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INVITED ARTICLE

On the 'expanded local mode' approach applied to the methane molecule: isotopic substitution $CH_2D_2 \leftarrow CH_4$

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On the basis of a compilation of the 'expanded local mode' model and the general isotopic substitution theory, sets of simple analytical relations between different spectroscopic parameters (harmonic frequencies, ω_λ, anharmonic coefficients, $x_{\lambda\mu}$, ro-vibrational coefficients, α_λ^β, different kinds of Fermi- and Coriolis-type interaction parameters) of the CH_2D_2 molecule are derived. All of them are expressed as simple functions of a few initial spectroscopic parameters of the mother, CH_4, molecule. Test calculations with the derived isotopic relations show that, in spite of a total absence of initial information about the CH_2D_2 species, the numerical results of the calculations have a very good correlation both with experimental data, and results of *ab initio* calculations.

Keywords: deuterated methanes; local mode model; isotopic relations; rotational and vibrational parameters

1. Introduction

Among numerous problems of chemical physics, the problem of as correct as possible extraction of physical information is one of the most fundamental. This type of information is strongly requested for the precise determination of intramolecular multi-dimensional potential surfaces (the last, in its turn, can be used in numerous applied problems of chemical physics), in different problems of astrophysics and planetology, the study of Earth atmosphere and environmental problems, etc. Reciprocally, the solution for a problem of correct extraction of physical information from high resolution spectra is based on the realization of two closely connected problems: mathematical modelling of intramolecular effects and interactions (first of all, again, the intramolecular potential function), and methods of assignments of spectral lines in experimentally recorded spectra. It should be mentioned that the latter (assignments of spectral lines), in many cases, is a very complicated problem, especially for the highly excited vibrational states with the presence of numerous accidental interactions.

As an illustration of such typical situations, the methane molecule and its different deuterated species can be mentioned. In spite of the fact there is a strong requirement for high accurate information about their high resolution spectra in the short wave region, on the one hand, and many-years extensive spectroscopic studies of both methane, CH_4, and its deuterated species, CH_3D, CH_2D_2, CHD_3 (see, e.g. [1, 2] where extensive references can be found – a complete list is not reproduced here), on the other hand, only the region below $6000\,cm^{-1}$ was studied in details. Up to now the study of the shorter wave region has been laborious, first of all, owing to the absence of the possibility to fulfill correct assignments of extremely complicated spectra for both methane, CH_4, itself, and any of its deuterated isotopomers (up to 2009, only some separate small wave regions above $6000\,cm^{-1}$ had been analysed with high resolution in [3–5] for the CH_4 molecule, and chromophore bands of the CHD_3 and CH_3D isotopomer were analysed in [6–11]; only recently, systematic investigations of the high resolution spectra in the region above $6000\,cm^{-1}$ of both methane, CH_4, and its three deuterated isotopomers have begun [12–21]). The only way to solve this problem as correctly as possible, is a qualitative prediction of line positions in the short wave region on the basis of spectroscopic parameters (rotational coefficients, harmonic frequencies and anharmonic coefficients, different kinds of Coriolis- and Fermi-type interaction coefficients). At the same time, the number of spectroscopic parameters in the

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Hamiltonian model is so high that their correct determination from the longer wave spectra and further use in the prediction of line positions in the shorter wave region is practically impossible. As a consequence, there is only one possibility to solve the problem of correct assignment of spectral lines in the short wave region. It is the reduction of the number of spectroscopic parameters in the Hamiltonian model to a minimum possible number. This can be done, for example, by the determination of relations between spectroscopic parameters of both the mother species, and relations between spectroscopic parameters of the mother and its different isotopic modifications.

In our recent publications (see, e.g. [22,23]) we have shown that the problem of determination of both the relations between spectroscopic parameters of a mother molecule, and of isotopic relations between spectroscopic parameters of different isotopic species of a molecule can be successfully solved for some types of polyatomic molecules as a result of compilation of the 'expanded local mode' approach (see [24–26]) and isotopic substitution theory [27,28]. In the present communication we apply the scheme used in [22,23] to derive isotopic relations for different spectroscopic parameters to the substitution $XH_2D_2 \leftarrow XH_4$ in methane type molecules.

The methane molecule is considered here for two reasons. Firstly, as mentioned above, it is an important object of study in a large number of both pure scientific, and applied problems. On the other hand, methane is the prototypical hydrocarbon, and one can expect that the scheme discussed in the present paper may be successfully applied to more complicated molecules and corresponding results can be considered as a good basis both in assignments of transitions in their, as a rule, very complicated high-resolution spectra, and in extraction of physical information from such spectra.

In Section 2 we reproduce briefly some results obtained recently for the CH_4 molecule which are the basis for further consideration. Section 3 gives some necessary information from the general isotopic substitution theory [27,28]. In Section 4, on the basis of the compilation of the 'expanded local mode approach' and isotopic substitution theory, we derive a set of simple enough isotopic relations between different spectroscopic parameters of the CH_4 mother and CH_2D_2 substituted species.

2. 'Expanded local mode' approach applied to the CH_4 molecule

The local mode ideas (the first extensive reviews of this method can be found in [29,30]; in [31], Lukka and

Halonen presented an exhaustive review of more recent papers on the subject; therefore we do not propose to carry out the same level of review in this paper) were successfully applied to the determination of connections between different spectroscopic parameters of some polyatomic molecules in a number of studies (see, e.g. [31–35]), etc. It should be mentioned that the traditional Local Mode approach only deals with stretching modes in a molecule and does not take into account the presence of bending modes. This circumstance considerably limits the possibilities of the Local Mode approach.

Earlier, in [24–26], the 'Expanded Local Mode' approach was derived which considerably extended the edges of the Local Mode approach and provided the possibility to take into account the presence of bending modes, as well. As was shown in [24–26], the clue point of the 'Expanded Local Mode' approach is the possibility to present the transformation coefficients, $l_{N\alpha\mu}$ (see, e.g. [36]), of a molecule in the form of simple analytical expressions. In its turn, as follows from general vibrational–rotational theory [37], all the spectroscopic parameters of a molecule depend on the values of the transformation coefficients, $l_{N\alpha\mu}$. It means that if it would be possible to express all the transformation coefficients, $l_{N\alpha\mu}$, in as simple a form as possible, then one may expect that any spectroscopic parameter of a molecule can be presented in a simple form also.

Such a procedure was realized in [23] by the authors of the present paper for the CH_4 molecule on the basis of an analysis of the Coriolis coefficients and the properties of the intramolecular potential function of methane. It was shown in [23] that the values of the $l_{N\alpha\mu}$ coefficients of the CH_4 molecule can be approximated with good accuracy (with less than 2% error) by a very simple form (see Table 1, which is reproduced from [23]). Analogously, it was shown in [23]) that the following relations between parameters $F_{i...j}$ of the intramolecular potential function of the CH_4 molecule are fulfilled also with good accuracy:

$$\frac{F_{33}}{267} = \frac{F_{11}}{272} = \frac{4F_{22}}{97\rho_e^2} = \frac{3F_{44}}{67\rho_e^2} = -\frac{2F_{34}}{19\rho_e}, \qquad (1)$$

$$\frac{2}{3}F_{244} = -\frac{7}{3}F_{222} = -\frac{2}{3}F_{444} = \rho_e F_{144} = \frac{4\rho_e}{5}F_{122}$$

$$= -\rho_e F_{234} = 2\rho_e F_{344} = \frac{\rho_e^2}{2}F_{233} = \rho_e^2 F_{334}$$

$$= -2\rho_e^2 F_{134} = \frac{\rho_e^3}{90}F_{111} = \frac{\rho_e^3}{90}F_{333}$$

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

and

$$F_{4444(2)} = 2F_{4444(1)} = 2F_{2244(2)} = 4F_{2222} = -\frac{13\rho_e}{7} F_{3444(1)}$$

$$= -\frac{39\rho_e}{7} F_{3444(2)} = -\frac{19\rho_e^2}{7} F_{3344(3)}$$

$$= -\frac{57\rho_e^2}{7} F_{3344(1)} = \frac{24\rho_e^2}{7} F_{2334} = -\frac{24\rho_e^2}{7} F_{2233(1)}$$

$$= -\frac{12\rho_e^2}{7} F_{2233(2)} = \frac{18\rho_e^3}{7} F_{3334(1)} = \frac{18\rho_e^3}{7} F_{3334(2)}$$

$$= \frac{\rho_e^4}{70} F_{1111} = \frac{\rho_e^4}{70} F_{1133} = \frac{\rho_e^4}{70} F_{1333}$$

$$= \frac{\rho_e^4}{70} F_{3333(1)} = \frac{\rho_e^4}{70} F_{3333(2)}. \tag{3}$$

All the other F_{ijkl} parameters have been taken equal to zero. The value ρ_e in Equations (1)–(3) is the equilibrium distance between the nuclei C and H.

On that basis, the following very simple, but, at the same time, correct enough relations can be derived, for example, between anharmonic, tetrahedral splitting, and ro-vibrational coefficients of CH_4:

$$x_{11} = \frac{21}{32} x_{12} = \frac{4}{17} x_{13} = 80 x_{14} = 80 x_{22} = \frac{28}{25} x_{23} = \frac{13}{5} x_{24}$$

$$= \frac{11}{25} x_{33} = \frac{9}{5} x_{34} = \frac{23}{10} x_{44} = -28 G_{22} = -\frac{21}{20} G_{33}$$

$$= 13 G_{34} = -\frac{13}{5} G_{44} = 20 S_{34} = -30 T_{23} = 25 T_{24}$$

$$= -\frac{19}{5} T_{33} = -27 T_{44} = -\frac{7}{32} \frac{\hbar}{\pi c m_H \rho_e^2} \approx -\frac{7}{3} B_e, \tag{4}$$

and

$$\frac{10}{11} Y_1 = -\frac{17}{44} Y_2^{(1)} = 13 Y_2^{(2)} = Y_3 = \frac{6}{11} Y_4^{(1)} = \frac{17}{5} Y_4^{(2)}$$

$$= -\frac{\hbar^2}{16\pi c \rho_e^4 (m_H^3 F_{11})^{1/2}} \approx -\frac{11}{3} \frac{B_e^2}{\omega_3} = -\frac{33}{49} \frac{x_{11}^2}{\omega_3}. \tag{5}$$

Notations in Equations (4) and (5) correspond to notations of [38]. In relations (4) the values $x_{\lambda\mu}$ are anharmonic coefficients; G_{22}, G_{33}, G_{34}, G_{44}, S_{34}, T_{23}, T_{24}, T_{33}, and T_{44} are different vibrational tetrahedral splitting parameters. In relations (5) the values Y_μ are rotational–vibrational coefficients; the superscript [1] marks parameters obtained in the model that neglects resonance interaction between the states $(v_1 v_2 v_3 v_4)$ and $(v_1 v_2 \pm 1 v_3 v_4 \mp 1)$. The superscript [2] marks parameters obtained in the model that takes into account such types of resonance interaction.

3. Some extraction from the isotopic substitution theory

Because the main goal of the present study is to derive simple isotopic relations between parameters of the mother, CH_4, and di-deuterated, CH_2D_2, methane isotopic species, it is suitable to make use of results of the general isotopic substitution theory. As was shown in [27], the following three relations are valid for an arbitrary isotopic substitution in any polyatomic molecule:

(1) A set of equations which allow one to determine all harmonic frequencies, ω'_v, of any isotopic substituted molecule as functions of harmonic frequencies, ω_λ, of a mother molecule and a set of coefficients $A_{\lambda\mu}$; or, conversely, to determine coefficients $A_{\lambda\mu}$ as functions of harmonic frequencies of the mother and substituted molecule:

$$\sum_\lambda A_{\mu\lambda} \omega_\lambda^2 \alpha_{\lambda v} = \alpha_{\mu v} \omega_v'^2. \tag{6}$$

Here the $\alpha_{v\lambda}$ are additional coefficients which also are determined from a solution of a set of Equations (6) and additional relations:

$$A_{\lambda\mu} = \sum_v \alpha_{\lambda v} \alpha_{\mu v}. \tag{7}$$

(2) From the above-mentioned relations, the second have the following form (m_N and m'_N are the masses of atoms before and after isotopic substitution):

$$A_{\lambda\mu} = \delta_{\lambda\mu} - \sum_{N\alpha} \frac{(m'_N - m_N)}{m'_N} l_{N\alpha\lambda} l_{N\alpha\mu}, \tag{8}$$

and they determine the $A_{\lambda\mu}$ coefficients via transformation coefficients, $l_{N\alpha\mu}$, of a mother isotopomer. Usually these transformation coefficients are known for any mother isotopomer.

(3) The third type of relations can be written as:

$$l'_{N\gamma\lambda} = \sum_{\alpha\mu} K_{\alpha\gamma}^e \left(\frac{m_N}{m'_N}\right)^{1/2} l_{N\alpha\mu} (\alpha^{-1})_{\lambda\mu} \tag{9}$$

and they provide the possibility of calculating transformation coefficients of a substituted isotopomer as functions of characteristics of a mother species. Here $K_{\alpha\gamma}^e$ 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 (6)–(9), α, β, $\gamma = x, y, z$ and λ, μ, v number the vibrational modes.

Table 1. Transformation coefficients, $l_{N\alpha\lambda}$, of CH$_4$ in the 'expanded local mode' model.

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

Note: [a]Here $A = 1/2(6^{1/2})$, $B = 1/20$

It is important, that the relations, Equations (6)–(9), allow one to obtain $l'_{N\gamma\lambda}$-transformation coefficients of any substituted molecule if one knows the corresponding $l_{N\alpha\mu}$ coefficients of a mother isotopic species. Unfortunately, because of the complexity, in the general case, results can be obtained only in a numerical form. On the other hand, if $l_{N\alpha\mu}$ coefficients of a mother molecule and $(\alpha^{-1})_{\lambda\mu}$ coefficients on the right-hand side of Equation (9) are more or less simple values, one may expect that the transformation coefficients $l'_{N\gamma\lambda}$ of a substituted molecule also can be obtained in a simple form.

4. Transformation, Coriolis, and ro-vibrational coefficients of the CH$_2$D$_2$ isotopomer

As was mentioned before, the presence of simple expressions for the $l_{N\alpha\mu}$-coefficients and $F_{i...j}$ potential parameters of the CH$_4$ molecule gives one the possibility to expect that analogous simple results can be obtained for the CH$_2$D$_2$ species as well.

As the first step of our analysis, transformation coefficients, $l'_{N\alpha\lambda}$, of the CH$_2$D$_2$ species were calculated. In this case, as was discussed in Section 3, Equations (9) were used, where $l_{N\alpha\mu}$ on the right-hand side should be taken from Table 1; the values $(\alpha^{-1})_{\lambda\mu}$ are obtained from the solution of Equations (6)–(8); elements of the rotational matrix, $K^e_{\alpha\gamma}$, in our case are determined in the following way:

$$
\begin{pmatrix} K^e_{xx} & K^e_{xy} & K^e_{xz} \\ K^e_{yx} & K^e_{yy} & K^e_{yz} \\ K^e_{zx} & K^e_{zy} & K^e_{zz} \end{pmatrix} = \begin{pmatrix} 1/2^{1/2} & -1/2^{1/2} & 0 \\ -1/2^{1/2} & -1/2^{1/2} & 0 \\ 0 & 0 & -1 \end{pmatrix}.
\tag{10}
$$

The results for the $l'_{N\alpha\lambda}$ coefficients of the CH$_2$D$_2$ molecule obtained in this way are presented in Table 2. In its turn, knowledge of the $l'_{N\alpha\lambda}$ values allows one to determine two sets of values which depend on $l'_{N\alpha\lambda}$, namely, Coriolis coefficients, $\zeta'^{\alpha}_{\lambda\mu}$, and ro-vibratonal coefficients, $a'^{\alpha\beta}_{\lambda}$, [36,37]:

$$
\zeta'^{\alpha}_{\lambda\mu} = \sum_{\beta\gamma} \epsilon_{\alpha\beta\gamma} \sum_N l'_{N\beta\lambda} l'_{N\gamma\mu}
\tag{11}
$$

and

$$
a'^{\alpha\beta}_{\lambda} = 2 \sum_{\gamma\delta\kappa} \epsilon_{\alpha\gamma\kappa} \epsilon_{\beta\delta\kappa} \sum_N m_N'^{1/2} r'^e_{N\gamma} l'_{N\delta\lambda}.
\tag{12}
$$

In our case, if one will take into account data from Table 2, the $\zeta'^{\alpha}_{\lambda\mu}$ and $a'^{\alpha\beta}_{\lambda}$ coefficients will have the form presented in Tables 3 and 4 (in those tables only non-zero values are presented).

