AMBIGUITY OF SPECTROSCOPIC PARAMETERS IN THE CASE OF ACCIDENTAL VIBRATION–ROTATION RESONANCES IN TETRAHEDRAL MOLECULES.
r^2J AND r^2J^2 TERMS FOR E–F_2 INTERACTING STATES ☆

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The ambiguity of spectroscopic parameters in the case of accidental vibration–rotation resonances in tetrahedral molecules is discussed. Equations are derived which relate different possible sets of r_2r_4J and $r_2^2J^2$ and $r_4^2J^2$ parameters obtained by fitting to experimental data. Perturbation calculations are generalized to give formulae consistent with various sets of fitted parameters for interacting ν_2 and ν_4 band of $^{12}CH_4$.

1. Relations between fitted parameters of interacting E–F_2 states

In a series of papers by the Dijon and Reading groups [1–8] it was proved that a simultaneous fit of energy levels of close-lying states of tetrahedral molecules enabled one to achieve much better accuracy compared to a fit within an isolated-state model. However, the parameters of interacting states deduced from experimental data are often rather different in different papers. These distinctions make it difficult to compare the results and to use the fitted values in order to refine the molecular potential function. In this paper we consider the Coriolis interacting E and F_2 states of tetrahedral molecules, using Champion's formalism [3,4] for an effective hamiltonian

$$H^{\mathrm{eff}} = P\mathcal{H}^{\mathrm{eff}}P, \tag{1}$$

where P is the projector onto the manifold of vibration–rotation wavefunctions of interacting states considered and

$$\mathcal{H}^{\mathrm{eff}} = \sum t_{s,s'}^{\Omega(K,L)\Gamma\Gamma'}\, T_{s,s'}^{\Omega(K,L)\Gamma\Gamma'}. \tag{2}$$

In the expansion (2) $T_{s,s'}^{\Omega(K,L)\Gamma\Gamma'} = ((-1)^K V_{s,s'}^{\Gamma\Gamma'(L)} \times R^{\Omega(K,L)})^{A_1}$ are the irreducible vibration–rotation r^2J^Ω type tensors and $t_{s,s'}^{\Omega(K,L)\Gamma\Gamma'}$ are adjustable parameters.

The symbolic notation r^nJ^Ω is used for a vibration–rotation operator having total degree n in vibrational operators (coordinates q_s, impulses p_t or creation a_s^+ and annihilation a_t operators) and total degree Ω in the rotational

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operators. Subindices denote vibrational modes. For example, the $r_2 r_4 J$ term corresponds to the well-known first-order Coriolis coupling term $(q_2 p_4 - p_2 q_4) J_\alpha$ between ν_2 and ν_4.

Recently it has been shown [9] that there are the unitary transformations

$$\tilde{\mathcal{H}}^{\text{eff}} = \ldots \mathrm{e}^{\mathrm{i}\mathcal{S}_2} \mathrm{e}^{\mathrm{i}\mathcal{S}_1} \mathcal{H}^{\text{eff}} \mathrm{e}^{(-\mathrm{i}\mathcal{S}_1)} \mathrm{e}^{(-\mathrm{i}\mathcal{S}_2)} \ldots , \tag{3}$$

which keep the form (2) of effective hamiltonian and its eigenvalues unaltered but change the values of some parameter in a wide range. According to table 1 of ref. [9] in the case of Coriolis interacting ν_2 and ν_4 fundamentals of XY_4 molecules the first allowed S-generator in eq. (3) is of the form

$$\mathcal{S}_1 = s_{2,4}^{1(1,\mathrm{F}_1)\mathrm{EF}_2} (V_{2,4}^{\mathrm{EF}_2(\mathrm{F}_1)} \times R^{1(1,\mathrm{F}_1)})^{\mathrm{A}_1} , \tag{4}$$

where the notations of refs. [3,4] are used for vibrational V and rotational R tensors. In eq. (4) the parameter $s_{2,4}^{1(1,\mathrm{F}_1)\mathrm{EF}_2}$ is free except for the order-of-magnitude condition

