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Theoretical Analysis of Spectroscopic Constants for Spherical Tops: ν_2, ν_4 Bands of AB_4 Molecules

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Extended analysis of the different sets of spectroscopic constants for ν_2, ν_4 bands of CH_4, CD_4, SiH_4 is performed taking into account the possibility of the unitary transformation of the corresponding effective Hamiltonians. Refined relations between different notations of tensor operators and spectroscopic constants are presented. The unitary equivalence between several different sets of constants is shown up to the λ^4 order.

I. INTRODUCTION

The rotational structure of ν_2 and ν_4 vibrational bands of tetrahedral molecules have been studied in detail experimentally. Such molecules like $^{12}CH_4$, $^{13}CH_4$ (*1-11*), CD_4 (*12-16*), SiH_4 (*17-21*), GeH_4 (*22-27*), CF_4 (*28-32*) are investigated with high accuracy. The treatment of the experimental data includes the construction of the effective Hamiltonian and fitting of the corresponding spectroscopic parameters. The number and the type of the chosen parameters depend widely not only on the accuracy and the number of the known spectral lines but on the investigators as well. There are several differences between the various models: (i) the difference in notation which results in numerical factors or sometimes in the transformation to linear combinations of parameters; (ii) the difference in terms included in the effective Hamiltonian. The more drastic the change in the models corresponds to the transformation from the isolated state model to the resonance one.

A variety of models used and of numerical values of the spectroscopic parameters for the same model make it difficult to use the spectroscopic constants to solve the inverse spectroscopic problem, to calculate the molecular properties, and even to extrapolate to more excited rovibrational levels.

This article is devoted to the comparative analysis of various sets of the spectroscopic constants for the same vibrational bands. SiH_4, CH_4, CD_4 molecules are considered as concrete examples. The most complete treatments of the experimental data for these molecules were made by two groups of scientists working in Dijon, France, and Reading, England (*5-8, 15, 16, 19, 20*). The comparison of the corresponding results requires: (i) transformation to unified notation; (ii) unitary transformation of the effective Hamiltonians to the same reduced form, taking into account the ambiguity of the effective Hamiltonians (*33-35*). Unfortunately, the connection between notations was not clear, so we specifically consider this problem in Section II. The notations of the operators must be suited for the unitary transformation of the tensor operators. We choose the notation introduced earlier for the tetrahedral molecules (*36*) which differs from Champion's notation (*38*) by known numerical factors.

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TABLE I

Relations between Spectroscopic Parameters Used in This Article and in Anterior Formalism: (a) Ground State Parameters; (b) ν_2 Isolated State Parameters; (c) ν_4 Isolated State Parameters; (d) ν_2, ν_4 Interaction Parameters

ⓐ λ^n	$u^{\Omega(K,A_1)}$	$t_0^{\Omega(K,A_1)}$ (38)	(47)
λ^0	$u^{2(0,A_1)}$	$-(\sqrt{3}/4)\ t_0^{2(0,A_1)}$	$-(\sqrt{3}/4)\ B_0$
λ^2	$u^{4(0,A_1)}$	$(3/16)\ t_0^{4(0,A_1)}$	$-(3/16)\ D_0$
λ^2	$u^{4(4,A_1)}$	$t_0^{4(4,A_1)}$	$-(\sqrt{15}/4\sqrt{2})\ D_t$
λ^4	$u^{6(0,A_1)}$	$-(3\sqrt{3}/64)\ t_0^{6(0,A_1)}$	$-(3\sqrt{3}/64)\ H_0$
λ^4	$u^{6(4,A_1)}$	$t_0^{6(4,A_1)}$	$(3\sqrt{5}/16\sqrt{2})\ H_{4t}$
λ^4	$u^{6(6,A_1)}$	$t_0^{6(6,A_1)}$	$-(\sqrt{231}/64\sqrt{2})\ H_{6t}$

ⓑ λ^n	$u_{2,2}^{\Omega(K,\Gamma)}$	$t_{2,2}^{\Omega(K,\Gamma)}$ (38)	(5, 19, 44)
λ^0	$u_{2,2}^{0}$	$\sqrt{2}\ t_{2,2}^{0(0,A_1)}$	$\sqrt{2}\ \nu_2$
λ^2	$u_{2,2}^{2(o,A_1)}$	$-(\sqrt{3}/2\sqrt{2})\ t_{2,2}^{2(0,A_1)}$	$-(\sqrt{3}/2\sqrt{2})\ (B_2 - B_0)$
λ^2	$u_{2,2}^{2(2,E)}$	$(1/\sqrt{2})\ t_{2,2}^{2(2,E)}$	$(\sqrt{3}/\sqrt{2})b_2 + (24\sqrt{3}/7\sqrt{2})C_6$
λ^3	$u_{2,2}^{3(3,A_2)}$	$-\ t_{2,2}^{3(3,A_2)}$	$-(1/2)\ d_2$
λ^4	$u_{2,2}^{4(0,A_1)}$	$(3/8\sqrt{2})\ t_{2,2}^{4(0,A_1)}$	$(3/8\sqrt{2})\ (D_0 - D_2)$
λ^4	$u_{2,2}^{4(4,A_1)}$	$t_{2,2}^{4(4,A_1)}$	$(\sqrt{15}/4)\ (D_{0t} - D_{2t})$
λ^4	$u_{2,2}^{4(2,E)}$	$(1/\sqrt{2})\ t_{2,2}^{4(2,E)}$	$-(3/4\sqrt{2})C_5 + (9/7\sqrt{2})C_6$
λ^4	$u_{2,2}^{4(4,E)}$	$(1/\sqrt{2})\ t_{2,2}^{4(4,E)}$	$-(3\sqrt{3}/\sqrt{14})\ C_6$
λ^5	$u_{2,2}^{5(3,A_2)}$	$-\ t_{2,2}^{5(3,A_2)}$	$(\sqrt{3}/8)\ d_2^{01}$

[1] This relation for d_{24} is supposed to be incorrect. See sections II and VI fof detail.

The equivalence of different sets of the spectroscopic parameters up to a unitary transformation was discussed for ν_4 band (*35*) and ν_2, ν_4 bands under resonance conditions (*34*, *37*), but the numerical comparison was realized only for low-order parameters (up to λ^2). In this paper the comparison is made for all spectroscopic parameters up to λ^4. The choice of the unitary transformation is discussed in Section III. The following sections are devoted to concrete molecules. We consider parameter sets which differ by a small unitary transformation and strongly different sets obtained for isolated and resonance model Hamiltonians.