5. Normal mode force parameters of CH$_2$D$_2$

As the next step, the obtained results can be used in formulas for different spectroscopic parameters which are both known in the general vibrational-rotational theory (see e.g. [39]), or can be derived on the basis of operator perturbation theory (see e.g. [37, 39–41]). As a consequence, in addition to the previous results obtained in Section 4, it is necessary to have information about harmonic frequencies, ω_λ, and, at least, cubic, $k_{\lambda\mu\nu}$, and quartic, $k_{\lambda\mu\nu\xi}$, normal mode force parameters. All these values can be derived on the basis of the knowledge of the parameters of an intramolecular potential function, V, which for the methane molecule has the form [42]:

$$
V = V^{(2)} + V^{(3)} + V^{(4)} + \ldots,
\tag{13}
$$

Table 2. Transformation coefficients, $l'_{N\alpha\lambda}$, of CH_2D_2 in the frame of the 'expanded local mode' model.[a]

$N\,\alpha/\lambda$	1	2	3	4	5	6	7	8	9
$1x$	$-C$	$-33C$	$13C$	$-40C$	0	0	0	$-32C$	$-23C$
$2x$	$-C$	$-33C$	$13C$	$-40C$	0	0	0	$32C$	$23C$
$3x$	$-33C$	$5C$	$-47C$	$-3C$	0	$-35C$	$-32C$	0	0
$4x$	$-33C$	$5C$	$-47C$	$-3C$	0	$35C$	$32C$	0	0
$5x$	$20C$	$24C$	$17C$	$35C$	0	0	0	0	0
$1y$	0	0	0	0	$35C$	$-C$	$-41C$	0	0
$2y$	0	0	0	0	$-35C$	$-C$	$-41C$	0	0
$3y$	$50C$	$-6C$	$-35C$	$-8C$	0	$47C$	$-31C$	0	0
$4y$	$-50C$	$6C$	$35C$	$8C$	0	$47C$	$-31C$	0	0
$5y$	0	0	0	0	0	$-26C$	$41C$	0	0
$1z$	$-3C$	$-48C$	$-5C$	$38C$	0	0	0	$-45C$	$4C$
$2z$	$3C$	$48C$	$5C$	$-38C$	0	0	0	$-45C$	$4C$
$3z$	0	0	0	0	$50C$	0	0	C	$52C$
$4z$	0	0	0	0	$-50C$	0	0	C	$52C$
$5z$	0	0	0	0	0	0	0	$36C$	$-33C$

Note: [a] Here $C = 1/50(3^{1/2})$.

Table 3. Non-zero values of Coriolis coefficients, $\zeta^{\alpha}_{\lambda\mu}$, of the CH_2D_2 molecule.[a]

$\alpha\lambda\mu$	value	$\alpha\lambda\mu$	value	$\alpha\lambda\mu$	value
$x\,1\,5$	$35D$	$y\,1\,8$	$-4D$	$z\,1\,7$	$33D$
$x\,2\,5$	$18D$	$y\,1\,9$	$28D$	$z\,2\,6$	$-4D$
$x\,3\,5$	$-21D$	$y\,2\,8$	$-5D$	$z\,2\,7$	$21D$
$x\,4\,5$	$-23D$	$y\,2\,9$	$18D$	$z\,3\,6$	$-49D$
$x\,5\,1$	$-35D$	$y\,3\,8$	$6D$	$z\,3\,7$	$-9D$
$x\,5\,2$	$-18D$	$y\,3\,9$	$38D$	$z\,4\,6$	$-11D$
$x\,5\,3$	$21D$	$y\,4\,8$	$-48D$	$z\,4\,7$	$28D$
$x\,5\,4$	$23D$	$y\,5\,6$	$-23D$	$z\,5\,8$	$15D$
$x\,6\,8$	$-5D$	$y\,5\,7$	$-21D$	$z\,5\,9$	$11D$
$x\,6\,9$	$38D$	$y\,6\,5$	$23D$	$z\,6\,2$	$4D$
$x\,7\,8$	$35D$	$y\,7\,5$	$21D$	$z\,6\,3$	$49D$
$x\,7\,9$	$-20D$	$y\,8\,1$	$4D$	$z\,6\,4$	$11D$
$x\,8\,6$	$5D$	$y\,8\,2$	$5D$	$z\,7\,1$	$-33D$
$x\,8\,7$	$-35D$	$y\,8\,3$	$-6D$	$z\,7\,2$	$-21D$
$x\,9\,6$	$-38D$	$y\,8\,4$	$48D$	$z\,7\,3$	$9D$
$x\,9\,7$	$20D$	$y\,9\,1$	$-28D$	$z\,7\,4$	$-28D$
		$y\,9\,2$	$-18D$	$z\,8\,5$	$-15D$
		$y\,9\,3$	$-38D$	$z\,9\,5$	$-11D$

Note: [a] Here $D = 1/50$.

Table 4. Non-zero values of the $a^{\lambda}_{\alpha\beta}$-coefficients of CH_2D_2.[a]

$\alpha\beta\lambda$	value	$\alpha\beta\lambda$	value
$1\,1\,1$	$-15F$	$2\,2\,2$	$35F$
$1\,1\,2$	$25F$	$2\,2\,3$	$-13F$
$1\,1\,3$	$14F$	$2\,2\,4$	$-5F$
$1\,1\,4$	$-15F$	$3\,2\,5$	$17F$
$2\,1\,6$	$-12F$	$1\,3\,8$	$-15F$
$2\,1\,7$	$-11F$	$1\,3\,9$	$-11F$
$3\,1\,8$	$-15F$	$2\,3\,5$	$17F$
$3\,1\,9$	$-11F$	$3\,3\,1$	$-24F$
$1\,2\,6$	$-12F$	$3\,3\,2$	$14F$
$1\,2\,7$	$-11F$	$3\,3\,3$	$-4F$
$2\,2\,1$	$-60F$	$3\,3\,4$	$15F$

Note: [a] Here $F = \frac{3^{1/2}}{25}(I^e)^{1/2}$, $I^e = \frac{8}{3}m\rho_e^2$ is the equilibrium moment of inertia of the CH_4 molecule.

where the quadratic part $V^{(2)}$ reads (in symmetrized coordinates notation):

$$V^{(2)} = \frac{1}{2}F_{11}S_1^2 + \frac{1}{2}F_{22}(S_{2a}^2 + S_{2b}^2) + \frac{1}{2}F_{33}(S_{3x}^2 + S_{3y}^2 + S_{3z}^2)$$
$$+ F_{34}(S_{3x}S_{4x} + S_{3y}S_{4y} + S_{3z}S_{4z})$$
$$+ \frac{1}{2}F_{44}(S_{4x}^2 + S_{4y}^2 + S_{4z}^2). \tag{14}$$

We do not present here the cubic, $V^{(3)}$, and quartic, $V^{(4)}$, parts of the function, Equation (13), because they are cumbersome. However, the reader can find them in Equations (10) and Table 4 of [42].

To obtain the analytical form of relations between the parameters F_{ij}, F_{ijk}, F_{ijkl} of Equations (13) and (14), on the one hand, and normal mode force parameters, ω_λ, $k_{\lambda\mu\nu}$, $k_{\lambda\mu\nu\xi}$, on the other hand, one can

(1) take into account connections between the parameters F_{ij}, F_{ijk}, F_{ijkl} and f_{rr}, $f_{r\alpha}$, $f_{\alpha\alpha}$, f_{rrr}, etc., which can be obtained on the basis of known relations from, e.g. [42]:

$$S_1 = \frac{1}{2}(r_1 + r_2 + r_3 + r_4),$$

$$S_{2_1} = \frac{1}{2(3^{1/2})}(2\alpha_{12} - \alpha_{13} - \alpha_{14} - \alpha_{23} - \alpha_{24} + 2\alpha_{34}),$$

$$S_{2_2} = \frac{1}{2}(\alpha_{13} - \alpha_{14} - \alpha_{23} + \alpha_{24}),$$

$$S_{3x} = \frac{1}{2}(r_1 - r_2 + r_3 - r_4),$$

$$S_{3y} = \frac{1}{2}(r_1 - r_2 - r_3 + r_4),$$

$$S_{3z} = \frac{1}{2}(r_1 + r_2 - r_3 - r_4),$$

$$S_{4x} = \frac{1}{2^{1/2}}(\alpha_{24} - \alpha_{13}),$$

$$S_{4y} = \frac{1}{2^{1/2}}(\alpha_{23} - \alpha_{14}),$$

$$S_{4z} = \frac{1}{2^{1/2}}(\alpha_{34} - \alpha_{12}); \tag{15}$$

(2) use corresponding general formulas which were derived in [43] and connect $\Delta r_N / \Delta \alpha_{NK}$ vibrational coordinates of a molecule with its normal mode coordinates, Q_λ:

$$\Delta r_N = \sum_\lambda C_\lambda^N Q_\lambda + \frac{1}{2} \sum_{\lambda\mu} C_{\lambda\mu}^N Q_\lambda Q_\mu$$
$$+ \frac{1}{6} \sum_{\lambda\mu\nu} C_{\lambda\mu\nu}^N Q_\lambda Q_\mu Q_\nu + \dots \tag{16}$$

and

$$\Delta \alpha_{NK} = \sum_\lambda C_\lambda^{NK} Q_\lambda + \frac{1}{2} \sum_{\lambda\mu} C_{\lambda\mu}^{NK} Q_\lambda Q_\mu$$
$$+ \frac{1}{6} \sum_{\lambda\mu\nu} C_{\lambda\mu\nu}^{NK} Q_\lambda Q_\mu Q_\nu + \dots, \tag{17}$$

where the coefficients $C_{...}^N$ and $C_{...}^{NK}$ have complicated enough forms, and we do not present them here. However, the reader can find them in [43].

If one takes into account Equations (13)–(17), data from Table 2, and relations (1)–(3), then one can obtain two sets of simple relations between normal mode force parameters, c_{ijk}/c_{ijkl}, of the mother, CH_4, and k'_{ijk}/k'_{ijkl}, of the substituted, CH_2D_2, species which are presented in Appendix 1.

6. Isotopic relations between spectroscopic parameters ω'_λ, $x'_{\lambda\mu}$, B^e_β, α'^β_λ of the CH_4 and CH_2D_2 species

Let us now use the results from Appendix 1 and Table 3 and 4 to derive isotopic relations between different spectroscopic parameters under substitution $CH_2D_2 \leftarrow CH_4$. First of all we consider harmonic frequencies, ω_λ, anharmonic coefficients, $x_{\lambda\mu}$, equilibrium rotational parameters, B^e_β, and ro-vibrational coefficients, α^β_λ, i.e. values presented in the unperturbed vibrational energies

$$E^{v_1,\dots,v_9} = \sum_\lambda \omega_\lambda \left(v_\lambda + \frac{1}{2}\right) + \sum_{\lambda\mu} x_{\lambda\mu} \left(v_\lambda + \frac{1}{2}\right)\left(v_\mu + \frac{1}{2}\right) + \dots \tag{18}$$

and in the formula for an effective rotational parameter:

$$B_\beta^{v_1,\dots,v_9} = B_\beta^e - \sum_\lambda \alpha_\lambda^\beta \left(v_\lambda + \frac{1}{2}\right) + \dots \tag{19}$$

In Equations (18) and (19), $\lambda, \mu = 1, \dots, 9$; $\alpha = x, y, z$.

6.1. Harmonic frequencies, ω'_λ

As follows from Equation (6), harmonic frequencies, ω'_λ, of the CH_2D_2 species can be obtained from the equation:

$$\det(\mathbf{AW} - \omega'^2 \mathbf{E}) = 0, \tag{20}$$

where $\mathbf{A}$ is the matrix with elements $A_{\lambda\mu}$, defined in Equation (8); $\mathbf{W}$ is the diagonal matrix with elements $W_{\lambda\lambda} = \omega_\lambda^2$; and $\mathbf{E}$ is the unit matrix. In this case, if one takes into account Equations (13) from [43] and data from Table 1 of the present paper, then the following relations can be obtained from the solution of Equation (20):

$$\frac{\omega_1^2}{120} = \frac{\omega_1'^2}{125} = \frac{\omega_2'^2}{18 + 27(3^{1/2})} = \frac{\omega_3'^2}{28} = \frac{\omega_4'^2}{23 - 5(3^{1/2})}$$
$$= \frac{\omega_5'^2}{62 - 22(3^{1/2})} = \frac{\omega_6'^2}{129} = \frac{\omega_7'^2}{49 - 19(3^{1/2})}$$
$$= \frac{\omega_8'^2}{69 + 3^{1/2}} = \frac{\omega_9'^2}{19 + 3^{1/2}} \tag{21}$$

Numerical values of the harmonic frequencies, ω'_λ, of CH_2D_2 obtained on the basis of derived relations, Equation (21), with the use of only one initial parameter, ω_1, of the CH_4 molecule from [23] are shown in column *I* of Table 5. For comparison, values of the same harmonic frequencies obtained from analysis of experimental data [13], and from *ab initio* calculations [44] are presented in columns *II* and *III*, respectively. It should be mentioned that, as is seen from comparison of data in columns *I*, on the one hand, and *II–III*, on the other hand, the calculated values are systematically (2–4 cm^{-1}) smaller than those from experiments or *ab initio* calculations. The reason is in the fact, that we used, in estimations with formula (21), the harmonic frequency, ω_1, of the CH_4 species from [23], as an initial value. Of course, the correspondence between data in columns *I* and *II–III* can be easily improved by simply shifting the initial CH_4 ω_1 value to a few cm^{-1} higher, see Equation (21). In any case, if one remembers that frequencies ω'_λ were obtained without any information about the CH_2D_2 molecule, the results used for comparison can be considered as quite satisfactory.

Table 5. Harmonic frequencies of the CH_2D_2 molecule (in cm^{-1}).

Parameter	I[a]	II[b]	III[c]
ω'_1	3103.07	3104.42	3102.5
ω'_2	2233.62	2237.99	2236.9
ω'_3	1468.64	1472.31	1470.9
ω'_4	1051.01	1054.44	1053.1
ω'_5	1356.72	1361.24	1360.1
ω'_6	3152.33	3159.79	3156.5
ω'_7	1113.34	1117.78	1116.2
ω'_8	2334.24	2339.57	2337.1
ω'_9	1263.74	1267.46	1265.7

Notes: [a]Calculated on the basis of Equation (21).
[b]Taken from analysis of experimental data [13].
[c]Taken from *ab initio* calculation [44].

6.2. Anharmonic coefficients, $x'_{\lambda\mu}$

To derive isotopic relations between anharmonic coefficients, $x'_{\lambda\mu}$, one can use corresponding general formulas, Equation (IV.20), from [39]. In this case, Equations (16), (17), (21) and data from Table 3 should be taken into account. As the result, one obtains the following:

$$x_{11} = -\frac{7}{3}B_e = \frac{9}{20}x'_{11} = 10x'_{12} = \frac{11}{26}x'_{13} = 7x'_{14} = \frac{6}{5}x'_{15}$$
$$= \frac{1}{9}x'_{16} = \frac{3}{2}x'_{17} = 900x'_{18} = \frac{11}{25}x'_{19} = \frac{23}{25}x'_{22} = 7x'_{23}$$
$$= \frac{19}{25}x'_{24} = \frac{9}{5}x'_{25} = -10x'_{26} = \frac{6}{5}x'_{27} = \frac{5}{24}x'_{28} = 3x'_{29}$$
$$= \frac{56}{5}x'_{33} = 7x'_{34} = 50x'_{35} = \frac{2}{5}x'_{36} = -\frac{19}{4}x'_{37} = 5x'_{38}$$
$$= -17x'_{39} = 41x'_{44} = -29x'_{45} = 12x'_{46} = -7x'_{47}$$
$$= \frac{23}{25}x'_{48} = 9x'_{49} = \frac{28}{5}x'_{55} = \frac{12}{21}x'_{56} = 70x'_{57} = \frac{8}{5}x'_{58}$$
$$= -7x'_{59} = \frac{2}{5}x'_{66} = \frac{33}{50}x'_{67} = -4x'_{68} = \frac{3}{5}x'_{69} = \frac{32}{5}x'_{77}$$
$$= \frac{21}{10}x'_{78} = -5x'_{79} = \frac{13}{19}x'_{88} = \frac{3}{2}x'_{89} = -10x'_{99}$$
$$= -\frac{7}{32}\frac{\hbar}{\pi cm\rho^2}. \tag{22}$$

It is important to note that while using the general formulas IV.20 from [39], we took into account the presence of possible Fermi-type resonance interactions between the following pairs of vibrational states: $(..v_2..v_4..)/(..v_2 \pm 1..v_4 \mp 2..)$, $(..v_2..v_7..)/(..v_2 \pm 1..v_7 \mp 2..)$, $(..v_1..v_3..)/(..v_1 \pm 1..v_3 \mp 2..)$, $(..v_1..v_9..)/(..v_1 \pm 1..v_9 \mp 2..)$, $(..v_3..v_6..v_7..)/(..v_3 \pm 1..v_6 \mp 1..v_7 \pm 1..)$, $(..v_5..v_6..v_9..)/(..v_5 \pm 1..v_6 \mp 1..v_9 \pm 1..)$, $(..v_4..v_8..v_9..)/(..v_4 \pm 1..v_8 \mp 1..v_9 \pm 1..)$, and $(..v_5..v_7..v_8..)/(..v_5 \pm 1..v_7 \pm 1..v_8 \mp 1..)$.