$$s_{2,4}^{1(1,\mathrm{F}_1)\mathrm{EF}_2} \lesssim \lambda^2 . \tag{5}$$

The transformation (3), (4) induces changes in the $r_2 r_4 J$ type Coriolis interaction parameter $t_{2,4}^{1(1,\mathrm{F}_1)\mathrm{EF}_2}$, and in all diagonal $r_2^2 J^2$ and $r_4^2 J^2$ type parameters $t_{s,s}^{2(K,L)\Gamma\Gamma}$. After calculation of the commutator $[\mathcal{S}_1, \mathcal{H}_1^{\text{eff}}]$ we find relations between the parameters of the transformed and untransformed effective hamiltonians

$$\tilde{t}_{2,4}^{1(1,\mathrm{F}_1)\mathrm{EF}_2} = t_{2,4}^{1(1,\mathrm{F}_1)\mathrm{EF}_2} + (\mathcal{E}_2 - \mathcal{E}_4) s_{2,4}^{1(1,\mathrm{F}_1)\mathrm{EF}_2} , \tag{6}$$

$$\tilde{t}_{s,s}^{2(K,L)\Gamma\Gamma} = t_{s,s}^{2(K,L)\Gamma\Gamma} + C^{2(K,L)\Gamma\Gamma} s_{2,4}^{1(1,\mathrm{F}_1)\mathrm{EF}_2} t_{2,4}^{1(1,\mathrm{F}_1)\mathrm{EF}_2} , \tag{7}$$

where $\mathcal{E}_2$ and $\mathcal{E}_4$ are ν_2 and ν_4 vibrational energies, $s = 2$ or 4, $\Gamma = \mathrm{E}$ or F_2, and the constants $C^{2(K,L)\Gamma\Gamma}$ are the following

$$\begin{aligned} &C^{2(0,\mathrm{A}_1)\mathrm{EE}} = -4/9, \quad C^{2(2,\mathrm{E})\mathrm{EE}} = -2/3\sqrt{3}, \\ &C^{2(0,\mathrm{A}_1)\mathrm{F}_2\mathrm{F}_2} = 8/27, \quad C^{2(2,\mathrm{E})\mathrm{F}_2\mathrm{F}_2} = -4/9, \quad C^{2(2,\mathrm{F}_2)\mathrm{F}_2\mathrm{F}_2} = 1/3. \end{aligned} \tag{8}$$

Substituting eq. (6) in eq. (7) we obtain that allowed variations $\Delta t = \tilde{t} - t$ of the parameters of an effective hamiltonian are related by the equation

$$\Delta t_{s,s}^{2(K,L)\Gamma\Gamma} = C^{2(K,L)\Gamma\Gamma} (\mathcal{E}_2 - \mathcal{E}_4)^{-1} \Delta t_{2,4}^{1(1,\mathrm{F}_1)\mathrm{EF}_2} t_{2,4}^{1(1,\mathrm{F}_1)\mathrm{EF}_2} . \tag{9}$$

It means that one can vary parameters in an effective hamiltonian (2) according to eq. (9) without changes in its eigenvalues. Such variation leads to the change of an effective eigenbasis $\{\Psi^{\text{eff}}\}$ only since it is equivalent to a unitary transformation (3), (4). For closely lying vibrational levels,

$$(\mathcal{E}_2 - \mathcal{E}_4) \approx \lambda^m \omega, \quad m \geqslant 1, \tag{10a}$$

one has

$$\Delta t_{2,4}^{1(1,\mathrm{F}_1)\mathrm{EF}_2} \lesssim \lambda^m t_{2,4}^{1(1,\mathrm{F}_1)\mathrm{EF}_2} , \tag{10b}$$

$$\Delta t_{s,s}^{2(K,L)\mathrm{F}_2\mathrm{F}_2} \approx t_{s,s}^{2(K,L)\mathrm{F}_2\mathrm{F}_2} , \tag{10c}$$

i.e. small variations in the $r_2 r_4 J$ type interaction parameter lead to relatively large variation in diagonal $r^2 J^2$ type parameters. In view of this result, distinctions between fitted values of parameters deduced by Gray and Robiette [2] and by Pierre et al. [5] may be explained as follows. In fact, Pierre et al. have determined from the experimental data an effective hamiltonian which is different from that of Gray and Robiette[‡]. Though these two ef-

