Further Analysis of Effective Hamiltonians for Triply Degenerate Fundamentals of Tetrahedral Molecules: Unambiguous Fit of $q^2J^5$ and $q^2J^6$ Terms for $\nu_4$ of $^{12}$CH$_4$

VL. G. TYUTEREV,* G. PIERRE,† J. P. CHAMPION,† V. I. PEREVALOV,* AND B. I. ZHILINSKI†

*Laboratory of Spectroscopy, Institute of Atmospheric Optics, Siberian Branch, Academy of Sciences of the USSR, Akademischeskii 1, 634055 Tomsk, USSR; †Laboratoire de Spectrochimie Moléculaire, Unité de Recherche associée au CNRS, Université de Dijon, 6 Bd Gabriel 21100 Dijon, France; and ‡Chemistry Department, Moscow State University, Moscow 117234, USSR

The further study of ambiguities among $q^2J^5$ and $q^2J^6$ terms in effective Hamiltonians for triply degenerate fundamentals of tetrahedral molecules is presented. It is shown that, in agreement with theory, $q^2J^5$ and $q^2J^6$ diagonal coupling parameters cannot be considered as constants having definite values for a given $F_2$ vibrational state, just like $q^2J^4$ terms previously studied [VL. G. Tyuterev, J. P. Champion, G. Pierre, and V. I. Perevalov, J. Mol. Spectrosc. 105, 113–138 (1984)]. The use of reduced Hamiltonians containing fewer (but unambiguous) parameters is suggested and applied to the $\nu_4$ band of $^{12}$CH$_4$.

0022-2852/86 $3.00

I. INTRODUCTION

In previous papers (1, 2), it was shown that $q^2J^4$-type diagonal coupling parameters of $F_2$ triply degenerate fundamentals of Td molecules are indeterminable from experimental data. In Refs. (2, 3), it was suggested to use a reduced effective Hamiltonian containing five unambiguous fourth-order parameters instead of six parameters in a conventional expansion. The separate analysis of the $\nu_4$ experimental data of $^{12}$CH$_4$ (4) based on the assignments of Ref. (5) has put some light on the practical consequences of ambiguities and on the efficiency of reduced effective Hamiltonians (3).

In the present article, we present a further study of effective Hamiltonians for triply degenerate $F_2$ fundamentals including $q^2J^5$ and $q^2J^6$ terms with application to the methane molecule. Such higher order terms are actually needed if very-high-resolution data including high-$J$ values are to be analyzed. As a matter of fact, the effective Hamiltonian for the ground state is generally developed to the sixth order (6), and even eighth order terms have been considered for the study of $\nu_3$ as an isolated band (7). The most recent analyses of the $\nu_4$ band have been achieved using effective Hamiltonians for the dyad ($\nu_2/\nu_4$) developed to the third or fourth order (5, 8). Although we restrict ourselves to the study of separate $F_2$ state Hamiltonians, all the properties and conclusions are equally valid for the $F_2$ part of dyad Hamiltonians.
II. FIRST TWO TRANSFORMATIONS OF EFFECTIVE HAMILTONIANS FOR $F_2$ STATES OF $T_d$ MOLECULES

According to Ref. (1) there exist unitary transformations of effective Hamiltonians which change the effective eigenbasis and the values of some parameters but keep the operator form and eigenvalues unaltered:

$$\hat{H}_{\text{eff}} = \ldots e^{i\hat{S}_3} e^{i\hat{S}_2} e^{i\hat{S}_1} \hat{H}_{\text{eff}} e^{-i\hat{S}_1} e^{-i\hat{S}_2} e^{-i\hat{S}_3} \ldots$$  \hspace{1cm} (1)

This is the reason for an ambiguity of these parameters in fitting experimental data.

Throughout this paper, we use the following simplified notation corresponding to the formalism of Champion (9):

$$\mathcal{S}_{m} = \sum_{\alpha, \Gamma, n} \mathcal{S}_{\alpha}(\Gamma, n) \mathcal{S}_{\alpha}(\Gamma, n')$$  \hspace{1cm} (2)

where

$$\mathcal{S}_{\alpha}(\Gamma, n) = \mathcal{S}_{\alpha}(\Gamma, n) F_2 F_2 = \{(-1)^{\alpha+1} V_{\alpha}^{F_2 F_2} F_2 \times R_{\alpha}(\Gamma, n)\} (4)$$

is an irreducible vibration-rotation tensor. Similarly the parameters involved in the effective Hamiltonian for $F_2$ fundamentals are simply designated by

$$t_{\alpha}(\Gamma, n) = t_{\alpha}(\Gamma, n) F_2 F_2.$$  \hspace{1cm} (3)

A list of allowed terms in $S_m$ generators is presented in Table III of Ref. (2).

**First Transformation**

The first transformation relating to the generator

$$S_1 = s^{3(3,F_2)} \mathcal{S}^{3(3,F_2)} = \lambda^3$$  \hspace{1cm} (4)

has been considered in Refs. (2, 3). It gives leading contributions to $q^2 J^4$-type diagonal coupling parameters $t^{(4,\Gamma, n+\alpha)}$ as well as to some higher order $q^2 J^n$ parameters. These contributions induce changes in $t^{(4,\Gamma, n+\alpha)}$ parameters which are related by $PTZ$ equations (1, 2). Combinations $W_i$ of $t^{(4,\Gamma, n)}$ parameters, invariant under transformations (4), have been determined for $\nu_4$ of CH$_4$ in Ref. (3).

In order to avoid the ambiguity associated with transformation (4), one can reduce the fourth-order part of the effective Hamiltonian by fixing one of the $t^{(4,\Gamma, n+\alpha)}$ parameters to a given value within the interval allowed by order of magnitude requirements according to Ref. (3).

**Second Transformation**

The second transformation is associated with the generator

$$S_2 = s^{4(4,F_2)} \mathcal{S}^{4(4,F_2)} = \lambda^4.$$  \hspace{1cm} (5)

We follow the Amat Nielsen ordering scheme; i.e., we assume that $q, p \sim 1$ and $J_{\alpha} \sim \lambda^{-1}$. In the tensor notation of Ref. (9), it means that

$$V_{\alpha}^{(\Gamma, n+\alpha)} \sim 1 \quad \text{and} \quad R_{\alpha}^{(\Gamma, n)} \sim \lambda^{-\alpha}$$

where $\lambda \sim (\kappa m / \omega)$ is a small Born–Oppenheimer parameter.
The leading contribution $\Delta H$ to the effective Hamiltonian is due to the vibrational part of the commutator:

$$[iS_2, H_1^{\text{eff}}]$$

where

$$H_1^{\text{eff}} = t^{(1, F_1)} T^{(1, F_1)}$$

$$\Delta H = \hat{H}^{\text{eff}} - H_1^{\text{eff}} = g_2 [S^{(4, F_1)}, T^{(1, F_1)}]_0 + \cdots$$

$$= \frac{g_2}{2} \sum_X \frac{\sqrt{|X|}}{3} \left\{ \left[ (\psi_{v, 0}^{F_2 F_3 F_4})_{X}^{*} - (\psi_{v, 0}^{F_2 F_3 F_4})_{X} \right] \times \left[ \left[ R^{(4, F_1)}, R^{(1, F_1)} \right]_A \right]_A^X + \cdots \right\} \tag{7}$$

where

$$g_2 = i s^{(4, F_1)} t^{(1, F_1)}.$$  

From the expressions of vibrational and rotational commutators presented in Appendixes 1 and 2, it follows that the commutator (7) contributes to $q^2 J^5$ terms:

$$\tilde{t}^{S(K, n\Gamma)} = t^{S(K, n\Gamma)} + \Delta t^{S(K, n\Gamma)}$$  

where $t$ and $\tilde{t}$ designate the $q^2 J^5$ parameters, respectively, before and after transformation (5) is achieved:

$$\Delta t^{S(K, n\Gamma)} = b^{S(K, n\Gamma)} s^{(4, F_1)} t^{(1, F_1)}.$$ \hspace{1cm} (9b)

