

Reduced Hamiltonian for 0100 and 0001 Interacting States of Tetrahedral XY_4 Molecules: Calculated r^2J^2 and r^2J^3 -Type Parameters for ν_2 and ν_4 Bands of Methane¹

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Ambiguity of the effective Hamiltonian for the interacting E and F_2 states of tetrahedral XY_4 molecules was studied. Unitary transformations to yield a reduced form of the Hamiltonian were suggested, the latter including only empirically determinable parameters. The r^2J^2 and r^2J^3 -type spectroscopic parameters for the 0001 and 0100 dyad of CH_4 molecule were calculated by means of contact transformations. It was shown that sets of spectroscopic parameters derived by several authors for the interacting ν_2 and ν_4 bands of CH_4 and SiH_4 may be related via certain unitary transformations. © 1985 Academic Press, Inc.

1. INTRODUCTION

It has already been shown (1, 2) that most high-order parameters of the effective Hamiltonians, \mathcal{H}^{eff} , for the degenerate vibrational states of spherical top molecules cannot be interpreted as spectroscopic constants. For example, there is one "degree of freedom" in the set of the four r^2J^4 -type parameters for a triply degenerate isolated F_2 state. The similar situation occurs for the r^2J^7 parameters of the isolated E state. The ambiguity is more pronounced in the case where resonating states are analyzed simultaneously. It is found that all the r^2J^2 - and r^2J^3 -type parameters and most other high-order parameters of the effective Hamiltonian for the tetrahedral XY_4 molecules cannot be unambiguously determined from experimental spectra. The ambiguity is caused by the fact that although \mathcal{H}^{eff} subjected to unitary transformations does retain its initial form and eigenvalues, it nevertheless leads to considerable changes in the adjusted parameters.

In this paper the 0100 and 0001 interacting states of the tetrahedral XY_4 molecules are treated in more detail.

Sections 3-6 discuss the ambiguous character of the effective Hamiltonian for the ν_2 - ν_4 dyad under small unitary transformations. Then the unitary transformation of \mathcal{H}^{eff} which inverts the signs of interaction operators is considered (Section 7). Furthermore, the relations derived are used to explain the pronounced discrepancies between the parameters for ν_2 and ν_4 interacting bands fitted by different authors for CH_4 and SiH_4 molecules (Section 8). In Section 9 r^2J^2 - and r^2J^3 -type parameters for the ν_2 and ν_4 interacting bands of methane are calculated using the anharmonic

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force field of Gray and Robiette (3) and the formulas of our previous paper (4). It is emphasized that the correct comparison of the calculated and fitted parameters is possible on the basis of relations derived in this paper. Finally, in Section 10 the reduced effective Hamiltonian is suggested. The awkward ambiguity in the parameters of the interacting states can be avoided by the use of this effective Hamiltonian.

2. EFFECTIVE HAMILTONIAN

The effective Hamiltonian is represented in terms of irreducible tensor operators of the Td point group (5, 6). For the 0100 and 0001 interacting states it may be written as

$$\mathcal{H} = \sum_{\substack{s,s'=2,4 \\ s \leq s'}} \sum_{\Omega, K, n, \Gamma} t_{s,s'}^{\Omega(K, n\Gamma)\Gamma_s \Gamma_{s'}} \mathbf{T}_{s,s'}^{\Omega(K, n\Gamma)\Gamma_s \Gamma_{s'}} \quad (1)$$

where

$$\mathbf{T}_{s,s'}^{\Omega(K, n\Gamma)\Gamma_s \Gamma_{s'}} = (-1)^K \mathbf{V}_{s,s'}^{\Gamma_s \Gamma_{s'}(\Gamma)} \times \mathbf{R}^{\Omega(K, n\Gamma)A_1}. \quad (2)$$

It should be noted that the notations introduced in Ref. (6) will be used throughout the paper. The tensor operator, $\mathbf{T}^{\Omega(0, A_1)\Gamma\Gamma}$, has the form

$$\mathbf{T}^{\Omega(0, A_1)\Gamma\Gamma} = [\Gamma]^{1/2} (-3^{1/2}/4)^{\Omega/2} (\mathbf{V}^{\Gamma\Gamma(A_1)} \times \mathbf{R}^{\Omega(0, A_1)A_1}). \quad (3)$$

Effective Hamiltonian (1) also contributes to the energy levels of some overtone and combination vibrational states. In this paper, we consider the effective Hamiltonian up to the third-order terms. This theoretical model was used by Pierre *et al.* (7).

3. AMBIGUITY OF EFFECTIVE HAMILTONIAN

The ambiguity of an effective Hamiltonian is due to the existence of small real unitary transformations

$$\begin{aligned} \tilde{\mathcal{H}} &= \cdots \exp(i\mathcal{S}) \mathcal{H} \exp(-i\mathcal{S}) \cdots \\ &= \mathcal{H} + [i\mathcal{S}, \mathcal{H}] + \frac{1}{2!} [i\mathcal{S}, [i\mathcal{S}, \mathcal{H}]] + \cdots \end{aligned} \quad (4)$$

which change the coefficients rather than the operators included in the effective Hamiltonian. For Hamiltonian (1) there are two possible types of transformations (4). These include transformations having diagonal generators (2)

$$\mathcal{S}_{s,s}^{\Omega(K, n\Gamma)\Gamma_s \Gamma_s} = \mathcal{S}_{s,s}^{\Omega(K, n\Gamma)\Gamma_s \Gamma_s} (-1)^{K-1} \mathbf{V}_{s,s}^{\Gamma_s \Gamma_s(\Gamma)} \times \mathbf{R}^{\Omega(K, n\Gamma)A_1} \quad (5)$$

and nondiagonal transformations

$$\mathcal{S}_{2,4}^{\Omega(K, n\Gamma)EF_2} = \mathcal{S}_{2,4}^{\Omega(K, n\Gamma)EF} (-1)^{K-1} \mathbf{V}_{2,4}^{EF_2(\Gamma)} \times \mathbf{R}^{\Omega(K, n\Gamma)A_1} \quad (6)$$

which appear to be more important. Possible generators up to the sixth power in the angular momentum are presented in Table I. The ambiguity of the effective Hamiltonian used by Pierre *et al.* (7) is due to the parameters of the \mathcal{S} generator marked with dotted line.

TABLE I

Independent Parameters of δ^5 -Generator up to Sixth Power in Angular Momentum

| ν_2 | ν_4 | $\nu_2 - \nu_4$ - Interaction | |
|-----------------------|-----------------------|-------------------------------|------------------------|
| $\Omega (k, \Gamma)$ | $\Omega (k, \Gamma)$ | $\Omega (k, n \Gamma)$ | |
| 5(5, E) | 3(3, F ₂) | 1(1, F ₁) | 5(3, F ₂) |
| 6(6, A ₂) | 4(4, F ₁) | 2(2, F ₂) | 5(5, 0F ₁) |
| | 5(3, F ₂) | 3(1, F ₁) | 5(5, 1F ₁) |
| | 5(5, E) | 3(3, F ₁) | 5(5, F ₂) |
| | 5(5, F ₂) | 3(3, F ₂) | 6(2, F ₂) |
| | 6(4, F ₁) | 4(2, F ₂) | 6(4, F ₁) |
| | 6(6, F ₁) | 4(4, F ₁) | 6(4, F ₂) |
| | | 4(4, F ₂) | 6(6, F ₁) |
| | | 5(1, F ₁) | 6(6, 0F ₂) |
| | | 5(3, F ₁) | 6(6, 1F ₂) |

