta^{vv'} J_z + \beta_J^{vv'} J_z J^2 + \beta_K^{vv'} J_z^3 + \beta_{JJ}^{vv'} J^4 J_z \\
& + \beta_{JK}^{vv'} J^2 J_z^3 + \cdots, \\
C^{vE,v'E} = & \frac{1}{2}\gamma^{vv'} + \frac{1}{2}\gamma_J^{vv'} J^2 + \gamma_K^{vv'} J_z^2 + \frac{1}{2}\gamma_{JJ}^{vv'} J^4 \\
& + \gamma_{JK}^{vv'} J^2 J_z^2 + \cdots + \gamma_{JJK}^{vv'} J^4 J_z^2 + \cdots, \\
D^{vE,v'E} = & \delta^{vv'} J_z + \delta_J^{vv'} J_z J^2 + \delta_K^{vv'} J_z^3 + \delta_{JJ}^{vv'} J_z J^4 \\
& + \delta_{JK}^{vv'} J^2 J_z^3 + \cdots, \\
F^{vE,v'E} = & \frac{1}{2}\kappa^{vv'} + \frac{1}{2}\kappa_J^{vv'} J_z^2 + \kappa_K^{vv'} J_z^2 + \frac{1}{2}\kappa_{JJ}^{vv'} J^4 \\
& + \kappa_{JK}^{vv'} J^2 J_z^2 + \cdots, \\
G^{vE,v'E} = & \theta^{vv'} J_z + \theta_J^{vv'} J_z J^2 + \theta_K^{vv'} J_z^3 + \theta_{JJ}^{vv'} J_z J^4 \\
& + \theta_{JK}^{vv'} J^2 J_z^3 + \cdots.
\end{aligned}
\tag{45}
$$

## 4. Effective rotational Hamiltonian matrix: perturbation theory

In this section, we present general formulae of the so-called projection modification of operator perturbation theory (see also [49]) that can be used then for the calculation of different spectroscopic parameters of the effective Hamiltonian, Equations (29)–(45). In that modification, the effective operator matrix has the form of Equation (29) (or Equation (30)), and the rotational operators $H^{i,j}$ on the right-hand side of Equation (29) can be obtained in accordance with

the general equation

$$
\begin{aligned}
H^{i,j} = & E_i^0 \delta_{ij} + \langle i|h|j\rangle + \frac{1}{2}\sum_{k\notin\Omega_{ij}} \langle i|h|k\rangle\langle k|h|j\rangle \\
& \times \left\{ \frac{1}{E_i^0 - E_k^0} + \frac{1}{E_j^0 - E_k^0} \right\} + \sum_{k,l\notin\Omega_{ij}} \langle i|h|k\rangle\langle k|h|l\rangle\langle l|h|j\rangle \\
& \times \left\{ \frac{1}{(E_i^0 - E_k^0)(E_i^0 - E_l^0)} + \frac{1}{(E_j^0 - E_k^0)(E_j^0 - E_l^0)} \right\} \\
& - \frac{1}{2}\sum_{\substack{k\notin\Omega_{ij}; \\ m\in\Omega_{ij}}} \frac{\langle i|h|m\rangle\langle m|h|k\rangle\langle k|h|j\rangle}{(E_i^0 - E_k^0)(E_m^0 - E_k^0)} \\
& - \frac{1}{2}\sum_{\substack{k\notin\Omega_{ij}; \\ m\in\Omega_{ij}}} \frac{\langle i|h|k\rangle\langle k|h|m\rangle\langle m|h|j\rangle}{(E_j^0 - E_k^0)(E_m^0 - E_k^0)} + \cdots O(\kappa^4).
\end{aligned}
\tag{46}
$$

Here $E_i^0$ and $|i\rangle$ are eigenvalues and eigenfunctions of the Hamiltonian $H_0$:

$$
H_0|i\rangle = E_i^0|i\rangle;
\tag{47}
$$

$H_0$ is the zero-order part (operator of a sum of harmonic oscillators) of the vibration-rotation Hamiltonian, Equation (15) (or Equation (23)),

$$
H^{\text{vib-rot}} \equiv H_0 + h.
\tag{48}
$$

$\Omega_{ij}$ is the space of states, $|i\rangle$ and $|j\rangle$, which are degenerate or interact with each other.

Using the symmetry adapted operators and wavefunctions of Section 2 in the general equation (46) is complicated even to second order, not to speak about third and higher orders of operator perturbation theory. Therefore, for our calculations, we used special codes realised on the basis of the computer languages MAPLE and MATHEMATICA. The results of our calculations for some of the most important spectroscopic parameters of XYZ$_3$ molecules are presented in the next section.

## 5. Some spectroscopic parameters of the XYZ$_3$ ($C_{3v}$) molecule as functions of structural and PES parameters

In this section, we use all the above information for deriving general equations which determine the most important spectroscopic parameters of the $H^{vv}$ Hamiltonian of the XYZ$_3$ ($C_{3v}$) molecule as functions of its structural parameters ($r_{XY}^e$, $r_{YZ}^e$, $\alpha_{XYZ}^e$, and $\alpha_{Z_iYZ_j}^e$) and parameters $k_a$ of the intramolecular potential energy surface (see Appendix C).

## 5.1.　*Anharmonic coefficients, $x_{ab}/x_{l_\lambda l_\mu}$*

It is well known (see, e.g. Refs. [46,47]) that the vibrational energy ($E^{vA_\lambda}$, or $E^{vE}$, in Equations (31) and (33)) of a symmetric top molecule can be represented by the following equation:

$$E^{v\cdots} = \sum_a \omega_a \left( v_a + \frac{d_a}{2} \right) + \sum_{a \leq b} x_{ab} \left( v_a + \frac{d_a}{2} \right)$$
$$\times \left( v_b + \frac{d_b}{2} \right) + \sum_{\lambda \leq \mu} x_{l_\lambda l_\mu} l_\lambda l_\mu + \cdots, \quad (49)$$

where $d = 1$ for non-degenerate vibrations (denoted by the indices $i, j, l, m$) and $d = 2$ for doubly degenerate vibrations ($\lambda, \mu, \nu$), $a = i, j, l, m, \ldots, \lambda, \mu, \nu, ..$

With the representation of the anharmonic potential as a Taylor expansion up to quartic terms, as given in Appendix C, the use of the operator perturbation theory from Section 4 with the operator, Equation (23) (see also Equations (C.1)–(C.3)), and symmetrised wave functions, Equations (24)–(28) (taking into account also the phase coefficients of functions from Appendix D), allows one to obtain the following relations for anharmonic coefficients:

$$x_{ii} = \frac{3}{2}k_{iiii} - \frac{15}{4}\frac{k_{iii}^2}{\omega_i} - \frac{1}{2}\sum_{j\neq i}\frac{k_{iij}^2}{\omega_j} - \sum_{j\neq i}\frac{k_{iij}^2}{8(\omega_j + 2\omega_i)}$$
$$- \sum_{j\neq i}\frac{k_{iij}^2}{8(\omega_j - 2\omega_i)}, \quad (50)$$

$$x_{ij} = k_{iijj} - \frac{3k_{iii}k_{ijj}}{\omega_i} - \frac{3k_{jjj}k_{iij}}{\omega_j} - \sum_{l\neq i,j}\frac{k_{iil}k_{jjl}}{\omega_l}$$
$$- \left\{ \frac{k_{ijj}^2}{2(\omega_i + 2\omega_j)} + \frac{k_{iij}^2}{2(\omega_j + 2\omega_i)} \right\}$$
$$+ \left\{ \frac{k_{ijj}^2}{2(\omega_i - 2\omega_j)} + \frac{k_{iij}^2}{2(\omega_j - 2\omega_i)} \right\}$$
$$- \sum_{l\neq i,j}\frac{k_{ijl}^2}{8}\left\{ \frac{1}{\omega_i + \omega_j + \omega_l} - \frac{1}{\omega_i + \omega_j - \omega_l} \right.$$
$$\left. - \frac{1}{\omega_i - \omega_j - \omega_l} + \frac{1}{\omega_i - \omega_j + \omega_l} \right\}, \quad (51)$$

$$x_{i\lambda} = k_{ii\lambda\lambda} - \frac{3k_{iii}k_{i\lambda\lambda}}{\omega_i} - \sum_{j\neq i}\frac{k_{iij}k_{j\lambda\lambda}}{\omega_j} - \frac{k_{i\lambda\lambda}^2}{2(\omega_i + 2\omega_\lambda)}$$
$$+ \frac{k_{i\lambda\lambda}^2}{2(\omega_i - 2\omega_\lambda)} - \sum_{\mu\neq\lambda}\frac{k_{i\lambda\mu}^2}{8}\left\{ \frac{1}{\omega_i + \omega_\lambda + \omega_\mu} \right.$$
$$\left. - \frac{1}{\omega_i + \omega_\lambda - \omega_\mu} + \frac{1}{\omega_i - \omega_\lambda + \omega_\mu} - \frac{1}{\omega_i - \omega_\lambda - \omega_\mu} \right\}$$
$$+ \frac{\omega_i^2 + \omega_\lambda^2}{\omega_i \omega_\lambda}B_x^e\left(\zeta_{i\lambda_2}^x\right)^2, \quad (52)$$

$$x_{\lambda\lambda} = \frac{3}{2}k_{\lambda\lambda\lambda\lambda} - \sum_i\frac{k_{i\lambda\lambda}^2}{2\omega_i} - \frac{15k_{\lambda\lambda\lambda}^2}{4\omega_\lambda} - \sum_{\mu\neq\lambda}\frac{k_{\lambda\lambda\mu}^2}{2\omega_\mu}$$
$$- \sum_i\frac{k_{i\lambda\lambda}^2}{8(\omega_i + 2\omega_\lambda)} - \sum_{\mu\neq\lambda}\frac{k_{\lambda\lambda\mu}^2}{8(\omega_\mu + 2\omega_\lambda)}$$
$$- \sum_i\frac{k_{i\lambda\lambda}^2}{8(\omega_i - 2\omega_\lambda)} - \sum_{\mu\neq\lambda}\frac{k_{\lambda\lambda\mu}^2}{8(\omega_\mu - 2\omega_\lambda)}, \quad (53)$$

$$x_{\lambda\mu} = k_{\lambda\lambda\mu\mu}^{(1)} + \frac{1}{2}k_{\lambda\lambda\mu\mu}^{(2)} - \sum_i\frac{k_{i\lambda\lambda}k_{i\mu\mu}}{\omega_i}$$
$$- \frac{k_{\lambda\lambda\mu}^2}{2(\omega_\mu + 2\omega_\lambda)} + \frac{k_{\lambda\lambda\mu}^2}{2(\omega_\mu - 2\omega_\lambda)}$$
$$- \frac{k_{\lambda\mu\mu}^2}{2(\omega_\lambda + 2\omega_\mu)} + \frac{k_{\lambda\mu\mu}^2}{2(\omega_\lambda - 2\omega_\mu)}$$
$$- \sum_i\frac{k_{i\lambda\mu}^2}{16}\left\{ \frac{1}{\omega_i + \omega_\lambda + \omega_\mu} + \frac{1}{\omega_i + \omega_\lambda - \omega_\mu} \right.$$
$$\left. + \frac{1}{\omega_i - \omega_\lambda + \omega_\mu} + \frac{1}{\omega_i - \omega_\lambda - \omega_\mu} \right\}$$
$$- \sum_{\nu\neq\lambda,\mu}\frac{k_{\lambda\mu\nu}^2}{8}\left\{ \frac{1}{\omega_\lambda + \omega_\mu + \omega_\nu} - \frac{1}{\omega_\lambda + \omega_\mu - \omega_\nu} \right.$$
$$\left. + \frac{1}{\omega_\lambda - \omega_\mu + \omega_\nu} - \frac{1}{\omega_\lambda - \omega_\mu - \omega_\nu} \right\}$$
$$+ \frac{\omega_\lambda^2 + \omega_\mu^2}{\omega_\lambda \omega_\mu}\left\{ B_x^e(\zeta_{\lambda_1\mu_2}^x)^2 + \frac{B_z^e}{2}(\zeta_{\lambda_1\mu_2}^z)^2 \right\}, \quad (54)$$

$$x_{l_\lambda l_\lambda} = -\frac{1}{2}k_{\lambda\lambda\lambda\lambda} + \frac{21}{4}\frac{k_{\lambda\lambda\lambda}^2}{\omega_\lambda} + \sum_{\mu\neq\lambda}\frac{k_{\lambda\lambda\mu}^2}{2\omega_\mu}$$
$$+ \sum_i\frac{k_{i\lambda\lambda}^2}{8(\omega_i + 2\omega_\lambda)} - \sum_{\mu\neq\lambda}\frac{k_{\lambda\lambda\mu}^2}{8(\omega_\mu + 2\omega_\lambda)}$$
$$+ \sum_i\frac{k_{i\lambda\lambda}^2}{8(\omega_i - 2\omega_\lambda)} - \sum_{\mu\neq\lambda}\frac{k_{\lambda\lambda\mu}^2}{8(\omega_\mu - 2\omega_\lambda)}$$
$$+ B_z^e(\zeta_{\lambda_1\lambda_2}^z)^2, \quad (55)$$

and

$$x_{l_\lambda l_\mu} = \sum_i\frac{k_{i\lambda\mu}^2}{16}\left\{ \frac{1}{\omega_i + \omega_\lambda + \omega_\mu} - \frac{1}{\omega_i + \omega_\lambda - \omega_\mu} \right.$$
$$\left. - \frac{1}{\omega_i - \omega_\lambda + \omega_\mu} + \frac{1}{\omega_i - \omega_\lambda - \omega_\mu} \right\}$$
$$+ \frac{k_{\lambda\lambda\mu}^2}{2}\left\{ \frac{2}{\omega_\mu} - \frac{1}{\omega_\mu + 2\omega_\lambda} - \frac{1}{\omega_\mu - 2\omega_\lambda} \right\}$$
$$+ \frac{k_{\lambda\mu\mu}^2}{2}\left\{ \frac{2}{\omega_\lambda} - \frac{1}{\omega_\lambda + 2\omega_\mu} - \frac{1}{\omega_\lambda - 2\omega_\mu} \right\}$$

$$-\sum_{\nu\neq\lambda,\mu}\frac{k_{\lambda\mu\nu}^2}{8}\left\{\frac{1}{\omega_\lambda+\omega_\mu+\omega_\nu}-\frac{1}{\omega_\lambda+\omega_\mu-\omega_\nu}\right.$$

$$-\frac{1}{\omega_\lambda-\omega_\mu+\omega_\nu}+\left.\frac{1}{\omega_\lambda-\omega_\mu-\omega_\nu}\right\}$$

$$+B_z^e(\zeta_{\lambda_1\mu_2}^z)^2-2B_x^e(\zeta_{\lambda_1\mu_2}^x)^2+2B_z^e\zeta_{\lambda_1\lambda_2}^z\zeta_{\mu_1\mu_2}^z. \quad (56)$$

It should be mentioned that Equations (50)–(54) agree with the analogous general equations from Ref. [46]. However, there are differences in the expressions for the $x_{l_t l_{t'}}$ parameters. In particular, these parameters in [46] have the following form (in Equations (57)–(58), we kept the notations from [46]):

$$x_{l_t l_t}=-\frac{1}{4}\left\{2k_{tttt}+\sum_{s'}k_{tts'}^2\frac{\omega_{s'}}{\left(4\omega_t^2-\omega_{s'}^2\right)}\right.$$

$$\left.-4\sum_\alpha\left(\zeta_{t,1;t,2}^{(\alpha)}\right)^2B_e^{\alpha\alpha}\right\} \quad (57)$$

and

$$x_{l_t l_{t'}}=\sum_\alpha\left(\zeta_{t,1;t,2}^{(\alpha)}\zeta_{t',1;t',2}^{(\alpha)}\right)B_e^{\alpha\alpha}, \quad (58)$$

which is different from the corresponding equations (55) and (56). Thus, we think that the corresponding equations in [46] are not correct.

