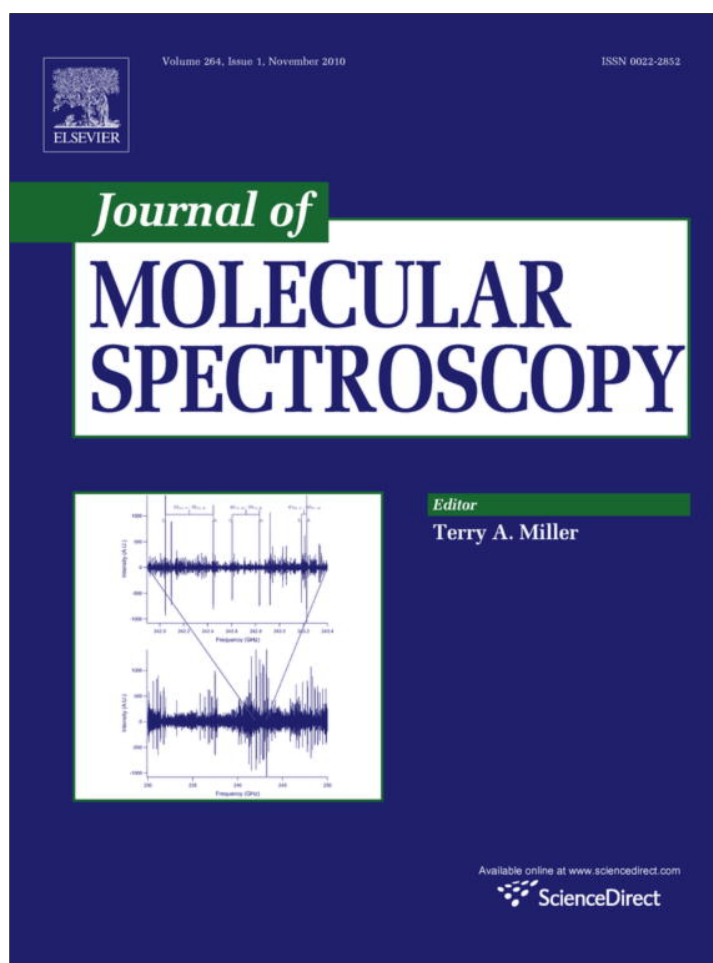


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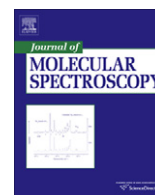
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On the “expanded local mode” approach applied to the methane molecule

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ABSTRACT

On the base of the “expanded local mode approach” (see, Ref. [12]) a simple expression of the ambiguity parameter $\sin \gamma$ of the CH_4 molecule is estimated and then, using empirical relations between $F_{i,j}$ force coefficients, simple relations between different spectroscopic parameters of the methane molecule are derived. Comparison with corresponding “experimental” values is made, that shows more than satisfactory correlations between both (predicted and obtained from experimental data) sets of parameters.

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1. Introduction

Methane (CH_4) is one of the main prototypical hydrocarbons and is of great importance in a variety of applications ranging from our understanding of the chemical bonding, structure and quantum dynamics, reaction kinetics to geology, astrophysics, atmospheric and environmental science. On that reason, during more than five last decades both the vibrational and ro-vibrational spectra of methane were a subject of numerous studies (see, for example, [1–3] where extensive references to spectroscopic and theoretical works can be found, the complete, very long list being not reproduced here).