4. FIRST-ORDER TRANSFORMATION

As one can see from Table I, the generator of the first transformation is (1, 8)

$$S_{2,4}^{1(1,F_1)EF_2} (V_{2,4}^{EF_2(F_1)} \times R^{1(1,F_1)A_1}). \tag{7}$$

For transformation [(4), (7)] to be small for $J \sim \lambda^{-1}$ one has to impose a restriction on the order of magnitude for the parameter $S_{2,4}^{1(1,F_1)EF_2}$

$$S_{2,4}^{1(1,F_1)EF_2} \ll \lambda^2 \tag{8}$$

where $\lambda^2 \sim (\bar{B}/\bar{\omega})$. This transformation affects the parameter $t_{2,4}^{1(1,F_1)EF_2}$ via the commutator of the generator (7) with $\mathcal{E}_2 T_{2,2}^{0(A_1)EE}$ and $\mathcal{E}_4 T_{4,4}^{0(A_1)F_2F_2}$ terms of the untransformed effective Hamiltonian

$$\tilde{t}_{2,4}^{1(1,F_1)EF_2} = t_{2,4}^{1(1,F_1)EF_2} + S_{2,4}^{1(1,F_1)EF_2} (\mathcal{E}_2 - \mathcal{E}_4). \tag{9}$$

Additionally, through the commutator

$$[iS_{2,4}^{1(1,F_1)EF_2} \mathbf{S}_{2,4}^{1(1,F_1)EF_2}, t_{2,4}^{1(1,F_1)EF_2} \mathbf{T}_{2,4}^{1(1,F_1)EF_2}],$$

it affects the diagonal coupling parameters $t_{s,s}^{2(2,\Gamma)1^s \Gamma_s}$ ($s = 2, 4$)

$$\begin{aligned} \tilde{t}_{2,2}^{2(2,E)EE} &= t_{2,2}^{2(2,E)EE} - \frac{2}{3\sqrt{3}} S_{2,4}^{1(1,F_1)EF_2} t_{2,4}^{1(1,F_1)EF_2}, \\ \tilde{t}_{4,4}^{2(2,E)F_2F_2} &= t_{4,4}^{2(2,E)F_2F_2} - \frac{4}{9} S_{2,4}^{1(1,F_1)EF_2} t_{2,4}^{1(1,F_1)EF_2}, \\ \tilde{t}_{4,4}^{2(2,F_2)F_2F_2} &= t_{4,4}^{2(2,F_2)F_2F_2} + \frac{1}{3} S_{2,4}^{1(1,F_1)EF_2} t_{2,4}^{1(1,F_1)EF_2} \end{aligned} \tag{10}$$

as well as the parameters $t_{s,s}^{2(0,A_1)\Gamma_s\Gamma_s}$ ($s = 2, 4$)

$$\begin{aligned}\tilde{t}_{2,2}^{2(0,A_1)EE} &= t_{2,2}^{2(0,A_1)EE} - \frac{4}{9} s_{2,4}^{1(1,F_1)EF_2} t_{2,4}^{1(1,F_1)EF_2}, \\ \tilde{t}_{4,4}^{2(0,A_1)F_2F_2} &= t_{4,4}^{2(0,A_1)F_2F_2} + \frac{8}{27} s_{2,4}^{1(1,F_1)EF_2} t_{2,4}^{1(1,F_1)EF_2}.\end{aligned}\quad (11)$$

The change in the second-order interaction parameter

$$\tilde{t}_{2,4}^{2(2,F_2)EF_2} = t_{2,4}^{2(2,F_2)EF_2} - \frac{1}{2\sqrt{3}} s_{2,4}^{1(1,F_1)EF_2} t_{4,4}^{1(1,F_1)F_2F_2} \quad (12)$$

induced by the first transformation is due to the commutator of S_1 with the term $t_{4,4}^{1(1,F_1)F_2F_2} \mathbf{T}_{4,4}^{1(1,F_1)F_2F_2}$. Major contributions of the first transformation to r^2J and r^2J^2 terms of methane-type molecules have been analyzed in a previous paper (8). The above transformation also contributes to the higher-order terms, e.g.,

$$\begin{aligned}\tilde{t}_{2,2}^{3(3,A_2)EE} &= t_{2,2}^{3(3,A_2)EE} + \frac{\sqrt{2}}{3\sqrt{3}} s_{2,4}^{1(1,F_1)EF_2} t_{2,4}^{2(2,F_2)EF_2}, \\ \tilde{t}_{4,4}^{3(1,F_1)F_2F_2} &= t_{4,4}^{3(1,F_1)F_2F_2} - \frac{2}{5} s_{2,4}^{1(1,F_1)EF_2} t_{2,4}^{2(2,F_2)EF_2}, \\ \tilde{t}_{4,4}^{3(3,F_1)F_2F_2} &= t_{4,4}^{3(3,F_1)F_2F_2} - \sqrt{\frac{2}{15}} s_{2,4}^{1(1,F_1)EF_2} t_{2,4}^{2(2,F_2)EF_2}.\end{aligned}\quad (13)$$

The details of the commutator calculations are presented in Ref. (2) and in the Appendix.

Equations (9)–(13) contain a free parameter, $s_{2,4}^{1(1,F_1)EF_2} \sim \lambda^2$. Therefore, there exist many sets $\{t_{s,s'}^{\Omega(K,\Gamma)\Gamma_s\Gamma_{s'}}\}$ ($s, s' = 2, 4$) of parameters t which provide the same vibration–rotation energies of the vibrational states considered. In order to remove this ambiguity in the fit of experimental energy levels one has to set a fixed value for one of the parameters involved in Eqs. (9)–(11). This value, for example, may be derived by perturbation calculations. Since admissible variations in the $t^{2(K,\Gamma)}$ parameters are of the order of the parameters themselves one can fix one of the parameters in Eqs. (10) and (11) to zero. On the contrary, the allowed variations $\Delta t_{2,4}^{1(1,F_1)EF_2}$ must lie in small range around the value

$$t_{2,4}^{1(1,F_1)EF_2} = \frac{3}{2} B \zeta_{24} \frac{\omega_2 + \omega_4}{(\omega_2 \omega_4)^{1/2}}, \quad (14)$$

i.e.,

$$|\Delta t_{2,4}^{1(1,F_1)EF_2}| \ll |t_{2,4}^{1(1,F_1)EF_2}|.$$

Otherwise the condition $s_{2,4}^{1(1,F_1)EF_2} \ll \lambda^2$ is violated and the convergence of the Hamiltonian expansion may be worse.

Substituting Eq. (9) in Eqs. (10) and (11) we find that allowed variations $\Delta t \equiv \tilde{t} - t$ of parameters of the effective Hamiltonian are related by the equations

$$\begin{aligned} \Delta t_{2,2}^{2(0,A_1)} &= -\frac{4}{9} X \Delta t_{2,4}^{1(1,F_1)}, & \Delta t_{4,4}^{2(0,A_1)} &= \frac{8}{27} X \Delta t_{2,4}^{1(1,F_1)}, \\ \Delta t_{2,2}^{2(2,E)} &= -\frac{2}{3\sqrt{3}} X \Delta t_{2,4}^{1(1,F_1)}, & \Delta t_{4,4}^{2(2,E)} &= -\frac{4}{9} X \Delta t_{2,4}^{1(1,F_1)}, \\ \Delta t_{4,4}^{2(2,F_2)} &= \frac{1}{3} X \Delta t_{2,4}^{1(1,F_1)}. \end{aligned} \quad (15)$$

where $X = t_{2,4}^{1(1,F_1)EF_2} / (\mathcal{E}_2 - \mathcal{E}_4)$. For the sake of simplicity some superscripts of the t parameters are omitted in Eqs. (15). For closely lying vibrational levels which satisfy the relation

$$\mathcal{E}_2 - \mathcal{E}_4 \sim \lambda^m \omega \quad (m \geq 1), \quad (16)$$

one has

$$\frac{\Delta t_{s,s}^{2(K,\Gamma)\Gamma_s\Gamma_s}}{t_{s,s}^{2(K,\Gamma)\Gamma_s\Gamma_s}} \sim \frac{\Delta t_{2,4}^{1(1,F_1)EF_2}}{\lambda^m t_{2,4}^{1(1,F_1)EF_2}}, \quad (17)$$

i.e., small variations in the interaction parameter lead to relatively large variations in the diagonal r^2J^2 -type parameters.