The coefficients $b^{S(K, n\Gamma)}$ are given by

$$b^{S(5, 0F_1)} = \frac{1}{3} \sqrt{\frac{11}{3}} K^{(4, 1 F_1 0 F_1)} \simeq 0.231435$$

$$b^{S(5, 1F_1)} = \frac{1}{3} \sqrt{\frac{11}{3}} K^{(4, 1 F_1 0 F_1)} \simeq 0.027546$$

$$b^{S(3, F_1)} = \frac{1}{9} \sqrt{\frac{10}{3}} \simeq 0.202860$$

$$b^{S(1, F_1)} = 0.$$  \hspace{1cm} (10)

The exact values of the isoscalar factors $K$ appearing in (10) are

$$K^{(4, 1 F_1 0 F_1)} = \frac{1}{12 \sqrt{55}} \left[ (87 - 17 \sqrt{21})^{1/2} + 3 \sqrt{7} (9 + \sqrt{21})^{1/2} \right] \simeq 0.362589$$

$$K^{(4, 1 F_1 1 F_1)} = - \frac{1}{12 \sqrt{55}} \left[ (87 - 17 \sqrt{21})^{1/2} - 3 \sqrt{7} (9 - \sqrt{21})^{1/2} \right] \simeq 0.043157.$$  

The parameter $s^{(4, F_1)}$ can be given any value within the interval determined by the order of magnitude requirement

$$s^{(4, F_1)} \ll \Delta.$$  \hspace{1cm} (11)

The transformation (5) satisfying the condition (11) changes the eigenbasis $\{ \psi^{\text{eff}} \}$ but keeps the operator form and eigenvalues of the effective Hamiltonian unchanged. The ordering in its expansion is not altered. The parameters $t^{S(5, 0F_1)}$ and $t^{S(3, F_1)}$ change...
essentially while \( t^{5(1,F_1)} \) is not affected. The contribution to \( t^{5(5,1,F_1)} \) is relatively small due to the relatively small value of the coefficient 
\[
K_{(5,1,F_1)}^{(5,1,F_1)}.
\]

III. BEHAVIOR OF \( q^2J^5 \)-TYPE DIAGONAL COUPLING PARAMETERS

Equations for Fifth-Order Parameters

Assuming that the fourth-order part of the effective Hamiltonian is reduced by fixing \( t^{4(4,F_2)} \) to zero \((1-3)\), allowed changes of the effective eigenbasis are due to the second transformation \((5)\). The corresponding changes of \( q^2J^5 \) parameters are related by linear equations which can be derived simply from Eqs. (9):

\[
\Delta t^{5(K,n,F_1)} = d^{5(K,n,F_1)} \Delta t^{5(5,0,F_1)}. \quad (12)
\]

The \( d \) constants have the following values:

\[
d^{5(5,1,F_1)} = b^{5(5,1,F_1)} / b^{5(5,0,F_1)} \approx 0.119025
\]
\[
d^{5(3,F_1)} = b^{5(3,F_1)} / b^{5(5,0,F_1)} \approx 0.876532
\]
\[
d^{5(1,F_1)} = 0. \quad (13a)
\]

It follows from Eqs. (9) and (13) that the parameters \( t^{5(5,0,F_1)} \), \( t^{5(5,1,F_1)} \), and \( t^{5(3,F_1)} \) cannot be unambiguously determined from experimental data, whereas \( t^{5(1,F_1)} \) has to be well defined. These conclusions may be tested by actual fits of experimental data. This is the subject of the next section.

Behavior of \( q^2J^5 \)-Fitted Parameters for \( v_4 \) of \( 12CH_4 \)

The experimental data used in the present work are those of Ref. (4) for which the experimental accuracy referred to in this paper is normally \( \delta_{\text{exper}} \sim 1-3 \times 10^{-3} \) cm\(^{-1}\).

In order to verify the validity of Eqs. (9)-(13), we made several fits of these data for various values of \( J_{\text{max}} \) and for different lengths of expansion of the effective Hamiltonian. For each fit, the parameter \( t^{5(5,0,F_1)} \) was fixed to a given value and only the three remaining fifth-order parameters \( t^{5(5,1,F_1)} \), \( t^{5(3,F_1)} \), and \( t^{5(1,F_1)} \) were adjusted. Repeating this procedure for a series of \( t^{5(5,0,F_1)} \) values, slightly shifted from one to the other, we made a point by point plot of the "experimental" lines which correspond to Eqs. (12) and (13).

Let us first discuss the case with \( Q_{\text{max}} = 5 \) and \( J_{\text{max}} = 10 \). It follows from Table I that the behavior of fitted fifth-order parameters is in qualitative agreement with Eqs. (12) and (13). The parameter \( t^{5(1,F_1)} \) is practically constant when \( t^{5(5,0,F_1)} \) varies from \(-10 \times 10^{-7}\) to \(+10 \times 10^{-7}\) cm\(^{-1}\). The changes of \( t^{5(5,1,F_1)} \) are relatively small (less than \( 5 \times 10^{-7}\) cm\(^{-1}\)) as expected from Eq. (12) in view of the small value of \( d^{5(5,1,F_1)} \), whereas the variation of \( t^{5(3,F_1)} \) is about \( 19 \times 10^{-7}\) cm\(^{-1}\). This behavior is clearly illustrated in Fig. 1. All the points associated with fitted values belong to straight lines; i.e., \( t^{5(K,F_1)} \) parameters obey linear equations of the type (12). However, the standard deviation of \( \sigma \) is not constant for this series of fits and has a pronounced minimum. As discussed in the previous paper (3), this behavior of \( \sigma \) does not contradict the general propositions of Section II and is a consequence of the effect of omitted higher order terms with
### TABLE I

Values of Fitted Parameters for \( v_4 \) of \(^{13}\)CH\(_4\) with \( J_{\text{max}} = 10 \) and \( \Omega_{\text{max}} = 5 \)