It should be mentioned that, in spite of the many-years essential efforts, only the region below 6000 cm^{-1} was analysed in details with a high resolution (only some separate small wave regions above 6000 cm^{-1} have been discussed in [1,4,5]). Recently, [6], high resolution spectra of the CH_4 molecule were experimentally recorded and preliminary theoretically analysed in the wide spectral region between 6000 cm^{-1} and $12\,000 \text{ cm}^{-1}$. The made analysis, on the one hand, allowed authors to obtain with a high accuracy (better than 0.001 cm^{-1}) centers of 12 new rovibrational bands and (on the base of analysis of 95 experimental band centers of the CH_4 molecule) a set of vibrational spectroscopic parameters. On the other hand, it was found that the absence of correct experimental information about some of the important for such kind analysis vibrational bands (e.g., $\nu_1 + \nu_2$ and/or $\nu_1 + \nu_3$) leads to ambiguity in the values of some of spectroscopic parameters. The analogous situations have been arisen also in our recent analysis

of the CH_2D_2 , Refs. [7–9], and $\text{CH}_3\text{D}/\text{CHD}_3$, [10], isotopomers of methane. One of the ways of eliminating of such kind ambiguities is to derive some relations between parameters of the model used for analysis. On the one hand, it will reduce the number of varied parameters and, on the other hand, will make the varied parameters more stable and physically suitable.

2. “Expanded local mode” approach and estimation of the parameter of ambiguity, $\sin \gamma$

As applied to the methane, CH_4 , molecule, some of such type relations are known in the literature, [11], and they have been obtained in the framework of the so-called “local mode” approach (see, [11] and references cited therein). Unfortunately, the local mode approach assumes the presence of stretching vibrations only in the model. At the same time, it is clear that the deformational motion is also important to understand of the processes taking place in the methane molecule.

The presence of the deformational motion can be taken into account if one will use the extension of a classical local mode model (namely, “expanded local mode” approach), that was derived in Refs. [12] and applied to asymmetric and symmetric top molecules, Refs. [13–16]. As was discussed in [12–16], the clue point of the “expanded local mode approach” is the possibility to present the transformation coefficients, $l_{N\alpha_i}$, of a molecule in the form of simple analytical expressions. As was shown in [12–16], peculiarities of some of the XY_2 (C_{2v} symmetry) and of the XY_3 (C_{3v} symmetry) molecules allow one to obtain such simple expression. At the same time, if one will remember that practically any spectroscopic parameter of a polyatomic molecule is a function of these $l_{N\alpha_i}$ -coefficients, then one may hope that

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those spectroscopic parameters also can be expressed in a simple form. As the consequence, simple enough relations between different spectroscopic parameters can be obtained.

Fortunately, for the methane molecule even considerably more simple analysis, than in Refs. [12–16], shows that very simple and, at the same time, numerically correct expressions are valid for the transformation $I_{N\alpha\lambda}$ -coefficients. For the beginning, we will remind that the exact transformation coefficients of the XY_4 (T_d symmetry) molecule have the form presented in Table 1 (reproduced from Ref. [17]), and all of them depend on one ambiguity coefficient, $\sin \gamma$. So, the main problem is, how to obtain that $\sin \gamma$ parameter in a simple as possible form.

In the above mentioned references [12–16] such type parameters have been estimated from the analysis of equations (at $\lambda \neq \mu$)

$$\left(\frac{\partial^2 V}{\partial Q_i \partial Q_\mu} \right)_{Q=0} = 0, \quad (1)$$

that correspond to the requirement that the vibrational coordinates Q are “normal” ones (here V is the intramolecular potential function of a molecule). In our case, we estimated the value of the $\sin \gamma$ parameter from analysis of (a) relations between the harmonic frequencies, ω_{λ} , of the CH_4 , [6,18], CH_2D_2 , [7], and CH_3D , CHD_3 , [10], isotopic species, and (b) experimental values of Coriolis coefficients from Ref. [19]. In the last case, it is necessary to take into account the definition of the Coriolis coefficients of an arbitrary polyatomic molecule (see, e.g., Refs. [20,21]):

$$\zeta_{\lambda\mu}^\alpha = \sum_{N\beta\gamma} \epsilon_{\alpha\beta\gamma} I_{N\beta\lambda} I_{N\gamma\mu}, \quad (2)$$

where $\alpha, \beta = x, y, z$; $\lambda, \mu = 1, 2_1, 2_2, 3_x, 3_y, 3_z, 4_x, 4_y, 4_z$ distinguish between different vibrational modes; ϵ is totally antisymmetric tensor.