In Table 6 (column *I*) one can see results of calculation with the relations of Equation (22). In this case, as in the previous subsection, only the single initial parameter, x_{11}, of the CH_4 species was taken from [23]. For comparison, values of corresponding $x'_{\lambda\mu}$-parameters obtained on the basis of *ab initio* calculations from [44] are shown in column *II* of Table 6. If one takes into account that the values of the $x'_{\lambda\mu}$-parameters in column *I* were calculated without any information about the CH_2D_2 species, and using only one x_{11} parameter of the CH_4 mother molecule, one can state a more than satisfactory correlation between values in both columns, with the exception of parameters x'_{13}, x'_{19}, x'_{24}, x'_{33}, x'_{36}, x'_{37}, x'_{44}, x'_{56}, x'_{59}, x'_{67}, x'_{69}, x'_{89}, and x'_{99}. Discrepancies in the values of the mentioned parameters can be explained very easily if one takes into account the following circumstance: to produce the isotopic relations, Equation (22), we used the above-mentioned set of vibrational resonance interactions. At the same time, the values of the parameters in column *II* (which are reproduced from [44]) were calculated from *ab initio* $F_{i,j}$ force parameters by taking into account only two types of vibrational interactions: $(..v_2..v_7..)/(..v_2 \pm 1..v_7 \mp 2..)$ and $(..v_4..v_8..v_9..)/(..v_4 \pm 1..v_8 \mp 1..v_9 \pm 1..)$. To illustrate the quality of the approach discussed in the present paper, we calculated the $x'_{\lambda\mu}$-parameters on the basis of the same *ab initio* $F_{i,j}$ force parameters from [44], but we took into account all eight above-mentioned resonance interactions. The results of that calculation are presented in column *III* of Table 6. One can see more than satisfactory correlations between the corresponding values in columns *III* and *I*. This circumstance can be considered as a good confirmation of the correctness and efficiency of the derived isotopic relations, Equation (22).

Also for comparison, column *IV* of Table 6 presents experimental values of the $x'_{\lambda\mu}$ anharmonic coefficients from [13]. Again, discrepancies between values of some parameters in columns *I* and *IV* can be explained by the fact that the analysis of experimental data in [13] was made by taking into account considerably smaller number of pairs of vibrationally interacting states than was made in our present analysis.

6.3. Equilibrium rotational parameters, B'^e_β, and ro-vibrational coefficients, α'^β_λ

Equilibrium rotational parameters, B'^e_β, of CH_2D_2 can be easily determined if one uses the known formula:

$$B'^e_\beta = \left(\frac{\hbar}{4\pi c I'^e_{\beta\beta}}\right), \tag{23}$$

Table 6. Anharmonic Parameters of the CH_2D_2 Molecule (in cm^{-1}).

Parameter	I[a]	II[b]	III[c]	IV[d]	Parameter	I[a]	II[b]	III[c]	IV[d]
x'_{11}	−27.82	−27.34	−27.34	−25.30	x'_{39}	0.74	0.65	0.65	−0.18
x'_{12}	−1.25	−0.83	−0.83	−3.29	x'_{44}	−0.31	−4.49	−0.05	−5.21
x'_{13}	−29.59	−7.25	−30.07	−15.23	x'_{45}	0.43	0.51	0.51	1.47
x'_{14}	−1.79	−2.05	−2.05	−2.42	x'_{46}	−1.04	−1.41	−1.41	−1.14
x'_{15}	−10.43	−11.75	−11.75	−11.75[e]	x'_{47}	1.79	0.73	0.73	−0.87
x'_{16}	−112.66	−115.08	−115.08	−114.11	x'_{48}	−13.61	−15.62	−14.99	−15.62[e]
x'_{17}	−8.35	−8.79	−8.79	−7.77	x'_{49}	−1.39	−1.91	−1.91	−2.57
x'_{18}	−0.01	0.40	0.40	−9.22	x'_{55}	−2.24	−2.21	−2.21	−2.65
x'_{19}	−28.45	−6.14	−28.22	−0.62	x'_{56}	−21.91	−12.87	−22.72	−11.91
x'_{22}	−13.61	−14.13	−14.13	−10.45	x'_{57}	−0.18	0.39	−0.15	0.39[e]
x'_{23}	−1.79	−2.07	−2.07	−3.61	x'_{58}	−7.82	−9.66	−8.79	−9.66[e]
x'_{24}	−16.47	0.85	−16.93	−0.57	x'_{59}	1.79	−8.76	2.43	−9.67
x'_{25}	−6.95	−7.32	−7.32	−7.32[e]	x'_{66}	−31.30	−31.64	−31.64	−31.57
x'_{26}	1.25	−0.51	1.81	−0.51[e]	x'_{67}	−18.97	−11.27	−18.29	−11.06
x'_{27}	−10.43	−8.02	−10.33	−1.75	x'_{68}	3.13	3.72	3.72	3.72[e]
x'_{28}	−60.09	−59.73	−59.74	−58.07	x'_{69}	−20.86	−10.82	−22.01	−12.73
x'_{29}	−4.17	−4.34	−4.34	−7.67	x'_{77}	−1.96	−1.88	−1.88	−6.59
x'_{33}	−1.12	−6.73	−1.03	−5.19	x'_{78}	−5.96	−7.00	−6.97	−7.00[e]
x'_{34}	−1.79	−1.54	−1.54	−1.98	x'_{79}	2.50	3.59	3.59	2.46
x'_{35}	−0.25	−0.45	−0.45	−0.45[e]	x'_{88}	−18.30	−18.58	−18.58	−15.26
x'_{36}	−31.30	−22.15	−32.35	−21.51	x'_{89}	−8.35	−15.62	−7.78	−9.15
x'_{37}	2.63	−7.53	2.68	−7.31	x'_{99}	1.25	−4.35	1.17	5.26
x'_{38}	−3.50	−3.07	−3.07	−3.90					

Notes: [a]Calculated on the basis of Equation (22).
[b]Taken from *ab initio* calculation [44].
[c]Calculated on the basis of *ab initio* $F_{i.j}$ parameters from [44], but with taking into account the same set of resonance interactions, those were used in deriving of isotopic relations, Equation (22).
[d]Taken from analysis of experimental data [13].
[e]Was fixed in [13] to the value of corresponding parameter from [44].

where

$$I'^e_{\beta\beta} = \sum_N m'_N \left[\sum_\gamma (r'^e_{N\gamma})^2 - (r'^e_{N\beta})^2 \right]. \quad (24)$$

The values $r'^e_{N\gamma}$ ($\gamma = x, y, z$) are equilibrium coordinates of nuclei of the CH_2D_2 molecule, that can be obtained from values of corresponding equilibrium coordinates, $r^e_{N\gamma}$, of CH_4 with the help of Equation (10). As a consequence, one obtains:

$$B^e = \frac{3}{2} B'^e_x = \frac{31}{18} B'^e_y = \frac{11}{9} B'^e_z = \frac{3\hbar}{32\pi cm\rho^2}. \quad (25)$$

Numerical values of the B'^e_β parameters, obtained with relations (25) and using the initial value, $5.29986\,cm^{-1}$, of the CH_4 molecule, are: $B'^e_x = 3.53324\,cm^{-1}$; $B'^e_y = 3.07734\,cm^{-1}$; $B'^e_z = 4.33625\,cm^{-1}$.

To derive isotopic relations for the ro-vibrational coefficients, α'^β_λ, one can use general formulas from [39], Equations (16), (17) and (21) of the present paper,

and data from Table 4. As a result, the following relations can be derived:

$$Y_3 = \frac{10}{11} Y_1 = -\frac{3}{2}\alpha'^x_1 = -\frac{6}{5}\alpha'^x_2 = 4\alpha'^x_3 = \frac{19}{10}\alpha'^x_4 = -2\alpha'^x_5$$
$$= -2\alpha'^x_6 = -\frac{37}{10}\alpha'^x_7 = -\frac{12}{5}\alpha'^x_8 = \frac{63}{2}\alpha'^x_9 = -\frac{24}{5}\alpha'^y_1$$
$$= -\frac{32}{25}\alpha'^y_2 = \frac{39}{10}\alpha'^y_3 = -\frac{13}{10}\alpha'^y_4 = \frac{34}{5}\alpha'^y_5 = -\frac{56}{25}\alpha'^y_6$$
$$= 4\alpha'^y_7 = -\frac{29}{20}\alpha'^y_8 = -5\alpha'^y_9 = -\frac{28}{25}\alpha'^z_1 = -\frac{17}{4}\alpha'^z_2$$
$$= -\frac{4}{5}\alpha'^z_3 = \frac{22}{25}\alpha'^z_4 = 4\alpha'^z_5 = -\frac{3}{2}\alpha'^z_6 = -\frac{12}{5}\alpha'^z_7$$
$$= -\frac{9}{10}\alpha'^z_8 = 3\alpha'^z_9 = -\frac{\hbar^2}{16\pi\rho^4 cm^{3/2}F_{11}^{1/2}}. \quad (26)$$

It should be mentioned that we took into account the presence of resonance interactions between all deformational states, and also interactions between the pairs of states $(..v_1..v_6..)/(..v_1 \pm 1..v_6 \mp 1..)$ and $(..v_2..v_8..)/(..v_2 \pm 1..v_8 \mp 1..)$.

Table 7. Ro-vibrational coefficients, $\alpha_\lambda'^\beta$, of the CH_2D_2 molecule (in $10^{-2}\,cm^{-1}$).

$\beta\lambda$	I[a]	II[b]	III[c]	$\beta\lambda$	I[a]	II[b]	III[c]	$\beta\lambda$	I[a]	II[b]	III[c]
$x1$	2.23	2.01	2.38	$y1$	0.70	1.99	0.70	$z1$	2.98	3.51	3.46
$x2$	2.78	2.70	2.97	$y2$	2.61	2.70	3.18	$z2$	0.79	0.94	0.81
$x3$	−0.84	−1.02	−8.76	$y3$	−0.86	−1.02	−11.07	$z3$	4.18	3.63	3.38
$x4$	−1.76	−1.49	1.68	$y4$	2.60	1.50	2.51	$z4$	−3.80	−4.14	3.46
$x5$	1.67	0.66	6.17	$y5$	−0.49	0.64	−3.39	$z5$	−0.84	−1.18	−4.98
$x6$	1.67	1.84	1.79	$y6$	1.49	1.85	1.52	$z6$	2.23	2.37	2.19
$x7$	0.90	1.02	6.40	$y7$	−0.84	1.02	2.01	$z7$	1.39	1.75	−3.60
$x8$	1.39	1.80	1.57	$y8$	2.30	1.80	1.91	$z8$	3.71	3.46	3.94
$x9$	−0.11	0.08	−5.57	$y9$	0.67	0.80	10.90	$z9$	−1.11	−1.00	2.84

Notes: [a]Calculated on the basis of Equation (26).
[b]Taken from analysis of experimental data [45].
[c]Taken from Table 11 of [46].

Table 8. Parameters of vibrational interactions in the CH_2D_2 molecule (in cm^{-1}).

Type of Interaction	Parameter	I[a]	Equation	II[b]
$(..v_1..v_6..)/(..v_1 \pm 2..v_6 \mp 2..)$	$^{(11,66)}F_0'$	−123.44	(30)	−125.84
$(..v_4..v_7..)/(..v_4 \pm 2..v_7 \mp 2..)$	$^{(44,77)}F_0'$	− 6.18	(30)	−13.67
$(..v_3..v_4..v_9..)/(..v_3 \pm 1..v_4 \pm 1..v_9 \mp 2..)$	$^{(34,99)}F_0'$	−1.34	(33)	1.75
$(..v_1..v_4..v_6..v_7..)/(..v_1 \pm 1..v_4 \mp 1..v_6 \mp 1..v_7 \pm 1..)$	$^{(17,46)}F_0'$	−7.54	(35)	−7.03
$(..v_3..v_5..v_7..v_9..)/(..v_3 \pm 1..v_5 \mp 1..v_7 \pm 1..v_9 \mp 1..)$	$^{(37,59)}F_0'$	−15.70	(35)	−17.42
$(..v_3..v_5..v_7..v_9..)/(..v_3 \pm 1..v_5 \mp 1..v_7 \pm 1..v_9 \pm 1..)$	$^{(39,57)}F_0'$	24.58	(35)	23.02
$(..v_5..v_5..v_7..v_9..)/(..v_4 \pm 1..v_5 \pm 1..v_7 \pm 1..v_9 \mp 1..)$	$^{(45,79)}F_0'$	8.31	(35)	7.44
$(..v_4..v_5..v_7..v_9..)/(..v_4 \pm 1..v_5 \mp 1..v_7 \mp 1..v_9 \pm 1..)$	$^{(49,57)}F_0'$	20.19	(35)	19.86
$(..v_1..v_9..)/(..v_1 \pm 1..v_9 \mp 2..)$	$^{(1,99)}F_0'$	−164.96	(47)	−158.02
$(..v_1..v_3..)/(..v_1 \pm 1..v_3 \mp 2..)$	$^{(1,33)}F_0'$	−87.98	(47)	−95.50
$(..v_2..v_4..)/(..v_2 \pm 2..v_4 \mp 2..)$	$^{(2,44)}F_0'$	67.68	(47)	72.75
$(..v_2..v_7..)/(..v_2 \pm 2..v_7 \mp 2..)$	$^{(2,77)}F_0'$	67.68	(47)	65.01
$(..v_3..v_6..v_7..)/(..v_3 \pm 1..v_6 \mp 1..v_7 \pm 1..)$	$^{(6,37)}F_0'$	−219.95	(47)	−218.61
$(..v_5..v_6..v_9..)/(..v_5 \pm 1..v_6 \mp 1..v_9 \pm 1..)$	$^{(6,59)}F_0'$	−219.96	(47)	−229.11
$(..v_4..v_8..v_9..)/(..v_4 \pm 1..v_8 \mp 1..v_9 \pm 1..)$	$^{(8,49)}F_0'$	73.32	(47)	68.45
$(..v_5..v_7..v_8..)/(..v_5 \pm 1..v_7 \pm 1..v_8 \mp 1..)$	$^{(8,57)}F_0'$	−20.95	(47)	−33.31

Notes: [a]Calculated on the basis of isotopic relations.
[b]Obtained from analysis of experimental data [45].

In column *I* of Table 7 one can see results of estimations of the ro-vibrational coefficients, $\alpha_\lambda'^\beta$, on the basis of Equation (26) using only one parameter Y_3 of the CH_4 species. Columns *II* of Table 7 presents, for comparison, values of the corresponding parameters obtained from the fit of experimental data [45]. One can see more than satisfactory correlations between all pairs of numerical values. Also for comparison, values of $\alpha_\lambda'^\beta$-coefficients from Table 11 of [46] are shown in column *III* of Table 7. Large enough differences between the values of the $\alpha_\lambda'^\beta$-coefficients (with $\lambda = 3, 5, 7, 9$) in column *III*, on the one hand, and in columns *I* and *II*, on the other hand, appeared because in [46] resonance interactions were not taken into account in $\alpha_\lambda'^\beta$.

7. Isotopic relations between spectroscopic parameters of the CH_4 and CH_2D_2 species: Fermi-type interactions

As is known, any Fermi-type resonance interaction in the C_{2v}-symmetry molecules (the CH_2D_2 is just a molecule of such type symmetry) is described by an operator of the following form (see, e.g. [47]):

$$H_{v\tilde{v}} = {}^{v\tilde{v}}F_0 + {}^{v\tilde{v}}F_K J_z^2 + {}^{v\tilde{v}}F_J J^2 + {}^{v\tilde{v}}F_{KK} J_z^4 + {}^{v\tilde{v}}F_{KJ} J_z^2 J^2$$
$$+ {}^{v\tilde{v}}F_{JJ} J^4 + \ldots + {}^{v\tilde{v}}F_{xy}(J_x^2 - J_y^2)$$
$$+ {}^{v\tilde{v}}F_{Kxy}\{J_z^2, (J_x^2 - J_y^2)\}_+ + 2\,{}^{v\tilde{v}}F_{Jxy} J^2(J_x^2 - J_y^2) + \ldots. \tag{27}$$

Here the first term is the pure vibrational part of the interaction; the other terms describe different types of

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rotational dependencies of the Fermi-type interaction caused by the presence in a molecule of rotation–vibration interactions.