| \( J(0, 1) \) | \( 10.29578(234) \) | \( 10.25679(201) \) | \( 10.25692(143) \) | \( 10.25707(89) \) | \( 10.25702(70) \) | \( 10.25701(64) \) | \( 10.25711(38) \) | \( 10.25718(32) \) | \( 10.25721(131) \) |
| \( 2(0, A_1) \) | \(-6.4075(133)\) | \(-6.4095(115)\) | \(-6.4111(81)\) | \(-6.4096(51)\) | \(-6.4096(39)\) | \(-6.4123(36)\) | \(-6.4132(41)\) | \(-6.4136(68)\) | \(-6.4136(88)\) |
| \( 2(0, \pi) \) | \(9.478(165)\) | \(9.4652(142)\) | \(9.4490(101)\) | \(9.4284(63)\) | \(9.4284(49)\) | \(9.4262(45)\) | \(9.4140(52)\) | \(9.4199(65)\) | \(9.4199(85)\) |
| \( 2(2, A_2) \) | \(-10.187(20)\) | \(-10.187(17)\) | \(-10.195(12)\) | \(-10.201(7)\) | \(-10.205(6)\) | \(-10.205(6)\) | \(-10.211(6)\) | \(-10.217(10)\) | \(-10.217(10)\) |
| \( 3(1, 1) \) | \(2.2617(305)\) | \(2.2623(263)\) | \(2.2651(186)\) | \(2.2674(116)\) | \(2.2674(90)\) | \(2.2662(83)\) | \(2.2690(95)\) | \(2.2680(158)\) | \(2.2650(148)\) |
| \( 3(3, 1) \) | \(1.8346(209)\) | \(1.8365(180)\) | \(1.8409(128)\) | \(1.8435(79)\) | \(1.8449(62)\) | \(1.8468(65)\) | \(1.8489(108)\) | \(1.8489(108)\) | \(1.8489(108)\) |
| \( 4(0, A_1) \) | \(8.59(108)\) | \(8.79(92)\) | \(8.95(65)\) | \(8.85(40)\) | \(8.80(31)\) | \(9.10(30)\) | \(8.99(36)\) | \(9.23(55)\) | \(9.23(55)\) |
| \( 4(2, A_1) \) | \(5.4402(152)\) | \(6.249(132)\) | \(7.946(53)\) | \(9.632(58)\) | \(10.499(45)\) | \(11.339(42)\) | \(12.201(48)\) | \(13.922(79)\) | \(13.922(79)\) |
| \( 4(2, \pi) \) | \(26.15(89)\) | \(25.30(76)\) | \(23.61(54)\) | \(23.04(41)\) | \(21.79(37)\) | \(20.37(34)\) | \(19.63(29)\) | \(17.98(46)\) | \(17.98(46)\) |
| \( 4(4, A_1) \) | \(5.84(108)\) | \(5.06(90)\) | \(4.19(55)\) | \(3.26(40)\) | \(2.77(31)\) | \(2.38(28)\) | \(1.80(33)\) | \(0.99(54)\) | \(0.99(54)\) |
| \( 4(4, \pi) \) | \(4.98(87)\) | \(5.92(75)\) | \(7.77(51)\) | \(9.52(33)\) | \(10.49(26)\) | \(11.40(24)\) | \(12.37(27)\) | \(14.23(55)\) | \(14.23(55)\) |
| \( 5(1, 1) \) | \(4.25(92)\) | \(4.29(79)\) | \(4.43(56)\) | \(4.55(35)\) | \(4.58(27)\) | \(4.54(25)\) | \(4.65(39)\) | \(4.66(48)\) | \(4.66(48)\) |
| \( 5(3, 1) \) | \(-2.89(92)\) | \(-2.99(82)\) | \(-2.99(82)\) | \(-6.75(36)\) | \(-6.75(36)\) | \(-6.75(36)\) | \(-10.52(26)\) | \(-12.47(29)\) | \(-12.47(29)\) |
| \( 5(5.0F1) \) | \(-10.2*\) | \(-10.2*\) | \(-10.2*\) | \(-10.2*\) | \(-10.2*\) | \(-10.2*\) | \(-10.2*\) | \(-10.2*\) | \(-10.2*\) |
| \( 5(5.1F1) \) | \(-5.85(38)\) | \(-5.85(38)\) | \(-5.85(38)\) | \(-5.85(38)\) | \(-5.85(38)\) | \(-5.85(38)\) | \(-5.85(38)\) | \(-5.85(38)\) | \(-5.85(38)\) |

* Fixed to zero.
As a matter of fact, unitary transformations like (1) do not change the Hamiltonian eigenvalues if the Hausdorff expansion is infinite or if omitted terms are completely negligible. These requirements are not satisfied in the considered case since some $q^2 J^6$ terms give a contribution to energy levels with $J = 10$ of the order of $10^{-2}$ cm$^{-1}$, significantly larger than the experimental accuracy ($1-3 \times 10^{-3}$ cm$^{-1}$). In fact, transformation (5) also contributes to higher order terms with $\Omega \geq 6$, and different tails in the expansion of the effective Hamiltonian are neglected, depending on the value of the $s^{(k,F)}$ parameter. In order to avoid the effect on the $q^2 J^5$ terms of the interruption of the Hamiltonian expansion, one can introduce the $q^2 J^6$ terms for the analysis, just to "protect" the considered $q^2 J^5$ parameters (Table II). In this case, the behavior of fitted $t^{(K,nF)}$ parameters is quite similar whereas the standard deviation $\sigma$ is practically constant (Fig. 1). When $t^{(3,0F)}$ is shifted within the interval allowed by order of magnitude requirements, the maximal variations of $\sigma$ are smaller than 0.0002 cm$^{-1}$ which is certainly below the experimental accuracy. The same is true for

$\Omega \geq 6$. The contribution of $q^2 J^6$ terms can be estimated simply from the values quoted in Table II.
<table>
<thead>
<tr>
<th></th>
<th>(1(1, F_1))</th>
<th>(10.25638(44))</th>
<th>(10.25643(42))</th>
<th>(10.25649(38))</th>
<th>(10.25668(41))</th>
<th>(10.25655(40))</th>
<th>(10.25655(40))</th>
<th>(10.25665(41))</th>
<th>(10.26656(41))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(2(0, A_1))</td>
<td>(-6.4045(41))</td>
<td>(-6.4051(42))</td>
<td>(-6.4054(37))</td>
<td>(-6.4053(36))</td>
<td>(-6.4032(39))</td>
<td>(-6.4032(39))</td>
<td>(-6.4031(39))</td>
<td>(-6.4031(39))</td>
<td>(-6.4031(39))</td>
</tr>
<tr>
<td>(2(0, E))</td>
<td>(8.4515(44))</td>
<td>(8.4518(48))</td>
<td>(8.4515(44))</td>
<td>(8.4515(44))</td>
<td>(8.4515(48))</td>
<td>(8.4515(48))</td>
<td>(8.4532(46))</td>
<td>(8.4532(46))</td>
<td>(8.4532(46))</td>
</tr>
<tr>
<td>(2(0, F_2))</td>
<td>(-10.175(5))</td>
<td>(-10.175(7))</td>
<td>(-10.177(6))</td>
<td>(-10.177(6))</td>
<td>(-10.177(6))</td>
<td>(-10.177(6))</td>
<td>(-10.177(6))</td>
<td>(-10.177(6))</td>
<td>(-10.177(6))</td>
</tr>
<tr>
<td>(3(1, F_1))</td>
<td>(2.2583(20))</td>
<td>(2.2583(20))</td>
<td>(2.2583(20))</td>
<td>(2.2583(20))</td>
<td>(2.2583(20))</td>
<td>(2.2583(20))</td>
<td>(2.2580(20))</td>
<td>(2.2580(20))</td>
<td>(2.2580(20))</td>
</tr>
<tr>
<td>(3(2, F_1))</td>
<td>(1.7863(26))</td>
<td>(1.7863(26))</td>
<td>(1.7863(26))</td>
<td>(1.7863(26))</td>
<td>(1.7863(26))</td>
<td>(1.7863(26))</td>
<td>(1.7863(26))</td>
<td>(1.7863(26))</td>
<td>(1.7863(26))</td>
</tr>
<tr>
<td>(3(2, A_1))</td>
<td>(6.706(76))</td>
<td>(6.706(78))</td>
<td>(6.706(76))</td>
<td>(6.706(76))</td>
<td>(6.706(76))</td>
<td>(6.706(76))</td>
<td>(6.706(76))</td>
<td>(6.706(76))</td>
<td>(6.706(76))</td>
</tr>
<tr>
<td>(3(4, A_1))</td>
<td>(19.54(41))</td>
<td>(19.54(41))</td>
<td>(19.54(41))</td>
<td>(19.54(41))</td>
<td>(19.54(41))</td>
<td>(19.54(41))</td>
<td>(19.54(41))</td>
<td>(19.54(41))</td>
<td>(19.54(41))</td>
</tr>
<tr>
<td>(3(4, E))</td>
<td>(19.35(40))</td>
<td>(19.35(40))</td>
<td>(19.35(40))</td>
<td>(19.35(40))</td>
<td>(19.35(40))</td>
<td>(19.35(40))</td>
<td>(19.35(40))</td>
<td>(19.35(40))</td>
<td>(19.35(40))</td>
</tr>
<tr>
<td>(3(4, F_2))</td>
<td>(8.91(46))</td>
<td>(8.91(46))</td>
<td>(8.91(46))</td>
<td>(8.91(46))</td>
<td>(8.91(46))</td>
<td>(8.91(46))</td>
<td>(8.91(46))</td>
<td>(8.91(46))</td>
<td>(8.91(46))</td>
</tr>
</tbody>
</table>

**Table II**

Values of Fitted Parameters for \(\nu_4\) of \(^13\text{CH}_4\) with \(J_{\text{max}} = 13\) and \(\Omega_{\text{max}} = 6\)