In the case (a), necessary information about value of the $\sin \gamma$ parameter can be obtained from the known in the isotopic substitution theory relations (see, Ref. [22]):

$$\sum_{\lambda} A_{\lambda\mu} \omega_{\lambda}^2 \alpha_{v\lambda} = \alpha_{v\mu} \omega_{\nu}^2 \quad (3)$$

and

$$\sum_{\nu} \alpha_{v\lambda} \alpha_{v\mu} = A_{\lambda\mu}, \quad (4)$$

where

$$A_{\lambda\mu} = \delta_{\lambda\mu} - \sum_{N\alpha} \frac{(m'_N - m_N)}{m'_N} I_{N\alpha\lambda} I_{N\alpha\mu}. \quad (5)$$

Table 1
Transformation Coefficients, $I_{N\alpha\lambda}$, of the CH_4 Molecule.^a

$N\alpha/\lambda$	1	2 ₁	2 ₂	3 _x	3 _y	3 _z	4 _x	4 _y	4 _z
1x	D	C ₁	C ₂	A ₃	-B ₃	-B ₃	A ₄	B ₄	B ₄
2x	-D	-C ₁	-C ₂	A ₃	-B ₃	B ₃	A ₄	B ₄	-B ₄
3x	-D	-C ₁	-C ₂	A ₃	B ₃	-B ₃	A ₄	-B ₄	B ₄
4x	D	C ₁	C ₂	A ₃	B ₃	B ₃	A ₄	-B ₄	-B ₄
5x	0	0	0	F	0	0	E	0	0
1y	-D	-C ₁	C ₂	-B ₃	A ₃	B ₃	B ₄	A ₄	-B ₄
2y	D	C ₁	-C ₂	-B ₃	A ₃	-B ₃	B ₄	A ₄	B ₄
3y	-D	-C ₁	C ₂	B ₃	A ₃	-B ₃	-B ₄	A ₄	B ₄
4y	D	C ₁	-C ₂	B ₃	A ₃	B ₃	-B ₄	A ₄	-B ₄
5y	0	0	0	0	F	0	0	E	0
1z	-D	2C ₁	0	-B ₃	B ₃	A ₃	B ₄	-B ₄	A ₄
2z	-D	2C ₁	0	B ₃	-B ₃	A ₃	-B ₄	B ₄	A ₄
3z	D	-2C ₁	0	-B ₃	-B ₃	A ₃	B ₄	B ₄	A ₄
4z	D	-2C ₁	0	B ₃	B ₃	A ₃	-B ₄	-B ₄	A ₄
5z	0	0	0	0	0	F	0	0	E

^a Here $D = \frac{1}{2\sqrt{3}}$, $C_1 = \frac{1}{2\sqrt{6}}$, $C_2 = \frac{1}{2\sqrt{2}}$, $A_3 = \frac{1}{2} \sin \gamma \sqrt{\frac{m}{M}}$, $A_4 = \frac{1}{2} \cos \gamma \sqrt{\frac{m}{M}}$, $B_3 = \cos \gamma / 2\sqrt{2}$, $B_4 = \sin \gamma / 2\sqrt{2}$, $E = -2 \cos \gamma \sqrt{\frac{m}{M}}$, $F = -2 \sin \gamma \sqrt{\frac{m}{M}}$, $M = mM/(4m + M)$.

and $I_{N\alpha\lambda}$ are the transformation coefficients of the “mother” isotopic species from Table 1. In this case, analytical solution of Eqs. (3) and (4) gives connections between harmonic frequencies of different isotopic species as functions of parameter $\sin \gamma$. In its turn, it allows one to obtain the value of the $\sin \gamma$ parameter on the basis of known “experimental” values of harmonic frequencies.