Strong Resonance Case

In the case of strong resonance it is convenient to rewrite relations (15) in another form where one of a $\Delta t_{s,s}^{2(K,\Gamma)\Gamma_s\Gamma_s}$ is regarded to be an independent variation. For example, Δt 's may be written as functions of $\Delta t_{4,4}^{2(2,F_2)F_2F_2}$

$$\begin{aligned} \Delta t_{2,2}^{2(0,A_1)} &= -\frac{4}{3} \Delta t_{4,4}^{2(2,F_2)}, & \Delta t_{4,4}^{2(0,A_1)} &= \frac{8}{9} \Delta t_{4,4}^{2(2,F_2)}, \\ \Delta t_{2,2}^{2(2,E)} &= -\frac{2}{\sqrt{3}} \Delta t_{4,4}^{2(2,F_2)}, & \Delta t_{4,4}^{2(2,E)} &= -\frac{4}{3} \Delta t_{4,4}^{2(2,F_2)}, \end{aligned} \quad (18)$$

$$\Delta t_{2,4}^{1(1,F_1)EF_2} = 3 \frac{\mathcal{E}_2 - \mathcal{E}_4}{t_{2,4}^{1(1,F_1)EF_2}} \Delta t_{4,4}^{2(2,F_2)F_2F_2}. \quad (19)$$

As one can see from Eq. (19) in the case of strong resonance [i.e., for $(\mathcal{E}_2 - \mathcal{E}_4) \leq \lambda^2 \omega$] the interaction parameter $t_{2,4}^{1(1,F_1)EF_2}$ has to be well defined in the fit because it cannot be changed considerably by transformations [(4), (7)] satisfying the order-of-magnitude restriction (8)

$$\Delta t_{2,4}^{1(1,F_1)EF_2} \leq \lambda^2 t_{2,4}^{1(1,F_1)EF_2}. \quad (20)$$

However, all the five diagonal r^2J^2 -type parameters may be changed from negative to positive values, including zero, by unitary transformation [(4), (7)]. Their changes are related by Eq. (18).

5. SECOND-ORDER TRANSFORMATION

According to Table I the allowed second-order \mathbf{S} generator in Eq. (4) is of the form

$$\mathbf{S}_2 = s_{2,4}^{2(2,F_2)EF_2} (-1)^{F_2} \mathbf{V}_{2,4}^{EF_2(F_2)} \times \mathbf{R}^{2(2,F_2)A_1} \quad (21)$$

where the parameters $s_{2,4}^{2(2,F_2)EF_2}$ is free except the order-of-magnitude condition

$$s_{2,4}^{2(2,F_2)EF_2} \ll \lambda^4. \quad (22)$$

Transformation [(4), (21)] induces changes in the interaction parameter $t_{2,4}^{2(2,F_2)EF_2}$ as well as in all the $t_{s,s'}^{3(K,T)T_3T_{3'}} (s, s' = 2, 4)$ parameters. After the calculation of the commutator $[\mathbf{S}_2, \tilde{\mathcal{H}}_1]$ we find relations between parameters of once-transformed and twice-transformed effective Hamiltonians. There is only second-order contribution

$$\tilde{t}_{2,4}^{2(2,F_2)EF_2} = t_{2,4}^{2(2,F_2)EF_2} + s_{2,4}^{2(2,F_2)EF_2} (\mathcal{C}_4 - \mathcal{C}_2). \quad (23)$$

Changes in the diagonal third-order parameters are described by the formulas

$$\begin{aligned} \tilde{t}_{2,2}^{3(3,A_2)EE} &= t_{2,2}^{3(3,A_2)EE} - \frac{1}{3} \sqrt{\frac{2}{3}} s_{2,4}^{2(2,F_2)EF_2} t_{2,4}^{1(1,F_1)EF_2} \\ \tilde{t}_{4,4}^{3(1,F_1)F_2F_2} &= t_{4,4}^{3(1,F_1)F_2F_2} + \frac{2}{5} s_{2,4}^{2(2,F_2)EF_2} t_{2,4}^{1(1,F_1)EF_2} \\ \tilde{t}_{4,4}^{3(3,F_1)F_2F_2} &= t_{4,4}^{3(3,F_1)F_2F_2} + \sqrt{\frac{2}{15}} s_{2,4}^{2(2,F_2)EF_2} t_{2,4}^{1(1,F_1)EF_2}. \end{aligned} \quad (24)$$

Changes in the nondiagonal parameters have quite similar form

$$\begin{aligned} \tilde{t}_{2,4}^{3(1,F_1)EF_2} &= t_{2,4}^{3(1,F_1)EF_2} - \frac{1}{5} s_{2,4}^{2(2,F_2)EF_2} t_{4,4}^{1(1,F_1)F_2F_2}, \\ \tilde{t}_{2,4}^{3(3,F_1)EF_2} &= t_{2,4}^{3(3,F_1)EF_2} - \frac{1}{\sqrt{30}} s_{2,4}^{2(2,F_2)EF_2} t_{4,4}^{1(1,F_1)F_2F_2}, \\ \tilde{t}_{2,4}^{3(3,F_2)EF_2} &= t_{2,4}^{3(3,F_2)EF_2} + \frac{1}{3\sqrt{6}} s_{2,4}^{2(2,F_2)EF_2} t_{4,4}^{1(1,F_1)F_2F_2}. \end{aligned} \quad (25)$$

In Eqs. (24) and (25) we use tildes for the parameters of the twice-transformed effective Hamiltonian whereas the untilded parameters are those of once transformed effective Hamiltonian. Equations (23)–(25) contain a free parameter $s_{2,4}^{2(2,F_2)EF_2}$. Therefore there occurs a linear dependence between the parameters $t_{s,s'}^{3(K,T)T_3T_{3'}} (s, s' = 2, 4)$ and the parameter $t_{2,4}^{2(2,F_2)EF_2}$. This linear dependence is to result in the ambiguity in the fit of the experimental energy levels. In order to remove this ambiguity one may fix one of these parameters.

As in the case of the first transformation we may rewrite Eqs. (23) and (24) in another form

$$\begin{aligned}\Delta t_{2,2}^{3(3,A_2)} &= -\frac{1}{3} \sqrt{\frac{2}{3}} Y \Delta t_{2,4}^{2(2,F_2)}, \\ \Delta t_{4,4}^{3(1,F_1)} &= \frac{2}{5} Y \Delta t_{2,4}^{2(2,F_2)}, \\ \Delta t_{4,4}^{3(3,F_1)} &= \sqrt{\frac{2}{15}} Y \Delta t_{2,4}^{2(2,F_2)}.\end{aligned}\quad (26)$$

Changes in the interaction parameters are related by equations

$$\begin{aligned}\Delta t_{2,4}^{3(1,F_1)} &= -\frac{1}{5} Z \Delta t_{2,4}^{2(2,F_2)}, \\ \Delta t_{2,4}^{3(3,F_1)} &= -\frac{1}{\sqrt{30}} Z \Delta t_{2,4}^{2(2,F_2)}, \\ \Delta t_{2,4}^{3(3,F_2)} &= \frac{1}{3\sqrt{6}} Z \Delta t_{2,4}^{2(2,F_2)}.\end{aligned}\quad (27)$$

As in Eq. (15) we omit here some trivial superscripts and assume that $\Delta t \equiv \tilde{t} - t$. Parameters Y and Z have the values

$$Y = \frac{t_{2,4}^{1(1,F_1)EF_2}}{\mathcal{E}_4 - \mathcal{E}_2}, \quad Z = \frac{t_{4,4}^{1(1,F_1)F_2F_2}}{\mathcal{E}_4 - \mathcal{E}_2}.\quad (28)$$

Equations (26) and (27) imply that variation of the interaction parameter $t_{2,4}^{2(2,F_2)EF_2}$ induces changes in the parameters $t_{s,s'}^{3(K,\Gamma)\Gamma_s\Gamma_{s'}}$ ($s, s' = 2, 4$).