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[‡] We do not mean differences in formalisms. There is a one-to-one correspondence between the notations of Robiette et al. and of Champion (see, for example, table 4 of ref. [4]).

fective hamiltonians have approximately the same eigenvalues, they have different eigenfunctions $\{\Psi^{\mathrm{eff}}\}$ and $\{\Psi^{\mathrm{eff}}\}'$.

2. Case of strong resonance

It is convenient to rewrite the relation (9) in another manner, considering one of $\Delta t_{s,s}^{2(K,L)\Gamma\Gamma}$ as an independent variation. Let us, for example, write Δt as a function of $\Delta t_{4,4}^{2(2,\mathrm{E})\mathrm{F}_2\mathrm{F}_2}$

$$\Delta t_{s,s}^{2(K,L)\Gamma\Gamma} = -\tfrac{9}{4} C^{2(K,L)\Gamma\Gamma} \Delta t_{s,s}^{2(2,\mathrm{E})\mathrm{F}_2\mathrm{F}_2}, \quad \Delta t_{2,4}^{1(1,\mathrm{F}_1)\mathrm{EF}_2} = -\tfrac{9}{4}[(\mathcal{E}_2 - \mathcal{E}_4)/t_{2,4}^{1(1,\mathrm{F}_1)\mathrm{EF}_2}]\, \Delta t_{4,4}^{2(2,\mathrm{E})\mathrm{F}_2\mathrm{F}_2}. \tag{11}$$

These relations are exactly equivalent to eq. (9), they are more convenient to consider a case of strong resonances, when $(\mathcal{E}_2 - \mathcal{E}_4) \to 0$ (formally $m \to \infty$ in eq. (10a)). In this case we have $\Delta t_{2,4}^{1(1,\mathrm{F}_1)\mathrm{EF}_2} \to 0$, thus one cannot change the interaction parameter by a transformation (3). It means that this parameter must become very well defined in the fit. However, all five diagonal r^2J^2 type parameters may be changed by the unitary transformation (3) from negative to positive values including zero. Their changes are related by eq. (11).

3. Ambiguity in perturbation calculations

It must be emphasized that the ambiguity considered is not a special feature of processing of experimental data. The similar ambiguity takes place in perturbation calculations. Let us consider the perturbation theory in the form of contact transformations (CT) [10–13]. A generalized version of CT applicable to accidental resonances is considered in ref. [11]. The aim of CT is to transform the initial vibration–rotation hamiltonian $H_{\text{vib-rot}} = H_0 + \lambda H_1 + \lambda^2 H_2 + ...$,

$$\mathcal{H}^{\mathrm{eff}} = ...\mathrm{e}^{\mathrm{i}\lambda^2 S_2}\,\mathrm{e}^{\mathrm{i}\lambda S_1} H_{\text{vib-rot}}\, \mathrm{e}^{-\mathrm{i}\lambda S_1}\,\mathrm{e}^{-\mathrm{i}\lambda^2 S_2} ... = H_0 + \lambda \mathcal{H}_1^{\mathrm{eff}} + \lambda^2 \mathcal{H}_2^{\mathrm{eff}} + ..., \tag{12}$$

in order to eliminate a coupling between different sets of interacting states. In the notations of ref. [11] this requirement may be written as $\mathcal{H}^{\mathrm{eff}} = \langle \mathcal{H}^{\mathrm{eff}} \rangle'$ where $\langle ... \rangle'$ is a block diagonal part with blocks associated to interacting states.

