AMBIGUITY OF SPECTROSCOPIC PARAMETERS
IN THE CASE OF ACCIDENTAL VIBRATION–ROTATION RESONANCES
IN TETRAHEDRAL MOLECULES.

\( r^2 J \) AND \( r^2 J' \) 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 \( r_2 r_4 J \) and \( r_2 J' \) parameters obtained by fitting to experimental data. Perturbation calculations are generalized to give formulae consistent with various sets of fitted parameters for interacting \( \nu_2 \) and \( \nu_4 \) band of \( ^{12}\text{CH}_4 \).

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

\[
H^{\text{eff}} = P \mathcal{K}^{\text{eff}} P,
\]

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

\[
\mathcal{K}^{\text{eff}} = \sum_{s,s'} t_{s,s'}^{\Omega(K,L)\Gamma'\Gamma} t_{s,s'}^{\Omega(K,L)\Gamma'\Gamma'}.
\]

In the expansion \((2)\) \( T_{s,s'}^{\Omega(K,L)\Gamma'\Gamma} = (-1)^K \sum_{s,s'}^{\Omega(K,L)\Gamma'\Gamma'} R^{\Omega(K,L)\Gamma'\Gamma'} \) are the irreducible vibration–rotation type tensors and \( r_{s,s'}^{\Omega(K,L)\Gamma'\Gamma'} \) are adjustable parameters.

The symbolic notation \( r^n J^{\Omega} \) 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 \( a_s \) operators) and total degree \( \Omega \) in the rotational

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operators. Subindices denote vibrational modes. For example, the $r_2r_4J$ term corresponds to the well-known first-order Coriolis coupling term $(q_2p_4-p_2q_4)J_\alpha$ between $\nu_2$ and $\nu_4$.

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

\[
\Theta_{\text{eff}} = \ldots e^{i\delta_2} e^{i\delta_1} \Theta e^{-i\delta_1} e^{-i\delta_2} \ldots ,
\]

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 $\nu_2$ and $\nu_4$ fundamentals of XY4 molecules the first allowed $S$-generator in eq. (3) is of the form

\[
\delta_1 = s_{1}^{(1,F_1)EF_2}(\gamma EF_2^2(F_1) \times R J_1(F_1)A_1 ,
\]

where the notations of refs. [3,4] are used for vibrational $V$ and rotational $R$ tensors. In eq. (4) the parameter $s_{1}^{(1,F_1)EF_2}$ is free except for the order-of-magnitude condition

\[
s_{1}^{(1,F_1)EF_2} \leq \lambda^2 .
\]

The transformation (3), (4) induces changes in the $r_2r_4J$ type Coriolis interaction parameter $\gamma_{1}^{(1,F_1)EF_2}$, and in all diagonal $r_2^2J^2$ and $r_4^2J^2$ type parameters $r_{2}^{2(K,L)\Gamma}$. After calculation of the commutator $[\delta_1, \Theta_{\text{eff}}]$ we find relations between the parameters of the transformed and untransformed effective Hamiltonians

\[
\gamma_{2}^{(1,F_1)EF_2} = \gamma_{2}^{(1,F_1)EF_2} \pm (\varepsilon_2 - \varepsilon_4) s_{1}^{(1,F_1)EF_2} ,
\]

\[
C_{2}^{2(K,L)\Gamma} = C_{2}^{2(K,L)\Gamma} \pm C_{2}^{2(F_1)EF_2} t_{2}^{1(F_1)EF_2} ,
\]

where $\varepsilon_2$ and $\varepsilon_4$ are $\nu_2$ and $\nu_4$ vibrational energies, $s = 2$ or $4$, $\Gamma = E$ or $F_2$, and the constants $C_{2}^{2(K,L)\Gamma}$ are the following

\[
C_{2}^{2(0,A_1)EF_2} = -4/9, \quad C_{2}^{2(2,E)EF_2} = -2/3\sqrt{3} ,
\]

\[
C_{2}^{2(0,A_1)EF_2} = 8/27, \quad C_{2}^{2(2,E)EF_2} = -4/9, \quad C_{2}^{2(2,F_2)EF_2} = 1/3 .
\]