TABLE I—*Continued*

ⓒ λ^n	$u_{4,4}^{\Omega(K,\Gamma)}$	$t_{4,4}^{\Omega(K,\Gamma)}$ (38)	(43)
λ^0	$u_{4,4}^{0}$	$\sqrt{3}\, t_{4,4}^{0}$	$\sqrt{3}\, \mathcal{D}_4$
λ^1	$u_{4,4}^{1(1,F_1)}$	$-(1/\sqrt{3})\, t_{4,4}^{1(1,F_1)}$	$-\sqrt{6}\, B\, \zeta_4$
λ^2	$u_{4,4}^{2(0,A_1)}$	$-(3/4)\, t_{4,4}^{2(0,A_1)}$	$-(3/4)\,(B_4 - B_0)$
λ^2	$u_{4,4}^{2(2,E)}$	$(1/\sqrt{2})\, t_{4,4}^{2(2,E)}$	$-(1/2\sqrt{2})\,\alpha_{220} - 3\sqrt{2}\,\alpha_{224}$
λ^2	$u_{4,4}^{2(2,F_2)}$	$(1/\sqrt{3})\, t_{4,4}^{2(2,F_2)}$	$-(\sqrt{3}/4)\,\alpha_{220} + 2\sqrt{3}\,\alpha_{224}$
λ^3	$u_{4,4}^{3(1,F_1)}$	$-(1/\sqrt{3})\, t_{4,4}^{3(1,F_1)}$	$-(3/4\sqrt{2})\, F_{110}$
λ^3	$u_{4,4}^{3(3,F_1)}$	$-(1/\sqrt{3})\, t_{4,4}^{3(3,F_1)}$	$-(\sqrt{15}/2)\, F_{134}$
λ^4	$u_{4,4}^{4(0,A_1)}$	$(3\sqrt{3}/16)\, t_{4,4}^{4(0,A_1)}$	$(3\sqrt{3}/16)\,(D_0 - D_4)$
λ^4	$u_{4,4}^{4(2,E)}$	$(1/\sqrt{2})\, t_{4,4}^{4(2,E)}$	$(\sqrt{3}/8\sqrt{2})G_{220} + (3\sqrt{3}/2\sqrt{2})G_{224}$
λ^4	$u_{4,4}^{4(2,F_2)}$	$(1/\sqrt{3})\, t_{4,4}^{4(2,F_2)}$	$(3/16)G_{220} - (3/2)G_{224}$
λ^4	$u_{4,4}^{4(0,A_1)}$	$t_{4,4}^{4(4,A_1)}$	$(3\sqrt{5}/4\sqrt{2})\,(D_{0t} - D_{044})$
λ^4	$u_{4,4}^{4(4,E)}$	$(1/\sqrt{2})\, t_{4,4}^{4(4,E)}$	$-(3\sqrt{7}/2\sqrt{2})G_{244} + (\sqrt{21}/4\sqrt{11})G_{246}$
λ^4	$u_{4,4}^{4(4,F_2)}$	$(1/\sqrt{3})\, t_{4,4}^{4(4,F_2)}$	$-(3\sqrt{21}/8)G_{244} - (\sqrt{7}/\sqrt{22})G_{246}$

ⓓ λ^n	$u_{2,4}^{\Omega(K,\Gamma)}$	$t_{2,4}^{\Omega(K,\Gamma)}$ (38)	(6, 19)
λ^1	$u_{2,4}^{1(1,F_1)}$	$-(1/\sqrt{3})\, t_{2,4}^{1(1,F_1)}$	$R_{24} - (1/10)\, F_{24b}$
λ^2	$u_{2,4}^{2(2,F_2)}$	$(1/\sqrt{3})\, t_{2,4}^{2(2,F_2)}$	$(\sqrt{3}/2\sqrt{2})\, d_{24}$ 1/
λ^3	$u_{2,4}^{3(1,F_1)}$	$-(1/\sqrt{3})\, t_{2,4}^{3(1,F_1)}$	$-(\sqrt{3}/4)F_{24a} - (3\sqrt{3}/80)F_{24b}$ $-(\sqrt{3}/4)\, R_{24}^{01}$
λ^3	$u_{2,4}^{3(3,F_1)}$	$-(1/\sqrt{3})\, t_{2,4}^{3(3,F_1)}$	$(1/4\sqrt{10})\, F_{24b}$
λ^3	$u_{2,4}^{3(3,F_2)}$	$-(1/\sqrt{3})\, t_{2,4}^{3(3,F_2)}$	$-(1/2\sqrt{2})\, F_{24c}$

II. SPECTROSCOPIC PARAMETER NOTATION

We follow the scheme of coupling the tensor operators introduced by Champion (*38*), but we use the tensor operators

$$U_{k,m}^{\Omega(K,\Gamma)} = [^{\epsilon}(a_k^{+} a_m)^{\Gamma} \times R^{\Omega(K,\Gamma)}]^{A_1} \tag{1}$$

without any additional numerical factors. To distinguish these two kinds of notations we use U for the operators and u for the parameters instead of T and t. The correspondence between the t and u parameters is defined by the normalization constants for V and by the additional relations for zero-rank operators (*38*). All required formulae are given in Tables Ia–d. The operators used by the Reading group sometimes are not irreducible with respect to group O(3). So we use the explicit expressions for the vibration–rotation operators given in Refs. (*5*, *6*, *43*, *44*) and transform them to the form (1). It must be noted that the orientation of the coordinate system made in Reading differs from that accepted in Dijon and in this article. Consequently, the following correspondence should be used for the components of the E-type irreducible operators:

$$q_{2a} = (q_2)^E_1, \qquad p_{2a} = (p_2)^E_1,$$

$$q_{2b} = -(q_2)^E_2, \qquad p_{2b} = -(p_2)^E_2, \tag{2}$$

where (a, b) is the Reading notation and $(1, 2)$ is the notation used in Dijon and the present article.

Some relations between parameters were correctly given in Ref. (*38*) but some are erroneous. We give the complete list of the relations in Table I. The most important points are illustrated below.