Strong Resonance Case

In this case it is convenient to choose variation of one of the diagonal coupling parameters $t_{s,s}^{3(K,\Gamma)\Gamma_s\Gamma_s}$ ($s = 2, 4$) to be independent. Let us, for example, take the parameter $t_{2,2}^{3(3,A_2)EE}$ as an independent one. Then Eqs. (26) may be written in the following form

$$\Delta \tilde{t}_{2,4}^{2(2,F_2)} = -\frac{3\sqrt{3}}{\sqrt{2}} \frac{\mathcal{E}_4 - \mathcal{E}_2}{t_{2,4}^{1(1,F_1)}} \Delta t_{2,2}^{3(3,A_2)}\quad (29)$$

and

$$\begin{aligned}\Delta \tilde{t}_{4,4}^{3(1,F_1)} &= -\frac{3}{5} \sqrt{6} \Delta t_{2,2}^{3(3,A_2)}, \\ \Delta \tilde{t}_{4,4}^{3(3,F_1)} &= -\frac{3}{5} \sqrt{5} \Delta t_{2,2}^{3(3,A_2)}.\end{aligned}\quad (30)$$

Changes in the interaction parameters are related by the equations

$$\begin{aligned}\Delta\tilde{t}_{2,4}^{3(1,F_1)} &= \frac{3}{5} \sqrt{\frac{3}{2}} C\Delta t_{2,2}^{3(3,A_2)}, \\ \Delta\tilde{t}_{2,4}^{3(3,F_1)} &= \frac{3}{2} \frac{1}{\sqrt{5}} C\Delta t_{2,2}^{3(3,A_2)}, \\ \Delta\tilde{t}_{2,4}^{3(3,F_2)} &= -\frac{1}{2} C\Delta t_{2,2}^{3(3,A_2)}\end{aligned}\quad (31)$$

where $C = t_{4,4}^{1(1,F_1)F_2F_2}/t_{2,4}^{1(1,F_1)EF_2}$.

For close-lying vibrational levels satisfying the relation $|\mathcal{E}_2 - \mathcal{E}_4| \leq \lambda^2\omega$ (strong resonance) the allowed changes in the value of the second-order interaction parameter induced by the second transformation are the order-of-magnitude less than the value of the parameter itself,

$$\Delta t_{2,4}^{2(2,F_2)EF_2} \leq \lambda^2 t_{2,4}^{2(2,F_2)EF_2}.$$

However, all the third-order r^2J^3 type parameters may be changed within a wide range by unitary transformation [(4), (21)]. Their variations are related by Eqs. (30) and (31).

It should be noted that even in the case of strong resonance there exists an essential ambiguity in the parameter $t_{2,4}^{2(2,F_2)EF_2}$ induced by the first transformation [see Eq. (9)].

6. THIRD-ORDER TRANSFORMATIONS

There are three generators of the third-order transformation

$$S_{2,4}^{3(1,F_1)EF_2} S_{2,4}^{3(1,F_1)EF_2}, \quad (32)$$

$$S_{2,4}^{3(3,F_1)EF_2} S_{2,4}^{3(3,F_1)EF_2}, \quad (33)$$

$$S_{2,4}^{3(3,F_2)EF_2} S_{2,4}^{3(3,F_2)EF_2}. \quad (34)$$

The commutators of these generators with $\mathcal{E}_2 \mathbf{T}_{2,2}^{0(0,A_1)EE}$ and $\mathcal{E}_4 \mathbf{T}_{4,4}^{0(0,A_1)F_2F_2}$ terms of the effective Hamiltonian contribute to the third-order interaction parameters

$$\tilde{t}_{2,4}^{3(1,F_1)EF_2} = t_{2,4}^{3(1,F_1)EF_2} + S_{2,4}^{3(1,F_1)EF_2} (\mathcal{E}_2 - \mathcal{E}_4), \quad (35)$$

$$\tilde{t}_{2,4}^{3(3,F_1)EF_2} = t_{2,4}^{3(3,F_1)EF_2} + S_{2,4}^{3(3,F_1)EF_2} (\mathcal{E}_2 - \mathcal{E}_4), \quad (36)$$

$$\tilde{t}_{2,4}^{3(3,F_2)EF_2} = t_{2,4}^{3(3,F_2)EF_2} + S_{2,4}^{3(3,F_2)EF_2} (\mathcal{E}_2 - \mathcal{E}_4). \quad (37)$$

Third-order transformations also affect all the fourth-order diagonal and interaction parameters of the r^2J^4 -type. The present discussion is limited to the third-order terms whose study is sufficient to perform the analysis of the data reported by Pierre *et al.* (7).

As one can see from Eqs. (35)–(37) the third-order transformations (32)–(34) are to result in uncertainties of the third-order interaction parameters $t_{2,4}^{3(K,\Gamma)EF_2}$. These

uncertainties must have the order $\lambda^6(\mathcal{E}_2 - \mathcal{E}_4)$, otherwise the contributions to the fourth-order parameters would exceed the values of these parameters by an order of magnitude.

7. SIGN INVERSION FOR ALL INTERACTION OPERATORS

Previous sections discuss only small transformations which do not disturb conventional ordering of the effective Hamiltonian. For the correct comparison of the calculated and fitted data (Section 9) we have to consider a unitary transformation of \mathcal{H}^{eff} which inverts the signs of all the interaction operators. This transformation is not small but it does not change conventional ordering of the effective Hamiltonian.

Let us write the block $\mathbf{H}^{\text{eff}} = \mathbf{P}\mathcal{H}^{\text{eff}}\mathbf{P}$ of the effective Hamiltonian (1) corresponding to the $\nu_2 - \nu_4$ dyad in the following form

$$\mathbf{H}^{\text{eff}} = \begin{pmatrix} \mathbf{H}_E & \mathbf{H}_{E-F_2} \\ \mathbf{H}_{E-F_2}^+ & \mathbf{H}_{F_2} \end{pmatrix} \quad (38)$$

where \mathbf{H}_E is a 2×2 "operator-matrix,"² \mathbf{H}_{F_2} is a 3×3 operator-matrix, and \mathbf{H}_{E-F_2} is a 2×3 interaction operator-matrix of the 0100 and 0001 vibrational states. The unitary transformation

$$\mathbf{U} = \begin{pmatrix} \mathbf{1}_E & 0 \\ 0 & -\mathbf{1}_{F_2} \end{pmatrix} \quad (39)$$

inverts the sign of the interaction block \mathbf{H}_{E-F_2}

$$\tilde{\mathbf{H}}^{\text{eff}} = \mathbf{U}^+\mathbf{H}^{\text{eff}}\mathbf{U} = \begin{pmatrix} \mathbf{H}_E & -\mathbf{H}_{E-F_2} \\ -\mathbf{H}_{E-F_2}^+ & \mathbf{H}_{F_2} \end{pmatrix}. \quad (40)$$

Here the notation $\mathbf{1}_E$ stands for the 2×2 unit matrix and $\mathbf{1}_{F_2}$ for the 3×3 unit matrix. Both \mathbf{H}^{eff} (38) and $\tilde{\mathbf{H}}^{\text{eff}}$ (40) have the same eigenvalues. Therefore the common sign of the interaction block is undeterminable from the experimental spectrum. Note that transformation (39) does not affect relative signs of the interaction parameters. Therefore one can avoid this kind of ambiguity by a proper choice of the sign of the first-order Coriolis coupling parameter $t_{2,4}^{(1,F_1)EF_2}$.

8. COMPARATIVE ANALYSIS OF THE FITTED SETS OF PARAMETERS FOR THE ν_2 AND ν_4 INTERACTING BANDS OF CH_4 AND SiH_4

The spectroscopic parameters for the ν_2 and ν_4 interacting bands of CH_4 deduced by different authors from the fit of the experimental data show pronounced discrepancies³ which involve even differences in signs and orders-of-magnitude of the parameters in question [see Table 13 in Ref. (5)]. A similar situation takes place in the case of the ν_2 and ν_4 interacting bands of SiH_4 . The object of this section is

² We use the term "operator-matrix" to emphasize that matrix elements in this case are rotational operators.