## 5.2. Ro-vibrational coefficients, $\alpha_b^\beta$

The ro-vibrational coefficients $\alpha_a^\beta$ are the parameters that describe the main part of the vibrational dependence of the rotational parameters, $B_\beta^v$:

$$B_\beta^v=B_\beta^e-\sum_b\alpha_b^\beta\left(v_b+\frac{d_b}{2}\right)+\cdots \quad (59)$$

To calculate the parameters $\alpha_b^\beta$, one should take into account that for the XYZ$_3$ ($C_{3v}$) molecule only the following $a_b^{\alpha\beta}$ coefficients (see Equations (20) and (21)) are different from zero: $a_i^{xx}=a_i^{yy}$, $a_i^{zz}$ ($i=1$, 2, or 3); $a_{\lambda_1}^{xz}=a_{\lambda_1}^{zx}=a_{\lambda_2}^{yz}=a_{\lambda_2}^{zy}$, and $a_{\lambda_1}^{xx}=-a_{\lambda_1}^{yy}=-a_{\lambda_2}^{xy}=-a_{\lambda_2}^{yx}$ ($\lambda=4$, 5, or 6); and, additionally, $B_x^e=B_y^e$. Taking into account these relations and the general equations (16)–(22), the use of operator perturbation theory from Section 4 allows one to obtain the following relations for the $a_b^{\alpha\beta}$ coefficients:

$$\alpha_i^\beta=-\frac{3}{2}\frac{(B_\beta^e)^3}{\omega_i}\left(\widetilde{a}_i^{\beta\beta}\right)^2-\frac{3\sqrt{2}}{\omega_i^{3/2}}\left(B_\beta^e\right)^2\widetilde{a}_i^{\beta\beta}k_{iii}$$

$$-\sum_{j\neq i}\frac{\sqrt{2}}{\omega_j^{3/2}}\left(B_\beta^e\right)^2\widetilde{a}_j^{\beta\beta}k_{iij}-\sum_\lambda\frac{(B_x^e\zeta_{i\lambda_2}^x)^2}{\omega_i\omega_\lambda}$$

$$\times\left\{\frac{(\omega_i+\omega_\lambda)^2}{\omega_i-\omega_\lambda}-\frac{(\omega_i-\omega_\lambda)^2}{\omega_i+\omega_\lambda}\right\}(1-\delta_{\beta z}), \quad (60)$$

$$\alpha_\lambda^x=\alpha_\lambda^y=-\frac{3}{4}\frac{(B_x^e)^2}{\omega_\lambda}\{2B_x^e(\widetilde{a}_{\lambda_1}^{xx})^2+B_z^e(\widetilde{a}_{\lambda_1}^{xz})^2\}$$

$$-\sum_i\frac{\sqrt{2}}{\omega_i^{3/2}}(B_x^e)^2\widetilde{a}_i^{xx}k_{i\lambda\lambda}$$

$$-\sum_{\mu\neq\lambda}\frac{(B_x^e\zeta_{\lambda_1\mu_2}^x)^2}{\omega_\lambda\omega_\mu}\left\{\frac{(\omega_\lambda+\omega_\mu)^2}{\omega_\lambda-\omega_\mu}-\frac{(\omega_\lambda-\omega_\mu)^2}{\omega_\lambda+\omega_\mu}\right\}$$

$$-\sum_i\frac{(B_x^e\zeta_{i\lambda_2}^x)^2}{2\omega_i\omega_\lambda}\left\{\frac{(\omega_\lambda+\omega_i)^2}{\omega_\lambda-\omega_i}-\frac{(\omega_\lambda-\omega_i)^2}{\omega_\lambda+\omega_i}\right\}, \quad (61)$$

and

$$\alpha_\lambda^z=-\frac{3}{2}\frac{B_x^e(B_z^e)^2}{\omega_\lambda}(\widetilde{a}_{\lambda_1}^{xz})^2-\sum_i\frac{\sqrt{2}}{\omega_i^{3/2}}(B_z^e)^2\widetilde{a}_i^{xx}k_{i\lambda\lambda}$$

$$-\sum_{\mu\neq\lambda}\frac{(B_z^e\zeta_{\lambda_1\mu_2}^z)^2}{\omega_\lambda\omega_\mu}\left\{\frac{(\omega_\lambda+\omega_\mu)^2}{\omega_\lambda-\omega_\mu}-\frac{(\omega_\lambda-\omega_\mu)^2}{\omega_\lambda+\omega_\mu}\right\}. \quad (62)$$

Equilibrium rotational parameters, $B_\beta^e$, and coefficients, $a_b^{\alpha\beta}$, are determined by Equations (19)–(22).

## 5.3. Centrifugal distortion coefficients $D_J$, $D_{JK}$, $D_K$, and parameter $\epsilon'$

Centrifugal distortion coefficients $D_J$, $D_{JK}$, $D_K$, and the parameter $\epsilon'$, which is responsible for the $a_1/a_2$ splittings in ($K=3$) rotational states in vibrational states of $A_1$ or $A_2$ symmetry, being calculated using the equations of Section 4, have the following form:

$$D_J^{A_\lambda}=D_J^E=\sum_i\left\{\frac{(B_x^e)^2\widetilde{a}_i^{xx}}{\omega_i}\right\}^2+\sum_\lambda\left\{\frac{(B_x^e)^2\widetilde{a}_{\lambda_1}^{xx}}{\omega_\lambda}\right\}^2, \quad (63)$$

$$D_{JK}^{A_\lambda}=D_{JK}^E=\sum_i\frac{2(B_x^e)^2\widetilde{a}_i^{xx}}{\omega_i^2}\{(B_z^e)^2\widetilde{a}_i^{zz}-(B_x^e)^2\widetilde{a}_i^{xx}\}$$

$$+\sum_\lambda\frac{2(B_x^e)^2}{\omega_\lambda^2}\{2(B_z^e)^2(\widetilde{a}_{\lambda_1}^{xz})^2-(B_x^e)^2(\widetilde{a}_{\lambda_1}^{xx})^2\}, \quad (64)$$

$$D_K^{A_\lambda}=D_K^E=\sum_i\left\{\frac{(B_x^e)^2\widetilde{a}_i^{xx}-(B_z^e)^2\widetilde{a}_i^{zz}}{\omega_i}\right\}^2$$

$$+\sum_\lambda\left\{\frac{B_x^e}{\omega_\lambda}\right\}^2\left\{(B_x^e\widetilde{a}_{\lambda_1}^{xx})^2-\left(2B_z^e\widetilde{a}_{\lambda_1}^{xz}\right)^2\right\}, \quad (65)$$

and

$$\epsilon'^{A_\lambda}=\epsilon'^E=\sum_\lambda\frac{1}{\omega_\lambda^2}\left(B_x^e\right)^3B_z^e\widetilde{a}_{\lambda_1}^{xx}\widetilde{a}_{\lambda_1}^{xz}. \quad (66)$$

### 5.4. Parameters of Coriolis splittings, $\eta^{vE}$, Coriolis interaction parameters, $\eta^{vA_1,vA_2}$, and Fermi interaction parameters, $\eta^{vnE,vmE}$

Using the $(-2B_z^e G_z J_z)$ part of the Hamiltonian $H^{\text{vib}-\text{rot}}$ in Equation (15) in the first-order term of operator perturbation theory (Section 4), one can easily obtain the main parts of three different types of spectroscopic parameters: parameters of Coriolis splittings $\eta^{vE}$, Equation (34), parameters $\eta^{vA_1,vA_2}$, Equation (39), and parameters $\eta^{vnE,vmE}$ ($n$, $m$ = 1, 2, ... and $n \neq m$), Equation (43), which describe Coriolis and Fermi interaction, respectively, between vibrational states having the same set of quantum numbers $v_a$, but different sets of quantum numbers $l_\lambda$. In this case, the result can be written as

$$\eta^{v\Gamma,v\Gamma'} = -2i B_z^e \left( c_\lambda \zeta_{\lambda_1\lambda_2}^z l_\lambda + c_\mu \zeta_{\mu_1\mu_2}^z l_\mu + c_\nu \zeta_{\nu_1\nu_2}^z l_\nu \right). \tag{67}$$

Here $\eta^{v\Gamma,v\Gamma'} = \eta^{vE,vE} \equiv \eta^{vE}$ is a parameter of the *k–l* splitting in Equation (34), $\eta^{v\Gamma,v\Gamma'} = \eta^{vA_1,vA_2}$ is a parameter of Coriolis resonance interaction in Equation (39), $\eta^{v\Gamma,v\Gamma'} = \eta^{vnE,vmE}$ is a parameter of Fermi resonance interaction in Equation (43), $\lambda$, $\mu$, $\nu$ are different combinations of values 4, 5, and/or 6, $l_\lambda$, $l_\mu$, and $l_\nu$ are vibrational quantum numbers in wavefunctions ($v_1$, $v_2$, $v_3$, $v_4$, $l_4$, $v_5$, $l_5$, $v_6$, $l_6$), and coefficients $c_\lambda$ for the most common situations are presented in Table 1. The following can be inferred from Table 1:

(1) The dependence of parameters $\eta^{\cdots}$ on the values of quantum numbers $l_\lambda/l_\mu/l_\nu$ is not trivial.

(2) The general equation (67) allows to connect with each other (and to make a prediction as a consequence) not only parameters of the *k–l* splitting in the *E* vibrational states, but also some Coriolis and Fermi resonance interaction parameters. The relations (67) do not depend on the values of the quantum numbers $v_\lambda/v_\mu/v_\nu$.

As an illustration of the adequateness of the relations obtained, we can mention the results of independent high-resolution analyses of the $\nu_5$ and $2\nu_5$ bands of the CHD$_3$ molecule from Refs. [50] and [51]. In this case, the parameter $\eta^{v_5=1E}$ from Ref. [50] is 3.565753 cm$^{-1}$ and $\eta^{v_5=2E}$ from Ref. [51] is $-2 \times 3.596929$ cm$^{-1}$. One can see an excellent agreement between both values. As one more illustration, we can mention the results of a preliminary ro-vibrational analysis of the $\nu_5 + \nu_6$ hybrid band of $^{13}$CH$_3$D [52] which can be compared with the results of the analysis of the fundamental bands $\nu_5$ and $\nu_6$ [53]. In this case, *k–l* splitting parameters in [53] are: $\eta^{v_5=1E} = -2.643331$ cm$^{-1}$ and $\eta^{v_6=1E} = +6.283671$ cm$^{-1}$. As seen from Table 1, one can expect that $\eta^{v_5=v_6=1A_1, v_5=v_6=1A_2} = +8.927002$ cm$^{-1}$ and $\eta^{v_5=v_6=1E} = -3.640340$ cm$^{-1}$. And, indeed, the cor-

responding parameters obtained from a preliminary fit to experimental data for the $\nu_5 + \nu_6$ hybrid band have the values +8.82 cm$^{-1}$ and $-3.53$ cm$^{-1}$, a more than satisfactory agreement between both pairs of values.

### 5.5. Parameters of the $a_1/a_2$ ($K = 1$) rotational splittings, $\gamma^{vE}$, Coriolis interaction parameters, $\gamma^{vA_\lambda,vE}$, and Fermi interaction parameters, $\gamma^{vnE,vmE}$

The parameters $\gamma^{vE}$ which describe the $a_1/a_2$ ($K = 1$) rotational splittings in the vibrational states of *E* symmetry, the Coriolis interaction parameters $\gamma^{vA_\lambda,vE}$, and the Fermi interaction parameters $\gamma^{vnE,vmE}$ are the main parameters related to the operators $(J_+^2 + J_-^2)/(J_+^2 - J_-^2)$ in Equations (35)–(36), (37)–(38), and (44)–(45). Using Equations (15)–(22) and (46) it can be shown that all these effects can be described by the parameters which have the form

$$\gamma^{v\Gamma,v\Gamma'} = d_\lambda^{(v)} \gamma_\lambda + d_\mu^{(v)} \gamma_\mu + d_\nu^{(v)} \gamma_\nu, \tag{68}$$

where $\lambda$, $\mu$, and $\nu$ are different, and

$$\gamma_\lambda = -\frac{3}{8} \frac{(B_x^e)^2 B_z^e}{\omega_\lambda} \left( \widetilde{a}_{\lambda_1}^{xz} \right)^2 - \frac{3}{\sqrt{2}} (B_x^e)^2 \widetilde{a}_{\lambda_1}^{xx} \frac{k_{\lambda\lambda\lambda}}{\omega_\lambda^{3/2}}$$
$$- \sum_{\mu'} \frac{1}{\sqrt{2}} (B_x^e)^2 \widetilde{a}_{\mu_1'}^{xx} \frac{k_{\lambda\lambda\mu'}}{\omega_{\mu'}^{3/2}} - \sum_i \frac{(B_x^e \zeta_{i\lambda_2}^x)^2}{4\omega_i \omega_\lambda}$$
$$\times \left\{ \frac{(\omega_i + \omega_\lambda)^2}{\omega_i - \omega_\lambda} + \frac{(\omega_i - \omega_\lambda)^2}{\omega_i + \omega_\lambda} \right\}. \tag{69}$$

(For $\gamma_\mu$ or $\gamma_\nu$ the index $\lambda$ on the right-hand side of Equation (69) should be changed to $\mu$ or $\nu$, respectively.) For $v_\lambda + v_\mu + v_\nu \leq 4$, non-zero values of coefficients $d_{\cdots}^{(\cdots)}$ are presented in Table 2.

As discussed in Section 5.4, Equations (68)–(69) allow one to make predictions of different parameters on the basis of known values of parameters $\gamma^{v_\lambda=1E}$ of the fundamental bands (the latter can be determined with high accuracy from the analysis of $a_1/a_2$ ($K = 1$) splittings in the fundamental bands). This is especially important for the prediction of resonance interaction parameters which are very often determined from the fit with poor reliability. It is also seen from Table 2 that the $a_1/a_2$ ($K = 1$) splitting parameters $\gamma^{vE}$ are non-zero for the fundamental bands, $v_\lambda$, but equal to zero for the first overtone, $2v_\lambda$, and combination, $v_\lambda + v_\mu$, bands.