Parameter C_6. This parameter is defined in Ref. (*44*) as a coefficient in the expression $(C_6/2)(TN + NT)$, where the operators T and N are given by

$$T = -(1/2)U^{3(3,A_2)}_{2,2}, \qquad N = (3/2)^{1/2}U^{2(2,E)}_{2,2}, \tag{3}$$

in accordance with Ref. (*38*). To calculate the rovibrational anticommutator

$$(C_6/2)(NT + TN) = -(C_6\sqrt{3}/4\sqrt{2})[U^{2(2,E)}_{2,2}, U^{3(3,A_2)}_{2,2}]_+ \tag{4}$$

we use the general expression for an anticommutator

$$[(V^\Gamma \times R^\Gamma)^{A_1}, (V^{\Gamma'} \times R^{\Gamma'})^{A_1}]_+$$
$$= \sum_{X\in\Gamma\times\Gamma'} (\sqrt{[X]}/2\sqrt{[\Gamma][\Gamma']})\{[V^\Gamma, V^{\Gamma'}]^X_+[R^\Gamma, R^{\Gamma'}]^X_+ + [V^\Gamma, V^{\Gamma'}]^X_-[R^\Gamma, R^{\Gamma'}]^X_-\}^{A_1} \tag{5}$$

which is similar to the commutator expression (*36*). Only the vibrational commutator of type E is nonzero in Ref. (*4*):

$$[V^\Gamma, V^{\Gamma'}]^E_- = i\sqrt{2}(a^+_2 a_2)^E. \tag{6}$$

The corresponding rotational commutator is

$$[R^{2(2,E)}, R^{3(3,A_2)}]^E_- = i\,\frac{96\sqrt{2}}{7}\,R^{2(2,E)} + i\,\frac{12\sqrt{6}}{7}\,R^{4(2,E)} - i\,\frac{12\sqrt{2}}{\sqrt{7}}\,R^{4(4,E)}.$$

Finally, the anticommutator (4) has the form

$$\frac{C_6}{2}\,[T, N]_+ = C_6\left\{\frac{9}{7\sqrt{2}}\,U^{4(2,E)}_{2,2} + \frac{24\sqrt{3}}{7\sqrt{2}}\,U^{2(2,E)}_{2,2} - \frac{3\sqrt{3}}{\sqrt{14}}\,U^{4(4,E)}_{2,2}\right\}. \tag{7}$$

Expression (7) enables one to find the contributions of C_6 to $u^{4(2,E)}_{2,2}$, $u^{2(2,E)}_{2,2}$, $u^{4(4,E)}_{2,2}$ listed in Table I. Expression (3) for the N operator also gives the relation for the C_5 parameter:

$$C_5 J^2 N = C_5(-\sqrt{3}/4) R^{2(0,A_1)} (\sqrt{3}/\sqrt{2}) U^{2(2,E)}_{2,2} = -(3/4\sqrt{2}) C_5 U^{4(2,E)}_{2,2}. \tag{8}$$

A short comment about α_{220}, α_{224}, G_{220}, G_{224} parameters: We follow the formulae for T_{220} and T_{224} operators given in Ref. (*43*) which differ from Hecht's expression for T_{224} (*47*) by 1/2 coefficient. This (1/2) coefficient causes, in particular, the error in the comparison of CD_4 parameters realized by Loete *et al.* (*16*).

Interaction parameters of ν_2, ν_4 bands. We treat the operators of F_1 and F_2 type used by the Reading group in the form (*6*)

$$\begin{aligned} l^{\alpha}_{24} &= (1/\sqrt{3}) \Omega^{+}_{24}{}^{(-)}(a^{+}_{2} a_4)^{F_1}_{\alpha} - (1/\sqrt{3}) \Omega^{-}_{24}{}^{(-)}(a^{+}_{2} a^{+}_{4})^{F_1}_{\alpha}, \\ m^{\alpha}_{24} &= -\Omega^{+}_{24}{}^{(-)}(a^{+}_{2} a_4)^{F_2}_{\alpha} - \Omega^{-}_{24}{}^{(-)}(a^{+}_{2} a^{+}_{4})^{F_2}_{\alpha}, \end{aligned} \tag{9}$$

where

$$\Omega^{\pm}_{24} = (\omega_4/\omega_2)^{1/2} \pm (\omega_2/\omega_4)^{1/2}.$$

For the fundamental transitions only the vibrational operators of the type $(a^{+}a)$ are important. The rotational parts of the operators having the parameters R_{24}, $R^{01}_{24} = F_{24a}$ and F_{24c} are, respectively, $R^{1(1,F_1)}$, $R^{3(1,F_1)}$, $R^{3(3,F_2)}$ up to a coefficient. For example,

$$\begin{aligned} & f_{24c}\{\sum_{\alpha} m^{\alpha}_{24}(J_{\alpha}(J^2_{\beta} - J^2_{\gamma}) + (J^2_{\beta} - J^2_{\gamma})J_{\alpha})\} \\ &\qquad = -(\Omega^{+}_{24}/2\sqrt{6}) f_{24c} \sum_{\alpha} {}^{(-)}(a^{+}_{2} a_4)^{F_2}_{\alpha} R^{3(3,F_2)}_{\alpha} \\ &\qquad = -(1/2\sqrt{2}) f_{24c} \Omega^{+}_{24} U^{3(3,F_2)}_{2,4} = -(1/2\sqrt{2}) F_{24c} U^{3(3,F_2)}_{2,4}. \end{aligned} \tag{10}$$

The rotational part of the operator corresponding to the F_{24b} parameter is constructed from J^3_{α}. These operators may be written as

$$J^3_{\alpha} = (1/4\sqrt{10}) R^{3(3,F_1)}_{\alpha} - (3\sqrt{6}/80\sqrt{2}) R^{3(1,F_1)}_{\alpha} - (1/10) R^{1(1,F_1)}_{\alpha}.$$

This relation leads to

$$f_{24b}\{\sum_{\alpha} l^{\alpha}_{24} J^3_{\alpha}\} = F_{24b}\left(\frac{1}{4\sqrt{10}} U^{3(3,F_1)}_{2,4} - \frac{3\sqrt{3}}{80} U^{3(1,F_1)}_{2,4} - \frac{1}{10} U^{1(1,F_1)}_{2,4}\right).$$

The parameter d_{24} requires special attention. Table I gives the relation for d_{24} obtained from the expression for the corresponding operator given in Ref. (*6*). Nevertheless, some clarifications are necessary because the numerical value of this parameter does not agree with some other sets of parameters (see Sect. VI). We may propose that the definition of the corresponding operator must include an additional factor.

III. TRANSFORMATION OF THE EFFECTIVE HAMILTONIANS

The effective Hamiltonians are defined up to a unitary transformation. The eigenvalues of the operator H and of the transformed operator $\tilde{H} = UHU^{-1}$ are the same and the eigenfunctions are connected by the unitary transformation $|\tilde{n}\rangle = U|n\rangle$. To compare different effective Hamiltonians we shall use the unitary transformations which do not alter the symmetry properties of the Hamiltonian and do not modify the order classification of the Hamiltonian terms. The generators S of such unitary

TABLE II

Commutators [*iS*, *H*] of the Hamiltonian Terms with *S* Generators [Including Fragments (a)–(e) and Guide (f)]