Our analysis of the ro-vibrational spectra of CH_2D_2 shows [13,14,45], at least, the following six types of pure vibrational resonance interactions should be taken into account if one wants to correctly describe high resolution spectra of that molecule:

(1) interaction of the type $\langle v|\dots|\tilde{v}\rangle \equiv \langle v_\lambda \dots v_\mu| \dots |v_\lambda \pm 2 \dots v_\mu \mp 2\rangle$, with $\lambda = 4$, $\mu = 7$, or $\lambda = 1$, $\mu = 6$;

(2) interaction of the type $\langle v|\dots|\tilde{v}\rangle \equiv \langle v_\lambda \dots v_\mu \dots v_\nu|\dots|v_\lambda \pm 2 \dots v_\mu \mp 1 \dots v_\nu \mp 1\rangle$, with $\lambda = 9$, $\mu = 3$, $\nu = 4$;

(3) interaction of the type $\langle v|\dots|\tilde{v}\rangle \equiv \langle v_\lambda \dots v_\mu \dots v_\nu \dots v_\xi|\dots|v_\lambda \pm 1 \dots v_\mu \pm 1 \dots v_\nu \mp 1 \dots v_\xi \mp 1\rangle$, where (a) $\lambda = 4$, $\mu = 5$, $\nu = 7$, $\xi = 9$; (b) $\lambda = 3$, $\mu = 7$, $\nu = 5$, $\xi = 9$; (c) $\lambda = 4$, $\mu = 9$, $\nu = 5$, $\xi = 7$; (d) $\lambda = 3$, $\mu = 9$, $\nu = 5$, $\xi = 7$; (e) $\lambda = 1$, $\mu = 7$, $\nu = 4$, $\xi = 6$.

(4) interaction of the type $\langle v|\dots|\tilde{v}\rangle \equiv \langle v_\lambda \dots v_\mu|\dots|v_\lambda \pm 1 \dots v_\mu \mp 1\rangle$, where $\lambda = 3$ and $\mu = 4$;

(5) interaction of the type $\langle v|\dots|\tilde{v}\rangle \equiv \langle v_\lambda \dots v_\mu|\dots|v_\lambda \pm 1 \dots v_\mu \mp 2\rangle$, where (a) $\lambda = 1$, $\mu = 3$, or 9, (b) $\lambda = 2$, $\mu = 4$, or 7;

(6) interaction of the type $\langle v|\dots|\tilde{v}\rangle \equiv \langle v_\lambda \dots v_\mu \dots v_\nu|\dots|v_\lambda \pm 1 \dots v_\mu \mp 1_\nu \mp 1\rangle$, where (a) $\lambda = 6$, $\mu = 3$, $\nu = 7$, or $\mu = 5$, $\nu = 9$, (b) $\lambda = 8$, $\mu = 4$, $\nu = 9$, or $\mu = 5$, $\nu = 7$.

7.1. Darling–Dennison interaction $\langle v_\lambda \dots v_\mu|\dots|v_\lambda \pm 2 \dots v_\mu \mp 2\rangle$

To discuss the main (pure vibrational) part of the Darling–Dennison interaction, the following formula was derived on the basis of the operator perturbation theory from [41]:

$$\langle v_\lambda \dots v_\mu|\dots|v_\lambda + 2 \dots v_\mu - 2\rangle = \langle v_\lambda + 2 \dots v_\mu - 2|\dots|v_\lambda \dots v_\mu\rangle$$
$$= \left(\frac{v_\lambda + 1}{2}\right)^{1/2}\left(\frac{v_\lambda + 2}{2}\right)^{1/2}\left(\frac{v_\mu}{2}\right)^{1/2}\left(\frac{v_\mu - 1}{2}\right)^{1/2}{}^{(\lambda\lambda,\mu\mu)}F_0',$$
(28)

where

$${}^{(\lambda\lambda,\mu\mu)}F_0' = k_{\lambda\lambda\mu\mu}' + \frac{k_{\lambda\lambda\lambda}'k_{\lambda\mu\mu}'}{2}\left(\frac{1}{\omega_\lambda'} + \frac{3\omega_\lambda'}{4\omega_\mu'^2 - \omega_\lambda'^2}\right)$$
$$+ \frac{k_{\mu\mu\mu}'k_{\lambda\lambda\mu}'}{2}\left(\frac{1}{\omega_\mu'} + \frac{3\omega_\mu'}{4\omega_\lambda'^2 - \omega_\mu'^2}\right) - k_{\lambda\lambda\mu}'^2$$
$$\times \left(\frac{1}{\omega_\mu'} + \frac{1}{2\omega_\lambda' - \omega_\mu'}\right) - k_{\lambda\mu\mu}'^2\left(\frac{1}{\omega_\lambda'} + \frac{1}{2\omega_\mu' - \omega_\lambda'}\right)$$

$$+ \sum_{\xi \neq \lambda, \mu} \frac{k_{\lambda\mu\xi}'^2}{4}\left(\frac{1}{\omega_\lambda' - \omega_\mu' - \omega_\xi'} + \frac{1}{\omega_\mu' - \omega_\lambda' - \omega_\xi'}\right)$$
$$- \sum_{\xi \neq \lambda, \mu} \frac{k_{\lambda\lambda\xi}'k_{\mu\mu\xi}'}{4}\left(\frac{1}{2\omega_\lambda' + \omega_\xi'} + \frac{1}{2\omega_\mu' + \omega_\xi'}\right)$$
$$+ \sum_{\xi \neq \lambda, \mu} \frac{k_{\lambda\lambda\xi}'k_{\mu\mu\xi}'}{4}\left(\frac{1}{2\omega_\lambda' - \omega_\xi'} + \frac{1}{2\omega_\mu' - \omega_\xi'}\right)$$
$$- \sum_\beta B_\beta'^e \left(\zeta_{\lambda\mu}'^\beta\right)^2 \frac{\left(\omega_\lambda' + \omega_\mu'\right)^2}{\omega_\lambda'\omega_\mu'}.$$
(29)

In Equation (29), if $\xi = 1$, and λ or $\mu = 3$ and/or 9, then the whole sum $\left(1/(2\omega_\lambda' - \omega_1') + 1/(2\omega_\mu' - \omega_1')\right)$ in the next to last term should be omitted. Also, if $\xi = 2$, and λ or $\mu = 4$ and/or 7, then the whole sum $(1/(2\omega_\lambda' - \omega_2') + 1/(2\omega_\mu' - \omega_2'))$ in the next to last term should be omitted.

Now, taking into account Equations (16), (17), (21), (25), and data from Table 3, one obtains:

$$\frac{32}{3}B^e = -\frac{101}{11}\ {}^{(44,77)}F_0' = -\frac{23}{50}\ {}^{(11,66)}F_0' = \frac{\hbar}{\pi c m \rho^2}.$$
(30)

The results of the estimation with isotopic relations (30) are shown in the first two lines of column *I* of Table 8. For comparison, column *II* presents the values of the same parameters obtained from an analysis of experimental rotation–vibration spectra [45]. One can see good correspondence of both results.

As the analysis shows, to derive formulas (analogous to Equations (28) and (29)) for the higher order interaction parameters, F_K', F_J', etc., in Equation (27), it is necessary to take into account, at least, fourth order perturbation theory. Because, on the one hand, it is a separate difficult problem and, on the other hand, values of these parameters must be 10^3–10^4 times smaller than values of the main, ${}^{(\lambda\lambda,\mu\mu)}F_0'$, parameters, we do not make an attempt here to discuss isotopic relations for these F_K', F_J', etc., parameters.

7.2. Interaction of the $\langle v_\lambda \dots v_\mu \dots v_\nu|\dots|v_\lambda \mp 2 \dots v_\mu \pm 1 \dots v_\nu \pm 1\rangle$ type

It is possible to show using the operator perturbation theory, that the resonance interaction of the type $\langle v_\lambda \dots v_\mu \dots v_\nu|\dots|v_\lambda \mp 2 \dots v_\mu \pm 1 \dots v_\nu \pm 1\rangle$ is described by the following expression:

$$\langle v_\lambda \dots v_\mu \dots v_\nu|\dots|v_\lambda - 2 \dots v_\mu + 1 \dots v_\nu + 1\rangle$$
$$= \langle v_\lambda - 2 \dots v_\mu + 1 \dots v_\nu + 1|\dots|v_\lambda \dots v_\mu \dots v_\nu\rangle$$
$$= \left(\frac{v_\lambda}{2}\right)^{1/2}\left(\frac{v_\lambda - 1}{2}\right)^{1/2}\left(\frac{v_\mu + 1}{2}\right)^{1/2}\left(\frac{v_\nu + 1}{2}\right)^{1/2}{}^{(\lambda\lambda,\mu\nu)}F_0',$$
(31)

where

$$^{(\lambda\lambda,\mu\nu)}F'_0 = k'_{\lambda\lambda\mu\nu} + \frac{3k'_{\lambda\lambda\lambda}k'_{\lambda\mu\nu}}{2}\left[\frac{1}{3\omega'_\lambda} + \frac{\omega'_\lambda}{(\omega'_\mu+\omega'_\nu)^2 - \omega'^2_\lambda}\right]$$

$$+ \frac{k'_{\lambda\mu\mu}k'_{\lambda\mu\nu}}{2}\left[\frac{\omega'_\mu+\omega'_\nu}{\omega'_\lambda(\omega'_\lambda - \omega'_\mu - \omega'_\nu)}\right.$$

$$\left. + \frac{3\omega'_\mu - \omega'_\nu}{(\omega'_\lambda+\omega'_\mu-\omega'_\nu)(\omega'_\lambda - 2\omega'_\mu)}\right] + \frac{k'_{\lambda\nu\nu}k'_{\lambda\mu\nu}}{2}$$

$$\times \left[\frac{\omega'_\mu+\omega'_\nu}{\omega'_\lambda(\omega'_\lambda - \omega'_\mu - \omega'_\nu)}\right.$$

$$\left. + \frac{3\omega'_\nu - \omega'_\mu}{(\omega'_\lambda+\omega'_\nu-\omega'_\mu)(\omega'_\lambda - 2\omega'_\nu)}\right] + k'_{\lambda\lambda\mu}k'_{\mu\mu\nu}$$

$$\times \left[\frac{\omega'_\mu}{4\omega'^2_\lambda - \omega'^2_\mu} + \frac{\omega'_\mu}{\omega'_\nu(2\omega'_\mu+\omega'_\nu)}\right] + k'_{\lambda\lambda\nu}k'_{\mu\nu\nu}$$

$$\times \left[\frac{\omega'_\nu}{4\omega'^2_\lambda - \omega'^2_\nu} + \frac{\omega'_\nu}{\omega'_\mu(2\omega'_\nu+\omega'_\mu)}\right]$$

$$- 2k'_{\lambda\lambda\mu}k'_{\lambda\lambda\nu}\left[\frac{\omega'_\lambda}{\omega'_\mu(2\omega'_\lambda - \omega'_\mu)} + \frac{\omega'_\lambda}{\omega'_\nu(2\omega'_\lambda - \omega'_\nu)}\right]$$

$$+ \sum_{\xi\neq\lambda,\mu,\nu}\frac{k'_{\lambda\mu\xi}k'_{\lambda\nu\xi}}{2}\left[\frac{\omega'_\xi}{(\omega'_\lambda - \omega'_\mu)^2 - \omega'^2_\xi}\right.$$

$$\left. + \frac{\omega'_\xi}{(\omega'_\lambda - \omega'_\nu)^2 - \omega'^2_\xi}\right] + \sum_{\xi\neq\lambda,\mu,\nu}\frac{k'_{\lambda\lambda\xi}k'_{\mu\nu\xi}}{4}$$

$$\times \left[\frac{2\omega'_\lambda + \omega'_\mu + \omega'_\nu - 2\omega'_\xi}{(2\omega'_\lambda - \omega'_\xi)(\omega'_\mu + \omega'_\nu - \omega'_\xi)}\right.$$

$$\left. - \frac{2\omega'_\lambda + \omega'_\mu + \omega'_\nu + 2\omega'_\xi}{(2\omega'_\lambda + \omega'_\xi)(\omega'_\mu + \omega'_\nu + \omega'_\xi)}\right]$$

$$- 2\sum_\beta B'^e_\beta\left(\zeta'\beta_{\lambda\mu}\zeta'^\beta_{\lambda\nu}\right)\frac{(\omega'_\lambda + \omega'_\mu)(\omega'_\lambda + \omega'_\nu)}{\omega'_\lambda(\omega'_\mu\omega'_\nu)^{1/2}}. \tag{32}$$

In Equation (32), the first term in the last square bracket should be omitted in the presence of resonance situations.

Now, we take again into account Equations (16), (17), (21), (25), and data from Table 3 in Equation (32), and obtain the following simple isotopic relation for the resonance interaction parameter $^{(99,34)}F'_0$, that is essential in the CH_2D_2 molecule:

$$\frac{32}{3}B^e = -\frac{85}{2}{}^{(99,34)}F'_0 = \frac{\hbar}{\pi cm\rho^2}. \tag{33}$$

As before, the result of the numerical estimation with relation (33) and comparison with the result obtained from experimental data are presented in Table 8. If one takes into account a small absolute value of the parameter $^{(99,34)}F'_0$, the result of the theoretical estimation can be considered as more than

satisfactory, in spite of the difference in signs of the calculated and experimental values. For the same reason as in the previous subsection, we do not consider here higher order interaction parameters, F'_K, F'_J, etc.

7.3. Interaction of the $\langle v_\lambda..v_\mu..v_\nu..v_\xi|..|v_\lambda \mp 1..v_\mu \mp 1..v_\nu \pm 1..v_\xi \pm 1\rangle$ type

Analogous to Subsection 7.2, it is possible to show that the resonance interaction of the type $\langle v_\lambda \ldots v_\mu \ldots v_\nu \ldots v_\xi| \ldots |v_\lambda \mp 1 \ldots v_\mu \mp 1 \ldots v_\nu \pm 1 \ldots v_\xi \pm 1\rangle$ is described by the following expression:

$$\langle v_\lambda \ldots v_\mu \ldots v_\nu \ldots v_\xi| \ldots |v_\lambda - 1 \ldots v_\mu$$
$$- 1 \ldots v_\nu + 1 \ldots v_\xi + 1\rangle$$
$$= \langle v_\lambda - 1 \ldots v_\mu - 1 \ldots v_\nu + 1 \ldots v_\xi$$
$$+ 1| \ldots |v_\lambda \ldots v_\mu \ldots v_\nu \ldots v_\xi\rangle$$
$$= \left(\frac{v_\lambda}{2}\right)^{1/2}\left(\frac{v_\mu}{2}\right)^{1/2}\left(\frac{v_\nu+1}{2}\right)^{1/2}\left(\frac{v_\xi+1}{2}\right)^{1/2}{}^{(\lambda\mu,\nu\xi)}F'_0, \tag{34}$$

where the formula for parameters $^{(\lambda\mu,\nu\xi)}F'_0$ is presented in the first subsection of Appendix 2.

As in the previous subsections, using Equation (64) from Appendix 2, Equations (16), (17), (21), (25), and data from Table 3 allows one to obtain the following simple isotopic relations for essential interaction parameters of the CH_2D_2 molecule:

$$\frac{32}{3}B^e = \frac{34}{5}{}^{(45,79)}F'_0 = -\frac{18}{5}{}^{(37,59)}F'_0 = \frac{14}{5}{}^{(49,57)}F'_0$$
$$= \frac{23}{10}{}^{(39,57)}F'_0 = -\frac{15}{2}{}^{(17,46)}F'_0 = \frac{\hbar}{\pi cm\rho^2} \tag{35}$$

Results of estimations of the values of interaction parameters, $^{(45,79)}F'_0$, $^{(37,59)}F'_0$, $^{(49,57)}F'_0$, $^{(39,57)}F'_0$, and $^{(17,46)}F'_0$, are presented in Table 8 (column *I*) together with the values of corresponding parameters obtained from analysis of experimental data (reproduced in column *II* from [45]).

7.4. Fermi-type interaction, $\langle v_\lambda \ldots v_\mu| \ldots |v_\lambda \pm 1 \ldots v_\mu \mp 1\rangle$

7.4.1. *Pure vibrational interaction coefficient,* $^{(\lambda,\mu)}F'_0$

The formula for the $^{(\lambda,\mu)}F'_0$-coefficient was obtained on the basis of operator perturbation theory in the following form:

$$\langle v_\lambda \ldots v_\mu| \ldots |v_\lambda + 1 \ldots v_\mu - 1\rangle$$
$$= \langle v_\lambda + 1 \ldots v_\mu - 1| \ldots |v_\lambda \ldots v_\mu\rangle$$
$$= \left(\frac{v_\lambda+1}{2}\right)^{1/2}\left(\frac{v_\mu}{2}\right)^{1/2}{}^{(\lambda,\mu)}F'_0, \tag{36}$$

where again the formula for parameters $^{(\lambda,\mu)}F_0'$ is presented in the second subsection of Appendix 2.