As an illustration of the adequacy of Equation (69), we made a calculation of the $\gamma^{v_5=1E}$ and $\gamma^{v_6=1E}$ parameters for the CH$_3$D and CHD$_3$ molecules using the potential parameters from Ref. [54]. The result is presented in Table 3. As seen from Table 3, there is a very good agreement between calculated and experimental values of the $\gamma^{v_6=1E}$ (CH$_3$D) and $\gamma^{v_5=1E}$ (CHD$_3$) parameters. The agreement

Table 1. Values of non-zero coefficients $c$, Equation (67), used for the determination of parameters $\eta$.

| $l_\lambda\, l_\mu\, l_\nu$ | $c_\lambda$ | $c_\mu$ | $c_\nu$ | $\Gamma\widetilde\Gamma^a$ | $l_\lambda\, l_\mu\, l_\nu$ | $c_\lambda$ | $c_\mu$ | $c_\nu$ | $\Gamma\widetilde\Gamma^a$ |
|---|---|---|---|---|---|---|---|---|---|
| 1 0 0 | 1 | | | $E$ | 2 2 0 | 1 | $-1$ | | $A_1/A_2$ |
| 2 0 0 | $-1$ | | | $E$ | 1 3 0 | 1 | | | 1E |
| 3 0 0 | $-1$ | | | $A_1/A_2$ | 1 3 0 | 1 | | | 2E |
| 4 0 0 | 1 | | | $E$ | 1 3 0 | | 1 | | 1E/2E |
| 5 0 0 | $-1$ | | | $E$ | 2 3 0 | $-1$ | | | 1E |
| 6 0 0 | $-1$ | | | $A_1/A_2$ | 2 3 0 | $-1$ | | | 2E |
| 1 1 0 | $-1$ | $-1$ | | $E$ | 2 3 0 | | 1 | | 1E/2E |
| 1 1 0 | $-1$ | 1 | | $A_1/A_2$ | 1 1 1 | 1 | 1 | $-1$ | 1E |
| 1 2 0 | $-1$ | 1 | | $E$ | 1 1 1 | 1 | $-1$ | 1 | 2E |
| 1 2 0 | $-1$ | $-1$ | | $A_1/A_2$ | 1 1 1 | $-1$ | 1 | 1 | 3E |
| 2 2 0 | 1 | 1 | | $E$ | 1 1 1 | 1 | 1 | 1 | $A_1/A_2$ |

$^a$In that column the type of parameter is presented: $\Gamma\widetilde\Gamma = E$ corresponds to the $\eta^{vE}$ $k$–$l$ splitting parameter of Equation (34); $\Gamma\widetilde\Gamma = A_1/A_2$ corresponds to the $\eta^{vA_1,vA_2}$ Coriolis interaction parameter of Equation (39); $\Gamma\widetilde\Gamma = E/E$ corresponds to the $\eta^{vE,vE}$ Fermi interaction parameter of Equation (43).

Table 2. Values of non-zero coefficients $d$, Equations (68) and (70), used for the determination of parameters $\gamma^{v\Gamma,v\Gamma'}$ and $\beta^{v\Gamma,v\Gamma'}$.

| $v_\lambda\, l_\lambda$ | $v_\mu\, l_\mu$ | $v_\nu\, l_\nu$ | $\Gamma$ | $\widetilde v_\lambda\widetilde l_\lambda$ | $\widetilde v_\mu\widetilde l_\mu$ | $\widetilde v_\nu\widetilde l_\nu$ | $\widetilde\Gamma$ | $d_\lambda^{(..)}$ | $d_\mu^{(..)}$ | $d_\nu^{(..)}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| 11 | 00 | 00 | $E$ | 11 | 00 | 00 | $E$ | 2 | | |
| 20 | 00 | 00 | $A_1$ | 22 | 00 | 00 | $E$ | 4 | | |
| 11 | 11 | 00 | $E$ | 11 | 11 | 00 | $A_1$ | 2 | 2 | |
| 11 | 11 | 00 | $E$ | 11 | 11 | 00 | $A_2$ | 2 | $-2$ | |
| 31 | 00 | 00 | $E$ | 31 | 00 | 00 | $E$ | 4 | | |
| 31 | 00 | 00 | $E$ | 33 | 00 | 00 | $A_1$ | $2\sqrt{3}$ | | |
| 31 | 00 | 00 | $E$ | 33 | 00 | 00 | $A_2$ | $2\sqrt{3}$ | | |
| 11 | 20 | 00 | $E$ | 11 | 20 | 00 | $E$ | 2 | | |
| 11 | 22 | 00 | $E$ | 11 | 22 | 00 | $A_1$ | 2 | | |
| 11 | 22 | 00 | $E$ | 11 | 22 | 00 | $A_2$ | 2 | | |
| 11 | 11 | 11 | 1E | 11 | 11 | 11 | 2E | 2 | | |
| 11 | 11 | 11 | 1E | 11 | 11 | 11 | 3E | | 2 | |
| 11 | 11 | 11 | 2E | 11 | 11 | 11 | 3E | | | 2 |
| 11 | 11 | 11 | 1E | 11 | 11 | 11 | $A_1$ | | | 2 |
| 11 | 11 | 11 | 1E | 11 | 11 | 11 | $A_2$ | | | $-2$ |
| 11 | 11 | 11 | 2E | 11 | 11 | 11 | $A_1$ | | 2 | |
| 11 | 11 | 11 | 2E | 11 | 11 | 11 | $A_2$ | | $-2$ | |
| 11 | 11 | 11 | 3E | 11 | 11 | 11 | $A_1$ | 2 | | |
| 11 | 11 | 11 | 3E | 11 | 11 | 11 | $A_2$ | $-2$ | | |
| $v_\lambda\, l_\lambda$ | $v_\mu\, l_\mu$ | $v_\nu\, l_\nu$ | $\Gamma$ | $\widetilde v_\lambda\widetilde l_\lambda$ | $\widetilde v_\mu\widetilde l_\mu$ | $\widetilde v_\nu\widetilde l_\nu$ | $\widetilde\Gamma$ | $d_\lambda^{(..)}$ | $d_\mu^{(..)}$ | $d_\nu^{(..)}$ |
| 40 | 00 | 00 | $A_1$ | 42 | 00 | 00 | $E$ | $-4\sqrt{3}$ | | |
| 42 | 00 | 00 | $E$ | 44 | 00 | 00 | $E$ | $-4$ | | |
| 20 | 20 | 00 | $A_1$ | 22 | 20 | 00 | $E$ | 4 | | |
| 20 | 22 | 00 | $E$ | 22 | 22 | 00 | $E$ | $2\sqrt{2}$ | | |
| 20 | 22 | 00 | $E$ | 22 | 22 | 00 | $A_1$ | $2\sqrt{2}$ | | |
| 20 | 22 | 00 | $E$ | 22 | 22 | 00 | $A_2$ | $-2\sqrt{2}$ | | |
| 11 | 31 | 00 | $E$ | 11 | 31 | 00 | $A_1$ | 2 | 4 | |
| 11 | 31 | 00 | $E$ | 11 | 31 | 00 | $A_2$ | 2 | $-4$ | |
| 11 | 31 | 00 | $E$ | 11 | 33 | 00 | 1E | | $\sqrt{6}$ | |
| 11 | 31 | 00 | $E$ | 11 | 33 | 00 | 2E | | $\sqrt{6}$ | |
| 11 | 31 | 00 | $A_1$ | 11 | 33 | 00 | 1E | | $\sqrt{6}$ | |
| 11 | 31 | 00 | $A_2$ | 11 | 33 | 00 | 1E | | $\sqrt{6}$ | |
| 11 | 31 | 00 | $A_1$ | 11 | 33 | 00 | 2E | | $-\sqrt{6}$ | |
| 11 | 31 | 00 | $A_2$ | 11 | 33 | 00 | 2E | | $-\sqrt{6}$ | |
| 11 | 33 | 00 | 1E | 11 | 33 | 00 | 1E | 2 | | |
| 11 | 33 | 00 | 2E | 11 | 33 | 00 | 2E | $-2$ | | |

Table 3. Values of some $a_1/a_2$ splitting parameters, $\gamma^{vE}$, of the $CH_3D$ and $CHD_3$ isotopomers.

| Parameter | CH$_3$D | | CHD$_3$ | |
| --- | --- | --- | --- | --- |
| | Calculated | Experimental [55] | Calculated | Experimental [50] |
| $\gamma^{v_5=1E}/10^{-3}$ cm$^{-1}$ | −1.03 | 0.72 | −5.87 | −5.95 |
| $\gamma^{v_6=1E}/10^{-3}$ cm$^{-1}$ | −16.90 | −17.53 | 12.1 | 16.8 |

between calculated and experimental values of the $\gamma^{v_5=1E}$ (CH$_3$D) and $\gamma^{v_6=1E}$ (CHD$_3$) parameters is not that good, and the differences between calculated and experimental values are $1.75 \times 10^{-3}$ cm$^{-1}$ for CH$_3$D and $4.7 \times 10^{-3}$ cm$^{-1}$ for CHD$_3$. However, even such discrepancies can be considered as acceptable if one takes into account the following:

(1) In one case, the discrepancy is about 25% of the absolute value of the parameter $\gamma_{calc}^{v_6=1E}$ (CHD$_3$).
(2) In the case of the parameter $\gamma^{v_5=1E}$ (CH$_3$D), the discrepancy is comparable with discrepancies for the parameters $\gamma^{v_6=1E}$ (CH$_3$D) and $\gamma^{v_5=1E}$ (CHD$_3$) even with different signs of experimental and calculated values. It should be mentioned also that we used in our calculations the *ab initio* PES from Ref. [54], and the relatively large difference between the values for $\gamma_{calc}^{v_6=1E}$ and $\gamma_{exp.}^{v_6=1E}$ of CHD$_3$ can be explained by possible uncertainties in PES parameters.

As one more illustration of the adequacy of the results, we compare the experimental values of the parameter $\gamma^{v_5=1E} = -0.5948 \times 10^{-2}$ cm$^{-1}$ from [50] with $\gamma^{v_5=2E} = -0.4451 \times 10^{-4}$ cm$^{-1}$ from [51] for CHD$_3$. As mentioned above, in the framework of the approximation used, the parameters $\gamma^{vE}$ of the first-overtone bands should be equal to zero. And, indeed, the absolute value of the parameter $\gamma^{v_5=2E}$ is less than 1% of the absolute value of the parameter $\gamma^{v_5=1E}$. The fact that the parameter $\gamma^{v_5=2E}$ is not equal to zero can be explained by the effects of higher orders.

### 5.6. Parameters $\beta^{vE}$, Coriolis interaction parameters $\beta^{vA_\lambda, vE}$, and Fermi interaction parameters $\beta^{vnE, vmE}$

The parameters $\beta^{vE}$, Equations (35) and (36), Coriolis interaction parameters $\beta^{vA_\lambda, vE}$, Equations (37) and (38), and Fermi interaction parameters $\beta^{vnE, vmE}$, Equations (44) and (45), are the main parameters related to the operators $[(J_+ \pm J_-), J_z]_+$ in the equations mentioned. It can be shown that all of these parameters can be expressed in the following form:

$$\beta^{v\Gamma, v\Gamma'} = d_\lambda^{(v)}\beta_\lambda + d_\mu^{(v)}\beta_\mu + d_\nu^{(v)}\beta_\nu, \qquad (70)$$

where the non-zero coefficients $d_{...}^{(...)}$ have exactly the same form as in Equation (68) and can be used from Table 2. In their turn, the parameters $\beta_\lambda$ have been determined as

$$\beta_\lambda = \frac{3\sqrt{2}}{8} \frac{(B_x^e)^2 B_z^e}{\omega_\lambda} \left(\widetilde{a}_{\lambda_1}^{xx}\widetilde{a}_{\lambda_1}^{xz}\right) + \frac{3}{2}(B_x^e)(B_z^e)\widetilde{a}_{\lambda_1}^{xz}\frac{k_{\lambda\lambda\lambda}}{\omega_\lambda^{3/2}}$$
$$+ \sum_\mu \frac{1}{2}(B_x^e)(B_z^e)\widetilde{a}_{\mu_1}^{xx}\frac{k_{\lambda\lambda\mu}}{\omega_\mu^{3/2}} + \sum_{\mu\neq\lambda}\frac{\left(B_x^e\zeta_{\mu_1\lambda_2}^x\right)\left(B_z^e\zeta_{\mu_1\lambda_2}^z\right)}{2\sqrt{2}\omega_\lambda\omega_\mu}$$
$$\times \left\{\frac{(\omega_\mu + \omega_\lambda)^2}{\omega_\mu - \omega_\lambda} + \frac{(\omega_\mu - \omega_\lambda)^2}{\omega_\mu + \omega_\lambda}\right\}. \qquad (71)$$

What has been said in Sections 2–5 is valid for every symmetric top XYZ$_3$ ($C_{3v}$) molecule. Moreover, it is also valid for every symmetric top XY$_3$ ($C_{3v}$) molecule taking into account that there are only two doubly degenerate vibrational modes in XY$_3$ instead of three in XYZ$_3$.

### 6. 'Expanded local mode' approach applied to the CH$_4$ molecule

Here we apply results obtained in Section 5 to derive isotopic relations for substitutions of the type CH$_3$D ← CH$_4$ and CHD$_3$ ← CH$_4$ in methane. In the present section, we summarise very briefly some results obtained in Ref. [35] for the CH$_4$ molecule in the framework of the 'expanded local mode' approach.

The classical local mode approach was extensively discussed in molecular spectroscopy originally by Mecke in the 1930s [56], and again in the 1980s and 1990s (see, e.g. [57–60], the discussion in [61], the review of the history in [19], and the later review in [62]). The approach was found to be very efficient for the study of the rotational-vibrational structure of highly excited vibrational states of XY$_2$ ($C_{2v}$ symmetry), XY$_3$($C_{3v}$), XY$_4$($T_d$), and some other types of molecules. By its basic statements, the local mode model assumes the following:

(1) Deformation motions in the molecule are neglected.
(2) The mass of the central nucleus X is assumed to be considerably greater than the masses $m$ of

the nuclei Y, i.e. in the limit, one has the ratio $m/M = 0$.

(3) The equilibrium angle between bonds X–Y is fixed for the $XY_2(C_{2v})$, $XY_3(C_{3v})$, and $XY_4(T_d)$ molecules.

(4) In the intramolecular potential function, only changes in the bond lengths are taken into account; the dependence on changes in interbond angles is neglected.

As a result, the local mode approach allows one to derive a set of simple relations between spectroscopic parameters of the molecule considered (see, e.g. Refs. [56–62]). Unfortunately, the above-mentioned limitations of the model are too serious, particularly because the deformation motions are not taken into account. It is clear that the deformation motions are important for understanding the processes taking place in the molecules.

The presence of the deformation motions can be taken into account by using the extension of a classical local mode model ('expanded local mode' approach) which was derived in Ref. [37] and applied to asymmetric [37,38,63], symmetric [39,64], and spherical top [35,36] molecules. The key point of the 'expanded local mode' model is the possibility to present the transformation coefficients, $l_{N\alpha\lambda}$, of a molecule in the form of simple analytical expressions. If one takes into account that spectroscopic parameters of a molecule are functions of these $l_{N\alpha\lambda}$ transformation coefficients (see, e.g. Refs. [47,48]), one may hope that these spectroscopic parameters also can be expressed in a simple form. In this case, all the results of the classical local mode model are reproduced by the 'expanded local mode model' for the corresponding molecules. Moreover, the 'expanded' model provides the possibility to consider the deformation motions as well, and to produce numerous additional simple relations between different spectroscopic parameters of the molecule considered.