ⓐ λ^n	H \ S	$S_{2,4}^{1(1,F_1)}$
λ^0	$U_{2,2}^{0}$	$-(1/\sqrt{2})\ U_{2,4}^{1(1,F_1)}$
	$U_{4,4}^{0}$	$(1/\sqrt{3})\ U_{2,4}^{1(1,F_1)}$
λ^1	$U_{4,4}^{1(1,F_1)}$	$(1/2)\ U_{2,4}^{2(2,F_2)} - (1/\sqrt{6})\ U_{2,4}^{1(1,F_1)}$
	$U_{2,4}^{1(1,F_1)}$	$(\sqrt{2}/\sqrt{3})\ U_{4,4}^{1(1,F_1)} + (\sqrt{2}/\sqrt{3})\ U_{2,2}^{2(2,E)} + (2\sqrt{2}/3)\ U_{4,4}^{2(2,E)}$ $-(1/\sqrt{3})\ U_{4,4}^{2(2,F_2)} + (2/3)\ U_{4,4}^{2(0,A_1)} - (\sqrt{2}/\sqrt{3})\ U_{2,2}^{2(0,A_1)}$
λ^2	$U_{2,2}^{2(2,E)}$	$U_{2,4}^{2(2,F_2)} + (\sqrt{2}/5)\ U_{2,4}^{3(1,F_1)}$ $-(\sqrt{3}/2\sqrt{5})\ U_{2,4}^{3(3,F_1)} - (1/2\sqrt{3})\ U_{2,4}^{3(3,F_2)}$
	$U_{2,2}^{2(0,A_1)}$	$-(1/\sqrt{2})\ U_{2,4}^{3(1,F_1)}$
	$U_{4,4}^{2(0,A_1)}$	$(1/\sqrt{3})\ U_{2,4}^{3(1,F_1)}$
	$U_{4,4}^{2(2,E)}$	$(2\sqrt{2}/5\sqrt{3})\ U_{2,4}^{3(1,F_1)} - (1/\sqrt{5})\ U_{2,4}^{3(3,F_1)}$
	$U_{4,4}^{2(2,F_2)}$	$-(1/\sqrt{2})\ U_{2,4}^{2(2,F_2)} - (1/5)\ U_{2,4}^{3(1,F_1)}$ $-(1/\sqrt{30})\ U_{2,4}^{3(3,F_1)} + (1/\sqrt{6})\ U_{2,4}^{3(3,F_2)}$
	$U_{2,4}^{2(2,F_2)}$	$(6/5)\ U_{4,4}^{1(1,F_1)} - 2\ U_{2,2}^{2(2,E)} + \sqrt{2}\ U_{4,4}^{2(2,F_2)}$ $+(2\sqrt{3}/5)U_{4,4}^{3(1,F_1)} + (\sqrt{2}/\sqrt{5})U_{4,4}^{3(3,F_1)} - (\sqrt{2}/\sqrt{3})U_{2,2}^{3(3,A_2)}$

ⓑ λ^n	H \ S	$S_{2,4}^{1(1,F_1)}$
λ^3	$U_{4,4}^{3(1,F_1)}$	$-(1/\sqrt{6})\ U_{2,4}^{3(1,F_1)}$
	$U_{4,4}^{3(3,F_1)}$	$(\sqrt{3}/2\sqrt{2})\ U_{2,4}^{3(3,F_1)} + (\sqrt{15}/2\sqrt{2})\ U_{2,4}^{3(3,F_2)}$
	$U_{2,2}^{3(3,A_2)}$	$-\sqrt{2}\ U_{2,4}^{3(3,F_2)}$
	$U_{2,4}^{3(1,F_1)}$	$(\sqrt{2}/\sqrt{3})U_{4,4}^{3(1,F_1)} + (\sqrt{2}/\sqrt{3})U_{2,2}^{4(2,E)} + (2\sqrt{2}/3)U_{4,4}^{4(2,E)}$ $-(1/\sqrt{3})U_{4,4}^{4(2,F_2)} + (2/3)U_{4,4}^{4(0,A_1)} - (\sqrt{2}/\sqrt{3})U_{2,2}^{4(0,A_1)}$
	$U_{2,4}^{3(3,F_1)}$	$-(9/7\sqrt{5})U_{2,2}^{4(2,E)} - (6\sqrt{3}/7\sqrt{5})U_{4,4}^{4(2,E)} - (3\sqrt{2}/7\sqrt{5})U_{4,4}^{4(2,F_2)}$ $-(\sqrt{3}/\sqrt{2})U_{4,4}^{3(3,F_1)} - (\sqrt{5}/\sqrt{21})U_{2,2}^{4(4,E)} - (2\sqrt{5}/3\sqrt{7})U_{4,4}^{4(4,E)}$ $+(\sqrt{5}/2\sqrt{42})U_{4,4}^{4(4,F_2)} + (\sqrt{2}/\sqrt{3})U_{2,2}^{4(4,A_1)} - (2/3)U_{4,4}^{4(4,A_1)}$
	$U_{2,4}^{3(3,F_2)}$	$2\sqrt{2}U_{2,2}^{3(3,A_2)} - (\sqrt{15}/\sqrt{2})U_{4,4}^{3(3,F_1)} - (3/7)U_{2,2}^{4(2,E)}$ $+(3\sqrt{2}/7)U_{4,4}^{4(2,F_2)} + (\sqrt{3}/\sqrt{7})U_{2,2}^{4(4,E)} + (3\sqrt{3}/2\sqrt{14})U_{4,4}^{4(4,F_2)}$

TABLE II—*Continued*

ⓒ λ^n	H \ S	$S_{2,4}^{2(2,F_2)}$
λ^0	$U_{2,2}^{0}$	$(1/\sqrt{2})\ U_{2,4}^{2(2,F_2)}$
	$U_{4,4}^{0}$	$-(1/\sqrt{3})\ U_{2,4}^{2(2,F_2)}$
λ^1	$U_{4,4}^{1(1,F_1)}$	$-(1/\sqrt{6})\ U_{2,4}^{2(2,F_2)} + (\sqrt{3}/5)\ U_{2,4}^{3(1,F_1)}$ $+ (1/\sqrt{10})\ U_{2,4}^{3(3,F_1)} - (1/3\sqrt{2})\ U_{2,4}^{3(3,F_2)}$
	$U_{2,4}^{1(1,F_1)}$	$2\ U_{2,2}^{2(2,E)} - \sqrt{2}\ U_{4,4}^{2(2,F_2)} - (2\sqrt{3}/5)\ U_{4,4}^{3(1,F_1)}$ $-(\sqrt{2}/\sqrt{5})\ U_{4,4}^{3(3,F_1)} + (\sqrt{2}/\sqrt{3})\ U_{2,2}^{3(3,A_2)}$
λ^2	$U_{2,2}^{2(2,E)}$	$(2\sqrt{3}/5)U_{2,4}^{3(1,F_1)} + (\sqrt{2}/\sqrt{5})U_{2,4}^{3(3,F_1)} - \sqrt{2}\ U_{2,4}^{3(3,F_2)}$
	$U_{2,2}^{2(0,A_1)}$ $U_{4,4}^{2(0,A_1)}$	nondiagonal operators of order λ^4
	$U_{4,4}^{2(2,E)}$	$-(2\sqrt{2}/\sqrt{3})\ U_{2,4}^{3(3,F_2)}$
	$U_{4,4}^{2(2,F_2)}$	$-(\sqrt{6}/5)\ U_{2,4}^{3(1,F_1)} + (4/\sqrt{5})\ U_{2,4}^{3(3,F_1)}$
	$U_{2,4}^{2(2,F_2)}$	$(4/5\sqrt{3})U_{4,4}^{4(0,A_1)} - (2\sqrt{2}/5)U_{2,2}^{4(0,A_1)} - (2\sqrt{2}/3\sqrt{5})U_{4,4}^{4(4,A_1)}$ $+ (2/\sqrt{15})U_{2,2}^{4(4,A_1)} - (4\sqrt{2}/7\sqrt{3})U_{4,4}^{4(2,E)} + (2\sqrt{2}/7)U_{2,2}^{4(2,E)}$ $-(2/7)U_{4,4}^{4(2,F_2)} + (2/\sqrt{21})U_{4,4}^{4(4,F_2)} + (4\sqrt{2}/3\sqrt{7})U_{4,4}^{4(4,E)}$ $-(2\sqrt{2}/\sqrt{21})U_{2,2}^{4(4,E)} - (2\sqrt{2}/5)U_{4,4}^{3(1,F_1)} + (8/\sqrt{15})U_{4,4}^{3(3,F_1)}$