Parameter Values:

- \(1(1, F_1)\): 10.25638(44), 10.25643(42), 10.25649(38), 10.25655(41), 10.25655(40), 10.25665(41), 10.26656(41)
- \(2(0, A_1)\): -6.4045(41), -6.4051(42), -6.4054(37), -6.4053(36), -6.4032(39), -6.4032(39), -6.4031(39), -6.4031(39), -6.4031(39)
- \(2(0, E)\): 8.4515(44), 8.4518(48), 8.4515(44), 8.4515(44), 8.4515(48), 8.4515(48), 8.4532(46), 8.4532(46), 8.4532(46)
- \(2(0, F_2)\): -10.175(5), -10.175(7), -10.177(6), -10.177(6), -10.177(6), -10.177(6), -10.177(6), -10.177(6), -10.177(6)
- \(3(1, F_1)\): 2.2583(20), 2.2583(20), 2.2583(20), 2.2583(20), 2.2583(20), 2.2583(20), 2.2580(20), 2.2580(20), 2.2580(20)
- \(3(2, F_1)\): 1.7863(26), 1.7863(26), 1.7863(26), 1.7863(26), 1.7863(26), 1.7863(26), 1.7863(26), 1.7863(26), 1.7863(26)
- \(3(2, A_1)\): 6.706(76), 6.706(78), 6.706(76), 6.706(76), 6.706(76), 6.706(76), 6.706(76), 6.706(76), 6.706(76)
- \(3(4, A_1)\): 19.54(41), 19.54(41), 19.54(41), 19.54(41), 19.54(41), 19.54(41), 19.54(41), 19.54(41), 19.54(41)
- \(3(4, E)\): 19.35(40), 19.35(40), 19.35(40), 19.35(40), 19.35(40), 19.35(40), 19.35(40), 19.35(40), 19.35(40)
- \(3(4, F_2)\): 8.91(46), 8.91(46), 8.91(46), 8.91(46), 8.91(46), 8.91(46), 8.91(46), 8.91(46), 8.91(46)

\(\sigma\): 0.0004, 0.0033, 0.0032, 0.0030, 0.0032, 0.0031, 0.0032, 0.0032
the parameter \( t^{(3,F_1)} \) supporting the above conclusion that there are no unique physically meaningful values for the parameters \( t^{(5,0,F_1)} \) and \( t^{(3,F_1)} \) for \( F_2 \) fundamentals of tetrahedral molecules.

Since in both series the points in Fig. 1 belong to straight lines, the associated parameters \( t^{(5,K,nF')} \) obey linear equations. The slopes of the lines give "experimental" values for the \( q^{(5,K,nF')} \) coefficients (Table III) which are to be compared with the theoretical values [Eq. (13a)]. Although these values do not coincide, they are in qualitative agreement: all variations \( \Delta t^{(5,1,F_1)} \), \( \Delta t^{(5,0,F_1)} \), and \( \Delta t^{(3,F_1)} \) have the same sign. \( d^{(5,1,F_1)} \) is the largest coefficient, \( d^{(5,0,F_1)} \) has the same positive sign but is noticeably smaller, while \( d^{(5,1,F_1)} \) is practically negligible. The largest discrepancy in \( d \) coefficients is about 0.13 in the case with \( \Omega \leq 5, J \leq 10 \) and about 0.18 in the case with \( \Omega \leq 6, J \leq 13 \), i.e., quite comparable with the discrepancies observed in the study of fourth-order parameters \( q^2J^4 \) reported previously (3).

The Account of Higher Order Corrections to Equation (13a)

An agreement between theoretical and "experimental" values of coefficients \( d^{(5,K,nF')} \) may be improved by account of high-order contributions in commutators of vibration-rotation tensor operators. As is described in Appendix 3, a variation \( \Delta t^{(5,K,nF')} \) induces a small transformation \( S_1 \) (4) in addition to the transformation \( S_2 \) (5) discussed in the previous sections. The transformation \( S_1 \) contributes to the \( q^2J^5 \) terms via commutators with the \( q^2J^2 \)-type operators. These contributions do not alter relation (12), but result in the corrections in values of coefficients \( d^{(5,K,nF')} \). When the parameter \( t^{(4,F_2)} \) is fixed, one has

\[
d^{(5,1,F_1)} = \left\{ K^{(4,1,5)}_{(F_1,F_1,F_1,F_1)} / K^{(4,1,5)}_{(F_1,F_1,F_1,0,F_1)} \right\} + 14 K^{(2,3,5)}_{(F,E,F_2,F_1,F_1)} 2^{(2,E)} / (\sqrt{6} K^{(4,1,5)}_{(F_1,F_1,F_1,0,F_1)} \, d^{(1,1,F_1)}) \]

\[
d^{(5,0,F_1)} = \left\{ \sqrt{10} / (3 \sqrt{11} K^{(4,1,5)}_{(F_1,F_1,F_1,0,F_1)}) \right\} + 28 t^{(2,E)} / (3 \sqrt{55} K^{(4,1,5)}_{(F_1,F_1,0,F_1)} \, d^{(1,1,F_1)}) \]

\[
d^{(3,F_1)} = -4 \sqrt{6} t^{(2,F_2)}/ (5 \sqrt{11} K^{(4,1,5)}_{(F_1,F_1,F_1,0,F_1)} \, d^{(1,1,F_1)}) + 14 t^{(2,F_2)}/ (9 \sqrt{55} K^{(4,1,5)}_{(F_1,F_1,0,F_1)} \, d^{(1,1,F_1)}) + 6 \sqrt{6} t^{(2,E)}/ (5 \sqrt{11} K^{(4,1,5)}_{(F_1,F_1,0,F_1)} \, d^{(1,1,F_1)}).
\]

The terms in braces coincide with the leading contributions given by Eq. (13a). The numerical values of the coefficients calculated using Eqs. (13b) are presented in the last column of Table III.

IV. THIRD TRANSFORMATION-SIXTH-ORDER \( q^2J^6 \) TERMS

The generator of the third transformation is the sum of three terms

\[
S_3 = S_{3a} + S_{3b} + S_{3c}
\]

3 Since only the slopes of the lines can be compared to the associated theoretical values, in Fig. 1, we have shifted the values of the \( t^{(5,K,nF')} \) parameters by an appropriate quantity \( \Delta e \) in such a manner that the corresponding lines have a common point of intersection, all angles being kept unaltered.
### TABLE III

Values of $d^{(K,w)}$ Constants Deduced from the Fits of Experimental $v_4$ Energy Levels of $^{12}$CH$_4$

<table>
<thead>
<tr>
<th>$\Omega \leq 5, J \leq 10$</th>
<th>$\Omega \leq 6, J \leq 13$</th>
<th>Theoretical, Eq.(13.a)</th>
<th>Theoretical, Eq.(13.b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S(5.5,1)_{d}$</td>
<td>0.2495(17)</td>
<td>0.3032(31)</td>
<td>0.119...</td>
</tr>
<tr>
<td>$S(3.3,1)_{d}$</td>
<td>0.9533(22)</td>
<td>1.0647(84)</td>
<td>0.876...</td>
</tr>
<tr>
<td>$S(1.1,1)_{d}$</td>
<td>0.0159(30)</td>
<td>0.0498(22)</td>
<td>0.036...</td>
</tr>
</tbody>
</table>

where

$$S_{3a} = S^{(5,E)} S^{(5,E)} = S^{(5,E)}(\pm) V_{5,F_2} \times R^{(5,E)}(41)$$

$$S_{3b} = S^{(5,F_2)} S^{(5,F_2)} = S^{(5,F_2)}(\pm) V_{5,F_2} \times R^{(5,F_2)}(41)$$

$$S_{3c} = S^{(3,F_2)} S^{(3,F_2)} = S^{(3,F_2)}(\pm) V_{5,F_2} \times R^{(3,F_2)}(41).$$