As to $CH_4$, it was shown in Ref. [35] that its transformation coefficients $l_{N\alpha\lambda}$ can be estimated with good accuracy (with less than 2% error) by a very simple form (see Table 4 which is reproduced here for convenience from [35]). Moreover, a set of simple approximate relations between different force field parameters are also fulfilled with good accuracy:

$$\frac{F_{33}}{267} = \frac{F_{11}}{272} = \frac{4F_{22}}{97\rho_e^2} = \frac{3F_{44}}{67\rho_e^2} = -\frac{2F_{34}}{19\rho_e}, \qquad (72)$$

$$\frac{2}{3}F_{244} = -\frac{7}{3}F_{222} = -\frac{2}{3}F_{444} = \rho_e F_{144} = \frac{4\rho_e}{5}F_{122}$$
$$= -\rho_e F_{234} = 2\rho_e F_{344} = \frac{\rho_e^2}{2}F_{233} = \rho_e^2 F_{334}$$

$$= -2\rho_e^2 F_{134} = \frac{\rho_e^3}{90}F_{111} = \frac{\rho_e^3}{90}F_{333}$$
$$= \frac{\rho_e^3}{90}F_{133} = -\frac{\rho_e^2}{30}F_{11}, \qquad (73)$$

and

$$F_{4444(2)} = 2F_{4444(1)} = 2F_{2244(2)} = 4F_{2222}$$
$$= -\frac{13\rho_e}{7}F_{3444(1)} = -\frac{39\rho_e}{7}F_{3444(2)}$$
$$= -\frac{19\rho_e^2}{7}F_{3344(3)} = -\frac{57\rho_e^2}{7}F_{3344(1)}$$
$$= \frac{24\rho_e^2}{7}F_{2334} = -\frac{24\rho_e^2}{7}F_{2233(1)}$$
$$= -\frac{12\rho_e^2}{7}F_{2233(2)} = \frac{18\rho_e^3}{7}F_{3334(1)}$$
$$= \frac{18\rho_e^3}{7}F_{3334(2)} = \frac{\rho_e^4}{70}F_{1111} = \frac{\rho_e^4}{70}F_{1133}$$
$$= \frac{\rho_e^4}{70}F_{1333} = \frac{\rho_e^4}{70}F_{3333(1)} = \frac{\rho_e^4}{70}F_{3333(2)}. \quad (74)$$

All the other $F_{ijkl}$ parameters are equal to zero, or close to zero, with a good accuracy of 1% –3%. The value $\rho_e$ is the equilibrium distance between the nuclei C and H.

## 7. Some results from the isotopic substitution theory

As was shown in [34], the following three statements are correct for an arbitrary isotopic substitution in a polyatomic molecule:

(1) A set of equations allows one to determine all harmonic frequencies, $\omega_c'$, of an isotopically substituted molecule as functions of harmonic frequencies, $\omega_a$, of a mother molecule and a set of coefficients $A_{ab}$; or, conversely, to determine coefficients $A_{ab}$ as functions of harmonic frequencies of the mother and substituted molecules:

$$\sum_a A_{ba}\omega_a^2\alpha_{ac} = \alpha_{bc}\omega_c'^2. \qquad (75)$$

Here $\alpha_{ac}$ (or $\alpha_{bc}$) are additional coefficients which are also determined from a solution of the set of equations (75) and additional relations:

$$A_{ab} = \sum_c \alpha_{ac}\alpha_{bc}. \qquad (76)$$

(2) From the statements above, the second equation (76) can take the following form ($m_N$ and $m_N'$ are the masses of atoms before and after isotopic

Table 4. Transformation coefficients, $l_{N\alpha\lambda}$, of $CH_4$ in the 'expanded local mode' model.[a]

| $N\alpha/\lambda$ | 1 | $2_1$ | $2_2$ | $3_x$ | $3_y$ | $3_z$ | $4_x$ | $4_y$ | $4_z$ |
|---|---|---|---|---|---|---|---|---|---|
| $1x$ | $\sqrt{2}A$ | $A$ | $\sqrt{3}A$ | $3\sqrt{3}B$ | $-4\sqrt{2}B$ | $-4\sqrt{2}B$ | $4\sqrt{3}B$ | $3\sqrt{2}B$ | $3\sqrt{2}B$ |
| $2x$ | $-\sqrt{2}A$ | $-A$ | $-\sqrt{3}A$ | $3\sqrt{3}B$ | $-4\sqrt{2}B$ | $4\sqrt{2}B$ | $4\sqrt{3}B$ | $3\sqrt{2}B$ | $-3\sqrt{2}B$ |
| $3x$ | $-\sqrt{2}A$ | $-A$ | $-\sqrt{3}A$ | $3\sqrt{3}B$ | $4\sqrt{2}B$ | $-4\sqrt{2}B$ | $4\sqrt{3}B$ | $-3\sqrt{2}B$ | $3\sqrt{2}B$ |
| $4x$ | $\sqrt{2}A$ | $A$ | $\sqrt{3}A$ | $3\sqrt{3}B$ | $4\sqrt{2}B$ | $4\sqrt{2}B$ | $4\sqrt{3}B$ | $-3\sqrt{2}B$ | $-3\sqrt{2}B$ |
| $5x$ | $0$ | $0$ | $0$ | $-6B$ | $0$ | $0$ | $-8B$ | $0$ | $0$ |
| $1y$ | $-\sqrt{2}A$ | $-A$ | $\sqrt{3}A$ | $-4\sqrt{2}B$ | $3\sqrt{3}B$ | $4\sqrt{2}B$ | $3\sqrt{2}B$ | $4\sqrt{3}B$ | $-3\sqrt{2}B$ |
| $2y$ | $\sqrt{2}A$ | $A$ | $-\sqrt{3}A$ | $-4\sqrt{2}B$ | $3\sqrt{3}B$ | $-4\sqrt{2}B$ | $3\sqrt{2}B$ | $4\sqrt{3}B$ | $3\sqrt{2}B$ |
| $3y$ | $-\sqrt{2}A$ | $-A$ | $\sqrt{3}A$ | $4\sqrt{2}B$ | $3\sqrt{3}B$ | $-4\sqrt{2}B$ | $-3\sqrt{2}B$ | $4\sqrt{3}B$ | $3\sqrt{2}B$ |
| $4y$ | $\sqrt{2}A$ | $A$ | $-\sqrt{3}A$ | $4\sqrt{2}B$ | $3\sqrt{3}B$ | $4\sqrt{2}B$ | $-3\sqrt{2}B$ | $4\sqrt{3}B$ | $-3\sqrt{2}B$ |
| $5y$ | $0$ | $0$ | $0$ | $0$ | $-6B$ | $0$ | $0$ | $-8B$ | $0$ |
| $1z$ | $-\sqrt{2}A$ | $2A$ | $0$ | $-4\sqrt{2}B$ | $4\sqrt{2}B$ | $3\sqrt{3}B$ | $3\sqrt{2}B$ | $-3\sqrt{2}B$ | $4\sqrt{3}B$ |
| $2z$ | $-\sqrt{2}A$ | $2A$ | $0$ | $4\sqrt{2}B$ | $-4\sqrt{2}B$ | $3\sqrt{3}B$ | $-3\sqrt{2}B$ | $3\sqrt{2}B$ | $4\sqrt{3}B$ |
| $3z$ | $\sqrt{2}A$ | $-2A$ | $0$ | $-4\sqrt{2}B$ | $-4\sqrt{2}B$ | $3\sqrt{3}B$ | $3\sqrt{2}B$ | $3\sqrt{2}B$ | $4\sqrt{3}B$ |
| $4z$ | $\sqrt{2}A$ | $-2A$ | $0$ | $4\sqrt{2}B$ | $4\sqrt{2}B$ | $3\sqrt{3}B$ | $-3\sqrt{2}B$ | $-3\sqrt{2}B$ | $4\sqrt{3}B$ |
| $5z$ | $0$ | $0$ | $0$ | $0$ | $0$ | $-6B$ | $0$ | $0$ | $-8B$ |

[a]Here $A = \frac{1}{2\sqrt{6}}$, $B = \frac{1}{20}$.

substitution):

$$A_{ab} = \delta_{ab} - \sum_{N\alpha} \frac{(m'_N - m_N)}{m'_N} l_{N\alpha a} l_{N\alpha b}, \quad (77)$$

and this determines the $A_{ab}$ coefficients via transformation coefficients, $l_{N\alpha a}$, of a mother isotopomer. Usually these transformation coefficients are known for every mother isotopomer.

(3) The third statement can be written as

$$l'_{N\gamma a} = \sum_{\alpha b} K^e_{\alpha\gamma} \left(\frac{m_N}{m'_N}\right)^{1/2} l_{N\alpha b}(\alpha^{-1})_{ab}, \quad (78)$$

and it provides the possibility to calculate the transformation coefficients of a substituted isotopomer as functions of the characteristics of a mother species. Here $K^e_{\alpha\gamma}$ is the matrix that provides a rotation of the molecular equilibrium coordinate axes from a mother species to a substituted one under isotopic substitution. In Equations (75)–(78), $\alpha$, $\beta,\gamma = x, y, z$ and $a, b, c$ enumerate the vibrational modes.

The relations (75)–(78) allow one to obtain the transformation coefficients $l_{N\gamma a}$ of any substituted molecule if one knows the corresponding coefficients $l_{N\alpha b}$ of a mother isotopic species. Unfortunately, because of the complexity in the general case, results can be obtained only in numerical form. On the other hand, if the coefficients $l_{N\alpha b}$ of a mother molecule and the coefficients $(\alpha^{-1})_{ab}$ on the right-hand side of Equation (78) have relatively simple values, one may expect that the transformation coefficients $l'_{N\gamma a}$

of a substituted molecule also can be obtained in a simple form.

## 8. Isotopic relations for $CH_3D$ and $CHD_3$

In the present section, we use the results derived above to obtain relatively simple isotopic relations between some of the most important spectroscopic parameters of $CH_3D$ and $CHD_3$, on one hand, and the spectroscopic parameters of the mother molecule, $CH_4$, on the other hand. In order to do so, we shall first discuss the transformation coefficients $l'_{N\gamma a}$, Coriolis coefficients $\zeta'^\alpha_{ab}$, ro-vibrational coefficients $a'^{\alpha\beta}_a$, and normal mode force field parameters of the $CH_3D$ and $CHD_3$ isotopomers.

### 8.1. Transformation coefficients, Harmonic frequencies, and equilibrium rotational parameters of $CH_3D$ and $CHD_3$

As a first step in the analysis, we (in accordance with Equation (78)) determine the transformation coefficients $l'_{N\gamma a}$ for both $CH_3D$ and $CHD_3$. In order to realise this

(1) the set of equations (75)–(76) should be solved with the values $A_{\lambda\mu}$ determined by Equation (77); and
(2) the elements, $K^e_{\alpha\gamma}$, of the matrix, which provide a rotation of the molecular equilibrium coordinate axes from a mother species to a substituted one, should be determined. The latter problem is solved easily, and the corresponding matrix is obtained in

Table 5. Transformation coefficients, $l'_{N\alpha b}$, of CH$_3$D in the framework of the 'expanded local mode' model.[a]

| $N\alpha/b$ | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|---|---|---|---|---|---|---|---|---|---|
| 1x | −47C | −5C | 17C | 63C | 0 | 14C | 0 | 5C | 0 |
| 2x | 23C | 3C | −9C | 15C | 28C | −40C | 31C | 24C | −11C |
| 3x | 23C | 3C | −9C | 15C | −28C | −40C | −31C | 24C | 11C |
| 4x | 0 | 0 | 0 | −C | 0 | 18C | 0 | 51C | 0 |
| 5x | 0 | 0 | 0 | −26C | 0 | 11C | 0 | −36C | 0 |
| 1y | 0 | 0 | 0 | 0 | −2C | 0 | −58C | 0 | 30C |
| 2y | 40C | 5C | −15C | 28C | 47C | 31C | −4C | −11C | 11C |
| 3y | −40C | −5C | 15C | −28C | 47C | −31C | −4C | 11C | 11C |
| 4y | 0 | 0 | 0 | 0 | −C | 0 | 18C | 0 | 51C |
| 5y | 0 | 0 | 0 | 0 | −26C | 0 | 11C | 0 | −36C |
| 1z | 16C | 2C | 43C | −23C | 0 | 34C | 0 | 38C | 0 |
| 2z | 16C | 2C | 43C | 11C | 20C | −17C | −29C | −19C | −33C |
| 3z | 16C | 2C | 43C | 11C | −20C | −17C | 29C | −19C | −33C |
| 4z | 5C | −80C | −12C | 0 | 0 | 0 | 0 | 0 | 0 |
| 5z | −15C | 31C | −32C | 0 | 0 | 0 | 0 | 0 | 0 |

[a]Here $C = \frac{1}{50\sqrt{3}}$.

the following form:

$$
\begin{pmatrix} K^e_{xx} & K^e_{xy} & K^e_{xz} \\ K^e_{yx} & K^e_{yy} & K^e_{yz} \\ K^e_{zx} & K^e_{zy} & K^e_{zz} \end{pmatrix}
= \begin{pmatrix} \sqrt{2/3} & -\sqrt{1/6} & -\sqrt{1/6} \\ 0 & -\sqrt{1/2} & \sqrt{1/2} \\ \sqrt{1/3} & \sqrt{1/3} & \sqrt{1/3} \end{pmatrix} \quad (79)
$$

both for CH$_3$D and CHD$_3$. From a solution of the Equations (75) and (76), one can obtain harmonic frequencies, $\omega_a$, $\alpha_{ab}$ coefficients, and, as a consequence, the transformation coefficients, $l'_{N\gamma a}$, from Equation (78). In this case, for the harmonic frequencies, the following results are obtained:

$$
\frac{\omega_1^2}{120} = \frac{\omega_2^2}{32} = \frac{\omega_3^2}{81 + 28\sqrt{3}} = \frac{\omega_4^2}{72 - 28\sqrt{3}}
$$
$$
= \frac{\omega_1'^2}{119 + 2\sqrt{3}} = \frac{\omega_2'^2}{66 + \sqrt{3}} = \frac{\omega_3'^2}{6 + 10\sqrt{3}}
$$
$$
= \frac{\omega_4'^2}{119 + 6\sqrt{3}} = \frac{\omega_5'^2}{14 + 9\sqrt{3}} = \frac{\omega_6'^2}{1 + 10\sqrt{3}}
\quad (80)
$$

for CH$_3$D and

$$
\frac{\omega_1^2}{120} = \frac{\omega_2^2}{32} = \frac{\omega_3^2}{81 + 28\sqrt{3}} = \frac{\omega_4^2}{72 - 28\sqrt{3}}
$$
$$
= \frac{\omega_1'^2}{122 + 3\sqrt{3}} = \frac{\omega_2'^2}{52 + 6\sqrt{3}} = \frac{\omega_3'^2}{5 + 5\sqrt{3}}
$$

$$
= \frac{\omega_4'^2}{64 + 4sqrt3} = \frac{\omega_5'^2}{14 + 5\sqrt{3}} = \frac{\omega_6'^2}{11 + 2\sqrt{2}}
\quad (81)
$$

for CHD$_3$. The $l'_{N\gamma b}$ coefficients are presented in Tables 5 and 6. The equilibrium rotational parameters, $B^e_\alpha$, can also be obtained very easily on the basis of Equation (79) in the following form for CH$_3$D:

$$
23B'^e_x = 23B'^e_y = 17B'^e_z = 17B^e \quad (82)
$$

and

$$
61B'^e_x = 61B'^e_y = 76B'^e_z = 38B^e \quad (83)
$$

for CHD$_3$.