7.4.2. Ro-vibrational interaction coefficient, $^{(\lambda,\mu)}F_K'$, $^{(\lambda,\mu)}F_J'$, and $^{(\lambda,\mu)}F_{xy}'$

Formulas for the corresponding $^{(\lambda,\mu)}F_{..}'$-coefficient were obtained in the following form:

$$\langle v_\lambda \ldots v_\mu | \ldots | v_\lambda + 1 \ldots v_\mu - 1 \rangle$$
$$= \langle v_\lambda + 1 \ldots v_\mu - 1 | \ldots | v_\lambda \ldots v_\mu \rangle$$
$$= \left(\frac{v_\lambda + 1}{2}\right)^{1/2} \left(\frac{v_\mu}{2}\right)^{1/2} {}^{(\lambda,\mu)}F_{..}', \quad (37)$$

where $^{(\lambda,\mu)}F_{..}' = {}^{(\lambda,\mu)}F_K'$, $^{(\lambda,\mu)}F_J'$, or $^{(\lambda,\mu)}F_{xy}'$;

$$2^{(\lambda,\mu)}F_K' = 2^{(\lambda,\mu)}F_z' - {}^{(\lambda,\mu)}F_x' - {}^{(\lambda,\mu)}F_y', \quad (38)$$

$$2^{(\lambda,\mu)}F_J' = {}^{(\lambda,\mu)}F_x' + {}^{(\lambda,\mu)}F_y', \quad (39)$$

$$2^{(\lambda,\mu)}F_{xy}' = {}^{(\lambda,\mu)}F_x' - {}^{(\lambda,\mu)}F_y', \quad (40)$$

and the formula for parameters $^{(\lambda,\mu)}F_\alpha'$ ($\alpha = x, y, z$) is presented in Appendix 2.

In the CH_2D_2 molecule, such kinds of resonance interaction correspond to only one situation, namely, $\lambda = 3$ and $\mu = 4$. In this case, isotopic relations were derived in the following form:

$$^{(3,4)}F_0' = \frac{92}{75} B^e \left[\frac{1}{2} V_1 + \frac{23}{10} V_2 - \frac{13}{5} V_3 - \frac{2}{125} V_4 - \frac{27}{100} V_5 \right.$$
$$\left. - \frac{57}{10} V_6 + \frac{39}{10} V_7 + \frac{17}{5} V_8 + \frac{11}{20} V_9 \right] \quad (41)$$

and

$$Y_3 = \frac{5}{2} {}^{(3,4)}F_x' = -\frac{8}{5} {}^{(3,4)}F_y' = \frac{6}{5} {}^{(3,4)}F_z'$$
$$= -\frac{\hbar^2}{16\pi c \rho^4 F_{11}^{1/2} m^{3/2}}. \quad (42)$$

Numerical calculations with relations (42) give the following result: $^{(3,4)}F_x' = -0.0134 \, \text{cm}^{-1}$, $^{(3,4)}F_y' = 0.0209 \, \text{cm}^{-1}$, and $^{(3,4)}F_z' = -0.0278 \, \text{cm}^{-1}$. Again as earlier, only one parameter (parameter Y_3 of the CH_4 molecule) was used as the initial one. Values of corresponding parameters taken from analysis of experimental data [45] are: $^{(3,4)}F_x' = -0.0163 \, \text{cm}^{-1}$, $^{(3,4)}F_y' = 0.0159 \, \text{cm}^{-1}$, and $^{(3,4)}F_z' = -0.0327 \, \text{cm}^{-1}$. If one takes into account that the predicted values were obtained without any information, at all, about CH_2D_2, one can mark a more than satisfactory correspondence between the predicted and experimental values.

7.5. Interaction of the $\langle v_\lambda..v_\mu..|..|v_\lambda \pm 1..v_\mu \mp 2..\rangle$ and $\langle v_\lambda..v_\mu..v_\nu..|..|v_\lambda \pm 1 \ldots v_\mu \mp 1 \ldots v_\nu \mp 1..\rangle$ types

It is very well known, that the main parts of such kinds of interactions are proportional to the corresponding cubic anharmonic parameters, $k_{\lambda\mu\nu}$. Namely,

$$\langle v_\lambda..v_\mu..|..|v_\lambda + 1..v_\mu - 2..\rangle =$$
$$\langle v_\lambda + 1..v_\mu - 2..|..|v_\lambda..v_\mu..\rangle =$$
$$\left(\frac{v_\lambda + 1}{2}\right)^{1/2} \left(\frac{v_\mu}{2}\right)^{1/2} \left(\frac{v_\mu - 1}{2}\right)^{1/2} {}^{(\lambda,\mu\mu)}F_0', \quad (43)$$

where

$$^{(\lambda,\mu\mu)}F_0' = k_{\lambda\mu\mu}', \quad (44)$$

and

$$\langle v_\lambda..v_\mu..v_\nu..|..|v_\lambda + 1..v_\mu - 1..v_\nu - 1..\rangle =$$
$$\langle v_\lambda + 1..v_\mu - 1..v_\nu - 1..|..|v_\lambda..v_\mu..v_\nu..\rangle =$$
$$\left(\frac{v_\lambda + 1}{2}\right)^{1/2} \left(\frac{v_\mu}{2}\right)^{1/2} \left(\frac{v_\nu}{2}\right)^{1/2} {}^{(\lambda,\mu\nu)}F_0', \quad (45)$$

where

$$^{(\lambda,\mu\nu)}F_0' = k_{\lambda\mu\nu}'. \quad (46)$$

On that basis, isotopic relations can be obtained easily in the following form:

$$-\frac{17}{5}(B^e \omega_3)^{1/2} = \frac{8}{3} {}^{(1,99)}F_0' = 5 {}^{(1,33)}F_0' = -\frac{13}{2} {}^{(2,44)}F_0'$$
$$= -\frac{13}{2} {}^{(2,77)}F_0' = 2 {}^{(6,37)}F_0' = 2 {}^{(6,59)}F_0'$$
$$= -6 {}^{(8,49)}F_0' = 21 {}^{(8,57)}F_0' = \frac{15}{2} {}^{(6,27)}F_0'. \quad (47)$$

Results of numerical estimations of the interaction parameters with relation (50) can be found in column I of Table 3 together with the corresponding values obtained from an analysis of the experimental data (column II). One can see good correlations of both sets of parameters.

8. Isotopic relations between spectroscopic parameters of the CH_4 and CH_2D_2 species: Coriolis-type interactions

As was discussed in [47], Coriolis-type interactions in an arbitrary asymmetric top molecule of the $C_{2\nu}$ symmetry group can be described by the three types of coupling operators $H^{\nu\tilde{\nu}}$, ($\nu \neq \tilde{\nu}$). In this case, if the

product $\Gamma = \Gamma^v \otimes \Gamma^{\tilde{v}}$ of the symmetry species of the states v and $\tilde{v}$ is equal to B_1, then the states v and $\tilde{v}$ are connected by a Coriolis resonance interaction of the form:

$$H_{v\tilde{v}} = \mathrm{i}J_z H_{v\tilde{v}}^{(1)} + \{J_x, J_y\}_+ H_{v\tilde{v}}^{(2)} + H_{v\tilde{v}}^{(2)}\{J_x, J_y\}_+ \\ + \{\mathrm{i}J_z, (J_x^2 - J_y^2)\}_+ H_{v\tilde{v}}^{(3)} + H_{v\tilde{v}}^{(3)}\{\mathrm{i}J_z, (J_x^2 - J_y^2)\}_+ + \ldots, \tag{48}$$

where $\{A, B\}$ denotes the anticommutator, $(AB + BA)$.

When $\Gamma = B_2$, then the following Coriolis interaction is allowed:

$$H_{v\tilde{v}} = \mathrm{i}J_y H_{v\tilde{v}}^{(1)} + H_{v\tilde{v}}^{(1)}\mathrm{i}J_y + \{J_x, J_z\}_+ H_{v\tilde{v}}^{(2)} + H_{v\tilde{v}}^{(2)}\{J_x, J_z\}_+ \\ + \{\mathrm{i}J_y, (J_x^2 - J_y^2)\}_+ H_{v\tilde{v}}^{(3)} + H_{v\tilde{v}}^{(3)}\{\mathrm{i}J_y, (J_x^2 - J_y^2)\}_+ + \ldots. \tag{49}$$

Finally, when $\Gamma = A_2$, a Coriolis interaction of the following type is possible:

$$H_{v\tilde{v}} = \mathrm{i}J_x H_{v\tilde{v}}^{(1)} + H_{v\tilde{v}}^{(1)}\mathrm{i}J_x + \{J_y, J_z\}_+ H_{v\tilde{v}}^{(2)} + H_{v\tilde{v}}^{(2)}\{J_y, J_z\}_+ \\ + \{\mathrm{i}J_x, (J_x^2 - J_y^2)\}_+ H_{v\tilde{v}}^{(3)} + H_{v\tilde{v}}^{(3)}\{\mathrm{i}J_x, (J_x^2 - J_y^2)\}_+ + \ldots. \tag{50}$$

The operators $H_{v\tilde{v}}^{(i)}$, $i = 1, 2, 3, \ldots$, in Equations (48)–(50) have the form:

$$H_{v\tilde{v}}^{(i)} = \frac{1}{2}\,{}^{v\tilde{v}}C^i + {}^{v\tilde{v}}C_K^i J_z^2 + \frac{1}{2}\,{}^{v\tilde{v}}C_J^i J^2 + {}^{v\tilde{v}}C_{KK}^i J_z^4 \\ + {}^{v\tilde{v}}C_{KJ}^i J_z^2 J^2 + \frac{1}{2}\,{}^{v\tilde{v}}C_{JJ}^i J^4 + {}^{v\tilde{v}}C_{KKK}^i J_z^6 \\ + {}^{v\tilde{v}}C_{KKJ}^i J_z^4 J^2 + {}^{v\tilde{v}}C_{KJJ}^i J_z^2 J^4 + \frac{1}{2}\,{}^{v\tilde{v}}C_{JJJ}^i J^6 + \ldots. \tag{51}$$

As in the previous section, analysis of the ro-vibrational spectra of the CH_2D_2 molecule [13,14,45], showed that the following three types of Coriolis interactions are mostly important when high resolution ro-vibrational analysis is fulfilled:

(1) interaction of the type $\langle v| \ldots |\tilde{v}\rangle \equiv \langle v_\lambda \ldots v_\mu| \ldots |v_\lambda \pm 1 \ldots v_\mu \mp 1\rangle$, with different combinations of indexes $\lambda, \mu = 3, 4, 5, 7, 9$ $\lambda \neq \mu$, or $\lambda = 1$, $\mu = 6$, or $\lambda = 2$, $\mu = 8$;
(2) interaction of the type $\langle v| \ldots |\tilde{v}\rangle \equiv \langle v_\lambda \ldots v_\mu| \ldots |v_\lambda \pm 1 \ldots v_\mu \mp 2\rangle$; in this case, $\mu = 3, 4, 5, 9$, if $\lambda = 6$, or $\mu = 3, 4, 5, 7$, if $\lambda = 8$;
(3) interaction of the type $\langle v| \ldots |\tilde{v}\rangle \equiv \langle v_\lambda \ldots v_\mu \ldots v_\nu| \ldots |v_\lambda \pm 1 \ldots v_\mu \mp 1 \ldots v_\nu \mp 1\rangle$, with $\mu/\nu = 3/9$ and $\lambda = 1, 6$, or $\mu/\nu = 4/7, 4/9$ and $\lambda = 2$, or $\mu/\nu = 4/5, 7/9$ and $\lambda = 8$.

8.1. Coriolis interaction $\langle v| \ldots |\tilde{v}\rangle \equiv \langle v_\lambda \ldots v_\mu| \ldots |v_\lambda \pm 1 \ldots v_\mu \mp 1\rangle$

In this case, the main interaction operators in Equations (48)–(51) have the following form:

$$\langle v_\lambda..v_\mu|..|v_\lambda + 1..v_\mu - 1\rangle \\ = \langle v_\lambda + 1..v_\mu - 1|..|v_\lambda..v_\mu\rangle^* \\ = \mathrm{i}J_\alpha\left(\frac{v_\lambda + 1}{2}\right)^{1/2}\left(\frac{v_\mu}{2}\right)^{1/2}{}^{(\lambda,\mu)}C_\alpha' + (J_\alpha J_\beta + J_\beta J_\alpha) \\ \times \left(\frac{v_\lambda + 1}{2}\right)^{1/2}\left(\frac{v_\mu}{2}\right)^{1/2}{}^{(\lambda,\mu)}C_{\alpha\beta}', \tag{52}$$

where

$$^{(\lambda,\mu)}C_\alpha' = 2\left(B_\alpha'^e \zeta_{\lambda\mu}'^\alpha\right)\frac{\omega_\mu' + \omega_\lambda'}{\left(\omega_\lambda'\omega_\mu'\right)^{1/2}}, \tag{53}$$

and

$$^{(\lambda,\mu)}C_{\alpha\beta}' = \frac{3}{2}\sum_\gamma \frac{B_\alpha'^e B_\beta'^e B_\gamma'^e}{\sqrt{\omega_\lambda'\omega_\mu'}}\left(\frac{4\pi c}{\hbar}\right)\left(a_\lambda'^{\alpha\gamma}a_\mu'^{\beta\gamma} + a_\mu'^{\alpha\gamma}a_\lambda'^{\beta\gamma}\right) \\ + \sqrt{2}B_\alpha'^e B_\beta'^e\left(\frac{4\pi c}{\hbar}\right)^{1/2}\left\{\frac{a_\lambda'^{\alpha\beta}k_{\lambda\lambda\mu}'}{\sqrt{\omega_\lambda'}}\frac{(\omega_\mu' + \omega_\lambda')^2 - 2\omega_\mu'^2}{\omega_\mu'\omega_\lambda'(2\omega_\lambda' - \omega_\mu')}\right. \\ \left. + \frac{a_\mu'^{\alpha\beta}k_{\lambda\mu\mu}'}{\sqrt{\omega_\mu'}}\frac{(\omega_\lambda' + \omega_\mu')^2 - 2\omega_\lambda'^2}{\omega_\lambda'\omega_\mu'(2\omega_\mu' - \omega_\lambda')}\right\} \\ + \sum_{\xi \neq \lambda,\mu}\frac{B_\alpha'^e B_\beta'^e}{\sqrt{2\omega_\xi'}}\left(\frac{4\pi c}{\hbar}\right)^{1/2}a_\xi'^{\alpha\beta}k_{\lambda\mu\xi}'\frac{2\omega_\xi'^2 - (\omega_\lambda' - \omega_\mu')^2}{\omega_\xi'\left[\omega_\xi'^2 - (\omega_\lambda' - \omega_\mu')^2\right]} \\ - \sum_{\xi \neq \lambda,\mu}\left[\left(B_\alpha'^e \zeta_{\lambda\xi}'^\alpha\right)\left(B_\beta'^e \zeta_{\mu\xi}'^\beta\right) + \left(B_\alpha'^e \zeta_{\mu\xi}'^\alpha\right)\left(B_\beta'^e \zeta_{\lambda\xi}'^\beta\right)\right] \\ \times \frac{(\omega_\lambda' - \omega_\xi')(\omega_\mu' - \omega_\xi')}{2\omega_\xi'\sqrt{\omega_\lambda'\omega_\mu'}}\left(\frac{1}{\omega_\mu' + \omega_\xi'} + \frac{1}{\omega_\lambda' + \omega_\xi'}\right) \\ + \sum_{\xi \neq \lambda,\mu}\left[\left(B_\alpha'^e \zeta_{\mu\xi}'^\alpha\right)\left(B_\beta'^e \zeta_{\lambda\xi}'^\beta\right) + \left(B_\alpha'^e \zeta_{\lambda\xi}'^\alpha\right)\left(B_\beta'^e \zeta_{\mu\xi}'^\beta\right)\right] \\ \times \frac{(\omega_\lambda' + \omega_\xi')(\omega_\mu' + \omega_\xi')}{2\omega_\xi'\sqrt{\omega_\lambda'\omega_\mu'}}\left(\frac{1}{\omega_\mu' - \omega_\xi'} + \frac{1}{\omega_\lambda' - \omega_\xi'}\right). \tag{54}$$

In the last formula, if $\omega_\xi' \approx \omega_\lambda'$, or $\omega_\xi' \approx \omega_\mu'$, then the last line should be omitted.

As earlier, corresponding isotopic relations obtained on the basis of Equations (52)–(54) have the following form:

$$\frac{32}{3}B^e = -99^{(1,6)}C_z' = -43^{(2,8)}C_y' = -10^{(3,5)}C_x' \\ = -\frac{88}{5}\,{}^{(3,7)}C_z' = \frac{31}{5}\,{}^{(3,9)}C_y' = -\frac{43}{5}\,{}^{(4,5)}C_x' \\ = \frac{28}{5}\,{}^{(4,7)}C_z' = 285^{(4,9)}C_y' = -\frac{54}{5}\,{}^{(5,7)}C_y' \\ = \frac{76}{5}\,{}^{(5,9)}C_z' = -10^{(7,9)}C_x' = \frac{\hbar}{\pi cm\rho^2} \tag{55}$$

Table 9. Coriolis interaction parameters of the $\langle v_\lambda v_\mu | \ldots | v_\lambda + 1 v_\mu - 1 \rangle$ -type resonance interactions (in cm^{-1}).