In the case (b), value of the $\sin \gamma$ parameter can be estimated directly from experimental value of some or another Coriolis coefficient in accordance with the formula (2). This way is considerably easier in comparison with the first one, especially if one will take into account that the value of one from the Coriolis coefficients of the $^{12}CH_4$ molecule (namely, $\zeta_{3x,3y}^z$) very close to zero. In this case, if to assume that $\zeta_{3x,3y}^z \approx 0$, then one will obtain

$$\sin \gamma \approx \frac{3}{5}. \quad (6)$$

Estimations on the basis of the (a)-way confirm this conclusion.

After that, all the transformation coefficients $I_{N\alpha\lambda}$ from Table 1, as well as, all the Coriolis parameters $\zeta_{\lambda\mu}^\alpha$, Eq. (2), and rotational-vibrational coefficients, Refs. [20,21]:

$$a_{\lambda}^{\alpha\beta} = 2 \sum_{\gamma\delta\kappa} \epsilon_{\alpha\gamma\kappa} \epsilon_{\beta\delta\kappa} \sum_N m_N^{1/2} T_{N\gamma}^e I_{N\gamma\lambda}, \quad (7)$$

(the values $r_{N\gamma}^e$ here are the equilibrium coordinates of atoms) can be expressed in a very simple form.

3. Relations between spectroscopic parameters of the CH_4 molecule and discussion

It is known (see, e.g., Ref. [23]) that, besides Coriolis ζ -coefficients, all both the rotational, and vibrational spectroscopic parameters depend on the harmonic frequencies, ω_{λ} , and anharmonic force coefficients ($c_{\lambda\mu\nu}$ and $d_{\lambda\mu\nu\xi}$ in the notations of Hecht [23]). On that reason, it is important to estimate a relative value of all the ω_{λ} , $c_{\lambda\mu\nu}$, and $d_{\lambda\mu\nu\xi}$ parameters and to derive corresponding simple analytical relations between them. We made this on the base of analysis of the quadratic, F_{ij} , cubic, F_{ijk} , and quartic, F_{ijkl} , force constants of the methane intramolecular potential function, V :

$$V = V^{(2)} + V^{(3)} + V^{(4)} + \dots, \quad (8)$$

where the quadratic part, $V^{(2)}$, has the form (in symmetry coordinate notations):

$$V^{(2)} = \frac{1}{2} F_{11} S_1^2 + \frac{1}{2} F_{22} (S_{2a}^2 + S_{2b}^2) + \frac{1}{2} F_{33} (S_{3x}^2 + S_{3y}^2 + S_{3z}^2) + F_{34} (S_{3x} S_{4x} + S_{3y} S_{4y} + S_{3z} S_{4z}) + \frac{1}{2} F_{44} (S_{4x}^2 + S_{4y}^2 + S_{4z}^2). \quad (9)$$

We do not present here the cubic, $V^{(3)}$, quartic, $V^{(4)}$, etc., parts of the intramolecular potential function because they are cumbersome. However, the reader can find them, e.g., in Eq. (10) and Table 4 of Ref. [24].

Data from some different sets of $F_{i..j}$ parameters, Refs. [25–27], were used for the above mentioned estimations. It was found that the following simple relations between $F_{i..j}$ parameters are suitable for satisfactory description of different both anharmonic force parameters, $c_{\lambda\mu\nu}$, and $d_{\lambda\mu\nu\xi}$ (see Appendix I from Ref. [23]), and different spectroscopic parameters of the CH_4 molecule:

$$\frac{F_{33}}{267} = \frac{F_{11}}{272} = \frac{4F_{22}}{97\rho_e^2} = \frac{3F_{44}}{67\rho_e^2} = -\frac{2F_{34}}{19\rho_e}, \quad (10)$$