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

\[
\Delta t_{2}^{2(K,L)\Gamma} = C_{2}^{2(K,L)\Gamma} (\varepsilon_2 - \varepsilon_4) \Delta t_{1}^{1(F_1)EF_2} t_{1}^{1(F_1)EF_2} .
\]

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,

\[
(\varepsilon_2 - \varepsilon_4) \approx \lambda^m \omega , \quad m \gg 1 ,
\]

one has

\[
\Delta t_{2}^{1(F_1)EF_2} \leq \lambda^m \Delta t_{2}^{(1,F_1)EF_2} ,
\]

\[
\Delta t_{2}^{2(K,L)EF_2} \approx t_{2}^{(2,F_2)EF_2} ,
\]

i.e. small variations in the $r_2r_4J$ type interaction parameter lead to relatively large variation in diagonal $r_2^2J^2$ 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-
fective hamiltonians have approximately the same eigenvalues, they have different eigenfunctions \( \{\psi_{\text{eff}}\} \) and \( \{\psi_{\text{eff}}'\} \).

2. Case of strong resonance

It is convenient to rewrite the relation (9) in another manner, considering one of \( \Delta t_{s,s}^{2(K,L),I,I'} \) as an independent variation. Let us, for example, write \( \Delta t \) as a function of \( \Delta t_{s,s}^{2(2,E),F_2,F_2} \)

\[
\Delta t_{s,s}^{2(K,L),I,I'} = -\frac{9}{4} C_{2(K,L),I,I'} \Delta t_{s,s}^{2(2,E),F_2,F_2} + \Delta t_{s,s}^{2(1,F_1),F_2,F_2} = -\frac{9}{4} [(\mathcal{E}_2 - \mathcal{E}_4)/(2,1,F_1)_{2,F_2}] \Delta t_{s,s}^{2(2,E),F_2,F_2}. \tag{11}
\]

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 \( \Delta t_{s,s}^{2(1,F_1),F_2,F_2} \to 0 \), 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 \( H_{\text{vib-rot}} = H_0 + \lambda H_1 + \lambda^2 H_2 + \ldots \)

\[
\mathcal{G}_{\text{eff}} = -\lambda^2 S_2 e^{i\lambda S_1} H_{\text{vib-rot}} e^{-i\lambda S_1} \ldots = H_0 + \lambda S_{\text{eff}} + \lambda^2 S_{\text{eff}} + \ldots \tag{12}
\]

in order to eliminate a coupling between different sets of interacting states. In the notations of ref. [11] this requirement may be written as \( \mathcal{G}_{\text{eff}} = (\mathcal{G}_{\text{eff}})' \) where \( (...)' \) 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

\[
i S_1 = (1/\Omega')(H_1) + (iZ_1)', \quad i S_2 = (1/\Omega')(H_2) + (iZ_2)', \ldots \tag{13}
\]

where \( Z_1 = \lambda \) is an arbitrary hermitean operator and the operation \( (1/\Omega')(\ldots) \) is inverse [11-13] to the commutator operation \([\ldots,H_0] \). In order to derive an effective hamiltonian which is invariant under the time reversal operation one has to consider only imaginary \( Z_n \) operators \( \dagger \). The terms including lowest powers of \( r \) and \( J \) operators which are totally symmetric with respect to Td group have the form

\[
Z_1 = z_1 (\nu_{2,4}^{EF_2(F_1)} \times R_{1,1}^{1,1,F_1} \lambda_1^1), \quad Z_2 = z_2 (\nu_{2,4}^{EF_2(F_2)} \times R_{1,1}^{1,1,F_1} \lambda_1^1), \quad \ldots
\]

where \( z_1 \leq \lambda^2, z_2 \leq \lambda^4 \) are the free parameters. The usual way to avoid this ambiguity in CT is to require \( \dagger \)

\[
i S_n' = 0, \quad i.e. \quad Z_n = 0, z_n = 0. \tag{15}
\]

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

\[
\text{CT} S_1 = (-i)(1/\Omega')(H_1) = \text{CT} S_{\text{centr}} + \text{CT} S_{\text{cor}} + \text{CT} S_{\text{anh}}. \tag{16}
\]

\( \dagger \) I.e. \( Z_n \) must change sign upon time reversal.