α	λ	μ	I[a]	II[b]	α	β	λ	μ	I[c]	II[b]
z	1	6	−0.57	−0.73	x	y	1	6	−0.019	−0.018
y	2	8	−1.32	−1.38	x	z	2	8	0.033	0.034
x	3	5	−5.68	−6.15	y	z	3	5	−0.024	−0.024
z	3	7	−3.23	−3.16	x	y	3	7	−0.017	−0.016
y	3	9	9.16	9.07	x	z	3	9	−0.030	−0.028
x	4	5	−6.60	−6.53	y	z	4	5	0.020	0.020
z	4	7	10.14	10.11	x	y	4	7	0.033	0.030
y	4	9	0.20	−0.11	x	z	4	9	0.006	0.005
y	5	7	−5.26	−5.32	x	z	5	7	−0.056	−0.054
z	5	9	3.74	3.76	x	y	5	9	−0.039	−0.039
x	7	9	−5.68	−5.75	y	z	7	9	−0.018	−0.017

Notes: [a]Calculated on the basis of Equation (55).
[b]Taken from analysis of experimental data [45].
[c]Calculated on the basis of Equation (56).

and

$$Y_3 = \frac{10}{11} Y_1 = \frac{9}{5} \, ^{(1,6)}C'_{xy} = -^{(2,8)}C'_{xz} = \frac{9}{5} \, ^{(3,4)}C'_{xx}$$
$$= -\frac{9}{5} \, ^{(3,4)}C'_{yy} = \frac{22}{25} \, ^{(3,4)}C'_{zz} = \frac{7}{5} \, ^{(3,5)}C'_{yz}$$
$$= 2^{(3,7)}C'_{xy} = \frac{28}{25} \, ^{(3,9)}C'_{xz} = -\frac{17}{10} \, ^{(4,5)}C'_{yz}$$
$$= -^{(4,7)}C'_{xy} = -6^{(4,9)}C'_{xz} = \frac{3}{5} \, ^{(5,7)}C'_{xz} = \frac{17}{20} \, ^{(5,9)}C'_{xy}$$
$$= \frac{19}{10} \, ^{(7,9)}C'_{yz} = -\frac{\hbar^2}{16\pi c \rho^4 F_{11}^{1/2} m^{3/2}}. \tag{56}$$

Calculations with Equations (55) and (56) give the results which are presented in columns *I* of Table 9. For comparison, columns *II* present values of corresponding interaction parameters obtained from analysis of experimental dada from Ref. [45]. One can see good correspondence between these two sets of results.

8.2. Coriolis interaction $\langle v| \ldots |\tilde{v}\rangle \equiv \langle v_\lambda \ldots v_\mu | \ldots | v_\lambda \pm 1 \ldots v_\mu \mp 2\rangle$

If one uses the operator perturbation theory (e.g. from [41]), then it is possible to show that the resonance interaction of the type $\langle v| \ldots |\tilde{v}\rangle \equiv \langle v_\lambda \ldots v_\mu | \ldots | v_\lambda \pm 1 \ldots v_\mu \mp 2\rangle$ can be obtained as:

$$\langle v_\lambda .. v_\mu |..| v_\lambda + 1 .. v_\mu - 2\rangle = \langle v_\lambda + 1 .. v_\mu - 2 |..| v_\lambda .. v_\mu \rangle^*$$
$$= iJ_\alpha \left(\frac{v_\lambda + 1}{2}\right)^{1/2} \left(\frac{v_\mu}{2}\right)^{1/2} \left(\frac{v_\mu - 1}{2}\right)^{1/2} \, ^{(\lambda,\mu\mu)}C'_\alpha$$
$$+ (J_\alpha J_\beta + J_\beta J_\alpha) \left(\frac{v_\lambda + 1}{2}\right)^{1/2} \left(\frac{v_\mu}{2}\right)^{1/2} \left(\frac{v_\mu - 1}{2}\right)^{1/2} \, ^{(\lambda,\mu\mu)}C'_{\alpha\beta}, \tag{57}$$

where

$$^{(\lambda,\mu\mu)}C'_\alpha = \sum_\beta 2(2^{1/2}) B'^e_\alpha B'^e_\beta \zeta'^\beta_{\lambda\mu} \left(\frac{4\pi c}{\hbar}\right)^{1/2} a'^{\alpha\beta}_\mu \frac{\omega'_\lambda + \omega'_\mu}{\omega'_\mu (\omega'_\lambda)^{1/2}}$$

$$- 3\left(B'^e_\alpha \zeta'^\alpha_{\lambda\mu}\right) \frac{k'_{\mu\mu\mu}}{(\omega'_\lambda \omega'_\mu)^{1/2}} \left[\frac{2\omega'_\lambda \omega'_\mu}{\omega'^2_\lambda - \omega'^2_\mu} + \frac{2\omega'_\mu + \omega'_\lambda}{3\omega'_\mu}\right]$$
$$+ 2\left(B'^e_\alpha \zeta'^\alpha_{\lambda\mu}\right) \frac{k'_{\lambda\lambda\mu}}{(\omega'_\lambda \omega'_\mu)^{1/2}} \left[\frac{2\omega'_\lambda \omega'_\mu}{\omega'^2_\lambda - \omega'^2_\mu} + \frac{\omega'^2_\lambda}{\omega'_\mu(2\omega'_\lambda - \omega'_\mu)}\right]$$
$$+ \sum_{\xi \neq \lambda, \mu} \left(B'^e_\alpha \zeta'^\alpha_{\lambda\xi}\right) \frac{k'_{\mu\mu\xi}}{2(\omega'_\lambda \omega'_\xi)^{1/2}} \left[\frac{\omega'_\lambda - \omega'_\xi}{\omega'_\lambda + \omega'_\xi}\right.$$
$$+ \frac{\omega'_\lambda - \omega'_\xi}{2\omega'_\mu + \omega'_\xi} - \frac{\omega'_\lambda + \omega'_\xi}{\omega'_\lambda - \omega'_\xi} - \frac{\omega'_\lambda + \omega'_\xi}{2\omega'_\mu - \omega'_\xi}\right]$$
$$+ \sum_{\xi \neq \lambda, \mu} \left(B'^e_\alpha \zeta'^\alpha_{\mu\xi}\right) \frac{k'_{\lambda\mu\xi}}{2(\omega'_\mu \omega'_\xi)^{1/2}} \left[\frac{\omega'_\xi - \omega'_\mu}{\omega'_\xi + \omega'_\mu} + \frac{\omega'_\xi - \omega'_\mu}{\omega'_\lambda + \omega'_\xi - \omega'_\mu}\right.$$
$$\left. + \frac{\omega'_\xi + \omega'_\mu}{\omega'_\mu - \omega'_\xi} + \frac{\omega'_\xi + \omega'_\mu}{\omega'_\lambda - (\omega'_\mu + \omega'_\xi)}\right]. \tag{58}$$

In Equation (58) the following conditions should be taken into account: (a) if $\xi = 1$ and $\lambda = 6$; or if $\xi = 2$ and $\lambda = 8$; or if $\xi = 1$ and $\mu = 3$, or 9; or if $\xi = 2$ and $\mu = 4$, or 7, then the two last terms in the before the last square bracket should be omitted; (b) if $\omega'_\xi = 3, 4, 5, 7$, or 9; or if $\omega'_\lambda \approx (\omega'_\mu + \omega'_\xi)$, then the two last terms in the last line should be omitted. As in the above section, we do not give here the formula for the $^{(\lambda,\mu\mu)}C'_{\alpha\beta}$ interaction coefficients because to realize this, one would have to take into account fourth-order perturbation theory corrections.

Again, the using of the same information, as in the before situation, allowed us to obtain simple isotopic relations:

$$\left(-\frac{32}{3} B^e Y_3\right)^{1/2} = \frac{18}{5} \, ^{(6,33)}C'_z = \frac{42}{5} \, ^{(6,55)}C'_z = 18^{(8,33)}C'_y$$
$$= -\frac{9}{5} \, ^{(8,44)}C'_y = \frac{24}{5} \, ^{(8,77)}C'_y = \frac{93}{25} \, ^{(8,99)}C'_y$$
$$= \frac{\hbar^{3/2}}{4\pi c \rho^3 m^{5/4} F_{11}^{1/4}}. \tag{59}$$

Table 10. Some Coriolis interaction parameters, $^{(\lambda,\mu\nu)}C'_\alpha$, of the CH_2D_2 molecule (in cm^{-1}).

α	λ	μ	ν	I^a	II^b
y	8	3	3	0.077	0.084
y	8	4	4	−0.077	−0.069
y	8	7	7	0.287	0.333
y	8	9	9	0.370	0.405
z	6	3	3	0.383	0.367
z	6	5	5	0.164	0.171
x	8	4	7	0.626	0.591
y	1	3	9	−0.383	−0.317
y	2	4	9	0.370	0.327
z	2	4	7	0.689	0.763
z	8	4	5	0.834	0.906
z	8	7	9	1.013	0.825

Notes: ^{a}Calculated on the basis of Equation (59) or (61).
^{b}Taken from analysis of experimental data [45].

In the columns *I* of Table 10 one can find values of Coriolis-interaction parameters, $^{(\lambda,\mu\mu)}C'_\alpha$, that were obtained on the basis of Equation (59). For comparison, values of corresponding parameters from [45] are shown in column *II* of Table 10.

8.3. Coriolis interaction $\langle v|.|\tilde{v}\rangle \equiv \langle v_\lambda.v_\mu.v_\nu|.|v_\lambda \pm 1.v_\mu \mp 1.v_\nu \mp 1\rangle$

For a description of the $\langle v|..|\tilde{v}\rangle \equiv \langle v_\lambda..v_\mu..v_\nu|..|v_\lambda \pm 1..v_\mu \mp 1..v_\nu \mp 1\rangle$ type Coriolis interactions, the following formula was obtained:

$$\langle v_\lambda..v_\mu..v_\nu|..|v_\lambda + 1..v_\mu - 1..v_\nu - 1\rangle$$
$$= \langle v_\lambda + 1..v_\mu - 1..v_\nu - 1|..|v_\lambda..v_\mu..v_\nu\rangle^*$$
$$= iJ_\alpha \left(\frac{v_\lambda + 1}{2}\right)^{1/2} \left(\frac{v_\mu}{2}\right)^{1/2} \left(\frac{v_\nu}{2}\right)^{1/2} {}^{(\lambda,\mu\nu)}C'_\alpha$$
$$+ (J_\alpha J_\beta + J_\beta J_\alpha)\left(\frac{v_\lambda + 1}{2}\right)^{1/2} \left(\frac{v_\mu}{2}\right)^{1/2} \left(\frac{v_\nu}{2}\right)^{1/2} {}^{(\lambda,\mu\nu)}C'_{\alpha\beta},$$

$$(60)$$

where the form of parameter $^{(\lambda,\mu\nu)}C'_{\alpha\beta}$ is presented in Appendix 3.

Analogous to the previous subsection, we do not consider here the $^{(\lambda,\mu\nu)}C'_{\alpha\beta}$-parameters. As regards the isotopic relations for the $^{(\lambda,\mu\nu)}C'_\alpha$ coefficients, they were derived in the following form:

$$\left(-\frac{32}{3}B^e Y_3\right)^{1/2} = -\frac{18}{5} {}^{(1,39)}C'_y = 2 {}^{(2,47)}C'_z = \frac{93}{25} {}^{(2,49)}C'_y$$
$$= \frac{33}{20} {}^{(8,45)}C'_z = \frac{11}{5} {}^{(8,47)}C'_x = \frac{34}{25} {}^{(8,79)}C'_z$$
$$= \frac{\hbar^{3/2}}{4\pi c \rho^3 m^{5/4} F_{11}^{1/4}}.$$

$$(61)$$

Results of numerical estimations with formula (61) are given in Column *I* of Table 10. Column *II* presents values of corresponding parameters obtained from experimental data [45]. Taking into account that calculated values were determined without any information about characters of the CH_2D_2 molecule (only two parameters, B_e and Y_3, of the CH_4 species were used as the initial value), correspondence between predicted values and those obtained from analysis of experimental data can be considered as quite satisfactory.

9. Discussion

The general simple scheme used in the present paper together with the results of [23] gives us the possibility to expect that

(a) analogous results can be derived for more complicated molecules for which the methane is the prototype molecule;
(b) the obtained results can be useful in the study of complicated ro-vibrational structures of high excited vibrational states of the CH_2D_2 molecule because they can provide a good prediction of, at least, the qualitative picture of spectra. As an illustration of such possibility, on Figure 1, trace IV, we present a small part of the synthetic ro-vibrational spectrum of the CH_2D_2 molecule in the region 3450–3460 cm^{-1}. The synthetic spectrum shown on Figure 1, trace IV is a compilation of three individual synthetic spectra of the bands $\nu_4 + 2\nu_9$, Figure 1, trace I, $\nu_2 + \nu_9$, Figure 1, trace II, and $\nu_3 + 2\nu_4$, Figure 1, trace III (these three bands are the strongest bands located in the region of 3450–3460 cm^{-1}). An experimental spectrum, recorded in the same region at a temperature of 78 K in [13,45] is shown on the upper part of Figure 1 (see Figure 1, trace V).

Some remarks concerning a construction of the synthetic spectra should be made.

(a) From comparison of the synthetic spectra on Figure 1, traces I–IV one can see that the spectra of separate bands are moved with respect to each other by values of 2–4 cm^{-1}. At the same time, the relative line positions in all three bands are correct, more or less. It would appear that the isotopic relations derived in the present paper give values of good relative accuracy for all predicted spectroscopic parameters (both vibrational, and rotational and resonance ones) of the CH_2D_2 molecule
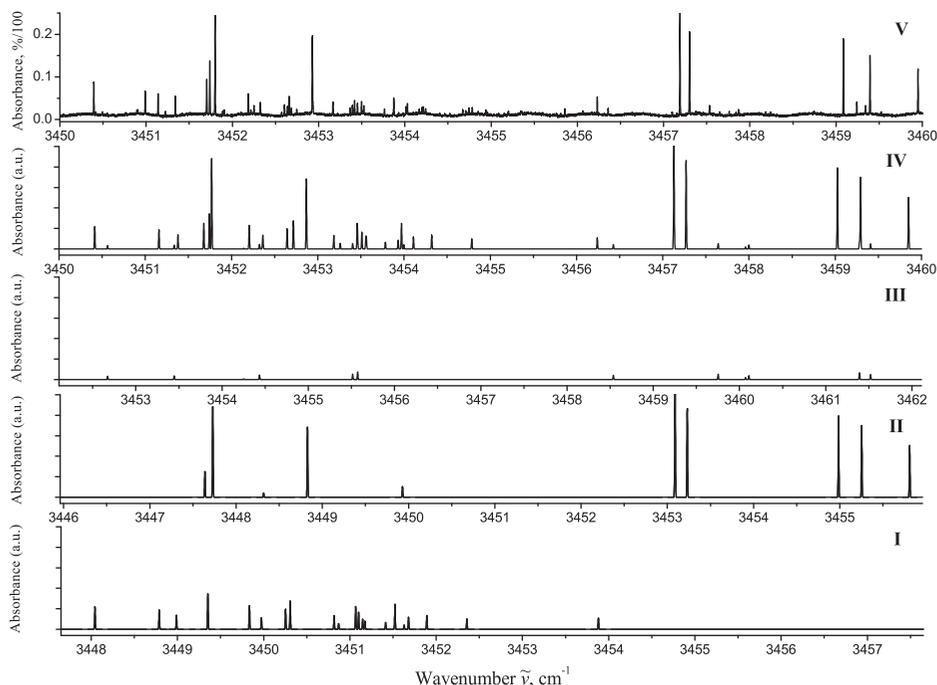
Figure 1. A small part of the high-resolution spectrum of CH_2D_2 in the region 3450–3460 cm^{-1}. The four bottom traces (I–IV) present simulated spectra. Traces I–III show the lines belonging to the bands, $\nu_4 + 2\nu_9$, $\nu_2 + \nu_9$, and $\nu_3 + 2\nu_4$, respectively. The sum of simulated spectra (I–III) is given by trace IV. The top trace (V) shows the experimentally recorded spectrum [13]. Experimental conditions: absorption path length, 10 m; sample pressure, 3 mbar; instrumental resolution, 0.0027 cm^{-1}; temperature 78 K.

(mistakes are the values of the order of some percents), but considerably worse absolute values for vibrational parameters (errors up to some cm^{-1}) in comparison with absolute errors in predicted values for rotational ones.

(b) From a comparison of experimental and synthetic spectra on Figure 1, traces V and IV, one can see that the correspondence of line positions between the two mentioned spectra is better than the correspondence in line strengths. It is an appearance of the following fact. When we calculated the line positions, we took into account the presence of the resonance interactions between the discussed bands, $\nu_4 + 2\nu_9$, $\nu_2 + \nu_9$, and $\nu_3 + 2\nu_4$, on the one hand, and some of the 'dark' bands (i.e. $\nu_4 + \nu_7 + \nu_9$, $2\nu_7 + \nu_9$, $\nu_4 + \nu_5 + \nu_7$, and some others), on the other hand. At the same time, because only transitions with low values of quantum number J are presented in the experimental low-temperature spectrum, the line strengths in the synthetic spectrum were estimated on the basis of only three main dipole moment parameters (one dipole moment parameter for one band; in this case, the ratio of absolute values of the mentioned main

dipole moment parameters was taken as $1:1.8:1/5^{1/2}$ for the bands $\nu_4 + 2\nu_9$, $\nu_2 + \nu_9$, and $\nu_3 + 2\nu_4$, respectively). Moreover, because of the absence of information about 'dark' bands, all their dipole moment parameters were taken as zero.