The leading contributions arise from the vibrational part of the commutator

$$[iS_{3}, H_{eff}^1]$$

where $H_{eff}^1$ is given by Eq. (6). According to Refs. (1, 2), we have

$$[iS_{3a}, H_{eff}^1] = \frac{g_{3a}}{2} \sum_{\Gamma \Gamma'} \sqrt{\frac{41}{6}} \left\{ \left[ V_{5,F_2}^{(5,E)}(F_2), V_{5,F_2}^{(5,F_2)}(F_1) \right]_{\Gamma \Gamma'} \times [R^{(5,E)}(41), R^{(1,F_1)}(1,F_1)]_{\Gamma \Gamma'} + \cdots \right\}$$

$$[iS_{3b}, H_{eff}^1] = \frac{g_{3b}}{2} \sum_{\Gamma \Gamma'} \sqrt{\frac{41}{3}} \left\{ \left[ V_{5,F_2}^{(5,F_2)}(F_2), V_{5,F_2}^{(5,F_2)}(F_1) \right]_{\Gamma \Gamma'} \times [R^{(5,F_2)}(41), R^{(1,F_1)}(1,F_1)]_{\Gamma \Gamma'} + \cdots \right\}$$

$$[iS_{3c}, H_{eff}^1] = \frac{g_{3c}}{2} \sum_{\Gamma \Gamma'} \sqrt{\frac{41}{3}} \left\{ \left[ V_{5,F_2}^{(3,F_2)}(F_2), V_{5,F_2}^{(3,F_2)}(F_1) \right]_{\Gamma \Gamma'} \times [R^{(3,F_2)}(41), R^{(1,F_1)}(1,F_1)]_{\Gamma \Gamma'} + \cdots \right\}.$$

All commutators and anticommutators involved in Eq. (16) are presented in the Appendixes. From their expressions it follows that the most important contributions from transformation (14) occur for $q^2j^0$ terms:

$$\Delta H_{eff} = \tilde{H}_{eff} - H_{eff} = [i(S_{3a} + S_{3b} + S_{3c}), H_{eff}^1]_{\Gamma} + \cdots$$

$$- t^{(1,F_1)} \sum_{j=a,b,c} \sum_{K,T} \sum_{N} b_j^{(K,N)} T_{\Gamma\Gamma'}^{(j,K,N)} F_2 F_2 + \cdots$$

where $s_j$ ($j = a, b, c$) designate, respectively, $S^{(5,E)}$, $S^{(5,F_2)}$, and $S^{(3,F_2)}$. The values of the coefficients $b_j^{(K,N)}$ are given in Table IV. If the parameters $S^{(3,F_2)}$ and $S^{(4,F_2)}$ of the first and second transformations are fixed in such a way that $t^{(2,F_2)} = 0$ and
HIGHER ORDER REDUCED HAMILTONIAN FOR $v_4$ OF $^{12}$CH$_4$

TABLE IV

Coefficients $b_{ij}^{(K,nf)}$ (with $j = a, b, c$) Determining the Changes Induced in $q^2J^6$ Parameters by the Third Transformation

<table>
<thead>
<tr>
<th></th>
<th>a</th>
<th>b</th>
<th>c</th>
</tr>
</thead>
<tbody>
<tr>
<td>$6(2, E)$</td>
<td>$b_3$ = 0</td>
<td>$b_1$ = 0</td>
<td>$-\sqrt{2}/7 \approx -0.202031$</td>
</tr>
<tr>
<td>$6(2, F_2)$</td>
<td>$b_3$ = 0</td>
<td>$b_1$ = 0</td>
<td>$\sqrt{2}/7 \approx 0.202031$</td>
</tr>
<tr>
<td>$6(4, E)$</td>
<td>$b_3$ = 0</td>
<td>$-\sqrt{2}/7 \approx -0.253533$</td>
<td>$\sqrt{2}/7 \approx 0.308507$</td>
</tr>
<tr>
<td>$6(4, F_2)$</td>
<td>$b_3 = -\frac{1}{11} \sqrt{33}/2 \approx -0.380300$</td>
<td>0</td>
<td>$\frac{1}{2} \sqrt{2}/14 \approx 0.231455$</td>
</tr>
</tbody>
</table>

$t^{5(0F_1)} = 0$, then the changes of $q^2J^6$ terms induced by a variation of the eigenbasis of $H^{*E}$ due to the third transformation are the following:

$$t^{5(K,nf)} = t^{5(K,nf)} + t^{1(1,F_1)} \times (\sum_{j=a,b,c} b_{ij}^{(K,nf)}S_{3j})$$

where $\Gamma \neq A_1$.

In order to find out the relations among allowed changes of $q^2J^6$ parameters, it is useful to rewrite Eq. (18) in a detailed form by taking into account vanishing values for the $b$ coefficients (Table IV):

\[
\begin{align*}
\Delta t^{6(2, E)} &= t^{1(1,F_1)}[b_{6(2,E)}S_{3c}] \\
\Delta t^{6(2, F_2)} &= t^{1(1,F_1)}[b_{6(2,F_2)}S_{3c}] \\
\Delta t^{6(4, E)} &= t^{1(1,F_1)}[b_{6(4,E)}S_{3b} + b_{6(4,E)}S_{3c}] \\
\Delta t^{6(4, F_2)} &= t^{1(1,F_1)}[b_{6(4,F_2)}S_{3a} + b_{6(4,F_2)}S_{3c}] \\
\Delta t^{6(6, E)} &= t^{1(1,F_1)}[b_{6(6,E)}S_{3b}] \\
\Delta t^{6(6,0F_2)} &= t^{1(1,F_1)}[b_{6(6,0F_2)}S_{3a} + b_{6(6,0F_2)}S_{3b}] \\
\Delta t^{6(6,1F_2)} &= t^{1(1,F_1)}[b_{6(6,1F_2)}S_{3a} + b_{6(6,1F_2)}S_{3b}].
\end{align*}
\]
It is clear that the variations of the two second-rank parameters [Eq. (19)] are directly connected but are independent of those of the sixth-rank parameters [Eq. (21)]. Among these three sixth-rank parameters, there are only 2 degrees of freedom corresponding to the two parameters $s_{3a}$ and $s_{3b}$. The variations of the fourth-rank parameters [Eq. (20)] are related with those of both second-rank and sixth-rank parameters.

Since there are three parameters in the generator $S_1$, three $q^2 f^6$ parameters can be given arbitrarily any value subject to order of magnitude requirements. We shall choose the variations $\Delta t^{(6,2,E)}$, $\Delta t^{(6,6,E)}$, and $\Delta t^{(6,6,F_1)}$ as arbitrary ones because in this case the associated equations can be solved in the most simple way to give

$$s_{3c} = [I^{(1,1,F_1)}/b_c^{(6,2,E)}]^{-1} \Delta t^{(6,2,E)}$$

$$s_{3b} = [I^{(1,1,F_1)}/b_b^{(6,6,F_1)}]^{-1} \Delta t^{(6,6,F_1)}$$

$$s_{3a} = [I^{(1,1,F_1)}/b_a^{(6,6,F_2)}]^{-1} [\Delta t^{(6,6,F_2)} - (b_a^{(6,6,F_2)}/b_b^{(6,6,E)}) \Delta t^{(6,6,E)}].$$  \hspace{1cm} (22)