The generators S_n are defined by commutator equations which have ambiguous solutions. In the notations of ref. [11] one has

$$\mathrm{i}S_1 = (1/\mathfrak{D}')(H_1) + \langle \mathrm{i}Z_1 \rangle', \quad \mathrm{i}S_2 = (1/\mathfrak{D}')(H_2^1) + \langle \mathrm{i}Z_2 \rangle', ..., \tag{13}$$

where $Z_1 \approx \lambda$ is an arbitrary hermitean operator and the operation $(1/\mathfrak{D}')(...)$ is inverse [11–13] to the commutator operation $[..., H_0]$. In order to derive an effective hamiltonian which is invariant under the time reversal operation one has to consider only imaginary Z_n operators [‡]. The terms including lowest powers of r and J operators which are totally symmetric with respect to $\mathrm{T_d}$ group have the from

$$Z_1 = z_1 (V_{2,4}^{\mathrm{EF}_2(\mathrm{F}_1)} \times R^{1(1,\mathrm{F}_1)})^{\mathrm{A}_1}, \quad Z_2 = z_2 ({}^{(-1)}V_{2,4}^{\mathrm{EF}_2(\mathrm{F}_2)} \times R^{1(1,\mathrm{F}_1)})^{\mathrm{A}_1}, \tag{14}$$

where $z_1 \lesssim \lambda^2, z_2 \lesssim \lambda^4$ are the free parameters. The usual way to avoid this ambiguity in CT is to require [≠]

$$\langle \mathrm{i}S_n \rangle' = 0, \quad \text{i.e.} \quad Z_n = 0, z_n = 0. \tag{15}$$

We denote the S-generators which satisfy the condition (15) by ${}^{\mathrm{CT}}S$

$${}^{\mathrm{CT}}S_1 = (-\mathrm{i})(1/\mathfrak{D}')(H_1) = {}^{\mathrm{CT}}S_1^{\mathrm{centrif}} + {}^{\mathrm{CT}}S_1^{\mathrm{cor}} + {}^{\mathrm{CT}}S_1^{\mathrm{anh}}. \tag{16}$$

[‡] I.e. Z_n must change sign upon time reversal.

[≠] Similar (but not the same for $n \geqslant 2$) conditions are applied in all degenerate or quasi-degenerate formulations of perturbation theory [13].

Operations $\langle\ldots\rangle'$ and $(1/\mathfrak{D}')(\ldots)$ of CT in terms of irreducible tensors $(V \times R)^{\mathrm{A}_1}$ [3,4] may be performed in a very simple way [14]

$$\begin{aligned}
&\langle({}^{\pm}V_{\{n_s\},\{m_s\}} \times R^{\Omega(K,\Gamma)})^{\mathrm{A}_1}\rangle' = \Delta({}^{\pm}V_{\{n_s\},\{m_s\}} \times R^{\Omega(K,\Gamma)})^{\mathrm{A}_1}, \\
&(1/\mathfrak{D}')({}^{\pm}V_{\{n_s\},\{m_s\}} \times R^{\Omega(K,\Gamma)})^{\mathrm{A}_1} = (1-\Delta)(-1)^{K}\mathrm{i}\Big(\sum_i n_i\omega_i - \sum_i m_i\omega_i\Big)^{-1} ({}^{\pm}V_{\{n_s\},\{m_s\}} \times R^{\Omega(K,\Gamma)})^{\mathrm{A}_1},
\end{aligned} \tag{17}$$

where $\Delta = 1$ if states $\Sigma_i n_i\omega_i$ and $\Sigma_i m_i\omega_i$ are in resonance (or coincide); $\Delta = 0$ if states $\Sigma_i n_i\omega_i$ and $\Sigma_i m_i\omega_i$ are not in resonance. For example, for XY_4 molecule we have