To illustrate the quality of our results, Table 7 presents numerical values of the harmonic wavenumbers of the CH$_3$D and CHD$_3$ species estimated using the isotopic relations (80)–(81) (column I). In this case, the 'basic' 'experimental' value of the parameter $\omega_1$(CH$_4$) = 3040.38 cm$^{-1}$ was taken from Ref. [35] (here we used the parameter $\omega_1$ of CH$_4$ as the 'basic' value in isotopic relations; however, one can also use another harmonic frequency of CH$_4$ as the 'basic' value). For comparison, values of the same parameters obtained from *ab initio* calculations [54] are shown in column IV of Table 7. It should be noted that in spite of the fact that the values of harmonic frequencies in column I were obtained without any information about the CH$_3$D and CHD$_3$ molecules, the results used for comparison can be considered as quite satisfactory. Columns II and III of Table 7 present the result of analogous calculations using

Table 6. Transformation coefficients, $l'_{N\alpha b}$, of CHD$_3$ in the framework of the 'expanded local mode' model.[a]

| $N\alpha/b$ | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|---|---|---|---|---|---|---|---|---|---|
| 1x | 2C | −46C | 20C | 60C | 0 | 6C | 0 | 16C | 0 |
| 2x | −C | 23C | −10C | 15C | 26C | −6C | 7C | −42C | 34C |
| 3x | −C | 23C | −10C | 15C | −26C | −6C | −7C | −42C | −34C |
| 4x | 0 | 0 | 0 | −0.7C | 0 | 70C | 0 | −14C | 0 |
| 5x | 0 | 0 | 0 | −37C | 0 | −18C | 0 | 32C | 0 |
| 1y | 0 | 0 | 0 | 0 | −0.4C | 0 | −10C | 0 | −62C |
| 2y | −2C | 40C | −17C | 26C | 45C | 7C | 2C | 34C | −4C |
| 3y | 2C | −40C | 17C | −26C | 45C | −7C | 2C | −34C | −4C |
| 4y | 0 | 0 | 0 | 0 | −0.7C | 0 | 70C | 0 | −14C |
| 5y | 0 | 0 | 0 | 0 | −37C | 0 | −18C | 0 | 32C |
| 1z | 0.1C | 16C | 38C | −22C | 0 | 37C | 0 | 9C | 0 |
| 2z | 0.1C | 16C | 38C | 11C | 19C | −18C | −32C | −5C | −8C |
| 3z | 0.1C | 16C | 38C | 11C | −19C | −18C | 32C | −5C | 8C |
| 4z | −83C | −9C | −11C | 0 | 0 | 0 | 0 | 0 | 0 |
| 5z | 24C | −17C | −44C | 0 | 0 | 0 | 0 | 0 | 0 |

[a]Here $C = \frac{1}{50\sqrt{3}}$.

the isotopic relations (80)–(81), but with the values of the 'basic' parameters $\omega_4(\mathrm{CH}_4) = 1345.3$ cm$^{-1}$ and $\omega_1(\mathrm{CH}_4) = 3036.2$ cm$^{-1}$ which were taken from the *ab initio* calculations [54]. One can see that the differences between values of the same quantities in columns I, II, and IV are no more than 0.05%. All the values in column III are smaller than the values of the corresponding parameters in columns I, II, and IV by 2–4 cm$^{-1}$ (about 0.15%–0.20% which can be considered to be a more than satisfactory accuracy of the predictions).

Table 7. Harmonic wavenumbers of the CH$_3$D and CHD$_3$ molecules (in cm$^{-1}$).

| Parameter | I[a] | II[b] | III[c] | IV[d] |
|---|---|---|---|---|
| | CH$_3$D | | | |
| $\omega'_1$ | 3071.4 | 3070.9 | 3067.2 | 3071.4 |
| $\omega'_2$ | 2284.2 | 2283.8 | 2281.1 | 2285.2 |
| $\omega'_3$ | 1340.3 | 1340.1 | 1338.5 | 1339.8 |
| $\omega'_4$ | 3157.1 | 3156.6 | 3152.8 | 3156.8 |
| $\omega'_5$ | 1509.7 | 1509.5 | 1507.7 | 1508.1 |
| $\omega'_6$ | 1187.9 | 1187.8 | 1186.3 | 1188.1 |
| | CHD$_3$ | | | |
| $\omega'_1$ | 3130.2 | 3129.7 | 3125.9 | 3130.5 |
| $\omega'_2$ | 2192.3 | 2191.9 | 2189.3 | 2191.3 |
| $\omega'_3$ | 1025.8 | 1025.6 | 1024.4 | 1025.4 |
| $\omega'_4$ | 2337.4 | 2337.1 | 2334.3 | 2337.0 |
| $\omega'_5$ | 1321.2 | 1321.0 | 1319.4 | 1321.4 |
| $\omega'_6$ | 1055.5 | 1055.4 | 1054.1 | 1055.5 |

[a]Calculated with Equations (80)–(81) (the 'experimental basic' value of the parameter $\omega_1(\mathrm{CH}_4) = 3040.38$ cm$^{-1}$ was taken from [26]).
[b]Calculated with Equations (80)–(81) (the '*ab initio* basic' value of the parameter $\omega_4(\mathrm{CH}_4) = 1345.3$ cm$^{-1}$ was taken from Table I (column 'cc-pVQZ') of [54]).
[c]Calculated with Equations (80)–(81) (the '*ab initio* basic' value of the parameter $\omega_1(\mathrm{CH}_4) = 3036.2$ cm$^{-1}$ was taken from Table I (column 'cc-pVQZ') of [54]).

### 8.2. Anharmonic coefficients, $x'_{ab}/x'_{l_\lambda l_\mu}$, and ro-vibrational coefficients, $\alpha'^\beta_b$, of CH$_3$D and CHD$_3$

The equations obtained in Sections 5.1 and 5.2, on one hand, and the information from Equations (72)–(74) and Tables 5 and 6, on the other hand, allow us to obtain the following approximate relations between anharmonic coefficients for CH$_3$D:

$$x_{11} \approx -\frac{7}{3}B_e = -\frac{7}{32}\frac{\hbar}{\pi cm\rho^2} = \frac{7}{10}x'_{11} = \frac{34}{5}x'_{12}$$
$$= \frac{15}{2}x'_{13} = \frac{3}{18}x'_{14} = \frac{13}{20}x'_{15} = \frac{11}{5}x'_{16} = \frac{9}{25}x'_{22}$$
$$= 2x'_{23} = -7x'_{24} = \frac{15}{4}x'_{25} = \frac{14}{25}x'_{26} = \frac{9}{5}x'_{33}$$
$$= \frac{6}{5}x'_{34} = 5x'_{35} = 6x'_{36} = \frac{2}{5}x'_{44} = \frac{2}{3}x'_{45} = \frac{3}{2}x'_{46}$$
$$= 7x'_{55} = 4x'_{56} = -92x'_{66} = -x'_{l_4 l_4} = 7x'_{l_4 l_5}$$
$$= 51x'_{l_4 l_6} = -34x'_{l_5 l_5} = \frac{5}{2}x'_{l_5 l_6} = -18x'_{l_6 l_6}, \quad (84)$$

and the following relations for CHD$_3$:

$$x_{11} \approx -\frac{7}{3}B_e = -\frac{7}{32}\frac{\hbar}{\pi cm\rho^2} = \frac{1}{5}x'_{11} = 6x'_{12} = \frac{32}{25}x'_{13}$$
$$= -\frac{28}{5}x'_{14} = \frac{3}{10}x'_{15} = 25x'_{16} = \frac{7}{5}x'_{22} = -\frac{4}{5}x'_{23}$$
$$= \frac{8}{25}x'_{24} = 3x'_{25} = \frac{6}{5}x'_{26} = \frac{7}{4}x'_{33} = \frac{3}{2}x'_{34} = 9x'_{35}$$
$$= -12x'_{36} = \frac{3}{5}x'_{44} = \frac{7}{4}x'_{45} = \frac{3}{2}x'_{46} = -30x'_{55}$$
$$= -245x'_{56} = 7x'_{66} = -\frac{7}{5}x'_{l_4 l_4} = -65x'_{l_4 l_5} = 17x'_{l_4 l_6}$$
$$= -40x'_{l_5 l_5} = -\frac{27}{2}x'_{l_5 l_6} = 25x'_{l_6 l_6}. \quad (85)$$

Table 8. Anharmonic parameters, $x'_{\lambda\mu}$ (in cm$^{-1}$).

| Parameter | CH$_3$D | | | | CHD$_3$ | | |
| | Calc.[a] | [54][b] | Exp.[c] | Calc.[d] | Calc.[e] | [54][b] | Exp.[c] |
| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
| $x'_{11}$ | −17.876 | −17.197 | −5.321 | −62.565 | | −59.221 | −58.994 |
| $x'_{12}$ | −1.840 | −1.878 | −2.555 | −2.086 | | −2.204 | −2.905 |
| $x'_{13}$ | −1.668 | −0.981 | 4.884 | −9.776 | | −9.731 | −9.193 |
| $x'_{14}$ | −75.078 | −72.771 | −99.022 | 2.234 | | 2.184 | 2.337 |
| $x'_{15}$ | −19.251 | −19.016 | −9.179 | −41.710 | −20.855 | −21.111 | −21.367 |
| $x'_{16}$ | −5.688 | −5.612 | −7.233 | −0.501 | | −0.309 | −1.406 |
| $x'_{22}$ | −34.758 | −31.167 | −27.944 | −8.938 | | −8.826 | 1.139 |
| $x'_{23}$ | −6.257 | −6.739 | −7.312 | 15.641 | | 15.727 | 3.096 |
| $x'_{24}$ | 1.788 | 1.639 | −7.730 | −39.103 | | −37.352 | −42.727 |
| $x'_{25}$ | −3.337 | −3.331 | −3.522 | −4.171 | | −4.017 | −5.220 |
| $x'_{26}$ | −22.345 | −22.266 | −17.587 | −10.428 | 4.813 | 4.674 | −2.489 |
| $x'_{33}$ | −6.952 | −6.802 | −7.759 | −7.150 | | −7.230 | −6.188 |
| $x'_{34}$ | −10.428 | − 9.440 | −10.517 | −8.342 | | −8.449 | −6.977 |
| $x'_{35}$ | −2.503 | −2.033 | −2.908 | −1.390 | | −1.029 | −2.795 |
| $x'_{36}$ | −2.086 | −1.091 | −3.073 | 1.043 | | 1.638 | 3.445 |
| $x'_{44}$ | −31.283 | −31.611 | −32.402 | −20.855 | | −18.601 | −16.349 |
| $x'_{45}$ | −18.770 | −14.611 | −8.373 | −7.150 | | −7.195 | −8.454 |
| $x'_{46}$ | −8.342 | −7.686 | −9.304 | −8.342 | | −8.402 | −11.044 |
| $x'_{55}$ | −1.788 | −1.874 | −4.417 | 0.417 | −4.813 | −4.604 | −4.552 |
| $x'_{56}$ | −3.128 | −4.068 | −5.090 | 0.051 | | 0.055 | 4.919 |
| $x'_{66}$ | 0.136 | 0.261 | 0.261 | −1.788 | −5.688 | −5.500 | −5.306 |
| $x'_{l_4 l_4}$ | 12.513 | 12.636 | 28.539 | 8.937 | | 8.252 | 8.560 |
| $x'_{l_4 l_5}$ | −1.788 | −1.721 | −7.062 | 0.193 | | −0.060 | 3.584 |
| $x'_{l_4 l_6}$ | −0.245 | −0.230 | 3.160 | −0.736 | | −0.729 | 1.143 |
| $x'_{l_5 l_5}$ | 0.368 | 0.384 | 2.380 | 0.313 | | 5.403 | 5.095 |
| $x'_{l_5 l_6}$ | −5.001 | −5.056 | −4.684 | 0.927 | | 0.921 | 5.894 |
| $x'_{l_6 l_6}$ | 0.695 | 0.645 | 1.516 | −0.501 | 3.128 | 3.251 | 2.871 |

[a]Calculated with Equation (84) (the 'basic' value of the parameter $x_{11}(CH_4) = -12.513$ cm$^{-1}$ was taken from [54]).
[b]Taken from Ref. [54].
[c]Taken from the analysis of experimental data, Ref. [6].
[d]Calculated using Equation (85) with $x_{11}(CH_4) = -12.513$ cm$^{-1}$.
[e]Calculated using Equation (88) with $x_{11}(CH_4) = -12.513$ cm$^{-1}$.

In Equations (84) and (85), $x_{11}$ is one of the anharmonic coefficients of the 'mother' CH$_4$ molecule. In accordance with [35], the parameter $x_{11}$ can be connected with the other $x_{\lambda\mu}$ anharmonic parameters of CH$_4$ (see Equation (18) of [35]). This implies that, in principle, any of the $x_{\lambda\mu}$ parameters of the CH$_4$ molecule can be used as the 'basic' value in Equations (84)–(85) for the numerical estimation of anharmonic parameters $x'_{\lambda\mu}$ of the CH$_3$D and CHD$_3$ isotopomers.

Analogous relations for the ro-vibrational coefficients $\alpha_b^\beta$ were obtained in the following form:

$$Y_3 = -\frac{\hbar^2}{16\pi\rho^4 cm^{3/2} F_{11}^{1/2}} = -2\alpha_1'^x = -\frac{22}{25}\alpha_2'^x$$
$$= 2\alpha_3'^x = -\frac{42}{25}\alpha_4'^x = \frac{28}{25}\alpha_5'^x = -\frac{19}{25}\alpha_6'^x = -\frac{3}{5}\alpha_1'^z$$
$$= -3\alpha_2'^z = \frac{7}{5}\alpha_3'^z = -3\alpha_4'^z = -\alpha_5'^z = \frac{21}{5}\alpha_6'^z \quad (86)$$

for CH$_3$D and

$$Y_3 = -\frac{\hbar^2}{16\pi\rho^4 cm^{3/2} F_{11}^{1/2}} = -\frac{39}{20}\alpha_1'^x = -2\alpha_2'^x$$
$$= -\frac{11}{5}\alpha_3'^x = -\frac{42}{25}\alpha_4'^x = \frac{13}{2}\alpha_5'^x = \frac{25}{2}\alpha_6'^x = -\frac{18}{5}\alpha_1'^z$$
$$= -\frac{8}{5}\alpha_2'^z = \frac{10}{3}\alpha_3'^z = -7\alpha_4'^z = \frac{44}{25}\alpha_5'^z = -\frac{29}{25}\alpha_6'^z \quad (87)$$

for CHD$_3$. Again, as in Equations (84)–(85), $Y_3$ is one of the four ro-vibrational parameters of the CH$_4$ molecule, and it is connected with the other three ro-vibrational parameters of CH$_4$ by Equation (19) of [35]. When the relations (84)–(87) were derived, we took into account the presence of resonance interactions between pairs of vibrational states, $(..v_1..v_5..)/(..v_1 \pm 1..v_5 \mp 2..)$, $(..v_3..v_5..)/(..v_3 \pm 1..v_5 \mp 1..)$, for CH$_3$D, and interactions between pairs of states, $(..v_1..v_5..)/(..v_1 \pm 1..v_5 \mp 2..)$, $(..v_2..v_6..)/$

$(..v_2 \pm 1..v_6 \mp 2..)$, $(..v_3 \ v_4 \ v_5..)/(..v_3 \pm 1 v_4 \mp 1 v_5 \pm 1..)$, $(..v_3..v_6..)/(..v_3 \pm 1..v_6 \mp 1..)$, for CHD$_3$.

Table 8 (columns 2 and 5) illustrates the suitability of the relations (84)–(85). In this case, as in the previous subsection, only the single initial parameter $x_{11} = -12.513$ cm$^{-1}$ of the CH$_4$ species was taken from Ref. [54] as the basic one. For comparison, values of the corresponding $x'_{\lambda\mu}$ parameters obtained on the basis of *ab initio* calculations from Ref. [54] are shown in columns 3 and 7 of Table 8. If one takes into account that the values of the $x'_{\lambda\mu}$ parameters in columns 2 and 5 were calculated without any information about CH$_3$D and CHD$_3$, and with using only one $x_{11}$ parameter of the CH$_4$ mother molecule, one can find a satisfactory agreement in most cases, with the exception of the parameters $x'_{15}$, $x'_{26}$, $x'_{55}$, $x'_{66}$, $x'_{l_5l_5}$, and $x'_{l_6l_6}$ of CHD$_3$. The discrepancies in the values of these parameters can be understood if one takes into account the following: to produce the isotopic relations, Equation (85), we took into account the presence of resonance interactions of the type $(..v_1..v_5..)/(..v_1 \pm 1..v_5 \mp 2..)$ and $(..v_2..v_6..)/(..v_2 \pm 1..v_6 \mp 2..)$. In [54] these interactions were not taken into account. To check the correctness of the approach used in the present study, we also derived isotopic relations analogous to relations, Equation (85), but without taking into account the resonance interactions mentioned. The results are as follows:

$$\frac{3}{5}x'_{15} = -\frac{13}{5}x'_{26} = \frac{13}{5}x'_{55} = \frac{11}{5}x'_{66} = -4x'_{l_6l_6} = x_{11}. \tag{88}$$

Column 6 of Table 8 shows the result of estimating the corresponding parameters on the basis of Equation (88). One can now find a good agreement of the results with the values of the parameters in column 7.