The variations of the remaining parameters can then be expressed as functions of the variations of the above-selected free parameters:

$$\Delta t^{(6,2,F_2)} = d_{2,F_2}^{(6,2,F_2)} \Delta t^{(6,2,E)}$$

$$\Delta t^{(6,4,E)} = d_{2,E}^{(6,4,E)} \Delta t^{(6,2,E)} + d_{6,E}^{(6,4,E)} \Delta t^{(6,6,E)}$$

$$\Delta t^{(6,4,F_2)} = d_{2,F_2}^{(6,4,F_2)} \Delta t^{(6,2,E)} + d_{6,F_2}^{(6,4,F_2)} \Delta t^{(6,6,E)} + d_{6,0,F_2}^{(6,4,F_2)} \Delta t^{(6,6,F_2)}$$

$$\Delta t^{(6,6,F_2)} = d_{6,F_2}^{(6,6,F_2)} \Delta t^{(6,6,E)} + d_{6,0,F_2}^{(6,6,F_2)} \Delta t^{(6,6,F_2)}$$ \hspace{1cm} (23)

where the $d$ coefficients have the following values:

$$d_{2,F_2}^{(6,2,F_2)} = -1; \hspace{0.5cm} d_{2,E}^{(6,4,E)} = -\sqrt{7}/3; \hspace{0.5cm} d_{2,F_2}^{(6,4,F_2)} = -\sqrt{21}/4$$

$$d_{6,F_2}^{(6,4,F_2)} = -21/111; \hspace{0.5cm} d_{6,E}^{(6,4,F_2)} = -21/22 K_{(F_2,F_1)0,F_2}^{(5,1,6)} \approx -0.607651$$

$$d_{6,F_2}^{(6,4,F_2)} = 11 \cdot 13 \hspace{0.5cm} \left( K_{(F_2,F_1)1,F_2}^{(5,1,6)} - K_{(F_2,F_1)0,F_2}^{(5,1,6)} / K_{(F_1,F_0)0,F_2}^{(5,1,6)} \right) \approx 1.25555$$

$$d_{6,F_2}^{(6,4,F_2)} = 1/11 \sqrt{105/13} \left( K_{(F_2,F_1)0,F_2}^{(5,1,6)} \right)^{-1} \approx 0.779726$$

$$d_{6,F_2}^{(6,4,F_2)} = K_{(F_2,F_1)0,F_2}^{(5,1,6)} / K_{(F_1,F_0)0,F_2}^{(5,1,6)} \approx -0.138128.$$ \hspace{1cm} (24)

Equations (23)-(24) can be used to relate the usual expansion of the effective Hamiltonian with a reduced effective Hamiltonian as described in the next section.
V. REDUCED HAMILTONIAN FOR F₂ FUNDAMENTALS OF Td MOLECULES UP TO THE SIXTH ORDER

In order to avoid the ambiguity associated with possible changes of the effective eigenbasis without changing the form and the eigenvalues of the effective Hamiltonian, one can simply remove free parameters. This procedure leads to a reduced effective Hamiltonian containing fewer adjustable parameters. The list of removable terms up to the sixth order is presented below:

(i) First, second, and third orders ($q^2J$, $q^2J^2$, and $q^2J^3$ terms): All terms are not removable.

(ii) Fourth order ($q^2J^4$ terms): Any one of the four parameters $t^{4(2,E)}$, $t^{4(2,F2)}$, $t^{4(4,E)}$, or $t^{4(4,F2)}$ can be removed. A detailed discussion about this reduction is presented in Ref. (3).

(iii) Fifth order ($q^2J^5$ terms): Any one of the two parameters $t^{5(5,0F1)}$ or $t^{5(3,F1)}$ can be removed. Fits using an unreduced fifth-order Hamiltonian and using two versions of reduced Hamiltonians (to the same order) are presented in Table V. The quality of the fit is not affected by reduction, although fewer parameters are adjusted. The parameter $t^{5(1,F2)}$ is not allowed to be removed since $t^{5(1,F2)} = 0$. The elimination of the parameter $t^{5(5,1F1)}$ requires a large transformation (5) which does not satisfy the

| TABLE V |
| Reducing the Fifth-Order Part of the Effective Hamiltonian |

| 1(1, F1) | 10.25655(39) | 10.25632(37) | 10.25669(39) |
| 2(0, A1) | -6.4043(37)  | -6.4037(37)  | -6.4024(36)  |
| 2(2, E)  | 8.4529(46)   | 8.4507(45)   | 8.4545(47)   |
| 2(2, F2) | -10.174(5)   | -10.173(5)   | -10.176(6)   |
| 3(1, F1) | 2.2600(45)   | 2.2562(40)   | 2.2633(42)   |
| 3(3, F1) | 1.17970(34)  | 1.16010(24)  | 1.7919(42)   |
| 4(0, A1) | 7.46(45)     | 7.20(46)     | 7.22(46)     |
| 4(2, E)  | 21.566(43)   | 21.86(36)    | 20.89(39)    |
| 4(2, F2) | 8.42(42)     | 9.49(45)     | 9.49(45)     |
| 4(4, E)  | 13.70(37)    | 13.70(36)    | 13.63(38)    |
| 4(4, F2) | 0.00*        | 0.00*        | 0.0*         |
| 5(1, F1) | 3.97(16)     | 3.86(15)     | 4.04(16)     |
| 5(3, F1) | 3.20(98)     | 8.69(7)      | 0.0*         |
| 5(5,0F1) | -1.49(86)    | 0.0*         | 4.39(6)      |
| 5(5,1F1) | -4.46(29)    | -4.04(11)    | -5.34(12)    |
| 6(0, A1) | 8.4(2)       | 8.6(2)       | 9.3(2)       |
| 6(2, E)  | 2.1(21)      | 5.6(20)      | -4.1(10)     |
| 6(2, F2) | 6.9(12)      | 6.1(12)      | 7.6(12)      |
| 6(4, A1) | 0.5(22)      | 0.43(20)     | 0.81(21)     |
| 6(4, E)  | -0.7(17)     | -0.7(16)     | -0.7(17)     |
| 6(6, F2) | -0.1(14)     | -0.1(13)     | -0.9(14)     |
| 6(6, A1) | -1.22(46)    | -1.18(36)    | -1.26(36)    |
| 6(6, E)  | 14.1(25)     | 9.9(2)       | 22.3(2)      |
| 6(6,0F2) | 0.0*         | 0.0*         | 0.0*         |
| 6(6,1F2) | 0.0*         | 0.0*         | 0.0*         |

σ 0.0030 0.0030 0.0032
condition (11) since $b^{(5,1F_1)} \approx 0.027$ is accidentally small. These proposals are confirmed by actual results of associated fits (Table VI).

(iv) Sixth order ($q^2J^6$ terms): Three of the seven parameters $t^{6(2,E)}$, $t^{6(2,F_2)}$, $t^{6(4,E)}$, $t^{6(4,F_0)}$, $t^{6(6,E)}$, $t^{6(6,F_2)}$, and $t^{6(6,1F_2)}$ can be removed. However, not any set of three is admissible. For example, $t^{6(2,E)}$ and $t^{6(2,F_2)}$ cannot be removed simultaneously. Similarly, all sixth-rank parameters cannot be removed simultaneously.

We suggest the removal from the effective Hamiltonian of the following five terms up to the sixth order: $t^{4(4,F_2)}$, $t^{5(5,0F_1)}$, $t^{6(2,E)}$, $t^{6(6,E)}$, and $t^{6(6,0F_2)}$.

The resulting reduced Hamiltonian contains 22 unambiguous parameters up to the sixth order, instead of 27 parameters in usual expansions. The parameters obtained by fitting the $v_4$ band of $^{12}$CH$_4$ using this reduced Hamiltonian are listed in Table VII.

VI. CONCLUSION

The processing of experimental $v_4$ energy levels of $^{12}$CH$_4$ performed in this paper confirms the propositions of Refs. (1, 2) in the case of higher order $q^2J^5$ and $q^2J^6$ diagonal coupling parameters. Just like $q^2J^4$ parameters (3), $q^2J^5$ and $q^2J^6$ parameters cannot be considered altogether as constants having definite values for a given $F_2$ vibrational state.