$$\begin{aligned}
\mathrm{i}^{\mathrm{CT}}S_1^{\mathrm{centrif}} &= (1/\sqrt{2})(B/\omega_1)^{3/2}[(a_1^+ - a_1)^{\mathrm{A}_1} \times R^{2(0,\mathrm{A}_1)}]^{\mathrm{A}_1} - \tfrac{1}{2}(B/\omega_2)^{3/2}[(a_2^+ - a_2)^{\mathrm{E}} \times R^{2(2,\mathrm{E})}]^{\mathrm{A}_1} \\
&\quad - \sqrt{3/8}\sum_{t=3,4}(B/\omega_t)^{3/2}\zeta_{2t}[(a_t^+ - a_t)^{\mathrm{F}_2} \times R^{2(2,\mathrm{F}_2)}]^{\mathrm{A}_1}, \\
\mathrm{i}^{\mathrm{CT}}S_1^{\mathrm{cor}} &= -\tfrac{1}{2}\mathrm{i}\sqrt{3}\,B\sum_{t=3,4}[\zeta_{2t}/(\omega_2\omega_t)^{1/2}]\{[(\omega_2 - \omega_t)/(\omega_2 + \omega_t)] \\
&\quad \times \{[(a_2^+ \times a_t^+)^{\mathrm{F}_1} - (a_2 \times a_t)^{\mathrm{F}_1}] \times R^{1(1,\mathrm{F}_1)}\}^{\mathrm{A}_1} \\
&\quad + [(\omega_2 + \omega_t)/(\omega_2 - \omega_t)]\{[(a_2^+ \times a_t)^{\mathrm{F}_1} - (a_t^+ \times a_2)^{\mathrm{F}_1}] \times R^{1(1,\mathrm{F}_1)}\}^{\mathrm{A}_1} \\
&\quad - \mathrm{i}\sqrt{6}\,B\sum_{t=3,4}\zeta_t[(a_t^+ \times a_t)^{\mathrm{F}_1} \times R^{1(1,\mathrm{F}_1)}]^{\mathrm{A}_1} \\
&\quad - \mathrm{i}\sqrt{3/2}\,B[\zeta_{34}/(\omega_3\omega_4)^{1/2}]\{[(\omega_3 - \omega_4)/(\omega_3 + \omega_4)]\{[(a_3^+ \times a_4^+)^{\mathrm{F}_1} - (a_3 \times a_4)^{\mathrm{F}_1}] \times R^{1(1,\mathrm{F}_1)}\}^{\mathrm{A}_1} \\
&\quad + [(\omega_3 + \omega_4)/(\omega_3 - \omega_4)]\{[(a_3^+ \times a_4)^{\mathrm{F}_1} - (a_4^+ \times a_3)^{\mathrm{F}_1}] \times R^{1(1,\mathrm{F}_1)}\}^{\mathrm{A}_1}\}.
\end{aligned} \tag{18}$$

In general, an effective hamiltonian is given by [13,11]

$$\mathcal{H}_1^{\mathrm{eff}}(Z_1) = \{\langle H_1\rangle'\} + [\langle \mathrm{i}Z_1\rangle', H_0], \tag{19a}$$

$$\mathcal{H}_2^{\mathrm{eff}}(Z_1, Z_2) = \{\langle H_2^1\rangle' + \tfrac{1}{2}\langle[\mathrm{i}^{\mathrm{CT}}S_1, H_1]\rangle'\} + [\langle \mathrm{i}Z_1\rangle', \langle H_1\rangle'] + [\langle \mathrm{i}Z_1\rangle', [\langle \mathrm{i}Z_1\rangle', H_0]] + [\langle \mathrm{i}Z_2\rangle', H_0]. \tag{19b}$$

Only the terms in braces were used in all the previous calculations by CT. We shall denote associate formulae for t-parameters by ${}^{\mathrm{CT}}t$ assuming that the conditions (15) of CT were used to calculate it. For XY_4 molecules we have in the case of resonance between ν_2 and ν_4

$${}^{\mathrm{CT}}t_{2,2}^{2(0,\mathrm{A}_1)\mathrm{EE}} = B^2/\omega_2 + 4\sqrt{3}K_{122}(B/\omega_1)^{3/2} + B^2(\zeta_{23}^2/\omega_2)(3\omega_2^2 + \omega_3^2)/(\omega_2^2 - \omega_3^2), \tag{20}$$

$${}^{\mathrm{CT}}t_{4,4}^{2(0,\mathrm{A}_1)\mathrm{F}_2\mathrm{F}_2} = B^2\zeta_{24}^2/\omega_4 + 4\sqrt{3}K_{144}(B/\omega_1)^{3/2} + \tfrac{4}{3}B^2(\zeta_{34}^2/\omega_4)(3\omega_4^2 + \omega_3^2)/(\omega_4^2 - \omega_3^2). \tag{21}$$