For comparison, columns 4 and 7 of Table 8 present experimental values of the $x'_{\lambda\mu}$ anharmonic coefficients from Ref. [6]. Again, one can find a satisfactory agreement between the parameters in most cases. However, one can see large differences between estimated and experimental values of the parameters $x'_{11}$, $x'_{14}$, $x'_{15}$, $x'_{45}$, $x'_{l_4l_4}$, $x'_{l_4l_5}$ for CH$_3$D, and of the parameters $x'_{22}$, $x'_{23}$, $x'_{26}$, $x'_{56}$, $x'_{l_5l_6}$ for CHD$_3$. In the second case, the presence of discrepancies can be explained by the neglect of interactions of the type $(..v_2..v_6..)/(..v_2 \pm 1..v_6 \mp 2..)$ in [6]. It is more difficult to explain the discrepancies in the values of parameters $x'_{45}$, $x'_{l_4l_4}$, and $x'_{l_4l_5}$ of CH$_3$D. One possible reason may be a strong correlation between the corresponding parameters which can lead to incorrectly fitted values. In any case, further analysis is desirable.

To illustrate the quality of the relations derived for the ro-vibrational coefficients $\alpha_b'^\beta$, we will consider results of the high-resolution analyses of the bands $v_3$, $v_5$, and $v_6$ of CH$_3$D [50]. Column 2 of Table 9 presents values of parameters $\alpha_b'^\beta$ ($\beta = x, z$; $b = 3, 5, 6$) predicted on the

Table 9. Some $\alpha_b'^\beta$ parameters of the CHD$_3$ molecule.

| Parameter | Calc.[a] | Exp.[b] | Exp.[c] |
|---|---|---|---|
| 1 | 2 | 3 | 4 |
| $\alpha_3'^x$/cm$^{-1}$ | 0.0152 | 0.0788 | 0.0194 |
| $\alpha_3'^z$/cm$^{-1}$ | −0.0100 | −0.0104 | |
| $\alpha_5'^x$/cm$^{-1}$ | −0.0051 | −0.0046 | |
| $\alpha_5'^z$/cm$^{-1}$ | −0.0190 | −0.0207 | |
| $\alpha_6'^x$/cm$^{-1}$ | −0.0027 | −0.0343 | −0.0036 |
| $\alpha_6'^z$/cm$^{-1}$ | 0.0288 | 0.0284 | |

[a]Calculated by the relations in Equation (87).
[b]Experimental values from Ref. [50].
[c]'Experimental' values corrected in accordance with Figure 3 (see text for details).

basis of relations (87). The values of the corresponding $\alpha$ parameters obtained from the fit of experimental data [50] are shown in column 3. One can find a satisfactory agreement between predicted and experimental values for the parameters $\alpha_5'^x$, $\alpha_5'^z$, $\alpha_3'^z$, and $\alpha_6'^z$. At the same time, the predicted values of the $\alpha_3'^x$ and $\alpha_6'^x$ parameters differ very much from the corresponding experimental values. To understand the situation, it is necessary to take into account the following:

(1) The band $v_5$ was considered in Ref. [50] as an isolated state. As is found from the discussion following Equation (87), resonance interactions also were neglected in deriving the relations for the coefficients $\alpha_5'^x$ and $\alpha_5'^z$.

(2) The bands $v_3$ and $v_6$ have been considered as interacting in [50]. In this case, it follows from the symmetry properties of the XYZ$_3$ ($C_{3v}$) molecule that the interaction is described by the operator, Equation (37). This implies that this interaction, on one hand, does not affect the $C^{(v_3=1)}$ and $C^{(v_6=1)}$ (as a consequence, the $\alpha_3'^z$ and $\alpha_6'^z$) parameters, but, on the other hand, strongly connects the parameters $B^{(v_3=1)}$ and $B^{(v_6=1)}$ ($\alpha_3'^x$ and $\alpha_6'^x$) with each other.

To illustrate these points, Figure 3 shows the dependence of the experimental values of $\alpha_3'^x$ (curve A) and $\alpha_6'^x$ (curve B) on the value of the resonance interaction parameter, $\alpha'$ (see Equation (37) and remarks after Equation (38)). The dashed horizontal lines (1) and (2) correspond to the values of the $\alpha_3'^x$ and $\alpha_6'^x$ parameters predicted with the relations (87). The dashed vertical line I indicates the experimental value of the Coriolis interaction parameter, $\alpha' \equiv \tilde{\alpha} = 1.701$ cm$^{-1}$, from Table 10 of Ref. [50]. In this case, the crossing of the line I with the curves A and B indicates the experimental values of the parameters $\alpha_3'^x$ and $\alpha_6'^x$ from Ref. [50]. To construct the curves A and B, we took experimental ro-vibrational energy levels of the states ($v_3 = 1$) and ($v_6 = 1$) from
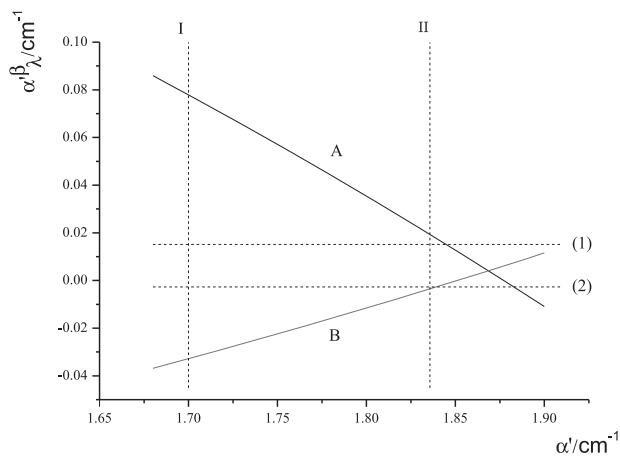
Figure 3. Dependence of the experimental values of $\alpha_3'^x$ (curve A) and $\alpha_6'^x$ (curve B) on the value of the resonance interaction parameter, $\alpha'$. The dashed horizontal lines (1) and (2) correspond to the values of the parameters $\alpha_3'^x$ and $\alpha_6'^x$ predicted with the relations (87). The dashed vertical line I indicates the 'experimental' value of the Coriolis interaction parameter, $\alpha' \equiv \tilde{\alpha} = 1.701$ cm$^{-1}$, from Table 10 of Ref. [50]. The dashed vertical line II corresponds to the value of the resonance interaction parameter, $\tilde{\alpha} = 1.836$ cm$^{-1}$, obtained from the theoretical prediction in the present paper on the basis of isotopic relation.

Ref. [50]. Then, we changed the value of the resonance interaction parameter, $\tilde{\alpha}$, in steps of 0.01 cm$^{-1}$ and, for every fixed value of the parameter $\tilde{\alpha}$, made a fit of the same set of spectroscopic parameters. As the analysis showed (and as one would expect because of a strong correlation between the parameters $\alpha_3'^x$ and $\alpha_6'^x$, on one hand, and the resonance interaction parameter, $\tilde{\alpha}$, on the other hand), the quality of fits (judged by the rms deviation) was practically unchanged for all fits, but the values of the $\alpha_3'^x$ and $\alpha_6'^x$ parameters obtained from fits were changed in accordance with the curves A and B. It should be mentioned that the vertical dashed line II in Figure 3 corresponds to the value of the resonance interaction parameter $\tilde{\alpha} = 1.836$ cm$^{-1}$ which was obtained from the theoretical prediction in the present paper on the basis of the isotopic relations. One can see that the curves A and B cross the lines (1) and (2) very close

Table 10. Centrifugal distortion coefficients $D'_J$, $D'_{JK}$, $D'_K$, and parameter $\epsilon'$.

| Parameter | CH$_3$D | | CHD$_3$ | |
|---|---|---|---|---|
| | Calc.[a] | Exp.[b] | Calc.[c] | Exp.[d] |
| $D'_J/10^{-4}$ cm$^{-1}$ | 0.503 | 0.526 | 0.479 | 0.495 |
| $D'_{JK}/10^{-4}$ cm$^{-1}$ | 1.189 | 1.264 | −0.372 | −0.383 |
| $D'_K/10^{-4}$ cm$^{-1}$ | −0.761 | −0.790 | 0.130 | 0.134 |
| $\epsilon'/10^{-4}$ cm$^{-1}$ | 0.030 | 0.032 | 0.054 | −0.289 |

[a]Calculated with Equation (89).
[b]Taken from the analysis of experimental data, Ref. [65].
[c]Calculated on the basis of Equation (90).
[d]Taken from the analysis of experimental data, Ref. [66].

to the line II. This implies that the fit, being made with the theoretically predicted value of the resonance interaction parameter $\tilde{\alpha}$, gives the 'experimental' values of the $\alpha_3'^x$ and $\alpha_6'^x$ parameters very close to the theoretically predicted ones. The values obtained for the parameters $\alpha_3'^x$ and $\alpha_6'^x$ are shown in column 4 of Table 9. One can see a reasonably good agreement between the $\alpha'$ values presented in the second and fourth columns.

### 8.3. Centrifugal distortion coefficients $D'_J$, $D'_{JK}$, $D'_K$, and parameter $\epsilon'$

As follows from Equations (19)–(22), the coefficients $a_{..}$ are proportional to $(B^e_{..})^{-1/2}$. This implies that both the centrifugal distortion coefficients, $D_J$, $D_{JK}$, $D_K$, and the parameter $\epsilon'$ are proportional to $(B^e_{..})^3/\omega^2_{..}$. Indeed, the use of Equations (71)–(74) in (54)–(57) leads to the following result for CH$_3$D:

$$\frac{B^3_e}{\omega^2_1} = \frac{8}{25}D'_J = \frac{13}{98}D'_{JK} = -\frac{11}{52}D'_K = \frac{27}{5}\epsilon' \quad (89)$$

and to

$$\frac{B^3_e}{\omega^2_1} = \frac{42}{125}D'_J = -\frac{54}{125}D'_{JK} = \frac{31}{25}D'_K = 3\epsilon' \quad (90)$$

for CHD$_3$. Here $B_e$ and $\omega_1$ are the parameters of the mother CH$_4$ molecule. Values with 'prime' belong to isotopically substituted species. Table 10 illustrates the validity of the relations obtained. The results of the calculation with isotopic relations are shown in columns 2 and 4 of Table 10. Columns 3 and 5 present the corresponding experimental values for the ground vibrational states from Refs. [65] and [66]. One can find a satisfactory agreement of all results with the exception of the parameter $\epsilon'$ of CHD$_3$. The discrepancy between the 'calculated' and 'experimental' values of the parameter $\epsilon'$ can be explained by the fact that in Ref. [66] the value of $\epsilon'$ was not varied, but was fixed. The variable parameter in [66] was $h'_3$. As discussed in Ref. [66], the parameters $\epsilon'$ and $h'_3$, as determined from the fit, are strongly correlated: a change of the parameter $\epsilon'$ will lead to a change of the parameter $h'_3$ without any change of the quality of the fit. Taking into account also the good agreement between calculated and experimental values of all other parameters in Table 10, one can conclude that the value $\epsilon' = 0.054 \times 10^{-4}$ cm$^{-1}$ is probably correct for CHD$_3$, and the large deviation of the 'experimental' value $-0.289 \times 10^{-4}$ cm$^{-1}$ from the calculated value is an artefact from the fit.

### 8.4. Isotopic relations for $\eta'^{v\Gamma,v\Gamma'}$, $\gamma'^{v\Gamma,v\Gamma'}$, and $\beta'^{v\Gamma,v\Gamma'}$

As in the previous sections, the use of Equations (80)–(83) in equations (67)–(71) allows one to obtain the following
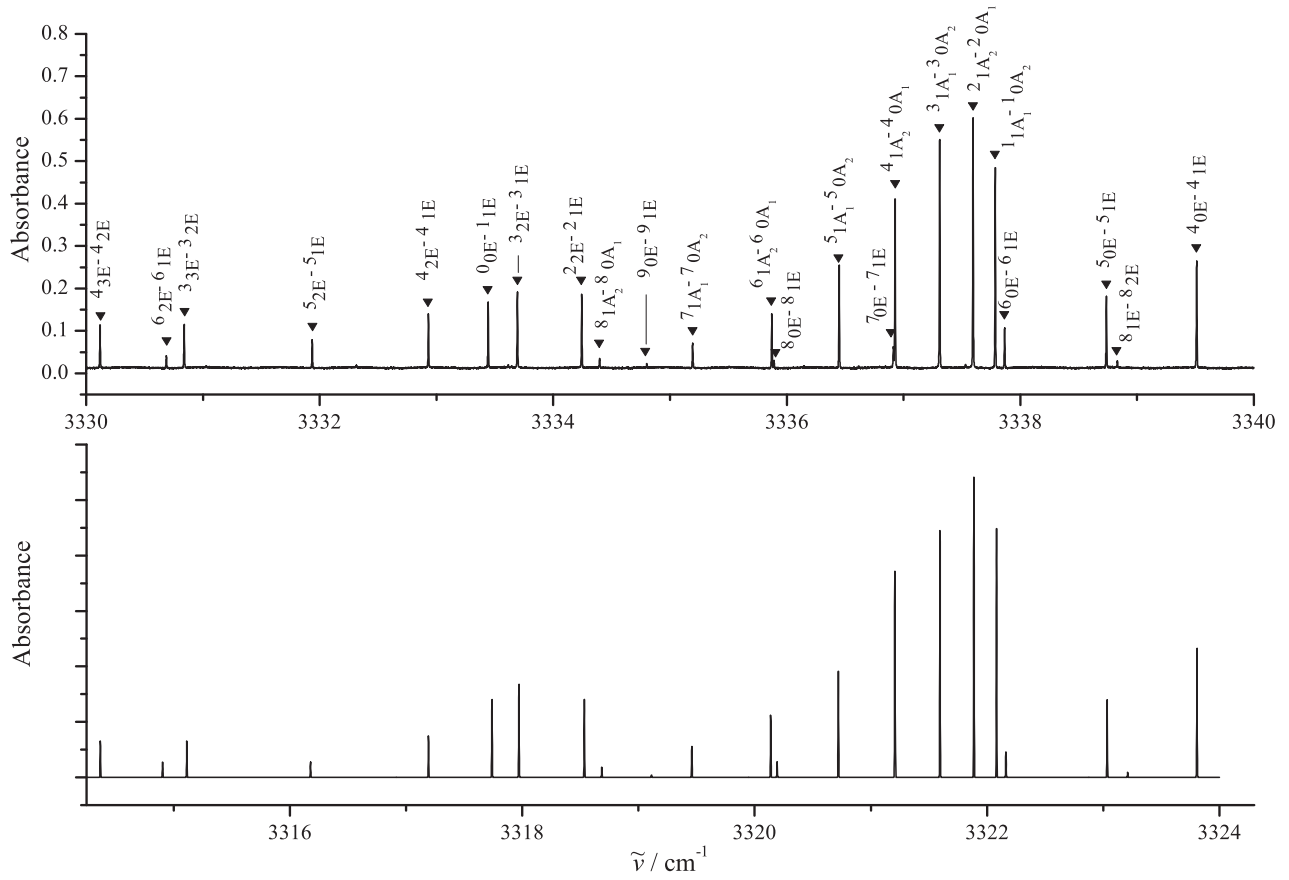
Figure 4.    A small part of the high-resolution spectrum of the $\nu_2 + \nu_6$ band of $^{12}CH_3D$ in the region of 3330–3340 cm$^{-1}$. The upper trace shows the experimental spectrum as decadic absorbance lg($I_0/I$) [6,8] with the experimental conditions: absorption path length, 10 m; sample pressure, 3 mbar; instrumental resolution, 0.0027 cm$^{-1}$; temperature, 80 K. The lower trace presents a simulated spectrum obtained with the use of parameters estimated on the basis of the isotopic relations. Assignments of transitions, $J_{K\Gamma}-J'_{K'\Gamma'}$, are shown in the upper trace: $J$, $K$, $\Gamma$ are the quantum numbers and symmetry of the upper ro-vibrational states; $J'$, $K'$, $\Gamma'$ are the quantum numbers and symmetry of the lower ro-vibrational states (see [4,6,8]).