³ We mean the discrepancies in the parameters recalculated for the same notation.

to demonstrate that these distinctions may be explained on the basis of the transformations considered above.

As an example we first discuss in detail two sets of fitted parameters of the $\nu_2 - \nu_4$ dyad of CH_4 deduced from experimental spectra by Pierre, Pierre, Champion, and Lutz (PPCL) (7) and by Gray and Robiette (GR) (9). Let us perform two successive transformations of the effective Hamiltonian with the PPCL parameters in such a way that the interaction parameter $t_{2,4}^{1(1,F_1)EF_2} = -9.6334 \text{ cm}^{-1}$ of Ref. (7) is converted into the parameter $\tilde{t}_{2,4}^{1(1,F_1)EF_2} = -9.52 \text{ cm}^{-1}$ of Ref. (9) and the interaction parameter $t_{2,4}^{2(2,F_2)EF_2} = -3.57 \times 10^{-2} \text{ cm}^{-1}$ of Ref. (7) is converted to zero as in Ref. (9). The generator of the first transformation is

$$S_1 = 5.097 \cdot 10^{-4} (\mathbf{V}_{2,4}^{EF_2(F_1)} \times \mathbf{R}^{1(1,F_1)})_{A_1}. \quad (41)$$

The parameters of the once transformed effective Hamiltonian are presented in the third column of Table II. The generator of the second transformation is

$$S_2 = -1.6737 \cdot 10^{-4} ({}^{(-1)}\mathbf{V}_{2,4}^{EF_2(F_2)} \times \mathbf{R}^{2(2,F_2)})_{A_1}. \quad (42)$$

Once can also see from Table II that the parameters of the twice-transformed PPCL Hamiltonian and the GR parameters [Ref. (9)] are in close agreement, except the

TABLE II

The Demonstration of Unitary Equivalence of Pierre-Pierre-Champion-Lutz (PPCL) (7) and Gray-Robiette (GR) (9) Parameters for Interacting ν_4 and ν_2 Bands of Methane

| cm^{-1} | $\Omega(K, \Gamma)$ | PPCL | a | b | GR |
|--------------------------------|-------------------------|----------|----------|----------|---------|
| ν_2 | $2(0, A_1) \times 10^2$ | -0.6640 | -0.4433 | -0.4433 | -0.3846 |
| | $2(2, E) \times 10^2$ | -3.1455 | -2.9544 | -2.9544 | -2.8025 |
| | $3(3, A_2) \times 10^3$ | -0.210 | -0.215 | -0.6536 | -0.6875 |
| $\nu_2 - \nu_4$ interaction | $1(1, F_1)$ | -9.6334 | -9.52 | -9.52 | -9.52 |
| | $2(2, F_2) \times 10^2$ | -3.570 | -3.7240 | 0 | 0 |
| | $3(1, F_1) \times 10^3$ | -0.0828 | | | 0 |
| | $3(3, F_1) \times 10^3$ | 0.2300 | | | 0 |
| | $3(3, F_2) \times 10^3$ | 0.1983 | | | 0 |
| ν_4 | $1(1, F_1)$ | 10.34721 | 10.34721 | 10.34721 | 10.3516 |
| | $2(0, A_1) \times 10^2$ | -0.1813 | -0.3284 | -0.3284 | -0.3106 |
| | $2(2, E) \times 10^2$ | -0.942 | -0.7213 | -0.7213 | -0.6879 |
| | $2(2, F_2) \times 10^2$ | -2.758 | -2.9235 | -2.9235 | -3.126 |
| | $3(1, F_1) \times 10^3$ | 0.5245 | 0.5319 | 1.1765 | 1.212 |
| | $3(3, F_1) \times 10^3$ | 0.2362 | 0.2429 | 0.8313 | 0.8892 |

a Once transformed PPCL-parameters

b Twice transformed PPCL-parameters

third-order interaction parameters. One can clearly choose the free parameters $S_{2,4}^{3(1,F_1)EF_2}$, $S_{2,4}^{3(3,F_1)EF_2}$, and $S_{2,4}^{3(3,F_2)EF_2}$ in Eqs. (32)–(34) so that the three transformed parameters $\tilde{t}_{2,4}^{3(1,F_1)EF_2}$, $\tilde{t}_{2,4}^{3(3,F_1)EF_2}$, and $\tilde{t}_{2,4}^{3(3,F_2)EF_2}$ are converted into zero by the third-order transformations (35) and (36). Thus the "unitary equivalence" of the two sets of parameters under consideration is proven. The remaining minor differences between the transformed PPCL parameters and those of Gray and Robiette may be explained by the following reasons. First, the expansion of \mathcal{H}^{eff} was differently truncated in Refs. (7) and (9), and besides, different experimental spectra were fitted. Second, there still exists a small contribution from higher-order commutators which may slightly modify the relations considered.

Analogous comparative analysis was made for spectroscopic parameters of the $\nu_2 - \nu_4$ interacting bands of SiH_4 fitted to the experimental spectra by Pierre *et al.* (10) and by Gray *et al.* (11). The results are presented in Table III. We made two successive transformations of the effective Hamiltonian reported by Pierre *et al.* (10). The first-order transformation was performed so that the interaction parameter $t_{2,4}^{1(1,F_1)EF_2} = -5.6147 \text{ cm}^{-1}$ of Ref. (10) was transformed into the parameter $\tilde{t}_{2,4}^{1(1,F_1)EF_2} = -4.9814 \text{ cm}^{-1}$ of Ref. (11), and the second-order transformation was performed in such a way as to convert the value of the once-transformed parameter $t_{2,2}^{3(3,A_2)EE} = -4.57 \times 10^{-5}$ into the value $\tilde{t}_{2,2}^{3(3,A_2)EE} = -60.8 \times 10^{-5}$ of Ref. (11). As one can see from Table III there is a reasonable agreement between the twice-transformed parameters of Ref. (10) and those of Ref. (11).

TABLE III

The Comparison of Pierre–Champion–Koslov–Smirnov (10) and Gray–Robiette–Johns (11) Spectroscopic Parameters for ν_2 and ν_4 Interacting Bands of Silane

| cm^{-1} | $\Omega (K, n \Gamma)$ | Pierre et al. | a | b | Gray et al. |
|--------------------------|-------------------------|---------------|---------|---------|-------------|
| ν_2 | $2(0, A_1) \times 10^2$ | -2.338 | 0.412 | 0.412 | 0.250 |
| | $2(2, E) \times 10^2$ | -2.938 | -0.556 | -0.556 | -0.429 |
| | $3(3, A_2) \times 10^5$ | -4.24 | -4.57 | -60.8 | -60.8 |
| $\nu_2 - \nu_4$ interac. | $1(1, F_1)$ | -5.6147 | -4.9814 | -4.9814 | -4.9814 |
| | $2(2, F_2) \times 10^2$ | -0.111 | -2.0369 | 0.3467 | 0 |
| ν_4 | $2(0, A_1) \times 10^2$ | 1.570 | -0.263 | -0.263 | -0.187 |
| | $2(2, E) \times 10^2$ | -2.624 | 0.126 | 0.126 | 0.099 |
| | $2(2, F_2) \times 10^2$ | 0.501 | -1.561 | -1.561 | -1.741 |
| | $3(1, F_1) \times 10^5$ | 16.75 | 17.24 | 99.88 | 103.25 |
| | $3(3, F_1) \times 10^5$ | -4.02 | -3.57 | 71.87 | 83.95 |

a Once transformed Pierre et al. parameters

b Twice transformed Pierre et al. parameters

9. CALCULATED r^2J^2 - AND r^2J^3 -TYPE PARAMETERS OF THE EFFECTIVE HAMILTONIAN FOR THE INTERACTING ν_2 AND ν_4 BANDS OF METHANE. COMPARISON WITH THE FITTED DATA

The formulas for the r^2J^2 - and r^2J^3 -type parameters of the effective Hamiltonian for the ν_2 and ν_4 interacting bands of tetrahedral XY_4 molecules have been derived in our recent paper⁴ (4) using the quasidegenerate formulation of contact transformations (13) and (14).