The formulae for ${}^{\mathrm{CT}}t_{2,2}^{2(2,\mathrm{E})\mathrm{EE}}$, ${}^{\mathrm{CT}}t_{4,4}^{2(2,\mathrm{F}_2)\mathrm{F}_2\mathrm{F}_2}$, ${}^{\mathrm{CT}}t_{4,4}^{2(2,\mathrm{E})\mathrm{F}_2\mathrm{F}_2}$ are presented in ref. [15] on‡. Other formations of perturbation theory (such as projector formulations) provide the same second-order formulae.

However, the condition (15) is not necessary and is applied for a formal simplicity only. In the general case we have due to the last terms in eqs. (19) the following expression:

$$t_{s,s}^{2(K,L)\Gamma\Gamma} = {}^{\mathrm{CT}}t_{s,s}^{2(K,L)\Gamma\Gamma} + z_1 C^{2(K,L)\Gamma\Gamma}({}^{\mathrm{CT}}t_{2,4}^{1(1,\mathrm{F}_1)\mathrm{EF}_2}), \quad t_{2,4}^{1(1,\mathrm{F}_1)\mathrm{EF}_2} = {}^{\mathrm{CT}}t_{2,4}^{1(1,\mathrm{F}_1)\mathrm{EF}_2} + z_1(\omega_2 - \omega_4), \tag{22}$$

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‡ There are some misprints in appendix II of ref. [15]. Formulae for $t^{2(0,\mathrm{A}_1)\Gamma\Gamma}$ must read as in eqs. (20), (21).

where $s = 2,4$ and the parameter $z_1 \lesssim \lambda^2$ is free. The ambiguity in eq. (13) is equivalent to unitary transformations of effective hamiltonians [13,11]

$$\mathcal{H}^{\mathrm{eff}}(Z_1, Z_2, ...) = ...\mathrm{e}^{\mathrm{i}Z_2}\mathrm{e}^{\mathrm{i}Z_1}\{^{\mathrm{CT}}\mathcal{H}^{\mathrm{eff}}(Z_n = 0)\}\mathrm{e}^{-\mathrm{i}Z_1}\mathrm{e}^{-\mathrm{i}Z_2}... . \tag{23}$$

With a suitable choice of arbitrary Z_n operators one can obtain in particular cases from (23) the results of any other perturbation methods.

4. How to compare calculated and fitted parameters? Reduced hamiltonian

If one equates directly the parameters calculated by perturbation treatment and parameters deduced from a fit of the experimental data it will not be quite correct due to the ambiguity considered above. The condition (15) deals nothing with the requirement to minimize a standard deviation which is applied in computer programs used in a fit. In fact, one has two different effective hamiltonians $^{(\mathrm{calc})}\mathcal{H}^{\mathrm{eff}}$ and $^{(\mathrm{fit})}\mathcal{H}^{\mathrm{eff}}$. Even if they have the same eigenvalues they may have different r^2J^2 parameters since these hamiltonians may have different eigenfunctions $\{\Psi^{\mathrm{eff}}\}$.