simple relations for the coefficients $\eta'^{v\Gamma,v\Gamma'}$, $\gamma'^{v\Gamma,v\Gamma'}$, and $\beta'^{v\Gamma,v\Gamma'}$ for CH$_3$D:

$$B_e = -10\eta'_4 = \frac{95}{49}\eta'_5 = -\frac{17}{20}\eta'_6, \tag{91}$$

$$Y_3 = -\frac{\hbar^2}{16\pi\rho^4 cm^{3/2}F_{11}^{1/2}} = -38\gamma'_4 = 32\gamma'_5$$
$$= 2\gamma'_6 = 15\beta'_4 = -8\beta'_5 = \frac{28}{5}\beta'_6, \tag{92}$$

and

$$B_e = -6\eta'_4 = -\frac{37}{25}\eta'_5 = \frac{89}{20}\eta'_6, \tag{93}$$

$$Y_3 = -\frac{\hbar^2}{16\pi\rho^4 cm^{3/2}F_{11}^{1/2}} = -18\gamma'_4 = \frac{28}{5}\gamma'_5$$
$$= -42\gamma'_6 = 18\beta'_4 = 7\beta'_5 = 30\beta'_6 \tag{94}$$

for CHD$_3$.

To illustrate the validity of the relations derived here, we compared the result of calculations with these relations and the experimental data from Refs. [55] and [50]. In particular, $\left(\frac{\eta'_6}{\eta'_5}\right)^{\text{calc}} = -2.281$, $\left(\frac{\eta'_6}{\eta'_5}\right)^{\text{exp}} = -2.310$ for CH$_3$D, and $\left(\frac{\eta'_5}{\eta'_6}\right)^{\text{calc}} = -3.007$, $\left(\frac{\eta'_5}{\eta'_6}\right)^{\text{exp}} = -3.097$ for CHD$_3$.

As an illustration of the quality of the results, a small part of the high-resolution spectrum of the $\nu_2 + \nu_6$ band of CH$_3$D is presented in Figure 4. The upper part of Figure 4 shows the experimental Fourier transform infrared spectrum recorded at ETH Zürich with the Bruker IFS 125 prototype (ZP 2001) at 80 K in a collisional-cooling cell [4,6,8]. The bottom part of Figure 4 presents a predicted spectrum obtained with the spectroscopic parameters as estimated from the isotopic relations derived here. The relative line strengths necessary for the comparison were calculated using only one dipole parameter and then calibrated with the strongest transition at 3337.5950 cm$^{-1}$. A simple Doppler profile was used for the line shapes. Noting that the prediction does not result from a fit, the agreement
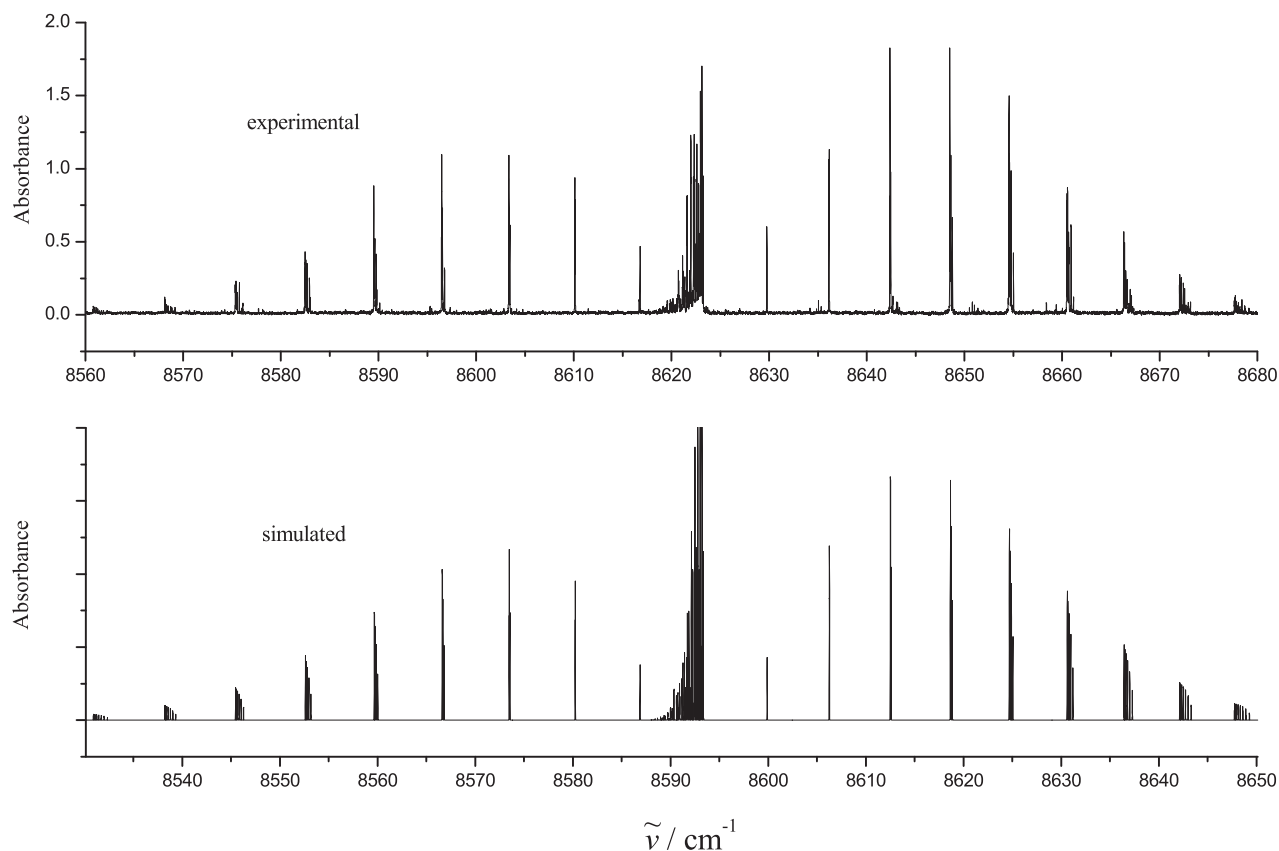
Figure 5. An overview spectrum of the $3\nu_1$ band of $^{12}CHD_3$. The upper trace shows the experimental spectrum (the spectrum has been recorded with the Zürich Fourier transform infrared spectrometer Bruker IFS prototype ZP 2001 [4,6,8,68,69] as decadic absorbance $\lg(I_0/I)$ with the experimental conditions: absorption path length, 10 m; sample pressure, 3 mbar; instrumental resolution, 0.0027 cm$^{-1}$; temperature, 80 K). The lower trace presents a predicted spectrum obtained with the use of parameters estimated on the basis of the isotopic relations.

with experiment is more than satisfactory for the overall pattern. One can see, however, that the wavenumber scale at the bottom of Figure 4 is shifted by about 15.7 cm$^{-1}$. This difference of about 0.4% between the experimental and calculated band centres of $\nu_2 + \nu_6$ can be considered as a satisfactory agreement, remembering that the accuracy of the isotopic relations was estimated to be within 0.1%–0.2% for the harmonic frequencies of the vibrations and somewhat less satisfactory for the anharmonic coefficients. Thus, applying a constant shift, one obtains an adequate prediction for the patterns which can be easily recognised in the experimental spectra. In this way, the results of the present paper can be helpful in the future in numerous cases for the assignment of transitions in excited vibrational states.

In further support of the above statements, we show in Figure 5 a prediction for the second stretching overtone band, $3\nu_1$, in the region 8560–8680 cm$^{-1}$ together with an experimental spectrum recorded at ETH Zürich with the Bruker IFS 125 prototype (ZP 2001) at 80 K [4,6,8,68,69]. The bottom part of Figure 5 presents a spectrum obtained

with the spectroscopic parameters which have been estimated from the isotopic relations without any adjustments to the experimental data for CHD$_3$. Again even in this high energy range, the relative line strengths have been successfully calculated using only one dipole moment parameter. A simple Doppler profile was used for the line shapes. The prediction for the pattern of relative line positions is excellent. Of course, the band centres are less well predicted by the isotopic relations, the difference between experimental and predicted values of the $3\nu_1$ band centre being about 30 cm$^{-1}$. The accuracy of the isotopic relations is estimated as 0.1%–0.2% for the harmonic frequencies and somewhat less for the anharmonic coefficients. Thus, a shift of 30 cm$^{-1}$ for the region of 8600 cm$^{-1}$ agrees with such an estimate for the accuracy. A small part of the spectrum shown in Figure 5 is presented in Figure 6. One can see a more than satisfactory agreement between experimental and predicted spectra. Small discrepancies in line strengths can be explained by the line intensities in the simulated spectrum being estimated using one dipole moment parameter only. These examples should provide ample illustration
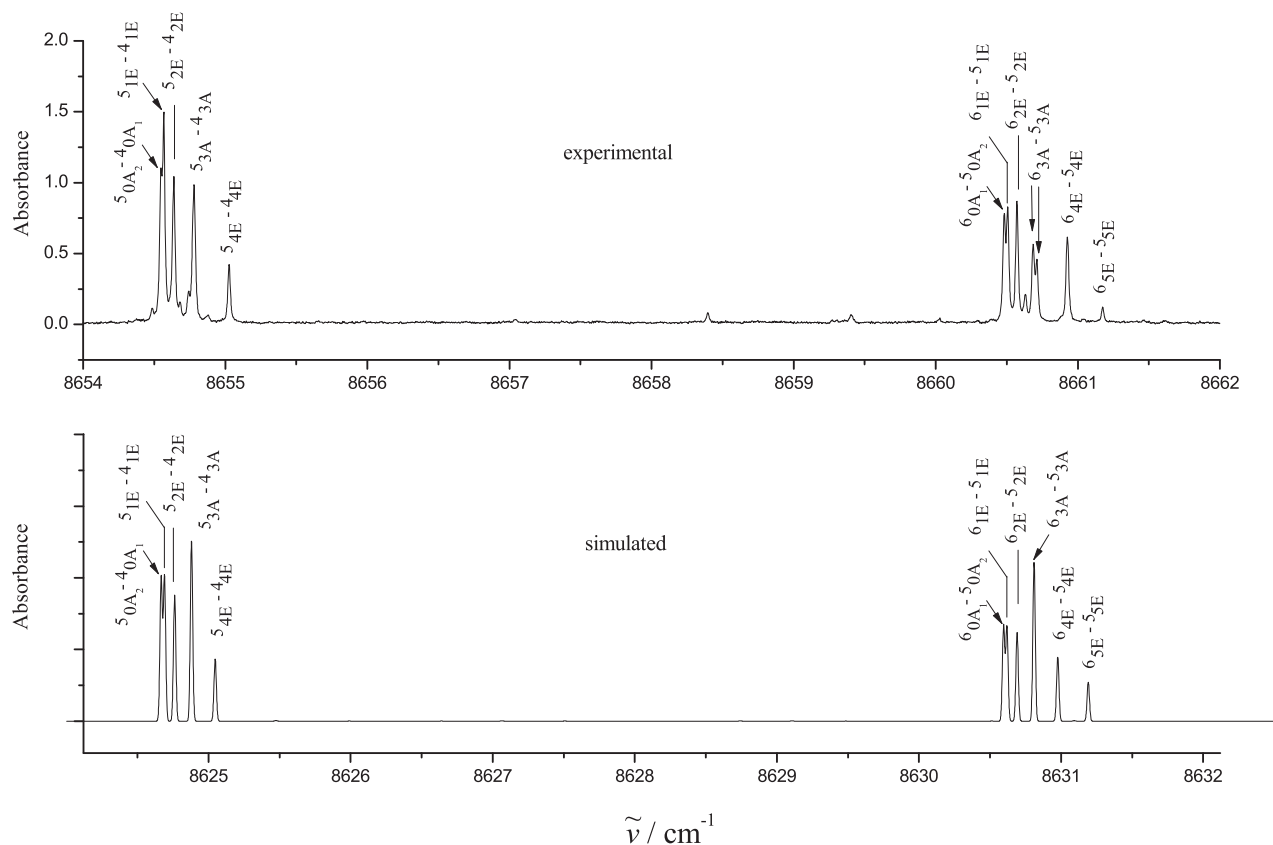
Figure 6.    A small part of the high-resolution spectrum of the $3\nu_1$ band of $^{12}CHD_3$ in the region of 8660–8670 cm$^{-1}$. The lower trace presents a predicted spectrum obtained with the use of parameters estimated on the basis of the isotopic relations. Assignments of transitions, $J_{K\Gamma}-J'_{K'\Gamma'}$, are shown: $J$, $K$, $\Gamma$ are the quantum numbers and symmetry of the upper ro-vibrational states; $J'$, $K'$, $\Gamma'$ are the quantum numbers and symmetry of the lower ro-vibrational states (see refs. [4,6,8,68,69] for the experiments and also caption to Fig. 5).

for the potential usefulness of the present theory in helping to assign spectra.

## 9.    Conclusions

Using operator perturbation theory, the low-order Taylor expansion of the intramolecular potential hypersurface, and symmetry properties of the $C_{3v}$ symmetric molecules in the framework of the 'expanded local mode' approach, we determined a set of relations which allow one to connect different types of spectroscopic parameters (parameters of diagonal blocks, Coriolis, and Fermi interaction parameters) for various isotopomers of XYZ$_3$ and also XY$_3$ ($C_{3v}$) molecules. Numerous isotopic relations are derived for the CH$_3$D ←CH$_4$ and CHD$_3$ ←CH$_4$ substitutions in methane. We have illustrated the success of these relations with examples comparing spectroscopic experiment with theory.

The obvious advantage of the simple analytical relations derived here is that they allow us to predict (or connect) directly the spectroscopic parameters of the effective Hamiltonians of different isotopomers, without passing through expensive numerical calculations of energy levels using

the multidimensional potential hypersurface. The disadvantages are related to the approximate nature of our results, depending on the model Hamiltonian used here. In particular, the uncertainties for the parameters obtained with the isotopic relations can be estimated to be between 0.1% and 0.4%. As a consequence, one finds a corresponding shift in absolute band positions between predicted and experimental spectra. However, the relative accuracies of predicted line positions are considerably better than their absolute values (as demonstrated by the examples shown in Figures 4–6). The reason is an error of only 0.1%–0.4 % even for the largest of rotational/centrifugal parameters which leads to a small error in predicted spectral patterns compared to the error in harmonic frequencies which leads to shifts in the band centres.