ⓓ λ^n	H \ S	$S_{2,4}^{3(1,F_1)}$	$S_{2,4}^{3(3,F_1)}$
λ^0	$U_{2,2}^{0}$	$-(1/\sqrt{2})\ U_{2,4}^{3(1,F_1)}$	$-(1/\sqrt{2})\ U_{2,4}^{3(3,F_1)}$
	$U_{4,4}^{0}$	$(1/\sqrt{3})\ U_{2,4}^{3(1,F_1)}$	$(1/\sqrt{3})\ U_{2,4}^{3(3,F_1)}$
λ^1	$U_{4,4}^{1(1,F_1)}$	$-(1/\sqrt{6})\ U_{2,4}^{3(1,F_1)}$	$-(\sqrt{15}/2\sqrt{2})U_{2,4}^{3(3,F_2)} + (\sqrt{3}/2\sqrt{2})U_{2,4}^{3(3,F_1)}$
	$U_{2,4}^{1(1,F_1)}$	$(\sqrt{2}/\sqrt{3})U_{4,4}^{3(1,F_1)} + (2/3)U_{4,4}^{4(0,A_1)}$ $-(\sqrt{2}/\sqrt{3})U_{2,2}^{4(0,A_1)} + (\sqrt{2}/\sqrt{3})U_{2,2}^{4(2,E)}$ $+ (2\sqrt{2}/3)U_{4,4}^{4(2,E)} - (1/\sqrt{3})U_{4,4}^{4(2,F_2)}$	$-(\sqrt{3}/\sqrt{2})U_{4,4}^{3(3,F_1)} - (9/7\sqrt{5})U_{2,2}^{4(2,E)}$ $-(6\sqrt{3}/7\sqrt{5})U_{4,4}^{4(2,E)} - (3\sqrt{2}/7\sqrt{5})U_{4,4}^{4(2,F_2)}$ $-(\sqrt{5}/\sqrt{21})U_{2,2}^{4(4,E)} - (2\sqrt{5}/3\sqrt{7})U_{4,4}^{4(4,E)}$ $+ (\sqrt{5}/2\sqrt{42})U_{4,4}^{4(4,F_2)} + (\sqrt{2}/\sqrt{3})U_{2,2}^{4(4,A_1)}$ $-(2/3)\ U_{4,4}^{4(4,A_1)}$

operators $U = \exp(iS)$ are given below for the case of resonance ν_2, ν_4 vibrational states of AB_4 molecules (*34, 36*)

$$S_{2,4}^{1(1,F_1)} = [^{(+)}(a_2^+ \times a_4)^{F_1} \times R^{1(1,F_1)}]^{A_1}$$

$$S_{2,4}^{2(2,F_2)} = [^{(-)}(a_2^+ \times a_4)^{F_2} \times R^{2(2,F_2)}]^{A_1}$$

TABLE II—*Continued*

ⓔ λ^n	H \ S	$S_{2,4}^{3(3,F_2)}$	$S_{4,4}^{3(3,F_2)}$
λ^0	$U_{2,2}^{0}$	$-(1/\sqrt{2})U_{2,4}^{3(3,F_2)}$	0
	$U_{4,4}^{0}$	$(1/\sqrt{3})U_{2,4}^{3(3,F_2)}$	0
λ^1	$U_{4,4}^{1(1,F_1)}$	$-(1/2\sqrt{6})U_{2,4}^{3(3,F_2)} - (\sqrt{15}/2\sqrt{2})U_{2,4}^{3(3,F_1)}$	$-(\sqrt{5}/\sqrt{2})U_{4,4}^{3(3,F_1)} + (3/7)U_{4,4}^{4(2,E)}$ $-(\sqrt{6}/7)U_{4,4}^{4(2,F_2)} - (\sqrt{3}/\sqrt{7})U_{4,4}^{4(4,E)}$ $-(3/2\sqrt{14})U_{4,4}^{4(4,F_2)}$
	$U_{2,4}^{1(1,F_1)}$	$-(\sqrt{15}/\sqrt{2})U_{4,4}^{3(3,F_1)} + 2\sqrt{2}\,U_{2,2}^{3(3,A_2)}$ $+(3\sqrt{2}/7)U_{4,4}^{4(2,F_2)} - (2/7)U_{2,2}^{4(2,E)}$ $+(3\sqrt{3}/2\sqrt{14})U_{4,4}^{4(4,F_2)} + (\sqrt{3}/\sqrt{7})U_{2,2}^{4(4,E)}$	$-(\sqrt{5}/2\sqrt{2})U_{2,4}^{3(3,F_1)} - (1/2\sqrt{2})U_{2,4}^{3(3,F_2)}$

ⓕ λ^n	$S_{2,4}^{1(1,F_1)}$	$S_{2,4}^{2(2,F_2)}$	$S_{2,4}^{3(1,F_1)}$	$S_{2,4}^{3(3,F_1)}$	$S_{2,4}^{3(3,F_2)}$	$S_{4,4}^{3(3,F_2)}$
λ^0	a	c	d	d	e	e
λ^1	a	c	d	d	e	e
λ^2	a	c				
λ^3	b					

$$S_{4,4}^{3(3,F_2)} = [^{(+)}(a_4^+ \times a_4)^{F_2} \times R^{3(3,F_2)}]^{A_1}$$

$$S_{2,4}^{3(3,F_2)} = [^{(+)}(a_2^+ \times a_4)^{F_2} \times R^{3(3,F_2)}]^{A_1}$$

$$S_{2,4}^{3(3,F_1)} = [^{(+)}(a_2^+ \times a_4)^{F_1} \times R^{3(3,F_1)}]^{A_1}$$

$$S_{2,4}^{3(1,F_1)} = [^{(+)}(a_2^+ \times a_4)^{F_1} \times R^{3(1,F_1)}]^{A_1}.$$