In column 1 of table 2 we present the direct calculation (with $z_1 = 0$) of the r_2r_4J and r^2J^2 parameters for ν_2–ν_4 of CH_4 which do not coincide with fitted values of Gray and Robiette. In collumns 2, 3 we try to make optimal choice of free parameter z_1 in eq. (22) requiring $^{\mathrm{calc}}t_{2,4}^{1(1,F_1)EF_2} = {}^{\mathrm{fit}}t_{2,4}^{1(1,F_1)EF_2}$ or $^{\mathrm{calc}}t_{2,2}^{2(2,E)EE} = {}^{\mathrm{fit}}t_{2,2}^{2(2,E)EE}$. With these choices $z_1 = ({}^{\mathrm{fit}}t_{2,4}^{1(1,F_1)} - {}^{\mathrm{CT}}t_{2,4}^{1(1,F_1)})/(\omega_2 - \omega_4)$ or $z_1 = \frac{3}{2}\sqrt{3}({}^{\mathrm{CT}}t_{2,2}^{2(2,E)} - {}^{\mathrm{fit}}t_{2,2}^{2(2,E)})/{}^{\mathrm{CT}}t_{2,4}^{1(1,F_1)}$, we have much better agreement for the parameters. In fact, making this choice one performs a unitary transformation (23) in order to match eigenbasis of $^{(\mathrm{calc})}\mathcal{H}^{\mathrm{eff}}$ to the eigenbasis of $^{(\mathrm{fit})}\mathcal{H}^{\mathrm{eff}}$. Formulae (22) of the generalized contact transformations in particular cases with appropriate choice of free parameter z_1 may describe with reasonable accuracy the fitted set of parameters found by Gray and Robiette or the set of Pierre et al.

Another possibility is to avoid the ambiguity by a restriction imposed on the form of $\mathcal{H}^{\mathrm{eff}}$. Let us consider a diagonal parameter $t_{l,j}^{2(m,L)LL}$. According to eqs. (7)–(10) its variation $\Delta t_{l,j}^{2(m,L)LL}$ is free. One can choose it in such a way that $t_{l,j}^{2(m,L)LL} = 0$. So one can fix $t_{l,j}^{2(m,L)LL}$ to zero or to other given value. After such restriction the transformation (3) is forbidden. We call such a hamiltonian a reduced effective hamiltonian $^{\mathrm{red}}\mathcal{H}^{\mathrm{eff}}$. Its parameters

Table 1
Comparison of the Pierre–Pierre–Champion–Lutz [5] and Gray–Robiette [2] fitted parameters (cm^{-1}) for ν_2 and ν_4 interacting bands of the methane molecule

	$\Omega(K,\Gamma)$	Fitted parameters of Pierre–Pierre–Champion–Lutz (PPCL) [a]	Parameters of unitary transformed PPCL-hamiltonian [b]	Fitted parameters of Gray and Robiette [c]
ν_2	$2(0,A_1)$	-0.6640×10^{-2}	-0.4433×10^{-2}	-0.3846×10^{-2}
	$2(2,E)$	-3.1455×10^{-2}	-2.9544×10^{-2}	-2.8025×10^{-2}
ν_2–ν_4 interaction	$1(1,F_1)$	-9.6344	-9.52	-9.52
ν_4	$2(0,A_1)$	-0.1813×10^{-2}	-0.3284×10^{-2}	-0.3106×10^{-2}
	$2(2,E)$	-0.942×10^{-2}	-0.7213×10^{-2}	-0.6879×10^{-2}
	$2(2,F_2)$	-2.758×10^{-2}	-2.9295×10^{-2}	-3.126×10^{-2}

[a] Ref. [5]. [b] $s_{2,4}^{1(1,F_1)EF_2} = 0.5155 \times 10^{-3}$. [c] Ref. [2].

Table 2
Comparison of $r_s^2J^2$ and r_2r_4J parameters (cm^{-1}) calculated by generalized contact transformations and deduced from simultaneous fit of experimental data on ν_2 and ν_4 interacting states of $^{12}CH_4$. $\Delta t/t = (\mathrm{fit}_t - \mathrm{calc}_t)/\mathrm{fit}_t$