(c) Because the experimental spectrum (Figure 1, trace V) was recorded [13,45] at a pressure of 3 mbar, the Doppler profile for the line shape was used in the construction of the synthetic spectra.

In any case, in spite of the fact of the total absence of initial information about the CH_2D_2 molecule (since only two parameters of the CH_4 molecule were used as the initial information in the derived isotopic relations), one can see more than satisfactory correlations between the synthetic and experimental spectra which can be considered as good confirmation of the validity of the results for the present paper.

10. Conclusion

We showed in the present study by using the CH_2D_2 molecule, as an example, that a compilation of the isotopic substitution theory [27,28], and the 'expanded

local mode' model [24–26], allows one to derive numerous simple isotopic relations which give us the possibility to make predictions of spectroscopic characteristics of CH_2D_2 without information about that species (in this case, only a very limited quantity of experimental information about the mother, CH_4, species can be used). The quality of the derived relations is confirmed by a comparison of the results of predictions with isotopic relations and results of analysis of experimental data. In this case, the majority of situations show good correlations between the predicted and 'experimental' results.

Up to now high resolution spectroscopy is an unique source of precise quantitative information about internal properties of polyatomic molecules. Such information can be provided by an analysis of the corresponding vibrational–rotational spectra. However, very often, for molecules with a large number of atoms (even 8–10), the possibility of analysis is very limited, first of all, because of the large number of necessary parameters in the hamiltonian. It is especially important for situations when accidental resonances appear in the spectra. The only way to improve the situation is to reduce the number of free parameters (deriving more or less correct relations between different parameters). If we take into account that methane is the prototypical hydrocarbon for a large number of more complicated organic molecules, it is possible to expect that the approach derived in the present paper will be helpful in future studies of such molecules.

Acknowledgements

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Appendix 1

Here we present relations between normal mode force parameters, c_{ijk}/c_{ijkl}, of the mother, CH_4, and k'_{ijk}/k'_{ijkl}, of the substituted, CH_2D_2, species:

$$36c_{111} = -\frac{9}{\pi\rho c}\left(\frac{\hbar^2 F_{11}}{m^3}\right)^{1/4} = -24k'_{111} = 118k'_{112} = 410k'_{113}$$

$$= -285k'_{114} = 135k'_{122} = 137k'_{123} = -355k'_{124} = 62k'_{133}$$

$$= 65k'_{134} = 700k'_{144} = 71k'_{155} = -\frac{125}{16}k'_{166} = 58k'_{167}$$

$$= 79k'_{177} = 98k'_{188} = -67k'_{189} = 32k'_{199} = 40k'_{222}$$

$$= 670k'_{223} = -300k'_{224} = -300k'_{234} = -77k'_{244} = 600k'_{255}$$

$$= 143k'_{266} = 90k'_{267} = -78k'_{277} = \frac{87}{7}k'_{288} = -147k'_{289}$$

$$= -2050k'_{299} = 445k'_{333} = 910k'_{334} = 722k'_{344}$$

$$= -300k'_{355} = -100k'_{366} = \frac{49}{2}k'_{367} = -122k'_{377}$$

$$= 780k'_{388} = -157k'_{389} = 167k'_{399} = -952k'_{444} = 314k'_{455}$$

$$= -162k'_{466} = 51k'_{467} = -151k'_{477} = 138k'_{488} = -71k'_{489}$$

$$= 108k'_{499} = -71k'_{568} = \frac{614}{25}k'_{569} = 255k'_{578} = -158k'_{579}; \quad (62)$$

$$\frac{3}{2}d_{1111} = \frac{23}{200}\frac{\hbar}{\pi\rho^2} \approx \frac{92}{75}B^e = \frac{1}{3}k'_{1111} = -\frac{7}{6}k'_{1112} = -\frac{11}{5}k'_{1113}$$

$$= 7k'_{1114} = 9k'_{1122} = -\frac{22}{25}k'_{1123} = -2k'_{1124} = -\frac{7}{51}k'_{1133}$$

$$= -\frac{11}{50}k'_{1134} = -\frac{6}{5}k'_{1144} = -\frac{9}{52}k'_{1155} = \frac{1}{19}k'_{1166}$$

$$= -\frac{1}{3}k'_{1167} = -\frac{8}{39}k'_{1177} = -70k'_{1188} = \frac{9}{20}k'_{1189}$$

$$= -\frac{1}{10}k'_{1199} = \frac{3}{2}k'_{1222} = \frac{22}{5}k'_{1223} = -\frac{7}{5}k'_{1224} = 2k'_{1233}$$

$$= \frac{13}{10}k'_{1234} = -k'_{1244} = -\frac{11}{5}k'_{1255} = -\frac{3}{7}k'_{1266} = -\frac{3}{5}k'_{1267}$$

$$= -\frac{11}{5}k'_{1277} = \frac{9}{22}k'_{1288} = -k'_{1289} = 2k'_{1299} = -\frac{9}{4}k'_{1333}$$

$$= -\frac{7}{5}k'_{1334} = -\frac{6}{5}k'_{1344} = \frac{7}{5}k'_{1355} = \frac{13}{25}k'_{1366} = -\frac{1}{25}k'_{1367}$$

$$= \frac{9}{24}k'_{1377} = 14k'_{1388} = \frac{4}{5}k'_{1389} = -\frac{14}{25}k'_{1399} = -13k'_{1444}$$

$$= -\frac{7}{5}k'_{1455} = \frac{6}{10}k'_{1466} = -\frac{1}{8}k'_{1467} = \frac{9}{10}k'_{1477} = -3k'_{1488}$$

$$= -k'_{1489} = -\frac{3}{5}k'_{1499} = \frac{7}{25}k'_{1568} = -\frac{1}{30}k'_{1569} = \frac{12}{25}k'_{1578}$$

$$= \frac{12}{25}k'_{1579} = \frac{3}{5}k'_{2222} = 7k'_{2223} = -\frac{7}{5}k'_{2224} = -12k'_{2233}$$

$$= 3k'_{2234} = -\frac{6}{25}k'_{2244} = -\frac{6}{5}k'_{2255} = -70k'_{2266} = \frac{6}{5}k'_{2267}$$

$$= -\frac{3}{10}k'_{2277} = \frac{12}{125}k'_{2288} = -\frac{9}{10}k'_{2289} = -\frac{3}{2}k'_{2299}$$

$$= 6k'_{2333} = 6k'_{2334} = -6k'_{2344} = -14k'_{2355} = -\frac{7}{10}k'_{2366}$$

$$= k'_{2367} = -9k'_{2377} = 4k'_{2388} = 3k'_{2389} = \frac{3}{2}k'_{2399} = -7k'_{2444}$$

$$= 4k'_{2455} = -3k'_{2466} = \frac{6}{5}k'_{2467} = -\frac{6}{5}k'_{2477} = \frac{3}{4}k'_{2488}$$

$$= -\frac{7}{50}k'_{2489} = \frac{9}{10}k'_{2499} = -k'_{2568} = 4k'_{2569} = \frac{7}{50}k'_{2578}$$

$$= -4k'_{2579} = 18k'_{3333} = 4k'_{3334} = 10k'_{3344} = 17k'_{3355}$$

$$= -\frac{1}{9}k'_{3366} = -9k'_{3367} = \frac{7}{10}k'_{3377} = -14k'_{3388} = -3k'_{3389}$$

$$= 2k'_{3399} = 7k'_{3444} = 4k'_{3455} = -\frac{1}{5}k'_{3466} = -5k'_{3467}$$

$$= \frac{1}{2}k'_{3477} = \frac{9}{10}k'_{3488} = -3k'_{3489} = \frac{6}{5}k'_{3499} = \frac{9}{10}k'_{3568}$$

$$= -\frac{14}{25}k'_{3569} = -3k'_{3578} = \frac{7}{20}k'_{3579} = 10k'_{4444} = -5k'_{4455}$$

$$= -\frac{6}{5}k'_{4466} = -2k'_{4467} = \frac{7}{5}k'_{4477} = -\frac{9}{51}k'_{4488} = 3k'_{4489}$$

$$= 15k'_{4499} = -2k'_{4568} = -\frac{4}{9}k'_{4569} = 3k'_{4578} = \frac{7}{10}k'_{4579} = 10k'_{5555}$$

$$= -\frac{1}{6}k'_{5566} = \frac{7}{5}k'_{5567} = 40k'_{5577} = -k'_{5588} = -k'_{5589} = \frac{3}{5}k'_{5599}$$

$$= \frac{4}{13}k'_{6666} = -5k'_{6667} = -\frac{1}{5}k'_{6677} = -5k'_{6688} = \frac{2}{5}k'_{6689}$$

$$= -\frac{1}{10}k'_{6699} = k'_{6777} = \frac{11}{10}k'_{6788} = \frac{7}{5}k'_{6789} = \frac{7}{10}k'_{6799}$$

$$= 5k'_{7777} = -\frac{7}{25}k'_{7788} = 3k'_{7789} = 3k'_{7799} = \frac{11}{20}k'_{8888} = 24k'_{8889}$$

$$= -\frac{7}{5}k'_{8899} = -3k'_{8999} = \frac{11}{10}k'_{9999} \tag{63}$$

Appendix 2. Parameters of Fermi-type (vibrational) interactions

In this appendix we present formulas used in the present paper for resonance interaction parameters of the Fermi-type (interactions between vibrational states of the same symmetry) as functions of fundamental characters of a methane-type molecule.

2.1. Interaction of the $\langle v_\lambda..v_\mu..v_\nu..v_\xi |..|v_\lambda \mp 1..v \mp 1 ..v_\nu \pm 1..v_\xi \pm 1\rangle$ type:

$$^{(\lambda\mu,\nu\xi)}F'_0 = k'_{\lambda\mu\nu\xi} + \sum_{\substack{\kappa,\theta=\lambda,\mu \\ (\kappa\neq\theta)}} \frac{k'_{\kappa\kappa\theta}k'_{\kappa\nu\xi}}{2}\left[\left(\frac{1}{\omega'_\theta} + \frac{1}{\omega'_\nu + \omega'_\xi - \omega'_\kappa}\right)\right.$$

$$\left. - \left(\frac{1}{2\omega'_\kappa + \omega'_\theta} + \frac{1}{\omega'_\kappa + \omega'_\nu + \omega'_\xi}\right)\right] - \sum_{\substack{\kappa,\theta=\lambda,\mu \\ (\kappa\neq\theta)}}\sum_{\substack{\eta,\tau=\nu,\xi \\ (\eta\neq\tau)}} \frac{k'_{\kappa\kappa\eta}k'_{\kappa\theta\tau}}{2}$$

$$\times\left[\left(\frac{1}{\omega'_\eta} + \frac{1}{\omega'_\kappa + \omega'_\theta - \omega'_\tau}\right) + \left(\frac{1}{2\omega'_\kappa - \omega'_\eta}\right.\right.$$

$$\left.\left. + \frac{1}{\omega'_\kappa + \omega'_\tau - \omega'_\theta}\right)\right] + \sum_{\substack{\eta,\tau=\nu,\xi \\ (\eta\neq\tau)}} \frac{k'_{\eta\eta\tau}k'_{\eta\lambda\mu}}{2}\left[\left(\frac{1}{\omega'_\tau}\right.\right.$$

$$\left.\left. + \frac{1}{\omega'_\lambda + \omega'_\mu - \omega'_\eta}\right) - \left(\frac{1}{2\omega'_\eta + \omega'_\tau} + \frac{1}{\omega'_\eta + \omega'_\lambda + \omega'_\mu}\right)\right]$$

$$- \sum_{\substack{\kappa,\theta=\lambda,\mu \\ (\kappa\neq\theta)}}\sum_{\substack{\eta,\tau=\nu,\xi \\ (\eta\neq\tau)}} \frac{k'_{\kappa\eta\eta}k'_{\theta\eta\tau}}{2}\left[\left(\frac{1}{\omega'_\kappa} + \frac{1}{\omega'_\eta + \omega'_\tau - \omega'_\theta}\right)\right.$$

$$\left. + \left(\frac{1}{2\omega'_\eta - \omega'_\kappa} + \frac{1}{\omega'_\theta + \omega'_\eta - \omega'_\tau}\right)\right] + \sum_{\rho\neq\lambda,\mu,\nu,\xi} \frac{k'_{\lambda\mu\rho}k'_{\nu\xi\rho}}{4}$$

$$\times\left[\left(\frac{1}{\omega'_\lambda + \omega'_\mu - \omega'_\rho} + \frac{1}{\omega'_\nu + \omega'_\xi - \omega'_\rho}\right)\right.$$

$$\left. - \left(\frac{1}{\omega'_\nu + \omega'_\xi + \omega'_\rho} + \frac{1}{\omega'_\lambda + \omega'_\mu + \omega'_\rho}\right)\right]$$

$$+ \sum_{\rho\neq\lambda,\mu,\nu,\xi}\sum_{\substack{\eta,\tau=\nu,\xi \\ (\eta\neq\tau)}} \frac{k'_{\lambda\eta\rho}k'_{\mu\tau\rho}}{4}\left[\left(\frac{1}{\omega'_\lambda - \omega'_\eta - \omega'_\rho}\right.\right.$$

$$\left. + \frac{1}{\omega'_\tau - \omega'_\mu - \omega'_\rho}\right) + \left.\left(\frac{1}{\omega'_\mu - \omega'_\tau - \omega'_\rho} + \frac{1}{\omega'_\eta - \omega'_\lambda - \omega'_\rho}\right)\right]$$

$$+ \sum_\beta \frac{2B'^e_\beta}{\left(\omega'_\lambda\omega'_\mu\omega'_\nu\omega'_\xi\right)^{1/2}}\left[\left(\zeta'^\beta_{\lambda\mu}\zeta'^\beta_{\nu\xi}\right)\left(\omega'_\mu - \omega'_\lambda\right)\left(\omega'_\xi - \omega'_\nu\right)\right]$$

$$- \sum_\beta \frac{2B'^e_\beta}{\left(\omega'_\lambda\omega'_\mu\omega'_\nu\omega'_\xi\right)^{1/2}}\left[\left(\zeta'^\beta_{\lambda\nu}\zeta'^\beta_{\mu\xi}\right)(\omega'_\nu + \omega'_\lambda)(\omega'_\mu + \omega'_\xi)\right.$$

$$\left. + \left(\zeta'^\beta_{\lambda\xi}\zeta'^\beta_{\mu\nu}\right)\left(\omega'_\lambda + \omega'_\xi\right)\left(\omega'_\mu + \omega'_\nu\right)\right]. \tag{64}$$

When $\rho = 6$, or 8, then a resonance situation can be produced in the first parentheses of the fourth line from the end. In this case, parentheses should be omitted.