\( \ddagger \) Similar (but not the same for \( n = 2 \)) conditions are applied in all degenerate or quasi-degenerate formulations of perturbation theory [13].
Operations \((\ldots)^v\) and \((1/\mathcal{D})^{(v)}\ldots\) of CT in terms of irreducible tensors \((V \times R)^A_1\) [3,4] may be performed in a very simple way [14]

\[
\langle \Delta^v V_{[n]}, [m]\rangle \times R^{(K,R)} )^A_1 = \Delta^v V_{[n]}, [m]\rangle \times R^{(K,R)} )^A_1 ,
\]

\[(1/\mathcal{D})^{(v)} V_{[n]}, [m]\rangle \times R^{(K,R)} )^A_1 = (1 - \Delta)^{(v)} K_1 (\sum n_i \omega_i - \sum m_i \omega_i )^{-1} \langle \Delta^v V_{[n]}, [m]\rangle \times R^{(K,R)} )^A_1 ,
\]

where \(\Delta = 1\) if states \(\Sigma n_i \omega_i\) and \(\Sigma m_i \omega_i\) are in resonance (or coincide); \(\Delta = 0\) if states \(\Sigma n_i \omega_i\) and \(\Sigma m_i \omega_i\) are not in resonance. For example, for XY\(_4\) molecule we have

\[i^{CT}_1 c_{\text{centrif}} = \frac{1}{2} (B/\omega_2)^{3/2} \left[ (a_1^+ - a_1^1) A_1 \times R^{(2,0)} \right] A_1 - \frac{1}{3} (B/\omega_2)^{3/2} \left[ (a_2^+ - a_2^1) \times R^{(2,0)} \right] A_1 ,
\]

\[i^{CT}_1 c_{\text{corr}} = -i \sqrt{3/8} B \sum_{\alpha = 2,4} \left[ \frac{\omega_2 - \omega_4}{\omega_2 + \omega_4} \right] \left[ (a_2^+ \times a_4^1) F_1 - (a_2^+ \times a_4^1) F_1 \right] R^{(1, F)} A_1 ,
\]

\[X \left[ (a_2^+ \times a_4^1) F_1 - (a_2^+ \times a_4^1) F_1 \right] \times R^{(1, F)} A_1 ,
\]

\[+ \frac{1}{2} \left[ (a_2^+ \times a_4^1) F_1 - (a_2^+ \times a_4^1) F_1 \right] \times R^{(1, F)} A_1 ,
\]

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

\[\mathcal{H}^\text{eff} = \{ [H_1] \} + \{ [iZ_1] \} + \{ [iZ_2] \} + \{ [iZ_3] \} + \{ [iZ_4] \} ,
\]

\[\mathcal{H}^\text{eff} = \{ [H_1] \} + \{ [iZ_1] \} + \{ [iZ_2] \} + \{ [iZ_3] \} + \{ [iZ_4] \} + \{ [iZ_5] \} ,
\]

Only the terms in braces were used in all the previous calculations by CT. We shall denote associate formulae for \(t\)-parameters by \(CT^T\) assuming that the conditions (15) of CT were used to calculate it. For XY\(_4\) molecules we have in the case of resonance between \(n_2\) and \(n_4\)

\[CT^T_{1, t, A_1}^{(2,0)} = B^2/\omega_2 + 4 \sqrt{3} K_{123} (B/\omega_1)^{3/2} + B^2 (\omega_2^2 + \omega_3^2) / (\omega_2 - \omega_3) ,
\]

\[CT^T_{1, t, A_1}^{(2,0)} = B^2 (\omega_2^2 + \omega_3^2) / (\omega_2 - \omega_3) ,
\]