	$\Omega(K,\Gamma)$	Direct perturbation calculations [a] $z_1 = 0$	Calculations by generalized CT [a] $z_1 = 5.95 \times 10^{-4}$	Calculations by generalized CT [a] $z_1 = 8.97 \times 10^{-4}$	Fitted values of Gray and Robiette [b]
ν_2	2(0,A$_1$)	-0.521×10^{-2}	-0.303×10^{-2}	-0.137×10^{-2}	-0.3846×10^{-2}
	2(2,E)	-3.135×10^{-2}	-2.946×10^{-2}	-2.8025×10^{-2}	-2.8025×10^{-2}
ν_2–ν_4 interaction	1(1,F$_1$)	-9.6321	-9.52	-9.43	-9.52
ν_4	2(0,A$_1$)	-0.064×10^{-2}	-0.209×10^{-2}	-0.320×10^{-2}	-0.3106×10^{-2}
	2(2,E)	-1.080×10^{-2}	-0.862×10^{-2}	-0.696×10^{-2}	-0.6879×10^{-2}
	2(2,F$_2$)	-2.893×10^{-2}	-3.057×10^{-2}	-3.181×10^{-2}	-3.126×10^{-2}
$\Sigma(\Delta t/t)^2$		1.11	0.22	0.42	

[a] Anharmonic force field of Gray and Robiette [16]. [b] Ref. [2].

are related to parameters of an unreduced one as follows

$$^{\mathrm{red}}t_{l,l}^{2(m,L')LL} = 0, \tag{24}$$

$$^{\mathrm{red}}t_{s,s}^{2(K,\Gamma')\Gamma\Gamma} = t_{s,s}^{2(K,\Gamma')\Gamma\Gamma} - \left(C^{2(K,\Gamma')\Gamma\Gamma}/C^{2(m,L')LL}\right)t_{l,l}^{2(m,L')LL}, \tag{25}$$

$$^{\mathrm{red}}t_{2,4}^{1(1,F_1)EF_2} = t_{2,4}^{1(1,F_1)EF_2} - \left[(\mathcal{E}_2 - \mathcal{E}_4)/C^{2(m,L')LL}\right] t_{l,l}^{2(m,L')LL}/t_{2,4}^{1(1,F_1)EF_2}. \tag{26}$$

It is possible to compare directly calculated and fitted parameters (see table 3) if the same way of reduction in a

Table 3
$r_s^2J^2$ and r_2r_4J parameters (cm^{-1}) of reduced effective hamiltonian for ν_2 and ν_4 interacting states of $^{12}CH_4$. The removed parameter is marked by asterisk. Parameters of reduced hamiltonian are recalculated with the use of eqs. (24)–(26)

	$\Omega(K,\Gamma)$	Using perturbation calculations [a]	Using fitted values of Gray and Robiette [b]	Using fitted values of Pierre et al. [c]
ν_2	2(0,A$_1$)	0.559×10^{-2}	0.377×10^{-2}	0.278×10^{-2}
	2(2,E)	-2.200×10^{-2}	-2.207×10^{-2}	-2.329×10^{-2}
ν_2–ν_4 interaction	1(1,F$_1$)	-9.078	-9.161	-9.149
ν_4	2(0,A$_1$)	-0.784×10^{-2}	-0.769×10^{-2}	-0.809×10^{-2}
	*2(2,E)	*0	*0	*0
	2(2,F$_2$)	-3.703×10^{-2}	-3.642×10^{-2}	-3.465×10^{-2}
$S_{2,4}^{1(1,F_1)EF_2}$		2.52×10^{-3}	1.63×10^{-3}	2.20×10^{-3}

[a] Anharmonic forc field of Gray and Robiette [16]. [b] Ref. [2]. [c] Ref. [5].

fit of the experimental data and in perturbation calculations is used.

We have used the anharmonic methane force field of Gray and Robiette [16] deduced from the fits of isolated states. Tables 2 and 3 make it clear that this force field is more consistent with fitted parameters of interacting ν_2 and ν_4 states of ref. [2] than it may seem from direct perturbation claculations (column 1 of tabel 2).

The second transformation in eq. (3) $\mathcal{S}_2 \sim Z_2$, which induces changes in $t_{2,4}^{2(2,F_2)EF_2}$ interaction parameter and in $t_{2,2}^{3(3,A_2)EE}$ and $t_{4,4}^{3(K,\Gamma)F_2F_2}$ diagonal parameters, has been discussed in ref. [9].

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