$$\begin{aligned} \frac{2}{3} F_{244} &= -\frac{7}{3} F_{222} = -\frac{2}{3} F_{444} = \rho_e F_{144} = \frac{4\rho_e}{5} F_{122} = -\rho_e F_{234} = 2\rho_e F_{344} \\ &= \frac{\rho_e^2}{2} F_{233} = \rho_e^2 F_{334} = -2\rho_e^2 F_{134} = \frac{\rho_e^3}{90} F_{111} = \frac{\rho_e^3}{90} F_{333} \\ &= \frac{\rho_e^3}{90} F_{133} = -\frac{\rho_e^2}{30} F_{11}, \end{aligned} \quad (11)$$

and

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

all the other F_{ijkl} -parameters have been taken equal to zero. The value ρ_e in Eqs. (10)–(12) is the equilibrium distance between the nuclei C and H.

Eq. (10) leads to the following simple relations between the harmonic frequencies, ω_i , of the CH₄ molecule:

$$\frac{\omega_1^2}{120} = \frac{\omega_2^2}{32} = \frac{\omega_3^2}{81 + 28\sqrt{3}} = \frac{\omega_4^2}{72 - 28\sqrt{3}}. \quad (13)$$

Additionally, as the analysis of data from Refs. [25–27] shown, suitable enough relations between the F_{11} , F_{1111} , and F_{1111} parameters of the potential function, Eq. (8), can be used:

$$F_{111} \approx -\frac{3}{\rho_e} F_{11} \quad (14)$$

and

$$F_{1111} \approx \frac{8}{\rho_e^2} F_{11}. \quad (15)$$

If to take now into account all the relations, Eqs. (10)–(15), then the following approximations for the cubic, c_{ijk} , and quartic, d_{ijkl} , anharmonic parameters (in normal-mode notations, Ref. [23]) can be obtained:

$$\begin{aligned}
 36c_{111} &= -177c_{122} = 11c_{133} = 268c_{134} = -51c_{144} \\
 &= -585c_{222} = -137c_{233} = -41c_{234} = -205c_{244} \\
 &= \frac{26}{5} c_{333} = 45c_{334} = 34c_{344} = 43c_{444} \\
 &= -\frac{9}{\pi c \rho_e} \left(\frac{h^2 F_{11}}{m_H^3} \right)^{1/4} \quad (16)
 \end{aligned}$$

and

$$\begin{aligned}
 \frac{2}{3} d_{1111} &= -\frac{10}{29} d_{1122} = \frac{1}{10} d_{1133} = -\frac{10}{47} d_{1144} = -10d_{2222} \\
 &= -\frac{10}{41} d_{2233} = -\frac{5}{22} d_{2234} = 5d_{2244} = 20d_{2244t} \\
 &= \frac{10}{33} d_{3333} = -\frac{2}{3} d_{3334} = -\frac{10}{69} d_{3344} = \frac{1}{4} d_{3344sb} \\
 &= -d_{3344t} = \frac{10}{3} d_{4444} = -10d_{4444t} = \frac{23}{200} \frac{h}{\pi c m_H \rho_e^2} \\
 &\approx \frac{92}{75} B_e. \quad (17)
 \end{aligned}$$

As the final step of analysis, the obtained simple relations between the Coriolis coefficients, harmonic frequencies, c -, and d -parameters were used to derive relations between different spectroscopic parameters of the CH₄ molecule. In this case, general formulas for

spectroscopic parameters from Refs. [23,28]¹ were used. As the result, we produce a set of simple relations that connect different vibrational, $x_{i\mu}$, rotational–vibrational Y_i , and different tetrahedral splitting parameters:

$$\begin{aligned}
 x_{11} &= \frac{21}{32} x_{12} = \frac{4}{17} x_{13} = 80x_{14} = 80x_{22} = \frac{28}{25} x_{23} = \frac{13}{5} x_{24} \\
 &= \frac{11}{25} x_{33} = \frac{9}{5} x_{34} = \frac{23}{10} x_{44} = -28G_{22} = -\frac{21}{20} G_{33} = 13G_{34} \\
 &= -\frac{13}{5} G_{44} = 20S_{34} = -30T_{23} = 25T_{24} = -\frac{19}{5} T_{33} \\
 &= -27T_{44} = -\frac{7}{32} \frac{h}{\pi c m_H \rho_e^2} \approx -\frac{7}{3} B_e, \quad (18)
 \end{aligned}$$