The formulae for \(CT^T_{2, t, A_1}^{(2,0)}\), \(CT^T_{2, t, A_1}^{(2,0)}\), \(CT^T_{2, t, A_1}^{(2,0)}\), \(CT^T_{2, t, A_1}^{(2,0)}\), \(CT^T_{2, t, A_1}^{(2,0)}\) are presented in ref. [15] on \(\dagger\). Other forms 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:

\[t_{2, t, A_1}^{(2,0)} = CT^T_{1, t, A_1}^{(2,0)} + z_1 t_{2, t, A_1}^{(2,0)} (CT^T_{1, t, A_1}^{(2,0)} EF_2) ,
\]

\[t_{1, t, A_1}^{(2,0)} EF_2 = CT^T_{1, t, A_1}^{(2,0)} EF_2 + z_1 (\omega_2 - \omega_4) ,
\]

\[\dagger\] There are some misprints in appendix II of ref. [15]. Formulae for \(t_{2, t, A_1}^{(2,0)}\) must read as in eqs. (20), (21).
where \( s = 2,4 \) and the parameter \( z_1 \leq \lambda^2 \) is free. The ambiguity in eq. (13) is equivalent to unitary transformations of effective hamiltonians \([13,11]\)

\[
\mathcal{H}^{\text{eff}}(Z_1, Z_2, \ldots) = \ldots e^{iZ_2} e^{iZ_1} \{ \mathcal{C} \mathcal{H}^{\text{eff}}(Z_n = 0) \} e^{-iZ_1} e^{-iZ_2} \ldots.
\] (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 \((\text{calc}) \mathcal{H}^{\text{eff}} \) and \((\text{fit}) \mathcal{H}^{\text{eff}} \). Even if they have the same eigenvalues they may have different \( r^2 J^2 \) parameters since these hamiltonians may have different eigenfunctions \{\Psi^{\text{eff}}\}.

In column 1 of table 2 we present the direct calculation (with \( z_1 = 0 \)) of the \( r_2 f_4 \) and \( r_2 J^2 \) parameters for \( \nu_2-\nu_4 \) of CH\(_4\) which do not coincide with fitted values of Gray and Robiette. In columns 2, 3 we try to make optimal choice of free parameter \( z_1 \) in eq. (22) requiring \( \text{calc} r_2 f_4(1,F_1)F_2 = \text{fit} r_2 f_4(1,F_1)F_2 \) or \( \text{calc} r_2 J^2(E_2,E) = \text{fit} r_2 J^2(E_2,E) \). With these choices \( z_1 = (\text{fit} r_2 f_4(1,F_1) - \text{calc} r_2 f_4(1,F_1)) / (\omega_2 - \omega_4) \) or \( z_1 = \frac{3}{2} \sqrt{3} (\text{fit} r_2 J^2(E_2,E) - \text{calc} r_2 J^2(E_2,E)) / (\text{calc} r_2 J^2(F_2,F_2) - \text{calc} r_2 J^2(F_2,F_2)) \), 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 \((\text{calc}) \mathcal{H}^{\text{eff}} \) to the eigenbasis of \((\text{fit}) \mathcal{H}^{\text{eff}} \). 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 \( \mathcal{H}^{\text{eff}} \). Let us consider a diagonal parameter \( t^2_{2m,L} \). According to eqs. (7)-(10) its variation \( \Delta t^2_{2m,L} \) is free. One can choose it in such a way that \( t^2_{2m,L} = 0 \). So one can fix \( t^2_{2m,L} \) to zero or to other given value. After such restriction the transformation (3) is forbidden. We call such a hamiltonian a reduced effective hamiltonian \( \text{red} \mathcal{H}^{\text{eff}} \). Its parameters