All the phenomenological conclusions presented in detail in Ref. (3) can be applied to the present case. The easiest way to overcome ambiguities in effective Hamiltonians is to reduce them by removing free parameters. Another way is to define invariant parameters by forming appropriate linear combinations of the usual parameters. Of course, these conclusions are equally valid for other formalisms subject to a careful calculation of the effect of ambiguities in each particular case as illustrated in the Appendix of Ref. (3).

| TABLE VI |
| Influence of the Elimination of Different $q^2J^4$ Terms from a Hamiltonian on the Accuracy of Fits |
| (Case $\alpha_{\text{max}} = 6$, $J_{\text{max}} = 13$) |

<table>
<thead>
<tr>
<th>$s(X,n\Gamma)$</th>
<th>$b$</th>
<th>$s(S=1,0)$</th>
<th>$5(5,0P_1)$</th>
<th>$5(3,F_2)$</th>
<th>$5(5,1P_2)$</th>
<th>$5(1,P_1)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>adjusted</td>
<td>4</td>
<td>3</td>
<td>3</td>
<td>5</td>
<td>6</td>
<td></td>
</tr>
</tbody>
</table>

Different types of reduction
\[ s \text{ constant reduction not allowed} \]
TABLE VII
Fitted Parameters of Unreduced and Reduced Effective Sixth-Order Hamiltonians for \(v_4\) of \(^{13}\text{CH}_4\)

<table>
<thead>
<tr>
<th></th>
<th>Unreduced</th>
<th>Reduced</th>
</tr>
</thead>
<tbody>
<tr>
<td>00(0, A1)</td>
<td>1310.763(1)</td>
<td>1310.763(1)</td>
</tr>
<tr>
<td>11(1, P1)</td>
<td>10.25713(33)</td>
<td>10.25711(33)</td>
</tr>
<tr>
<td>20(0, A1)</td>
<td>-6.4031(36)</td>
<td>-6.4022(36)</td>
</tr>
<tr>
<td>22(2, E  )</td>
<td>8.4381(33)</td>
<td>8.4396(33)</td>
</tr>
<tr>
<td>22(2, P2)</td>
<td>-10.186(8)</td>
<td>-10.186(8)</td>
</tr>
<tr>
<td>31(1, P1)</td>
<td>2.2643(24)</td>
<td>2.2694(29)</td>
</tr>
<tr>
<td>33(3, P1)</td>
<td>1.7143(46)</td>
<td>1.8012(25)</td>
</tr>
<tr>
<td>40(0, A1)</td>
<td>7.26(46)</td>
<td>7.10(46)</td>
</tr>
<tr>
<td>42(2, A2)</td>
<td>21.38(280)</td>
<td>11.47(7)</td>
</tr>
<tr>
<td>42(2, E  )</td>
<td>1.0(118)</td>
<td>21.2(3)</td>
</tr>
<tr>
<td>42(2, P2)</td>
<td>29.7(123)</td>
<td>8.8(42)</td>
</tr>
<tr>
<td>44(4, E  )</td>
<td>54.1(193)</td>
<td>13.3(37)</td>
</tr>
<tr>
<td>44(4, P2)</td>
<td>26.0(133)</td>
<td>0.*</td>
</tr>
<tr>
<td>51(1, F1)</td>
<td>0.951(183)</td>
<td>4.46(7)</td>
</tr>
<tr>
<td>53(3, F1)</td>
<td>21.11(500)</td>
<td>4.66(10)</td>
</tr>
<tr>
<td>55(5,OF1)</td>
<td>16.94(492)</td>
<td>0.*</td>
</tr>
<tr>
<td>60(0, A1)</td>
<td>-4.99(264)</td>
<td>-3.66(6)</td>
</tr>
<tr>
<td>62(2, E  )</td>
<td>9.2(2)</td>
<td>9.5(2)</td>
</tr>
<tr>
<td>62(2, P2)</td>
<td>23.1(73)</td>
<td>0.*</td>
</tr>
<tr>
<td>64(4, A1)</td>
<td>16.1(27)</td>
<td>11.7(6)</td>
</tr>
<tr>
<td>64(4, E  )</td>
<td>9.22(27)</td>
<td>8.95(18)</td>
</tr>
<tr>
<td>64(4, P2)</td>
<td>22.7(78)</td>
<td>0.*</td>
</tr>
<tr>
<td>66(6, A1)</td>
<td>27.6(87)</td>
<td>-4.7(7)</td>
</tr>
<tr>
<td>66(6, E  )</td>
<td>-2.13(37)</td>
<td>-1.00(8)</td>
</tr>
<tr>
<td>66(6, P2)</td>
<td>33.2(75)</td>
<td>0.*</td>
</tr>
<tr>
<td>66(6,OF2)</td>
<td>-1.84(367)</td>
<td>2.10(53)</td>
</tr>
</tbody>
</table>

\(\sigma\) 0.0030 0.0030

\(N\) 27 22

APPENDIX I

Using the general definition of irreducible tensor commutators

\[ [A^{\Gamma_1}, B^{\Gamma_2}]^{\Gamma} = (A^{\Gamma_1} \times B^{\Gamma_2})^{\Gamma} - (-1)^{\Gamma_1 + \Gamma_2} (B^{\Gamma_2} \times A^{\Gamma_1})^{\Gamma}, \]

We obtain the following expressions for the vibrational commutators in Champion's notation (9):

\[ \left[ (-)^{\Gamma_1} V_{A1}^{F_1F_2} F_1, (-)^{\Gamma_2} V_{B1}^{F_1F_2} F_1 \right] = \frac{i}{\sqrt{3}} (-)^{\Gamma_1} V_{A1}^{F_1F_2}, \]

\[ \left[ (+)^{\Gamma_1} V_{A1}^{F_2F_1} E_1, (-)^{\Gamma_2} V_{B1}^{F_2F_1} F_2 \right] = \frac{i}{\sqrt{3}} (+)^{\Gamma_1} V_{A1}^{F_2F_1}, \]

\[ \left[ (+)^{\Gamma_1} V_{A1}^{F_2F_1} E_1, (-)^{\Gamma_2} V_{B1}^{F_2F_1} F_2 \right] = \frac{i}{\sqrt{3}} (+)^{\Gamma_1} V_{A1}^{F_2F_1}. \]
The general expression has the form

\[
(-)^{\varphi_r} V_{4,4}^{F_2 F_3 (F_3)} (-)^{\varphi_r} V_{4,4}^{F_2 F_3 (F_3)} = (-)^{\varphi_r} V_{4,4}^{F_2 F_3 (F_3)} \left[ (-1)^{\Gamma_1 + \Gamma_2} - (-1)^{\Gamma} \right] \sqrt{\Gamma} \left( \frac{\Gamma F_2 F_3 \Gamma}{F_2 F_3 \Gamma} \right) R_{4(4, F_1)}^{(1, F_1)}
\]

where

\[
\varphi_r = 0 \quad \Gamma = A_1, E, F_2
\]

\[
\varphi_r = 1 \quad \Gamma = A_2, F_1.
\]

### Appendix 2

Using the general definition of irreducible tensor anticommutators,

\[
[A^{(1)}, B^{(2)}]_\Gamma = (A^{(1)} \times B^{(2)})^\Gamma + (-1)^{\Gamma_1 + \Gamma_2 + \Gamma} (B^{(2)} \times A^{(1)})^\Gamma.
\]

The leading contributions to rotational “anticommutators” are given by

\[
[R^{5(5, E)}, R^{(1, F_1)}]_{F_1} = -2 \sqrt{\frac{11}{3}} K_{(5, 1, 3, 5)}^{(4, 1, 3, 5)} R^{(5, 0, F_1)}
\]

\[
- 2 \sqrt{\frac{11}{3}} K_{(5, 1, 3, 5)}^{(4, 1, 3, 5)} R^{(5, 1, F_1)} - 2 \sqrt{\frac{10}{3}} R^{(5, F_1)}
\]

\[
[R^{5(5, F_2)}, R^{(1, F_1)}]_{F_2} = 2 \sqrt{\frac{13}{3}} K_{(5, 5, F_2)}^{(4, 1, 6, 5)} R^{(6, 0, F_2)} + 2 \sqrt{\frac{13}{3}} K_{(5, 5, F_2)}^{(4, 1, 6, 5)} R^{(6, 1, F_2)} + 2 \sqrt{\frac{35}{11}} R^{(6, F_2)}
\]

\[
[R^{5(5, E)}, R^{(1, F_1)}]_{F_1} = - \sqrt{\frac{10}{11}} R^{(5, 0, E)} + \sqrt{\frac{210}{11}} R^{(6, 4, E)}
\]

\[
[R^{5(5, F_2)}, R^{(4, F_1)}]_{F_2} = 2 \sqrt{\frac{13}{3}} K_{(5, 5, F_2)}^{(4, 1, 6, 5)} R^{(6, 0, F_2)} + 2 \sqrt{\frac{13}{3}} K_{(5, 5, F_2)}^{(4, 1, 6, 5)} R^{(6, 1, F_2)}
\]

\[
[R^{5(5, F_2)}, R^{(4, F_1)}]_{F_1} = 3 \sqrt{\frac{3}{14}} R^{(6, F_2)} + \frac{6\sqrt{2}}{7} R^{(6, 2, F_2)}.
\]