and

$$\begin{aligned}
 \frac{10}{11} Y_1 &= -\frac{17}{44} Y_2^{(1)} = 13Y_2^{(2)} = Y_3 = \frac{6}{11} Y_4^{(1)} = \frac{17}{5} Y_4^{(2)} \\
 &= -\frac{h^2}{16\pi c \rho_e^4 (m_H^3 F_{11})^{1/2}} \approx -\frac{11}{3} \frac{B_e^2}{\omega_3} = -\frac{33}{49} \frac{x_{11}^2}{\omega_3}. \quad (19)
 \end{aligned}$$

In relations (19) 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 type resonance interaction.

To illustrate the efficiency of the obtained results, column 2 of Tables 2 and 3 presents the results of numerical calculations with the formulas (18) and (19). We would like to emphasize that in those calculations only two parameters (ρ_e and F_{11} , or ω_3 and B_e) are independent. The values of all other parameters are estimated on the base of these two initial ones. For comparison, columns 3 and 4 of Tables 2 and 3 show the values of corresponding vibrational parameters from Refs. [25] and [6], and of rotational–vibrational parameters from Refs. [19] and [29], respectively. In the most cases one can see good correlation between the results obtained on the base of the derived relations, on the one hand, and the results obtained on the base of both the ab initio calculations, [25], and the fit of experimental data, [6,19,29], on the other hand. Some more or less significant discrepancy can be seen only between calculated and “experimental” values of the parameters $Y_2^{(2)}$ and $Y_4^{(2)}$ (differences equal +0.0040 cm⁻¹ and -0.0080 cm⁻¹, respectively). However, this discrepancy can be easily understood if one will remember that, in accordance with the general vibrational–rotational theory (see, e.g., Ref. [20]), there is a strong connection between the rotational parameters of strongly interacting vibrational states (states (0100) and (0001) in our case), on the one hand, and resonance interaction parameter (Coriolis interaction parameter, $X_{E F_2}^{1(1,F_2)} = -9.63$ cm⁻¹, in notations of Ref. [19]), on the other hand. However, it should be mentioned that this numerical value of the parameter $X_{E F_2}^{1(1,F_2)}$ was reproduced in [19] from earlier paper, Ref. [31] where the value of the parameter $X_{E F_2}^{1(1,F_2)}$ is (-9.63 ± 0.42) cm⁻¹. It is not difficult to estimate that the decrease of the absolute value of the parameter $X_{E F_2}^{1(1,F_2)}$ by 0.42 cm⁻¹ changes “experimental” values of the parameters $Y_2^{(2)}$ and $Y_4^{(2)}$ up to -0.0016 cm⁻¹ and -0.0068 cm⁻¹, respectively. In its turn, these values already are close to the predicted values of the parameters $Y_2^{(2)}$ and $Y_4^{(2)}$.

As the resume of the above said, one can expect that the simple relations obtained in the present paper may to give a correct qualitative picture of the peculiarities in the complicated spectra of the methane molecule. At the same time, it would not be strange, if the derived simple model with only two free parameters gives not very

¹ Formulas in Refs. [23,28] are exactly the same with the exception of the fact that the resonance interaction between the states $(v_1 v_2 v_3 v_4)$ and $(v_1 v_2 \pm 1 v_3 v_4 \mp 1)$ are taken into account in Ref. [28].

Table 2
Vibrational spectroscopic parameters of the $^{12}\text{CH}_4$ molecule (in cm^{-1}).