We list here all S generators which lead to the main contributions to the diagonal Hamiltonian terms of order λ, λ^2, λ^3, λ^4 and to nondiagonal terms of order λ, λ^2, λ^3. This set of generators is sufficient for the analysis of the modern treatment of the experimental data. The effective operators used today include either a complete set of the operators (diagonal and nondiagonal) up to λ^3 (*8, 20, 16*) or some nondiagonal operators and the diagonal ones up to λ^4 (*5, 6, 15, 19*). The higher order operators (λ^6 in Ref. (*19*), etc.) may sometimes be added but the corresponding coefficients are poorly determined and we shall not consider them here.

The general expression for the S generator used in the present study is

$$U = \exp i(s_{2,4}^{1(1,F_1)}S_{2,4}^{1(1,F_1)} + s_{2,4}^{2(2,F_2)}S_{2,4}^{2(2,F_2)} + s_{4,4}^{3(3,F_2)}S_{4,4}^{3(3,F_2)}$$
$$+ s_{2,4}^{3(3,F_2)}S_{2,4}^{3(3,F_2)} + s_{2,4}^{3(3,F_1)}S_{2,4}^{3(3,F_1)} + s_{2,4}^{3(1,F_1)}S_{2,4}^{3(1,F_1)}).$$

The U operator includes six free parameters which are restricted by the requirement of the fixed order classification of the Hamiltonian terms. The transformed Hamiltonian may be written in the form of the commutator expansion

$$\exp(iS)H\exp(-iS) = H + [iS, H] + (1/2)[iS, [iS, H]] + \cdots. \tag{11}$$

All terms must be taken into account which contribute to the parameters of the transformed Hamiltonian of the same order as the characteristic difference between these parameters. If s parameters are considerably smaller than their limiting values, the first commutator in Eq. (11) is sufficient. The multiple commutators become essential for a rather large value of the s parameter.

Some simplified transformations of the effective operators were done earlier for ν_4 (*35*) and resonant ν_2, ν_4 (*34, 37*) bands. Only the main contributions and the first commutators were taken into account in these works. The unitary equivalence of the spectroscopic parameter sets for ν_2, ν_4 bands was shown only up to the terms of the first and second order of magnitude (*34, 37*). In this paper we take into account the nonleading contributions as well and make the calculations for the terms up to λ^4.

The main technical difficulty is the calculation of the rovibrational commutators of the tensor operators. The method of calculation was outlined earlier (*35, 39, 40*) and discussed in Ref. (*36*) in detail. We list in Tables IIa–f the rovibrational com-

TABLE III

Comparison of the Spectroscopic Parameters for ν_2, ν_4 Bands of $^{28}SiH_4$ Obtained in Refs. (*19*) and (*20*)

λ^n	$\Omega(K,\Gamma)$ $U_{k,m}$ k,m	$\Omega(K,\Gamma)$	Parameters from (19)	Transformed values (a)	weight	(b)	weight	Parameters from (20)
λ^0	2,2	0	1373.1462	1373.1462	0	1373.1462	0	1373.1274
	4,4	0	1582.1816	1582.1816		1582.1816		1582.1851
λ^1	4,4	$1(1,F_1)$	-3.4841	-3.4998	1	-3.5009	0	-3.49479
	2,4	$1(1,F_1)$	2.876	3.24555		3.2705	1	3.24167
λ^2	2,2	$2(2,E)$	$-0.3079\ 10^{-2}$	$-2.0855\ 10^{-2}$	10^3	$-2.1991\ 10^{-2}$	0	$-2.0777\ 10^{-2}$
	2,2	$2(0,A_1)$	$-0.155\ 10^{-2}$	$1.488\ 10^{-2}$		$1.599\ 10^{-2}$	0	$1.4315\ 10^{-2}$
	4,4	$2(0,A_1)$	$0.1398\ 10^{-2}$	$-1.2024\ 10^{-2}$		$-1.2929\ 10^{-2}$	0	$-1.1773\ 10^{-2}$
	4,4	$2(2,E)$	$7.00\ 10^{-4}$	$-1.834\ 10^{-2}$		$-1.959\ 10^{-2}$	0	$-1.8551\ 10^{-2}$
	4,4	$2(2,F_2)$	$-1.005\ 10^{-2}$	$0.248\ 10^{-2}$		$0.328\ 10^{-2}$	0	$0.2891\ 10^{-2}$
	2,4	$2(2,F_2)$	0	$-0.1124\ 10^{-2}$		$-0.0681\ 10^{-2}$	$5\cdot 10^2$	$-0.0643\ 10^{-2}$
λ^n	k,m	$\Omega(K,\Gamma)$	Parameters from (19)	(a)	weight	(b)	weight	Parameters from (20)
λ^3	2,2	$3(3,A_2)$	$6.08\ 10^{-4}$	$0.542\ 10^{-4}$	10^4	$0.367\ 10^{-4}$	0	$0.424\ 10^{-4}$
	4,4	$3(1,F_1)$	$-5.9609\ 10^{-4}$	$-1.3420\ 10^{-4}$		$-1.237\ 10^{-4}$	0	$-0.967\ 10^{-4}$
	4,4	$3(3,F_1)$	$-4.847\ 10^{-4}$	$-0.419\ 10^{-4}$		$-0.277\ 10^{-4}$	0	$0.232\ 10^{-4}$
	2,4	$3(1,F_1)$	$-1.94\ 10^{-4}$	$0.948\ 10^{-4}$		$1.189\ 10^{-4}$	$5\ 10^3$	$0.971\ 10^{-4}$
	2,4	$3(3,F_1)$	0	$-0.942\ 10^{-4}$		$-0.890\ 10^{-4}$	$5\ 10^3$	$-1.001\ 10^{-4}$
	2,4	$3(3,F_2)$	0	$0.075\ 10^{-4}$		$0.364\ 10^{-4}$	$5\ 10^3$	$-0.224\ 10^{-4}$
λ^4	2,2	$4(0,A_1)$	$4.852\ 10^{-6}$	$0.855\ 10^{-6}$	10^5	$1.341\ 10^{-6}$	$2\ 10^4$	0
	2,2	$4(4,A_1)$	$-1.0095\ 10^{-5}$	$0.899\ 10^{-6}$		$0.672\ 10^{-6}$	$2\ 10^4$	0
	2,2	$4(2,E)$	$0.78\ 10^{-6}$	$-0.46\ 10^{-6}$		$-0.007\ 10^{-6}$	$2\ 10^4$	0
	2,2	$4(4,E)$	$1.395\ 10^{-5}$	$1.51\ 10^{-6}$		$0.40\ 10^{-6}$	$2\ 10^4$	0
	4,4	$4(0,A_1)$	$-2.890\ 10^{-6}$	$-0.723\ 10^{-6}$		$-1.15\ 10^{-6}$	$2\ 10^4$	0
	4,4	$4(4,A_1)$	$9.12\ 10^{-6}$	$-0.85\ 10^{-6}$		$-0.696\ 10^{-6}$	$2\ 10^4$	0
	4,4	$4(2,E)$	$1.144\ 10^{-5}$	$1.39\ 10^{-6}$		$1.36\ 10^{-6}$	$2\ 10^4$	0
	4,4	$4(4,E)$	$2.42\ 10^{-6}$	$1.21\ 10^{-6}$		$0.78\ 10^{-6}$	$2\ 10^4$	0
	4,4	$4(2,F_2)$	$7.31\ 10^{-6}$	$-0.24\ 10^{-6}$		$-1.27\ 10^{-6}$	$2\ 10^4$	0
	4,4	$4(4,F_2)$	$3.04\ 10^{-6}$	$3.04\ 10^{-6}$		$1.31\ 10^{-6}$	$2\ 10^4$	0