The importance of our results can be seen in light of the following observations. In the analysis of the high-resolution ro-vibrational spectra of highly excited states, it is often necessary to include many interacting vibrational levels. In such a situation, there frequently arise correlations between various parameters of the diagonal and the resonance coupling parameters in the blocks

corresponding to the polyads of strongly coupled levels, as given by Equations (39)–(45). These correlations then prevent the unambiguous simultaneous determination of all the parameters of the effective Hamiltonian to a fit of the experimental data. By using the numerous simple theoretical relations derived in the present work, one can then remove many of the correlations and ambiguities. Thus, it is possible to provide an analysis of spectra of one isotopomer by using theoretical predictions obtained from the relations to spectroscopic parameters of another isotopomer. It is also possible to use the theoretical relations derived here in a simultaneous analysis of spectroscopic data for several different isotopomers. Finally, the theoretical relations derived in the present work can also be used for a consistency check of spectroscopic parameters derived independently for different isotopomers. Thus, we think that the results of the present work will prove useful in many spectroscopic analysis in the future. Further interesting applications of the general approach described here would concern $^{13}$C Substitution in $CH_4$, given the recent progress in the high resolution spectra and analysis of methane isotopomers [67–70].

## Acknowledgements

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## Appendix A.  G-matrix elements for the $C_{3v}$ symmetry group

$${}^{(J)}G_{NA_1}^m = \frac{(-i)^J}{\sqrt{2}}(1+\delta_{N,0})^{-1/2}(\delta_{m,3N}+(-1)^{(J+3N)}\delta_{m,-3N}),$$

$${}^{(J)}G_{NA_2}^m = \frac{(-i)^{J+1}}{\sqrt{2}}(1-2\delta_{N,0})(1+\delta_{N,0})^{-1/2}(\delta_{m,3N}+(-1)^{(J+3N+1)}\delta_{m,-3N}),$$

$${}^{(J)}G_{NE1}^m = \frac{(-i)^J}{\sqrt{2}}(\delta_{m,3N+1}+(-1)^{(J+3N+1)}\delta_{m,-(3N+1)}),$$

$${}^{(J)}G_{NE2}^m = \frac{(-i)^{J+1}}{\sqrt{2}}(\delta_{m,3N+1}+(-1)^{(J+3N)}\delta_{m,-(3N+1)}),$$

$${}^{(J)}G_{(N+1+\{(J-1)/3\})E1}^m = \frac{(-i)^J}{\sqrt{2}}(\delta_{m,3N+2}+(-1)^{(J+3N)}\delta_{m,-(3N+2)}),$$

$${}^{(J)}G_{(N+1+\{(J-1)/3\})E2}^m = \frac{(-i)^{J-1}}{\sqrt{2}}(\delta_{m,3N+2}+(-1)^{(J+3N+1)}\delta_{m,-(3N+2)}).$$

The index $N$ takes the following values:
$N = 0, 1, \ldots, \{J/3\}$ for the states of $A_1$ and $A_2$ symmetry;
$N = 0, 1, \ldots, \{(J-1)/3\}$ for the states of $E$ symmetry.
The nomenclature of the rotational states is shown in Figure 2.

## Appendix B.  Symmetrised rotational operators

In this appendix, we present the first (with the degree $\Omega \leq 3$) non-zero irreducible rotational operators of the $SO_3$ and $C_{3v}$ symmetry groups that have been used in the present paper.

### B.1.  Rotational operators symmetrised in the $SO_3$ symmetry group

In accordance with Equations (1)–(3), the symmetrised rotational operators, $R_n^{\Omega(K)}$ ($0 \leq \Omega \leq 3$, and $0 \leq K \leq 3$), can be obtained in the following form:

$$R_{+1}^{1(1)} = -J_+ = -\frac{1}{\sqrt{2}}(J_x - iJ_y) \quad J_+|Jk\rangle = \frac{1}{\sqrt{2}}(J(J+1) - k(k+1))^{\frac{1}{2}}|Jk+1\rangle$$

$$R_{-1}^{1(1)} = J_- = \frac{1}{\sqrt{2}}(J_x + iJ_y) \quad J_-|Jk\rangle = \frac{1}{\sqrt{2}}(J(J+1) - k(k-1))^{\frac{1}{2}}|Jk-1\rangle,$$

$$R_0^{1(1)} = J_0 \qquad\qquad J_0|Jk\rangle = k|Jk\rangle \tag{B.1}$$

$$R_0^{2(2)} = \sqrt{\frac{3}{2}} J_0^2 - \frac{1}{\sqrt{6}} J^2$$

$$R_{\pm 1}^{2(2)} = \mp \frac{1}{\sqrt{2}} [J_0, J_\pm]_+$$

$$R_{\pm 2}^{2(2)} = J_\pm^2$$

$$R_0^{2(0)} = -\frac{1}{\sqrt{3}} J^2, \tag{B.2}$$

$$R_0^{3(3)} = -\frac{3}{\sqrt{10}} J^2 J_0 + \sqrt{\frac{5}{2}} J_0^3 + \frac{1}{\sqrt{10}} J_0$$

$$R_{\pm 1}^{3(3)} = \pm \frac{3}{2\sqrt{15}} J_\pm J^2 \mp \frac{\sqrt{15}}{4} (J_\pm J_0^2 + J_0^2 J_\pm) \pm \frac{3}{4\sqrt{15}} J_\pm$$

$$R_{\pm 2}^{3(3)} = \frac{\sqrt{3}}{2} (J_0 J_\pm^2 + J_\pm^2 J_0)$$

$$R_{\pm 3}^{3(3)} = \mp J_\pm^3$$

$$R_{\pm 1}^{3(1)} = \pm \frac{1}{\sqrt{3}} J^2 J_\pm$$

$$R_0^{3(1)} = -\frac{1}{\sqrt{3}} J^2 J_0, \tag{B.3}$$

where $J^2 = \sum_\alpha J_\alpha^2$.

## B.2. Rotational operators symmetrised in the $C_{3v}$ symmetry group

The use of the results of the above subsection in the general relations, Equation (5), allows one to determine rotational operators symmetrised in the $C_{3v}$ group:

$$R^{1(1,A_2)} = J_0 = J_z$$

$$R_1^{1(1,E)} = -\frac{i}{\sqrt{2}} (J_- - J_+) = J_y$$

$$R_2^{1(1,E)} = \frac{1}{\sqrt{2}} (J_- + J_+) = J_x, \tag{B.4}$$

$$R^{2(0,A_1)} = -\frac{J^2}{\sqrt{3}}$$

$$R^{2(2,A_1)} = -\sqrt{\frac{3}{2}} J_0^2 + \frac{1}{\sqrt{6}} \sum_\alpha J_\alpha^2$$

$$R_1^{2(2,1E)} = \frac{1}{2} ([J_0, J_-]_+ + [J_0, J_+]_+)$$

$$R_2^{2(2,1E)} = \frac{i}{2} ([J_0, J_-]_+ - [J_0, J_+]_+)$$

$$R_1^{2(2,2E)} = -\frac{1}{\sqrt{2}} (J_+^2 + J_-^2)$$

$$R_2^{2(2,2E)} = \frac{i}{\sqrt{2}} (J_-^2 - J_+^2), \tag{B.5}$$

and

$$R^{3(1,A_2)} = -\frac{J^2 J_0}{\sqrt{3}}$$

$$R_1^{3(1,E)} = \frac{i}{\sqrt{6}} J^2 (J_- - J_+)$$

$$R_2^{3(1,E)} = -\frac{1}{\sqrt{6}} J^2 (J_- + J_+)$$

$$R^{3(3,A_1)} = \frac{i}{\sqrt{2}} (J_-^3 - J_+^3)$$

$$R^{3(3,1A_2)} = -\frac{1}{\sqrt{2}} (J_-^3 + J_+^3)$$

$$R^{3(3,2A_2)} = \frac{3}{\sqrt{10}} J^2 J_0 - \sqrt{\frac{5}{2}} J_0^3 - \frac{1}{\sqrt{10}} J_0$$

$$R_1^{3(3,1E)} = \frac{i}{\sqrt{2}} \left\{ \frac{3}{2\sqrt{15}} (J_+ - J_-) J^2 \right.$$
$$\left. - \frac{\sqrt{15}}{4} \left[ (J_+ - J_-) J_0^2 + J_0^2 (J_+ - J_-) \right] \right\}$$
$$+ \frac{3i}{4\sqrt{30}} (J_+ - J_-)$$

$$R_2^{3(3,1E)} = \frac{1}{\sqrt{2}} \left\{ \frac{3}{2\sqrt{15}} (J_+ + J_-) J^2 \right.$$
$$\left. - \frac{\sqrt{15}}{4} \left[ (J_+ + J_-) J_0^2 + J_0^2 (J_+ + J_-) \right] \right\}$$
$$+ \frac{3}{4\sqrt{30}} (J_+ + J_-)$$

$$R_1^{3(3,2E)} = \frac{i\sqrt{3}}{2\sqrt{2}} \left\{ J_0 (J_+^2 - J_-^2) + (J_+^2 - J_-^2) J_0 \right\}$$

$$R_2^{3(3,2E)} = -\frac{\sqrt{3}}{2\sqrt{2}} \left\{ J_0 (J_+^2 + J_-^2) + (J_+^2 + J_-^2) J_0 \right\}. \tag{B.6}$$

## Appendix C. Anharmonic part of the intramolecular potential energy surface of the XYZ$_3$ molecule

Here we present the anharmonic part of the intramolecular potential energy surface of the XYZ$_3$ molecule in symmetrised form:

$$V_{\text{anh}} = V_{\text{anh}}^{(3)} + V_{\text{anh}}^{(4)} + \cdots, \tag{C.1}$$

where

$$V_{\text{anh}}^{(3)} = \sum_{i \le j \le l} k_{ijl} q_i q_j q_l + \sum_{i, \lambda \le \mu} k_{i\lambda\mu} q_i (q_{\lambda_1} q_{\mu_1} + q_{\lambda_2} q_{\mu_2})$$
$$+ \sum_{\lambda \le \mu \le \nu} k_{\lambda\mu\nu} (q_{\lambda_1} q_{\mu_1} q_{\nu_1}$$
$$- q_{\lambda_1} q_{\mu_2} q_{\nu_2} - q_{\lambda_2} q_{\mu_2} q_{\nu_1} - q_{\lambda_2} q_{\mu_1} q_{\nu_2}), \tag{C.2}$$

$$V_{\text{anh}}^{(4)} = \sum_{i \le j \le l \le m} k_{ijlm} q_i q_j q_l q_m$$

$$+ \sum_{i \le j, \lambda \le \mu} k_{ij\lambda\mu} q_i q_j (q_{\lambda_1} q_{\mu_1} + q_{\lambda_2} q_{\mu_2})$$

$$+ \sum_{i, \lambda \le \mu \le \nu} k_{i\lambda\mu\nu} q_i (q_{\lambda_1} q_{\mu_1} q_{\nu_1} - q_{\lambda_1} q_{\mu_2} q_{\nu_2}$$

$$- q_{\lambda_2} q_{\mu_2} q_{\nu_1} - q_{\lambda_2} q_{\mu_1} q_{\nu_2})$$

$$+ \sum_{\lambda < \mu} k^{(1)}_{\lambda\lambda\mu\mu} (q_{\lambda_1}^2 + q_{\lambda_2}^2)(q_{\mu_1}^2 + q_{\mu_2}^2)$$

$$+ \sum_{\lambda < \mu} k^{(2)}_{\lambda\lambda\mu\mu} (q_{\lambda_1} q_{\mu_2} - q_{\lambda_2} q_{\mu_1})^2$$

$$+ \sum_{\lambda; \mu \ne \lambda; \nu \ne \lambda, \mu} k^{(1)}_{\lambda\lambda\mu\nu} (q_{\lambda_1}{}^2 + q_{\lambda_2}{}^2)(q_{\mu_1} q_{\nu_1} + q_{\mu_2} q_{\nu_2})$$

$$+ \sum_{\lambda; \mu \ne \lambda; \nu \ne \lambda, \mu} k^{(2)}_{\lambda\lambda\mu\nu} (q_{\lambda_1} q_{\mu_2} - q_{\lambda_2} q_{\mu_1})(q_{\lambda_1} q_{\nu_2} - q_{\lambda_2} q_{\nu_1})$$

$$+ \sum_{\lambda} k_{\lambda\lambda\lambda\lambda} (q_{\lambda_1}^2 + q_{\lambda_2}^2)^2$$

$$+ \sum_{\lambda, \mu \ne \lambda} k_{\lambda\lambda\lambda\mu} (q_{\lambda_1}{}^2 + q_{\lambda_2}{}^2)(q_{\lambda_1} q_{\mu_1} + q_{\lambda_2} q_{\mu_2}). \quad \text{(C.3)}$$

## Appendix D. Symmetrised wavefunctions of the doubly degenerate harmonic oscillator

$$(v \, 0 \, a_1) = |v \, 0\rangle;$$

$$(v \, 6p \ne 0 \, a_1) = \frac{1}{\sqrt{2}}(|v \, 6p\rangle + |v - 6p\rangle),$$

$$(v \, 6p \, a_2) = -\frac{i}{\sqrt{2}}(|v \, 6p\rangle - |v - 6p\rangle);$$

$$(v \, 6p + 1 \, e_1) = \frac{1}{\sqrt{2}}(|v \, 6p + 1\rangle - |v - (6p + 1)\rangle),$$

$$(v \, 6p + 1 \, e_2) = \frac{i}{\sqrt{2}}(|v \, 6p + 1\rangle + |v - (6p + 1)\rangle);$$

$$(v \, 6p + 2 \, e_1) = \frac{1}{\sqrt{2}}(|v \, 6p + 2\rangle + |v - (6p + 2)\rangle),$$

$$(v \, 6p + 2 \, e_2) = -\frac{i}{\sqrt{2}}(|v \, 6p + 2\rangle - |v - (6p + 2)\rangle);$$

$$(v \, 6p + 3 \, a_1) = \frac{1}{\sqrt{2}}(|v \, 6p + 3\rangle - |v - (6p + 3)\rangle),$$

$$(v \, 6p + 3 \, a_2) = -\frac{i}{\sqrt{2}}(|v \, 6p + 3\rangle + |v - (6p + 3)\rangle);$$

$$(v \, 6p + 4 \, e_1) = \frac{1}{\sqrt{2}}(|v \, 6p + 4\rangle + |v - (6p + 4)\rangle),$$

$$(v \, 6p + 4 \, e_2) = \frac{i}{\sqrt{2}}(|v \, 6p + 4\rangle - |v - (6p + 4)\rangle),$$

$$(v \, 6p + 5 \, e_1) = \frac{1}{\sqrt{2}}(|v \, 6p + 5\rangle - |v - (6p + 5)\rangle),$$

$$(v \, 6p + 5 \, e_2) = -\frac{i}{\sqrt{2}}(|v \, 6p + 5\rangle + |v - (6p + 5)\rangle).$$

Here, in the symmetrised functions $(v \, l\gamma)$, the value $l \ge 0$. At the same time, functions $|v \, l\rangle$ are the eigenfunctions of a doubly degenerate harmonic oscillator (see, e.g. Equations (III.9) and (III.10) of Ref. [46]), and $l = -v, -v + 2, -v + 4, \ldots, v - 4, v - 2, v$ in those, $|v \, l\rangle$, functions.