Parameter 1	From (13) and (18) 2	From Ref.[25] 3	From Ref.[6] 4
ω_1^a	3040.38	3036.2	3040.38
ω_2	1570.05	1570.4	1569.87
ω_3	3158.40	3157.1	3153.38
ω_4	1345.53	1345.3	1346.10
x_{11}^b	-12.518	-12.476	-12.560
x_{12}	-19.075	-18.485	-14.453
x_{13}	-53.202	-52.487	-52.562
x_{14}	-0.156	-0.706	-3.516
x_{22}	-0.156	-0.295	-1.159
x_{23}	-11.176	-12.847	-11.907
x_{24}	-4.815	-5.207	-5.571
x_{33}	-28.450	-28.336	-25.615
x_{34}	-6.954	-8.243	-8.212
x_{44}	-5.443	-5.854	-6.508
G_{22}	0.447	-0.426	0.366
G_{33}	11.922	11.544	9.406
G_{34}	-0.962	-0.742	-0.715
G_{44}	4.815	5.020	5.026
T_{23}	0.416	0.406	0.357
T_{24}	-0.501	-0.907	-0.906
T_{33}	3.294	3.246	3.332
T_{44}	0.463	0.535	0.545
S_{34}	-0.625	0.016	-0.022

^a The “basic” “experimental” value of the parameter ω_1 was taken from Ref. [30].

^b Necessary for calculations value of the parameter $\rho_e = 1.0855 \text{ \AA}$ was taken from Ref. [9].

Table 3
Rotational–vibrational spectroscopic parameters of the $^{12}\text{CH}_4$ molecule (in cm^{-1}).

Parameter 1	From (19) 2	From Ref. [19] 3	From Ref. [29] 4
Y_3^a	-0.0334	-0.0357	-0.0434
Y_1	-0.0367	-0.0377	
$Y_2^{(1)b}$	0.0864		0.0879
$Y_2^{(2)c}$	-0.0026	-0.0066	
$Y_4^{(1)b}$	-0.0612		-0.0648
$Y_4^{(2)c}$	-0.0098	-0.0018	

^a Calculated on the base of the values of ω_1 from Ref. [30] and ρ_e from Ref. [9]. All the other parameters are obtained from the relations (19) with the using of the value of the parameter Y_3 as an initial one.

^b Resonance interaction between the states $(v_1 v_2 v_3 v_4)$ and $(v_1 v_2 \pm 1 v_3 v_4 \mp 1)$ does not taken into account.

^c Resonance interaction between the states $(v_1 v_2 v_3 v_4)$ and $(v_1 v_2 \pm 1 v_3 v_4 \mp 1)$ is taken into account.

good quantitative correspondence between values predicted on their basis and high accurate experimental data. However, as the analysis showed, even such simple two-parameter model can provide more than satisfactory quantitative predictions. As the illustration, experimental values of the band centers for the three lowest poliads ($N = \frac{1}{2}, 1$, and $\frac{3}{2}$, where $N = v_1 + \frac{v_2}{2} + v_3 + \frac{v_4}{2}$, and v_1, v_2, v_3, v_4 are the vibrational quantum numbers of the considered states) of the methane molecule from Ref. [3] are given in column 4 of Table 4. Results of prediction of the same band center values on the basis of two parameters, $\omega_1 = 3040.38 \text{ cm}^{-1}$ from Ref. [30] and $x_{11} = -12.518 \text{ cm}^{-1}$ from Ref. [9] (see, column 2 of Table 2 and footnotes to that Table) are shown in the column 2 of Table 4. One can see that the correspondence between data in columns 2 and 4 is not very good. However, the situation can be considerably improved if one will use the two mentioned parameters, ω_1 and x_{11} , not from the literature, but adapted to the experimental data. In particular, column 3 of Table 4 presents the results of prediction on the basis of the values $\omega_1 = 3016.215 \text{ cm}^{-1}$ and $x_{11} = -10.546 \text{ cm}^{-1}$ (the lasts have been obtained from the fit of five band centers: $2\nu_2(A_1), 2\nu_2(E), 2\nu_4(A_1), 2\nu_4(E)$, and $2\nu_4(F_2)$).