mutators sufficient to make the transformation of any effective operator for resonant ν_2, ν_4 bands with the accuracy of λ^4.

The general scheme of the comparison of two sets of the spectroscopic parameters includes the following stages. (i) Recalculation of the parameters of each set in the notation used in this article (see Table I). (ii) The construction of the parameter-dependent variety of the effective Hamiltonians by the use of Table II. This stage results in a six-parameter variety of the effective Hamiltonians. (iii) The application of the least-squares procedure. This stage gives the numerical values of the s parameters minimizing the square difference between the parameters of the considered sets. We use the weight factors proportional to the reciprocal values of the corresponding parameters. We can tell if the parameter sets agree or do not agree only after the comparison of the unitary transformed parameters. The following sections are devoted to the realization of such a procedure for concrete molecules. Here, for example, we discuss shortly stage (ii) of the problem for ν_2, ν_4 bands treatment of $^{12}CH_4$.

Table II enables one to write all nonzero contributions of $i[S, H]_-$ and multiple

TABLE IV

Characteristics[a] of the Unitary Transformations Relating the Treatments of ν_2, ν_4 Bands for $^{28}SiH_4$ Made by Pierre *et al.* (*20*) and by Gray *et al.* (*19*)

N	k,m	Ω(K,Γ)	$s_{k,m}^{\Omega(K,\Gamma)}$ parameters	
			(a)	(b)
1	2,4	$1(1,F_1)$	$-6.5828\ 10^{-3}$	$-7.0266\ 10^{-3}$
2	2,4	$2(2,F_2)$	$-2.1505\ 10^{-4}$	$-2.2068\ 10^{-4}$
3	4,4	$3(3,F_2)$	$2.7814\ 10^{-6}$	$2.5241\ 10^{-6}$
4	2,4	$3(3,F_2)$	$-2.9293\ 10^{-6}$	$-3.5213\ 10^{-6}$
5	2,4	$3(3,F_1)$	$4.3293\ 10^{-6}$	$4.2469\ 10^{-6}$
6	2,4	$3(1,F_1)$	$0.9042\ 10^{-6}$	$0.6911\ 10^{-6}$

Correlation matrix (a)

2	0.19753				
3	0.00260	0.00069			
4	0.00479	0.01676	-0.30808		
5	-0.00494	-0.06280	0.15969	0.12569	
6	0.01051	-0.05140	0.30712	0.22612	0.39410

Mean square deviations from (20)

λ^n	(19)	(a)	(b)	weight	(20)
λ^1	$2.59\ 10^{-1}$	$4.48\ 10^{-3}$	$2.08\ 10^{-2}$	1	0
λ^2	$1.46\ 10^{-2}$	$3.73\ 10^{-4}$	$1.07\ 10^{-3}$	10^3	0
λ^3	$3.92\ 10^{-4}$	$3.35\ 10^{-5}$	$3.51\ 10^{-5}$	10^4	0
λ^4	$7.82\ 10^{-6}$	$1.34\ 10^{-6}$	$1.00\cdot\ 10^{-7}$	10^5	0
$\lambda^1 - \lambda^4$	7.58	$2.65\ 10^{-1}$	$5.63\ 10^{-1}$		0

[a] (i) Parameters of the S generator; (ii) correlation matrix for s parameters; and (iii) mean square deviations of the transformed parameters from Ref. (*20*).

commutators to each operator $U^{\Omega(K,\Gamma)}_{k,m}$ and to corresponding parameter $u^{\Omega(K,\Gamma)}_{k,m}$. Let us consider the operator $U^{1(1,F_1)}_{2,4}$. It can be seen from Table II that the contribution to it is due to the commutators of $s^{1(1,F_1)}_{2,4}S^{1(1,F_1)}_{2,4}$ with several terms of the Hamiltonian. The most important terms are of order λ^0. They lead to the following contributions

$$\begin{aligned}&\tilde{u}^{1(1,F_1)}_{2,4}U^{1(1,F_1)}_{2,4}\\ &\quad = u^{1(1,F_1)}_{2,4}U^{1(1,F_1)}_{2,4} + i[s^{1(1,F_1)}_{2,4}S^{1(1,F_1)}_{2,4},\ u^0_{2,2}U^0_{2,2} + u^0_{4,4}U^0_{4,4} + u^{1(1,F_1)}_{4,4}U^{1(1,F_1)}_{4,4}]_- .\end{aligned}$$

The commutator calculation (Table II) gives

$$(\tilde{u}^{1(1,F_1)}_{2,4} - u^{1(1,F_1)}_{2,4})U^{1(1,F_1)}_{2,4} = s^{1(1,F_1)}_{2,4}\left(-\frac{1}{\sqrt{2}}u^0_{2,2} + \frac{1}{\sqrt{3}}u^0_{4,4} - \frac{1}{\sqrt{6}}u^{1(1,F_1)}_{4,4}\right)U^{1(1,F_1)}_{2,4}. \qquad (12)$$

Only the leading contributions are listed because for $\nu_2 - \nu_4 \approx 222\ \text{cm}^{-1}$ ($^{12}CH_4$) other terms are smaller than 1%. The numerical value of $s^{2(2,F_2)}_{2,4}$ is 10–10^2 times smaller and that of $s^{3(K,\Gamma)}_{k,m}$ is 10^3–10^4 times smaller (see Sects. IV–VII), so the contributions from these generators may be neglected. Relations similar to (12) may be written for other