<table>
<thead>
<tr>
<th>( \Omega(K, \Gamma) )</th>
<th>Fitted parameters of Pierre–Pierre–Champion–Lutz (PPCL) ( \alpha) )</th>
<th>Parameters of unitary transformed PPCL-hamiltonian ( \beta) )</th>
<th>Fitted parameters of Gray and Robiette ( \gamma) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \nu_2 )</td>
<td>( 2(0,A_1) )</td>
<td>(-0.6640 \times 10^{-2})</td>
<td>(-0.4433 \times 10^{-2})</td>
</tr>
<tr>
<td></td>
<td>( 2(2,E) )</td>
<td>(-3.1455 \times 10^{-2})</td>
<td>(-2.9544 \times 10^{-2})</td>
</tr>
<tr>
<td>( \nu_2-\nu_4 ) interaction</td>
<td>( 1(1,F_1) )</td>
<td>(-9.6344)</td>
<td>(-9.52)</td>
</tr>
<tr>
<td>( \nu_4 )</td>
<td>( 2(0,A_1) )</td>
<td>(-0.1813 \times 10^{-2})</td>
<td>(-0.3281 \times 10^{-2})</td>
</tr>
<tr>
<td></td>
<td>( 2(2,E) )</td>
<td>(-0.2492 \times 10^{-2})</td>
<td>(-0.7213 \times 10^{-2})</td>
</tr>
<tr>
<td></td>
<td>( 2(2,F_2) )</td>
<td>(-0.2578 \times 10^{-2})</td>
<td>(-2.9295 \times 10^{-2})</td>
</tr>
</tbody>
</table>

\( \alpha) \) Ref. [5]. \( \beta) S_{2}^{(2,F_2)}F_2 = 0.5155 \times 10^{-3}. \( \gamma) \) Ref. [2].
Table 2
Comparison of $r_{2}^2 J^2$ and $r_{2}F_{4}J$ parameters (cm$^{-1}$) calculated by generalized contact transformations and deduced from simultaneous fit of experimental data on $v_2$ and $v_4$ interacting states of $^{12}$CH$_4$. $\Delta tf = (\text{fit} - \text{calc})/\text{fit}$

<table>
<thead>
<tr>
<th>$\Omega(K, \Gamma)$</th>
<th>Direct perturbation calculations a) $z_1 = 0$</th>
<th>Calculations by generalized CT a) $z_1 = 5.95 \times 10^{-4}$</th>
<th>Calculations by generalized CT b) $z_1 = 8.97 \times 10^{-4}$</th>
<th>Fitted values of Gray and Robiette b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$v_2$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$2(0,A_1)$</td>
<td>$-0.521 \times 10^{-2}$</td>
<td>$-0.303 \times 10^{-2}$</td>
<td>$-0.137 \times 10^{-2}$</td>
<td>$-0.3846 \times 10^{-2}$</td>
</tr>
<tr>
<td>$2(2,E)$</td>
<td>$-3.135 \times 10^{-2}$</td>
<td>$-2.946 \times 10^{-2}$</td>
<td>$-2.8025 \times 10^{-2}$</td>
<td>$-2.8025 \times 10^{-2}$</td>
</tr>
<tr>
<td>$v_2 - v_4$ interaction</td>
<td>$1(1,F_1)$</td>
<td>$-9.6321$</td>
<td>$-9.52$</td>
<td>$-9.43$</td>
</tr>
<tr>
<td>$v_4$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$2(0,A_1)$</td>
<td>$-0.064 \times 10^{-2}$</td>
<td>$-0.209 \times 10^{-2}$</td>
<td>$-0.320 \times 10^{-2}$</td>
<td>$-0.3106 \times 10^{-2}$</td>
</tr>
<tr>
<td>$2(2,E)$</td>
<td>$-1.080 \times 10^{-2}$</td>
<td>$-0.862 \times 10^{-2}$</td>
<td>$-0.696 \times 10^{-2}$</td>
<td>$-0.6879 \times 10^{-2}$</td>
</tr>
<tr>
<td>$2(2,F_2)$</td>
<td>$-2.893 \times 10^{-2}$</td>
<td>$-3.057 \times 10^{-2}$</td>
<td>$-3.181 \times 10^{-2}$</td>
<td>$-3.126 \times 10^{-2}$</td>
</tr>
<tr>
<td>$\Sigma(\Delta tf)^2$</td>
<td></td>
<td>$1.11$</td>
<td>$0.22$</td>
<td>$0.42$</td>
</tr>
</tbody>
</table>