Our choice of normal coordinates and of the bases of irreducible representations coincides with that of Refs. (3, 15), i.e. the parameters $\epsilon_x, \epsilon_y, \epsilon_z$ ($\epsilon_z = 2\pi/3 + \epsilon_y = 4\pi/3 + \epsilon_x$) of orientation of doubly degenerate normal coordinates are taken all through the paper as $\epsilon_z = \pi$ and the Coriolis coupling constants $\zeta_{2b4z}^{\tilde{z}} = -\sin \gamma \times \cos \epsilon_z$ and $\zeta_{2b3z}^{\tilde{z}} = \cos \gamma \cos \epsilon_z$ [Ref. (16)] have the forms

$$\zeta_{2b4z}^{\tilde{z}} = \sin \gamma \equiv \zeta_{24}, \quad \zeta_{2b3z}^{\tilde{z}} = -\cos \gamma \equiv \zeta_{23}.$$

In the second column of Table IV our calculated parameters for the $\nu_2 - \nu_4$ dyad are listed. These calculations are performed using the perturbation formulas of Ref. (4) and the anharmonic force field of Gray and Robiette (3). These results will be referred to as "direct" calculations. The molecular parameters used are summarized in Table V.

Pierre *et al.* (7) chose another set of orientation parameters associated with $\epsilon_z = 0$, therefore, all the interaction parameters of their paper have opposite signs. Before the comparison of the calculated and fitted parameters of Ref. (7) one has first to perform transformation (40) which changes the signs of the interaction parameters and is equivalent to the appropriate change of orientation of doubly degenerate coordinates.

As one can see from Tables III and IV the parameters derived by the "direct" perturbation calculations do not coincide with the fitted parameters of Gray and Robiette (9) nor with the fitted parameters of Pierre *et al.* (7). There are especially large discrepancies in the case of the r^2J^3 -type parameters. However, there are no real contradictions between the calculated and fitted parameters in this case since these sets of parameters may be matched by the unitary transformations considered in Sections 4-7.

Let us consider, for example, the calculated parameters and the PPCL parameters. The second-order transformation (4) having the generator

$$\mathbf{S}_2 = -7.25 \cdot 10^{-5} {}^{(-1)}\mathbf{V}_{2,4}^{EF_2(F_2)} \times \mathbf{R}^{2(2,F_2)A_1} \quad (43)$$

transforms the set of directly calculated parameters into the set (column 3 of Table IV) which is rather close to the fitted parameters of Ref. (7). The free parameter $s_{2,4}^{2(2,F_2)EF_2}$ is chosen so that the calculated value $t_{2,2}^{3(3,A_2)EE} = -0.020 \times 10^{-3} \text{ cm}^{-1}$ is converted by transformation (4) into the CCPL value $\tilde{t}_{2,2}^{3(3,A_2)EE} = -0.210 \times 10^{-3} \text{ cm}^{-1}$. The first-order transformation [(4), (7)] appears to be negligible in this case.

The conclusion of the present section may be summarized as follows. The direct perturbation calculations using contact transformation result in the effective Hamiltonian ${}^{(CT)}\mathcal{H}^{\text{eff}}$ which does not necessarily coincide with the effective Hamiltonian

⁴ There are some misprints in Appendix II of this paper. The true formulas for $t_{2,2}^{2(0,A_1)EE}$ and $t_{4,4}^{2(0,A_1)F_2F_2}$ parameters are presented in Ref. (8) or in Errata (12).

TABLE IV

The Comparison of Theoretical and Experimental Values of Spectroscopic Parameters for Interacting ν_2 and ν_4 Bands of Methane Molecule

| cm^{-1} | $\Omega (K, n \Gamma)$ | Our direct calculations ^a | Unitary transformed parameters | PPCL parameters ^b |
|--------------------------------|-------------------------|--------------------------------------|--------------------------------|------------------------------|
| ν_2 | $2(0, A_1) \times 10^2$ | -0.521 | -0.521 | -0.6640 |
| | $2(2, E) \times 10^2$ | -3.135 | -3.135 | -3.146 |
| | $3(3, A_2) \times 10^3$ | -0.020 | -0.210 | -0.210 |
| $\nu_2 - \nu_4$ Interaction | $1(1, F_1)$ | +9.6321 | -9.6321 | -9.6334 |
| | $2(2, F_2) \times 10^2$ | +5.366 | -3.771 | -3.570 |
| ν_4 | $1(1, F_1)$ | 10.2446 | 10.2446 | 10.34721 |
| | $2(0, A_1) \times 10^2$ | -0.064 | -0.064 | -0.1813 |
| | $2(2, E) \times 10^2$ | -1.080 | -1.080 | -0.942 |
| | $2(2, F_2) \times 10^2$ | -2.893 | -2.893 | -2.758 |
| | $3(1, F_1) \times 10^3$ | 0.251 | 0.530 | 0.525 |
| | $3(3, F_1) \times 10^3$ | -0.014 | 0.241 | 0.236 |

^a The formulas of Ref.(4) and anharmonic force field of Ref.(3) were used.

^b Ref.(7).

${}^{(ft)}\mathcal{H}^{\text{eff}}$ deduced from the fit of the experimental data. Even if these two effective Hamiltonians have the same eigenvalues they may still have different parameters since they may have different eigenfunctions $\{\Psi^{\text{eff}}\}$. The additional transformation [(4), (43)] which matches the eigenbases of ${}^{(CT)}\mathcal{H}^{\text{eff}}$ to the eigenbases of ${}^{(ft)}\mathcal{H}^{\text{eff}}$ of Ref. (7) makes it evident that there is, in fact, a good agreement between the calculated and fitted data for the $\nu_2 - \nu_4$ interacting bands of CH_4 (see, for example, columns 3 and 4 of Table IV).

10. REDUCED EFFECTIVE HAMILTONIAN FOR THE 0100 AND 0001 INTERACTING STATES OF T_d MOLECULES

In order to avoid the considered kind of ambiguity we suggest the use of the reduced effective Hamiltonian⁵ for the $\nu_2 - \nu_4$ interacting vibrational states.

Some terms may be removed from the Hamiltonian (1) by appropriate choice of

⁵ The term "reduced Hamiltonian" was introduced first by Watson (17) in his study of the centrifugal distortion Hamiltonian of asymmetric molecules. The reduction procedure has been generalized to interacting states of asymmetric top molecules in Ref. (18). For degenerate vibrational states of spherical top molecules the reduced Hamiltonians were suggested in Refs. (1, 2). The reduction of r^2J^2 -terms for the $\nu_2 - \nu_4$ interacting states has been discussed in Ref. (8).

TABLE V

The Molecular Parameters Used for the Calculations of r^2J^2 - and r^2J^3 -type Spectroscopic Parameters for ν_2 and ν_4 Interacting Bands of $^{12}\text{CH}_4$ [All parameters are taken from Ref. (3)]

| constants | values in cm^{-1} | constants | values |
|------------|----------------------------|---------------------------------------|---------|
| ω_1 | 3025 | $\zeta_{23}^z \equiv \zeta_{2b}^z 3z$ | -0.7974 |
| ω_2 | 1583 | $\zeta_{24}^z \equiv \zeta_{2b}^z 4z$ | 0.6034 |
| ω_3 | 3157 | $\zeta_{34}^z \equiv \zeta_{3x}^z 4y$ | 0.7218 |
| ω_4 | 1367 | $\zeta_3^z \equiv \zeta_{3x}^z 3y$ | 0.0462 |
| B_e | 5.321 | $\zeta_4^z \equiv \zeta_{4x}^z 4y$ | 0.4538 |