### Appendix 3: Higher Order Contributions to \( q^2 J^4 \) and \( q^2 J^3 \) Terms

The second transformation (5) results in the contributions to \( q^2 J^4 \) terms via the commutator of the type \([V, V'], [R, R']\) [see the last term in Eq. (7) of the Ref. (2)]:

\[
\Delta t^{4(4, A_1)} = \frac{4\sqrt{5}}{9} s^{(4, F_1)}_{4(4, F_1)}
\]

\[
\Delta t^{4(4, F_2)} = \frac{1}{3} \sqrt{\frac{7}{2}} s^{(4, F_1)}_{4(4, F_1)}
\]

\[
\Delta t^{4(4, E)} = \frac{2\sqrt{14}}{9} s^{(4, F_1)}_{4(4, F_1)}
\]

\[
\Delta t^{4(2, F_2)} + \Delta t^{4(2, F_2)} - \Delta t^{4(0, A_1)} - 0.
\]
The resulting changes in $q^2J^4$-type parameters (A3.1)–(A3.4) have to be two orders less than the associated changes $\Delta t^{4(2, E)} = (\sqrt{2}/7) d^{4(2, E)}(3, F_1) t^{1(1, F_1)}$ induced by the first transformation (4) if the condition $s^{3(3, F_2)} \ll \lambda^6$ [see Refs. (2, 3)] and the condition (11) are satisfied. Formally one could use the transformation (5) in order to eliminate one more term from the $q^2J^4$ part of the Hamiltonian by appropriate choice of $s^{4(4, F_1)}$ in Eqs. (A3.1)–(A3.3). However, it would violate the condition (11) and results in a deterioration of a quality of a fit [see Table VIII of Ref. (3)]. The more consistent way is to use the procedure of the reduction which does not result in a reordering of the Hamiltonian expansion and does not worsen its convergence as is discussed in Refs. (2, 3) and in Section V.

The validity of Eqs. (A3.1)–(A3.4) may be verified using the results of the fits of experimental data presented in the Table II. Let us consider two effective Hamiltonians corresponding to any two columns of the Table II. These Hamiltonians are equivalent since $\sigma$ in both cases is practically the same. In order to relate them up to fifth-order terms, one needs two unitary transformations of the types (5) and (4). The associated parameters $s^{3(3, F_2)}$ and $s^{4(4, F_1)}$ are the solutions of the following equations:

$$\Delta t^{4(4, F_1)} = \frac{\sqrt{3}}{2\sqrt{14}} s^{3(3, F_2)} t^{1(1, F_1)} + \frac{\sqrt{7}}{3\sqrt{2}} s^{4(4, F_1)} t^{1(1, F_1)} + \cdots = 0 \quad (A3.5)$$

$$\Delta s^{5(5, 0, F_1)} = \frac{1}{3} \sqrt{\frac{11}{3}} K^{4(4, 1, 5)}_{(F_1, F_1, 0, F_1)} s^{4(4, F_1)} t^{1(1, F_1)} + \cdots = \text{constant}. \quad (A3.6)$$

The transformation involving $s^{4(4, F_1)}$ has been discussed in Section II. It follows from Eq. (A3.5) that a variation $\Delta s^{5(5, 0, F_1)}$ and the requirement $\Delta t^{4(4, F_1)} = 0$ result in auxiliary fifth-order transformation of the type (2) with the parameter

$$s^{3(3, F_2)} = -14 \Delta t^{4(4, F_1)} / (\sqrt{11} K^{4(4, 1, 5)}_{(F_1, F_1, 0, F_1)} t^{1(1, F_1)}) \sim \lambda^8. \quad (A3.7)$$

The sixth-order contributions of the latter transformation to $q^2J^5$ terms are presented as corrections in Eqs. (13b).

Both transformations provide fifth-order contributions to $q^2J^4$ terms. Associated variations of the parameters may be written as

$$\Delta t^{4(K, T)} = e^{4(K, T)} \Delta t^{3(3, F_2)} \quad (A3.8)$$

where the calculated coefficients $e^{4(K, T)}$ are the following:

$$e^{4(4, A_1)} = 4 \sqrt{5} / (\sqrt{3} 3 K^{4(4, 1, 5)}_{(F_1, F_1, 0, F_1)}) \quad (A3.9)$$

$$e^{4(2, E)} = 2 \sqrt{2} / (\sqrt{11} K^{4(4, 1, 5)}_{(F_1, F_1, 0, F_1)}) \quad (A3.10)$$

$$e^{4(2, F_2)} = -2 \sqrt{2} / (\sqrt{11} K^{4(4, 1, 5)}_{(F_1, F_1, 0, F_1)}) \quad (A3.11)$$

$$e^{4(4, E)} = e^{4(0, A_1)} = 0. \quad (A3.12)$$

The results of processing of experimental $v_4$ data for $^{12}$CH$_4$ presented in Table II are in agreement with Eqs. (A3.8)–(A3.12). The values of fitted $t^{4(K, T)}$ parameters displayed in the Table II with reasonable accuracy obey linear equations of the type (A3.8). The comparison of theoretical and "experimental" values of $e^{4(K, T)}$ coefficients is presented in the Table VIII.
TABLE VIII
Comparison of Theoretical Values of $e^{4\nu_{4}}$ Constants with These Deduced from the Fits
of Experimental $\nu_{4}$ Energy Levels of $^{12}$CH$_{4}$

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Theoretical Eqs. (A2.3)-(A2.12)</th>
<th>Deduced from Table II</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\epsilon(4, \nu_{4})$</td>
<td>4.25</td>
<td>4.6 (3)</td>
</tr>
<tr>
<td>$\epsilon(2, \nu_{3})$</td>
<td>2.35</td>
<td>3.1 (9)</td>
</tr>
<tr>
<td>$\epsilon(2, \nu_{3})$</td>
<td>-2.35</td>
<td>-3.3 (8)</td>
</tr>
<tr>
<td>$\epsilon(4, \nu_{5})$</td>
<td>0</td>
<td>-0.5 (10)</td>
</tr>
<tr>
<td>$\epsilon(0, \nu_{2})$</td>
<td>0</td>
<td>0.0 (8)</td>
</tr>
</tbody>
</table>

Note that in Tables I and II, we examine the behavior of parameters in the wide region which is larger than an interval allowed by order-of-magnitude considerations. The distinction in $r^{5(5,0\nu_{3})}$ between left and right sets is $\Delta r^{5(5,0\nu_{3})} = 2 \times 10^{-6}$ cm$^{-1}$. According to the Amat-Nielsen ordering scheme, one should consider $\Delta r^{5(K, \nu)} \sim r^{5(K, \nu)} \sim \lambda^{10 \nu} \sim 10^{-7}$ cm$^{-1}$, otherwise the condition (11) should be violated. Within an allowed interval restricted by two nearby sets of Table II, the variations in fitted values of $r^{4(K, \nu)}$ parameter are not important, as should be expected from the general scheme of the reduction (2).

RECEIVED: September 10, 1985

REFERENCES