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

are related to parameters of an unreduced one as follows

$$\tilde{t}_{1,1,1}^{2(m,L')LL} = 0,$$

$$\tilde{t}_{2}^{2(K,\Gamma)\Gamma \Gamma} = \frac{(C^{2(K,\Gamma)\Gamma \Gamma}/C^{2(m,L')LL})\tilde{t}_{1,1}^{2(m,L')LL}},$$

$$\tilde{t}_{2,4}^{1(1,F_1)EF_2} = \tilde{t}_{2,4}^{1(1,F_1)EF_2} - [(E_2 - E_4)/C^{2(m,L')LL}] \tilde{t}_{1,1}^{2(m,L')LL}/\tilde{t}_{2,4}^{1(1,F_1)EF_2}. (26)$$

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

Table 3
$r_{2}^2 J^2$ and $r_{2}F_{4}J$ parameters (cm$^{-1}$) of reduced effective hamiltonian for $v_2$ and $v_4$ 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)

<table>
<thead>
<tr>
<th>$\Omega(K, \Gamma)$</th>
<th>Using perturbation calculations a)</th>
<th>Using fitted values of Gray and Robiette b)</th>
<th>Using fitted values of Pierre et al. c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$v_2$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$2(0,A_1)$</td>
<td>$0.559 \times 10^{-2}$</td>
<td>$0.377 \times 10^{-2}$</td>
<td>$0.278 \times 10^{-2}$</td>
</tr>
<tr>
<td>$2(2,E)$</td>
<td>$-2.200 \times 10^{-2}$</td>
<td>$-2.207 \times 10^{-2}$</td>
<td>$-2.329 \times 10^{-2}$</td>
</tr>
<tr>
<td>$v_2 - v_4$ interaction</td>
<td>$1(1,F_1)$</td>
<td>$-9.078$</td>
<td>$-9.161$</td>
</tr>
<tr>
<td>$v_4$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$2(0,A_1)$</td>
<td>$0.784 \times 10^{-2}$</td>
<td>$0.769 \times 10^{-2}$</td>
<td>$0.809 \times 10^{-2}$</td>
</tr>
<tr>
<td>*$2(2,E)$</td>
<td>*0</td>
<td>*0</td>
<td>*0</td>
</tr>
<tr>
<td>$2(2,F_2)$</td>
<td>$-3.703 \times 10^{-2}$</td>
<td>$-3.642 \times 10^{-2}$</td>
<td>$-3.465 \times 10^{-2}$</td>
</tr>
<tr>
<td>$\Sigma(\Delta tf)^2$</td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

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 $\nu_2$ and $\nu_4$ states of ref. [2] than it may seem from direct perturbation calculations (column 1 of table 2).

The second transformation in eq. (3) $\mathcal{C}_2 \rightarrow Z_2$, which induces changes in $t^{2(2, F_2)}\mathcal{F}_2\mathcal{F}_2$ interaction parameter and in $t^{2(3, A_2)}\mathcal{F}_2\mathcal{F}_2$ and $t^{4(4, F_2)}\mathcal{F}_2\mathcal{F}_2$ diagonal parameters, has been discussed in ref. [9].

References