| K_{1je} | values in cm^{-1} | K_{1je} | values in cm^{-1} |
|-------------------------------|----------------------------|-------------------------------|----------------------------|
| K_{111} | -149.3 | $K_{234} \equiv K_{2a} 3z 4z$ | -24.5 |
| $K_{122} \equiv K_{12a} 2a$ | 7 | $K_{244} \equiv K_{2a} 4z 4z$ | -6 |
| $K_{133} \equiv K_{13x} 3x$ | -162.3 | $K_{333} \equiv K_{3x3y} 3z$ | -171.8 |
| $K_{134} \equiv K_{13x} 4x$ | -3.2 | $K_{334} \equiv K_{3x} 3y 4z$ | -21 |
| $K_{144} \equiv K_{14x} 4x$ | 38.2 | $K_{344} \equiv K_{3x} 4y 4z$ | -25.5 |
| $K_{222} \equiv K_{2a} 2a 2a$ | -8.8 | $K_{444} \equiv K_{4x} 4y 4z$ | -21.2 |
| $K_{233} \equiv K_{2a} 3z 3z$ | -15.3 | | |

free parameters in S generators (5, 6). The resulting reduced effective Hamiltonian contains a smaller number of adjustable parameters compared to expansion (1). From the practical point of view, in order to obtain the reduced Hamiltonian one has to fix to zero (or to other given values) the removable parameters in expansion (1). The number of removable terms coincides with the number of free parameters in S generators. The fixed parameters must be chosen so that transformations having generators (5, 6) become forbidden. In order to avoid the ambiguity caused by transformation (7) one may fix to zero one of the parameters $t_{s,s}^{2(K,T)\Gamma_s\Gamma_s}$ ($s = 2, 4$). Let this parameter be $t_{4,4}^{2(2,E)F_2F_2}$. This choice is equivalent to the unitary transformation of the effective Hamiltonian with generator (7), where

$$S_{2,4}^{1(1,F_1)EF_2} = \frac{9}{4} \frac{t_{4,4}^{2(2,E)F_2F_2}}{t_{2,4}^{1(1,F_1)EF_2}} \quad (44)$$

The parameters of the reduced Hamiltonian are related to the parameters of the

unreduced one in the following way. For the interaction parameter $\text{red} t_{2,4}^{1(1,F_1)EF_2}$ one has

$$\text{red} t_{2,4}^{1(1,F_1)EF_2} = t_{2,4}^{1(1,F_1)EF_2} + \frac{9}{4} \frac{\mathcal{E}_2 - \mathcal{E}_4}{t_{2,4}^{1(1,F_1)EF_2}} t_{4,4}^{2(2,E)F_2F_2}. \quad (45)$$

For the diagonal coupling parameters these relations may be written as

$$\begin{aligned} \text{red} t_{2,2}^{2(0,A_1)} &= t_{2,2}^{2(0,A_1)} - t_{4,4}^{2(2,E)}, \\ \text{red} t_{2,2}^{2(2,E)} &= t_{2,2}^{2(2,E)} - \frac{\sqrt{3}}{2} t_{4,4}^{2(2,E)} \end{aligned} \quad (46)$$

and

$$\text{red} t_{4,4}^{2(0,A_1)} = t_{4,4}^{2(0,A_1)} + \frac{2}{3} t_{4,4}^{2(2,E)}, \quad (47a)$$

$$\text{red} t_{4,4}^{2(2,E)} = 0 \quad (\text{fixed}), \quad (47b)$$

$$\text{red} t_{4,4}^{2(2,F_2)} = t_{4,4}^{2(2,F_2)} + \frac{3}{4} t_{4,4}^{2(2,E)}. \quad (47c)$$

It should be noted that this transformation gives rise to the contributions to the higher-order terms as well.

To avoid the ambiguity caused by the transformation having generator (21) one may for example fix to zero one of the parameters $t_{s,s}^{3(K,\Gamma)\Gamma_s}$ ($s = 2, 4$). Let this parameter be $t_{2,2}^{3(3,A_2)EE}$. This choice is equivalent to the unitary transformation of the effective Hamiltonian having generator (21), where

$$s_{2,4}^{2(2,F_2)EF_2} = \frac{3\sqrt{3}}{\sqrt{2}} \frac{t_{2,2}^{3(3,A_2)EE}}{t_{2,4}^{1(1,F_1)EF_2}}. \quad (48)$$

The third-order parameters of the reduced Hamiltonian are related to those of the once-transformed Hamiltonian [the transformation having generator (44)] in the following way

$$\text{red} t_{2,2}^{3(3,A_2)} = 0 \quad (\text{fixed}), \quad (49a)$$

$$\text{red} t_{4,4}^{3(1,F_1)} = t_{4,4}^{3(1,F_1)} + \frac{3}{5} \sqrt{6} t_{2,2}^{3(3,A_2)}, \quad (49b)$$

$$\text{red} t_{4,4}^{3(3,F_1)} = t_{4,4}^{3(3,F_1)} + \frac{3}{5} \sqrt{5} t_{2,2}^{3(3,A_2)}. \quad (49c)$$

For the interaction parameter $t_{2,4}^{2(2,F_2)EF_2}$ one has

$$\text{red} t_{2,4}^{2(2,F_2)} = t_{2,4}^{2(2,F_2)} + \frac{3\sqrt{3}}{\sqrt{2}} \frac{\mathcal{E}_4 - \mathcal{E}_2}{t_{2,4}^{1(1,F_1)EF_2}} t_{2,2}^{3(3,A_2)}. \quad (50)$$

After the restrictions of the types (47b) and (49a) are imposed, there are no longer "degrees of freedom" in the effective eigenbasis $\{\Psi^{\text{eff}}\}$. Transformations (7) and (21) become forbidden, i.e., one cannot perform them without violating Eqs. (47b) and (49a). This is the reason why one can expect to have unambiguous calculations based on the reduced Hamiltonian. This proposition is confirmed by Table VI where the parameters of the reduced Hamiltonian for the ν_2 and ν_4 interacting bands of methane recalculated from those of Refs. (7) and (9) are presented. The differences between the values of the parameters in Table VI are much less

TABLE VI

The Parameters of the Reduced Hamiltonian for the ν_2 and ν_4 Interacting Bands of Methane

| | $\Omega(K, \Gamma)$ in cm^{-1} | a | b | c |
|--------------------------------|---|--------|--------|--------|
| ν_2 | $2(0, A_1) \times 10^2$ | 0.278 | 0.303 | 0.559 |
| | $2(2, E) \times 10^3$ | -2.330 | -2.207 | -2.200 |
| | $3(3, A_2) \times 10^3$ | 0 | 0 | 0 |
| $\nu_2 - \nu_4$ interaction | $1(1, F_1)$ | -9.144 | -9.159 | -9.072 |
| | $2(2, F_2) \times 10^2$ | -6.296 | -6.623 | -6.626 |
| ν_4 | $2(0, A_1) \times 10^2$ | -0.809 | -0.769 | -0.784 |
| | $2(2, E) \times 10^2$ | 0 | 0 | 0 |
| | $2(2, F_2) \times 10^2$ | -3.465 | -3.642 | -3.703 |
| | $3(1, F_1) \times 10^3$ | 0.216 | 0.202 | 0.221 |
| | $3(3, F_1) \times 10^3$ | -0.045 | -0.033 | -0.041 |

a - recalculated parameters of Ref.(9);

b - recalculated parameters of Ref.(7);

c - our direct calculated parameters.

pronounced than the corresponding differences for the parameters of an unreduced Hamiltonian (see Tables II and IV).

The reduction procedure can be easily generalized to higher-order terms. The number of the adjustable parameters of unreduced and reduced Hamiltonians for the interacting 0100 and 0001 states of tetrahedral XY_4 molecules is presented in Table VII.