2.2. Fermi-type interaction, $\langle v_\lambda\ldots v_\mu|\ldots|v_\lambda \pm 1\ldots v_\mu\mp 1\rangle$: pure vibrational interaction coefficient, $^{(\lambda,\mu)}F'_0$:

$$^{(\lambda,\mu)}F'_0 = \frac{3}{2}k'_{\lambda\lambda\lambda\mu}V_\lambda + \frac{3}{2}k'_{\lambda\mu\mu\mu}V_\mu + \sum_{\xi\neq\lambda,\mu} k'_{\lambda\mu\xi\xi}V_\xi$$

$$- \sum_{\substack{i,j=\lambda,\mu}}^{i\neq j} \frac{3k'_{iii}k'_{iij}}{4}\left\{\frac{10}{3\omega'_i} + \frac{1}{\omega'_j} + \frac{6\omega'_i + \omega'_j}{4\omega'^2_i - \omega'^2_j}\right\}V_i$$

$$+ \sum_{\substack{i,j=\lambda,\mu}}^{i\neq j} \frac{k'_{iij}k'_{ijj}}{4}\left\{\frac{2\omega'_j}{4\omega'^2_i - \omega'^2_j} - \frac{6\omega'_j + \omega'_i}{4\omega'^2_j - \omega'^2_i} - \frac{4\omega'_i + \omega'_j}{\omega'_i\omega'_j}\right\}V_i$$

$$- \sum_{\xi\neq\lambda,\mu} \frac{3k'_{\lambda\mu\xi}k'_{\xi\xi\xi}}{2\omega'_\xi}\frac{2\omega'^2_\xi - \left(\omega'_\lambda - \omega'_\mu\right)^2}{\omega'^2_\xi - \left(\omega'_\lambda - \omega'_\mu\right)^2}V_\xi$$

$$- \sum_{\xi\neq\lambda,\mu,\nu}\sum_{\nu\neq\lambda,\mu} \frac{k'_{\lambda\mu\nu}k'_{\nu\xi\xi}}{2\omega'_\nu}\frac{2\omega'^2_\nu - \left(\omega'_\lambda - \omega'_\mu\right)^2}{\omega'^2_\nu - \left(\omega'_\lambda - \omega'_\mu\right)^2}V_\xi$$

$$- \sum_{\substack{i,j=\lambda,\mu}}^{i\neq j}\sum_{\xi\neq\lambda,\mu} \frac{k'_{iij}k'_{i\xi\xi}}{2}\left\{\frac{2}{\omega'_i} + \frac{1}{\omega'_j} + \frac{1}{2\omega'_i - \omega'_j}\right\}V_\xi$$

$$+ \sum_{\xi\neq\lambda,\mu} 2k'_{\lambda\xi\xi}k'_{\mu\xi\xi}\left\{\frac{\omega'_\xi}{\omega'^2_\lambda - 4\omega'^2_\xi} + \frac{\omega'_\xi}{\omega'^2_\mu - 4\omega'^2_\xi}\right\}V_\xi$$

$$+ \sum_{\xi\neq\lambda,\mu}\sum_{\nu\neq\lambda,\mu,\xi} \frac{k'_{\lambda\xi\nu}k'_{\mu\xi\nu}}{4}\left\{\frac{\omega'_\xi + \omega'_\nu}{\omega'^2_\lambda - (\omega'_\xi + \omega'_\nu)^2}\right.$$

$$\left. + \frac{\omega'_\xi + \omega'_\nu}{\omega'^2_\mu - (\omega'_\xi + \omega'_\nu)^2}\right\}V_\xi - \sum_{\substack{i,j=\lambda,\mu}}^{i\neq j}\sum_{\xi\neq\lambda,\mu} \frac{k'_{ii\xi}k'_{ij\xi}}{4}$$

$$\times\left\{\frac{2(\omega'_i - \omega'_j)}{(\omega'_i - \omega'_j)^2 - \omega'^2_\xi} + \frac{3\omega'_i + \omega'_j + 2\omega'_\xi}{(2\omega'_i + \omega'_\xi)(\omega'_i + \omega'_j + \omega'_\xi)}\right\}V_\xi$$

$$- \sum_{\substack{i,j=\lambda,\mu}}^{i\neq j}\sum_{\xi\neq\lambda,\mu} \frac{k'_{ii\xi}k'_{ij\xi}}{8}\left\{\frac{4(\omega'_i - \omega'_j)^2 - 8\omega'^2_\xi}{\omega'_\xi(\omega'_i - \omega'_j)^2 - \omega'^3_\xi}\right.$$

$$\left. + \frac{3\omega'_i + \omega'_j + 2\omega'_\xi}{(2\omega'_i + \omega'_\xi)(\omega'_i + \omega'_j + \omega'_\xi)}\right\}V_i + \sum_{\xi\neq\lambda,\mu} 2\sum_\beta B'^e_\beta \zeta'^\beta_{\lambda\xi}\zeta'^\beta_{\mu\xi}$$

$$\times \frac{\omega_\xi'^2 + \omega_\lambda' \omega_\mu'}{\omega_\xi' \left(\omega_\lambda' \omega_\mu'\right)^{1/2}} V_\xi - \sum_{i,j=\lambda,\mu}^{i\neq j} \sum_{\xi\neq\lambda,\mu} \frac{k_{ii\xi}' k_{ij\xi}'}{4}$$

$$\times \left\{ \frac{3\omega_i' + \omega_j' - 2\omega_\xi'}{(2\omega_i' - \omega_\xi')(\omega_i' + \omega_j' - \omega_\xi')} \right\} V_\xi + \sum_{i,j=\lambda,\mu}^{i\neq j} \sum_{\xi\neq\lambda,\mu} \frac{k_{ii\xi}' k_{ij\xi}'}{8}$$

$$\times \left\{ \frac{3\omega_i' + \omega_j' - 2\omega_\xi'}{(2\omega_i' - \omega_\xi')(\omega_i' + \omega_j' - \omega_\xi')} \right\} V_i + \sum_{\xi\neq\lambda,\mu} \sum_{\nu\neq\lambda,\mu,\xi} \frac{k_{\lambda\xi\nu}' k_{\mu\xi\nu}'}{8}$$

$$\times \left\{ \frac{1}{\omega_\lambda' + \omega_\xi' - \omega_\nu'} + \frac{1}{\omega_\mu' + \omega_\xi' - \omega_\nu'} \right\} V_\xi - \sum_{\xi\neq\lambda,\mu} \sum_{\nu\neq\lambda,\mu,\xi}$$

$$\frac{k_{\lambda\xi\nu}' k_{\mu\xi\nu}'}{8} \left\{ \frac{1}{\omega_\lambda' + \omega_\nu' - \omega_\xi'} + \frac{1}{\omega_\mu' + \omega_\nu' - \omega_\xi'} \right\} V_\xi. \tag{65}$$

Here

$$V_i = \left(\frac{v_i + \tilde{v}_i}{2} + \frac{1}{2} \right),$$

and v_i and $\tilde{v}_i$ are the vibrational quantum numbers in the left and right wave functions of Equation (36). When $i = 3$ and $\xi = 1$ or $i = 4$ and $\xi = 2$, then the third and fourth lines from the end in Equation (65) should be omitted because of resonance interactions between corresponding vibrational states. For the same reason, when $\xi = 7$ and $\nu = 6$ or $\xi = 9$ and $\nu = 8$, then the next to last line should be omitted. Analogously, when $\nu = 7$ and $\xi = 6$ or $\nu = 9$ and $\xi = 8$, then the last line should be omitted.

2.3. Fermi-type interaction, $\langle v_\lambda \cdots v_\mu | \cdots | v_\lambda \pm 1 \cdots v_\mu \mp 1 \rangle$: ro-vibrational interaction coefficient, $^{(\lambda,\mu)}F_K'$, $^{(\lambda,\mu)}F_J'$ and $^{(\lambda,\mu)}F_{xy}'$:

$$^{(\lambda,\mu)}F_\alpha' = 3 \sum_\gamma \frac{(B_\alpha'^e)^2 B_\gamma'^e}{\sqrt{\omega_\lambda' \omega_\mu'}} \left(\frac{4\pi c}{\hbar} \right) a_\lambda'^{\alpha\gamma} a_\mu'^{\alpha\gamma}$$

$$+ \sqrt{\frac{2}{\omega_\lambda'}} (B_\alpha'^e)^2 \left(\frac{4\pi c}{\hbar} \right)^{1/2} a_\lambda'^{\alpha\alpha} k_{\lambda\lambda\mu}' \frac{(\omega_\mu' + \omega_\lambda')^2 - 2\omega_\mu'^2}{\omega_\mu' \omega_\lambda' - (2\omega_\lambda' - \omega_\mu')}$$

$$+ \sqrt{\frac{2}{\omega_\mu'}} (B_\alpha'^e)^2 \left(\frac{4\pi c}{\hbar} \right)^{1/2} a_\mu'^{\alpha\alpha} k_{\lambda\mu\mu}' \frac{(\omega_\lambda' + \omega_\mu')^2 - 2\omega_\lambda'^2}{\omega_\lambda' \omega_\mu' - (2\omega_\mu' - \omega_\lambda')}$$

$$+ \sum_{\xi\neq\lambda,\mu} \frac{(B_\alpha'^e)^2}{\sqrt{2\omega_\xi'}} \left(\frac{4\pi c}{\hbar} \right)^{1/2} a_\xi'^{\alpha\gamma} k_{\xi\lambda\mu}' \frac{2\omega_\xi'^2 - (\omega_\lambda' - \omega_\mu')^2}{\omega_\xi' \left[\omega_\xi'^2 - (\omega_\lambda' - \omega_\mu')^2 \right]}$$

$$- \sum_{\xi\neq\lambda,\mu} (B_\alpha'^e \zeta_{\xi\lambda}'^\alpha)(B_\alpha'^e \zeta_{\xi\lambda}'^\alpha)$$

$$\times \frac{(\omega_\lambda' + \omega_\xi')(\omega_\mu' + \omega_\xi')}{\omega_\xi' \sqrt{\omega_\lambda' \omega_\mu'}} \left(\frac{1}{\omega_\xi' - \omega_\lambda'} + \frac{1}{\omega_\xi' - \omega_\mu'} \right)$$

$$- \sum_{\xi\neq\lambda,\mu} (B_\alpha'^e \zeta_{\xi\lambda}'^\alpha)(B_\alpha'^e \zeta_{\xi\mu}'^\alpha) \frac{(\omega_\lambda' - \omega_\xi')(\omega_\mu' - \omega_\xi')}{\omega_\xi' \sqrt{\omega_\lambda' \omega_\mu'}}$$

$$\times \left(\frac{1}{\omega_\xi' + \omega_\lambda'} + \frac{1}{\omega_\xi' + \omega_\mu'} \right). \tag{66}$$

In Equation (66), $\alpha = x, y$, or z; if $\omega_\xi' \approx \omega_\lambda'$, or $\omega_\xi' \approx \omega_\mu'$, then the before last line in Equation (66) should be put to zero.

Appendix 3. Parameters of Coriolis interactions of the $\langle v | . | \tilde{v} \rangle \equiv \langle v_\lambda . v_\mu . v_\nu | . | v_\lambda \pm 1 . v_\mu \mp 1 . v_\nu \mp 1 \rangle$ type

$$^{(\lambda,\mu\nu)}C_\alpha' = \frac{2(2^{1/2})B_\alpha'^e}{\left(\omega_\lambda' \omega_\mu' \omega_\nu'\right)^{1/2}} \left(\frac{4\pi c}{\hbar} \right)^{1/2} \sum_\beta \left[a_\lambda'^{\alpha\beta} \left(B_\beta'^e \zeta_{\mu\nu}'^\beta \right) \left(\omega_\mu' - \omega_\nu' \right) \right.$$

$$\left. + a_\mu'^{\alpha\beta} \left(B_\beta'^e \zeta_{\lambda\nu}'^\beta \right) \left(\omega_\lambda' + \omega_\nu' \right) + a_\nu'^{\alpha\beta} \left(B_\beta'^e \zeta_{\lambda\mu}'^\beta \right) \left(\omega_\lambda' + \omega_\mu' \right) \right]$$

$$+ \left(B_\alpha'^e \zeta_{\mu\nu}'^\alpha \right) \left(k_{\lambda\mu\mu}' + k_{\lambda\nu\nu}' \right) \frac{\omega_\mu' - \omega_\nu'}{\left(\omega_\mu' \omega_\nu'\right)^{1/2}} \left(\frac{1}{\omega_\lambda'} + \frac{1}{\omega_\mu' + \omega_\nu'} \right)$$

$$+ \frac{\omega_\mu' + \omega_\nu'}{\left(\omega_\mu' \omega_\nu'\right)^{1/2}} \left[\left(B_\alpha'^e \zeta_{\nu\mu}'^\alpha \right) k_{\lambda\mu\mu}' \left(\frac{1}{\omega_\mu' - \omega_\nu'} + \frac{1}{\omega_\lambda' - 2\omega_\mu'} \right) \right.$$

$$\left. + \left(B_\alpha'^e \zeta_{\mu\nu}'^\alpha \right) k_{\lambda\nu\nu}' \left(\frac{1}{\omega_\mu' - \omega_\nu'} + \frac{1}{\omega_\lambda' - 2\omega_\nu'} \right) \right]$$

$$+ \left(B_\alpha'^e \zeta_{\lambda\mu}'^\alpha \right) \frac{k_{\lambda\lambda\nu}'}{\left(\omega_\lambda' \omega_\mu'\right)^{1/2}} \left[\frac{4\omega_\lambda' \omega_\mu'}{\omega_\lambda'^2 - \omega_\mu'^2} + \frac{2\omega_\lambda' \left(\omega_\lambda' + \omega_\mu' - \omega_\nu' \right)}{\omega_\nu' \left(2\omega_\lambda' - \omega_\nu' \right)} \right]$$

$$+ \left(B_\alpha'^e \zeta_{\lambda\nu}'^\alpha \right) \frac{k_{\lambda\lambda\mu}'}{\left(\omega_\lambda' \omega_\nu'\right)^{1/2}} \left[\frac{4\omega_\lambda' \omega_\nu'}{\omega_\lambda'^2 - \omega_\nu'^2} + \frac{2\omega_\lambda' \left(\omega_\lambda' + \omega_\nu' - \omega_\mu' \right)}{\omega_\mu' \left(2\omega_\lambda' - \omega_\mu' \right)} \right]$$

$$- \left(B_\alpha'^e \zeta_{\lambda\mu}'^\alpha \right) \frac{k_{\mu\mu\nu}'}{\left(\omega_\lambda' \omega_\mu'\right)^{1/2}} \left[\frac{4\omega_\lambda' \omega_\mu'}{\omega_\lambda'^2 - \omega_\mu'^2} + \frac{2\omega_\mu' \left(\omega_\lambda' + \omega_\mu' + \omega_\nu' \right)}{\omega_\nu' \left(2\omega_\mu' + \omega_\nu' \right)} \right]$$

$$- \left(B_\alpha'^e \zeta_{\lambda\nu}'^\alpha \right) \frac{k_{\mu\nu\nu}'}{\left(\omega_\lambda' \omega_\nu'\right)^{1/2}} \left[\frac{4\omega_\lambda' \omega_\nu'}{\omega_\lambda'^2 - \omega_\nu'^2} + \frac{2\omega_\nu' \left(\omega_\lambda' + \omega_\nu' + \omega_\mu' \right)}{\omega_\mu' \left(2\omega_\nu' + \omega_\mu' \right)} \right]$$

$$+ \sum_{\xi\neq\lambda,\mu,\nu} \frac{\left(B_\alpha'^e \zeta_{\nu\xi}'^\alpha \right)}{2} \frac{k_{\lambda\mu\xi}'}{\left(\omega_\nu' \omega_\xi'\right)^{1/2}} \left\{ \left(\frac{\omega_\xi' - \omega_\nu'}{\omega_\xi' + \omega_\nu'} + \frac{\omega_\xi' - \omega_\nu'}{\omega_\xi' + \omega_\lambda' - \omega_\mu'} \right) \right.$$

$$\left. - \left(\frac{\omega_\xi' + \omega_\nu'}{\omega_\xi' - \omega_\nu'} + \frac{\omega_\xi' + \omega_\nu'}{\omega_\xi' - \omega_\lambda' + \omega_\mu'} \right) \right\} + \sum_{\xi\neq\lambda,\mu,\nu} \frac{\left(B_\alpha'^e \zeta_{\mu\xi}'^\alpha \right)}{2} \frac{k_{\lambda\nu\xi}'}{\left(\omega_\mu' \omega_\xi'\right)^{1/2}}$$

$$\times \left\{ \left(\frac{\omega_\xi' - \omega_\mu'}{\omega_\xi' + \omega_\mu'} + \frac{\omega_\xi' - \omega_\mu'}{\omega_\xi' + \omega_\lambda' - \omega_\nu'} \right) - \left(\frac{\omega_\xi' + \omega_\mu'}{\omega_\xi' - \omega_\mu'} + \frac{\omega_\xi' + \omega_\mu'}{\omega_\xi' - \omega_\lambda' + \omega_\nu'} \right) \right\}$$

$$+ \sum_{\xi\neq\lambda,\mu,\nu} \frac{\left(B_\alpha'^e \zeta_{\lambda\xi}'^\alpha \right)}{2} \frac{k_{\mu\nu\xi}'}{\left(\omega_\lambda' \omega_\xi'\right)^{1/2}} \left\{ \left(\frac{\omega_\lambda' - \omega_\xi'}{\omega_\lambda' + \omega_\xi'} + \frac{\omega_\lambda' - \omega_\xi'}{\omega_\mu' + \omega_\nu' + \omega_\xi'} \right) \right.$$

$$\left. - \left(\frac{\omega_\lambda' + \omega_\xi'}{\omega_\lambda' - \omega_\xi'} + \frac{\omega_\lambda' + \omega_\xi'}{\omega_\mu' + \omega_\nu' - \omega_\xi'} \right) \right\}. \tag{67}$$

Here, if $\omega_\mu' \approx \omega_\nu'$, then the square bracket lines 4 and 5 of Equation (67) should be totally omitted. If $\lambda = 1$, and $\mu = 3$, or 9; or if $\lambda = 2$, and $\mu = 4$, or 7, then the fourth line should be omitted. Analogously, if $\lambda = 1$, and $\nu = 3$, or 9; or if $\lambda = 2$, and $\nu = 4$, or 7, then the fifth line should be omitted. If $\xi = 3$, 4, 5, 7, or 9, then the first parentheses of line 11 and the second parentheses of line 12 should be omitted. For the resonance situations ($\lambda = 1$ and $\xi = 6$; $\lambda = 6$ and $\xi = 1$; $\lambda = 2$ and $\xi = 8$; $\lambda = 8$ and $\xi = 2$) in the last line should be omitted.