Table 4
Values of band centers of three lowest poliads of the CH_4 molecule (in cm^{-1}).

Band ($v_1 v_2 v_3 v_4; l_2 l_3 l_4; T$) 1	Calc. I ^a 2	Calc. II ^b 3	Exp. [3] 4
(0001; 001; F_2)	1318.06	1311.70	1310.76
(0100; 100; E)	1537.01	1528.55	1533.33
(0002; 000; A_1)	2605.98	2598.01	2587.04
(0002; 002; F_2)	2631.17	2627.03	2614.26
(0002; 002; E)	2640.43	2619.22	2624.62
(0101; 101; F_2)	2845.25	2832.82	2830.32
(0101; 101; F_1)	2854.26	2839.57	2846.07
(1000; 000; A_1)	2917.23	2911.69	2916.48
(0010; 010; F_2)	3020.24	3016.90	3019.49
(0200; 000; A_1)	3072.80	3056.01	3063.65
(0200; 200; E)	3074.59	3057.52	3065.14
(0003; 001; F_2)	3900.78	3889.11	3870.49
(0003; 003; A_1)	3939.31	3922.18	3909.20
(0003; 003; F_1)	3948.57	3930.36	3920.51
(0003; 003; F_2)	3957.47	3937.88	3930.92
(0102; 102; F_1)	4154.54	4137.04	4128.76
(0102; 102; A_1)	4159.79	4141.48	4132.86
(0102; 102; F_2)	4162.55	4143.79	4142.86
(0102; 102; E)	4169.58	4149.72	4151.21
(0102; 102; A_2)	4175.82	4155.01	4161.85
(1001; 001; F_2)	4235.14	4223.26	4223.46
(0011; 011; F_2)	4329.97	4320.70	4319.21
(0011; 011; E)	4329.97	4322.90	4322.18
(0011; 011; F_1)	4334.39	4325.31	4322.59
(0011; 011; A_1)	4329.10	4320.85	4322.70
(0201; 001; F_2)	4374.07	4353.57	4348.72
(0201; 201; F_1)	4383.03	4361.11	4363.61
(0201; 201; F_2)	4390.20	4367.15	4378.95
(1100; 100; E)	4435.16	4424.17	4435.12
(0110; 110; F_1)	4542.74	4533.22	4537.55
(0110; 110; F_2)	4549.39	4538.84	4543.76
(0300; 100; E)	4609.19	4587.55	4592.03
(0300; 300; A_2)	4612.76	4590.57	4595.27
(0300; 300; A_1)	4612.76	4590.57	4595.50

^a Calculated with $\omega_1 = 3040.38 \text{ cm}^{-1}$ and $x_{11} = -12.518 \text{ cm}^{-1}$ (see text, for details).

^b Calculated with $\omega_1 = 3016.215 \text{ cm}^{-1}$ and $x_{11} = -10.546 \text{ cm}^{-1}$ (see text, for details).

One can see considerably better, than in the first case, correspondence between predicted and experimental data.

4. Conclusion

Obtained results can be used both in pure vibrational analysis and, especially, in analysis of complicated ro-vibrational spectra of high excited vibrational states of the methane molecule. One may expect also that, being compiled with the general isotopic substitution theory, the obtained results will allow one to derive analogous simple relations both between different spectroscopic parameters of separate isotopic species of the methane molecule, and to construct simple isotopic relations which will express any spectroscopic parameters of any “daughter” isotopic species as a simple function of one–two spectroscopic parameters of the “mother”, CH_4 molecule. In its turn, it is difficult to overestimate an importance of such kind relations for study of complicated rotational–vibrational spectra of the methane isotopomers, especially in high frequency spectral region. It is necessary to mention also, that the quantitative accuracy of relations can be increased if one will increase the number of free parameters up to three–four. In this case, of course, the derived model should be slightly changed.

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