TABLE VII

The Numbers of Parameters of Unreduced and Reduced Hamiltonians for Interacting 0100 and 0001 States of the Tetrahedral XY_4 Molecules

| Type of operators | Unreduced Hamiltonian | | Reduced Hamiltonian | |
|----------------------|-----------------------|--------------------------|-----------------------|--------------------------|
| | Diagonal operators | Interaction operators | Diagonal operators | Interaction operators |
| r^2J | 1 | 1 | 1 | 1 |
| r^2J^2 | 5 | 1 | 4 | 1 |
| r^2J^3 | 3 | 3 | 2 | 3 |
| r^2J^4 | 10 | 3 | 6 | 3 |
| r^2J^5 | 5 | 6 | 1 | 6 |
| r^2J^6 | 16 | 6 | 7 | - |

We recommend to truncate the expansion of *self* for methane and silane as indicated in Table by dotted lines

11. CONCLUSIONS

The major conclusion is that the r^2J^Ω -type parameters ($\Omega \geq 2$) of the interacting ν_2 and ν_4 bands of XY_4 molecules are not spectroscopic constants. There are many sets of such parameters. The distinctions between these sets are due to nonphysical distinctions in the eigenfunctions of associated effective Hamiltonians. In order to make consistent comparisons of the fitted parameters of different studies or comparison of the fitted and calculated parameters, one has to take into account transformations (5) and (6). A possible way of performing an unambiguous fit of experimental data is to use the reduced effective Hamiltonian.

The above conclusions have been recently verified in a series of actual fits of experimental energy levels of the ν_2 and ν_4 interacting bands of CH_4 and SiH_4 performed together with Champion and Pierre (19) using computer programs developed by Dijon group. The behavior of the fitted parameters appears to be in agreement with the relations discussed in the present paper.

APPENDIX

*Calculation of the Commutators and Anticommutators
of Rotational Tensor Operators*

Rotational tensor commutators and anticommutators are calculated using the following formula

$$[\mathbf{R}^{\Omega_1(J_1, t_1 \Gamma_1)}, \mathbf{R}^{\Omega_2(J_2, t_2 \Gamma_2)}]_{\pm}^{\chi} = \frac{1}{\sqrt{[\chi]}} \sum_{t_3 J_3} \sum_{\delta} (1 \pm (-1)^{J_1+J_2+J_3}) \times (-1)^{J_3} \sqrt{2J_3 + 1} K_{t_1 \Gamma_1}^{J_1} K_{t_2 \Gamma_2}^{J_2} K_{t_3 \Gamma_3}^{J_3} ((J_1 J_2 | \delta J_3)) \mathbf{R}^{\Omega_1+\Omega_2-\delta(J_3, t_3 \chi)}$$

where $K_{t_i \Gamma_i}^{J_i}$ are isoscalar coefficients tabulated, for example in Ref. (5), and $((J_1 J_2 | \delta J_3))$ are genealogical coefficients [Ref. (20)]. The definition and detailed discussion of calculation of vibration-rotation tensor commutators can be found in the Appendix of Ref. (2). We give here the list of the rotational anticommutators used in the present work.

$$\begin{aligned} [\mathbf{R}^{1(1, F_1)}, \mathbf{R}^{1(1, F_1)}]_{+}^{2(2, F)} &= -2\mathbf{R}^{2(2, F)}, \\ [\mathbf{R}^{1(1, F_1)}, \mathbf{R}^{1(1, F_1)}]_{+}^{2(2, F_2)} &= -2\mathbf{R}^{2(2, F_2)}, \\ [\mathbf{R}^{1(1, F_1)}, \mathbf{R}^{1(1, F_1)}]_{+}^{2(0, A_1)} &= -2\mathbf{R}^{2(0, A_1)}, \\ [\mathbf{R}^{2(2, F_2)}, \mathbf{R}^{1(1, F_1)}]_{+}^{3(3, A_2)} &= 2\mathbf{R}^{3(3, A_2)}, \\ [\mathbf{R}^{2(2, F_2)}, \mathbf{R}^{1(1, F_1)}]_{+}^{3(1, F_1)} &= \frac{4}{5} \sqrt{3} \mathbf{R}^{3(1, F_1)}, \\ [\mathbf{R}^{2(2, F_2)}, \mathbf{R}^{1(1, F_1)}]_{+}^{3(3, F_1)} &= 2 \sqrt{\frac{2}{5}} \mathbf{R}^{3(3, F_1)}, \\ [\mathbf{R}^{2(2, F_2)}, \mathbf{R}^{1(1, F_1)}]_{+}^{3(3, F_2)} &= 2 \sqrt{\frac{2}{3}} \mathbf{R}^{3(3, F_2)}. \end{aligned}$$

Calculation of the Commutators of Vibrational Tensor Operators

The vibrational commutators of the present paper may be calculated using the general relation

$$[(\mathbf{a}_i^+ \times \mathbf{a}_j)^{\Gamma_1}, (\mathbf{a}_k^+ \times \mathbf{a}_l)^{\Gamma_2}]_-^{\Gamma} = \delta_{j,k} \left\{ \begin{matrix} \Gamma_i & \Gamma_k & \Gamma_1 \\ \Gamma_2 & \Gamma & \Gamma_l \end{matrix} \right\} (-1)^{\Gamma_i + \Gamma_l + \Gamma} \sqrt{[\Gamma_1][\Gamma_2]} (\mathbf{a}_i^+ \times \mathbf{a}_l)^{\Gamma} \\ - \delta_{i,l} \left\{ \begin{matrix} \Gamma_k & \Gamma_i & \Gamma_2 \\ \Gamma_1 & \Gamma & \Gamma_j \end{matrix} \right\} (-1)^{\Gamma_k + \Gamma_j + \Gamma_1 + \Gamma_2} \sqrt{[\Gamma_1][\Gamma_2]} (\mathbf{a}_k^+ \times \mathbf{a}_j)^{\Gamma}$$

where $\left\{ \begin{matrix} \Gamma_i & \Gamma_k & \Gamma_1 \\ \Gamma_2 & \Gamma & \Gamma_l \end{matrix} \right\}$ is 6 Γ symbol of the Td group. From this formula one readily obtains the vibrational commutators

$$[\mathbf{V}_{2,4}^{EF_2(F_1)}, (-1)\mathbf{V}_{2,4}^{EF_2(F_1)}]_-^E = -i \sqrt{\frac{2}{3}} \mathbf{V}_{2,2}^{EE(E)} - i \frac{2\sqrt{2}}{3} \mathbf{V}_{4,4}^{F_2F_2(E)},$$

$$[\mathbf{V}_{2,4}^{EF_2(F_1)}, (-1)\mathbf{V}_{2,4}^{EF_2(F_1)}]_-^{F_2} = \frac{i}{\sqrt{3}} \mathbf{V}_{4,4}^{F_2F_2(F_2)},$$

$$[\mathbf{V}_{2,4}^{EF_2(F_1)}, (-1)\mathbf{V}_{2,4}^{EF_2(F_1)}]_-^{A_1} = i \sqrt{\frac{2}{3}} \mathbf{V}_{2,2}^{EE(A_1)} - i \frac{2}{3} \mathbf{V}_{4,4}^{F_2F_2(A_1)},$$

$$[\mathbf{V}_{2,4}^{EF_2(F_1)}, (-1)\mathbf{V}_{4,4}^{F_2F_2(F_1)}]_-^{F_2} = -\frac{i}{2} \mathbf{V}_{2,4}^{EF_2(F_2)},$$

$$[(-1)\mathbf{V}_{2,4}^{EF_2(F_2)}, (-1)\mathbf{V}_{2,4}^{EF_2(F_1)}]_-^{A_2} = -i \sqrt{\frac{2}{3}} \mathbf{V}_{2,2}^{EE(A_2)},$$

$$[(-1)\mathbf{V}_{2,4}^{EF_2(F_2)}, (-1)\mathbf{V}_{2,4}^{EF_2(F_1)}]_-^{F_1} = i \mathbf{V}_{4,4}^{F_2F_2(F_1)},$$

$$[(-1)\mathbf{V}_{2,4}^{EF_2(F_2)}, (-1)\mathbf{V}_{4,4}^{F_2F_2(F_1)}]_-^{F_2} = -\frac{i}{2\sqrt{3}} (-1)\mathbf{V}_{2,4}^{EF_2(F_2)},$$

$$[(-1)\mathbf{V}_{2,4}^{EF_2(F_2)}, (-1)\mathbf{V}_{4,4}^{F_2F_2(F_1)}]_-^{F_1} = \frac{i}{2} (-1)\mathbf{V}_{2,4}^{EF_2(F_1)}.$$

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