TABLE V

Example of the Minimization of the Mean Square Deviation between the Transformed Parameters from Ref. (*19*) and Parameters from Ref. (*20*) for $^{28}SiH_4$

λ^n	$U^{\Omega(K,\Gamma)}_{k,m}$ k,m	$\Omega(K,\Gamma)$	Difference between (19) and (20)	Difference between(19) and transformed values	Weight
λ^0	2,2	0	$-1.88\ 10^{-2}$	$-1.83\ 10^{-2}$	0
	4,4	0	$0.35\ 10^{-2}$	$0.35\ 10^{-2}$	0
λ^1	4,4	$1(1,F_1)$	$-1.064480\ 10^{-2}$	$-1.564772\ 10^{-2}$	$2.8867\ 10^{-1}$
	2,4	$1(1,F_1)$	$3.656712\ 10^{-2}$	$3.695538\ 10^{-2}$	$2.8867\ 10^{-1}$
λ^2	2,2	$2(2,E)$	$-1.769806\ 10^{-2}$	$-1.777595\ 10^{-2}$	$2.8867\ 10^{2}$
	2,2	$2(0,A_1)$	$1.586779\ 10^{-2}$	$1.644053\ 10^{-2}$	$2.8867\ 10^{2}$
	4,4	$2(0,A_1)$	$-1.317225\ 10^{-2}$	$-1.342363\ 10^{-2}$	$2.8867\ 10^{2}$
	4,4	$2(2,E)$	$-1.925098\ 10^{-2}$	$-1.904132\ 10^{-2}$	$2.8867\ 10^{2}$
	4,4	$2(2,F_2)$	$1.294650\ 10^{-2}$	$1.253439\ 10^{-2}$	$2.8867\ 10^{2}$
	2,4	$2(2,F_2)$	$-6.431680\ 10^{-4}$	$-1.124602\ 10^{-3}$	$2.8867\ 10^{2}$
λ^3	2,2	$3(3,A_2)$	$-5.656000\ 10^{-4}$	$-5.537357\ 10^{-4}$	$2.8867\ 10^{3}$
	4,4	$3(1,F_1)$	$4.993849\ 10^{-4}$	$4.616870\ 10^{-4}$	$2.8867\ 10^{3}$
	4,4	$3(3,F_1)$	$5.079133\ 10^{-4}$	$4.427641\ 10^{-4}$	$2.8867\ 10^{3}$
	2,4	$3(3,F_1)$	$-1,001703\ 10^{-4}$	$-9.426083\ 10^{-5}$	$2.8867\ 10^{3}$
	2,4	$3(1,F_1)$	$2.915907\ 10^{-4}$	$2.892102\ 10^{-4}$	$2.8867\ 10^{3}$
	2,4	$3(3,F_2)$	$-2.245892\ 10^{-5}$	$7.505454\ 10^{-6}$	$2.8867\ 10^{3}$
λ^4	2,2	$4(0,A_1)$	$-4.852520\ 10^{-6}$	$-3.997441\ 10^{-6}$	$2.8867\ 10^{4}$
	2.2	$4(4,A_1)$	$1.009547\ 10^{-5}$	$1.099484\ 10^{-5}$	$2.8867\ 10^{4}$
	2,2	$4(2,E)$	$-7.803430\ 10^{-7}$	$-1.245138\ 10^{-6}$	$2.8867\ 10^{4}$
	2,2	$4(4,E)$	$-1.395674\ 10^{-5}$	$-1.244200\ 10^{-5}$	$2.8867\ 10^{4}$
	4,4	$4(0,A_1)$	$2.880359\ 10^{-6}$	$2.166666\ 10^{-6}$	$2.8867\ 10^{4}$
	4,4	$4(4,A_1)$	$-9.123297\ 10^{-6}$	$-9.978882\ 10^{-6}$	$2.8867\ 10^{4}$
	4,4	$4(2,E)$	$-1.144830\ 10^{-5}$	$-1.005313\ 10^{-5}$	$2.8867\ 10^{4}$
	4,4	$4(4,E)$	$-2.420626\ 10^{-6}$	$-1.207117\ 10^{-6}$	$2.8867\ 10^{4}$
	4,4	$4(2,F_2)$	$-7.308750\ 10^{-6}$	$-7.551858\ 10^{-6}$	$2.8867\ 10^{4}$
	4,4	$4(4,F_2)$	$-3.041290\ 10^{-6}$	$2.566178\ 10^{-9}$	$2.8867\ 10^{4}$

operators. They are the basis for the comparative analysis of different sets, say I and II, of spectroscopic parameters. For one given set of spectroscopic parameters these formulae enable one to construct a parametric variety. Using parameters (*8*) as initial ones we have

$$\tilde{u}_{2,4}^{1(1,F_1)} = 5.5618 - s_{2,4}^{1(1,F_1)}220.151.$$

Now we can choose the $s_{2,4}^{1(1,F_1)}$ parameter to minimize the difference between the parameters of sets I and II. (We take Ref. (*8*) as set I and Ref. (*38*) as set II.) We may now put $\tilde{u}_{2,4}^{1(1,F_1)}$ equal to the corresponding parameter of set II. This requirement yields the numerical value of the *s* parameter. After that we can find in the same way the numerical value of the $s_{2,4}^{2(2,F_2)}$ parameter without any least-squares procedure. For the concrete example considered we have

$$\begin{aligned} s_{2,4}^{1(1,F_1)} &= 2.53 \times 10^{-2} & s_{2,4}^{3(3,F_1)} &= -5.94 \times 10^{-6} \\ s_{2,4}^{2(2,F_2)} &= 4.19 \times 10^{-4} & s_{2,4}^{3(3,F_2)} &= -0.34 \times 10^{-6} \\ s_{2,4}^{3(1,F_1)} &= 4.07 \times 10^{-6} & s_{4,4}^{3(3,F_2)} &\approx 10^{-6}. \end{aligned} \tag{13}$$

TABLE VI

Comparison of the Spectroscopic Parameters for ν_2, ν_4 Bands of $^{12}CH_4$ Obtained in Refs. (*8*) and (*38*).

λ^n	$U_{k,m}^{\Omega(K,\Gamma)}$ k,m	$\Omega(K,\Gamma)$	Parameters from (8)	Transformed values	Parameters from (38)	weight
λ^0	2,2	0	2168.4779	2168.4779	2168.4739	0
	4,4	0	2270.2952	2270.2952	2270.2589	
λ^1	4,4	$1(1,F_1)$	-5.97396	-5.91868	-5.91171	1
	2,4	$1(1,F_1)$	5.5618	$3.22\ 10^{-2}$	0	
λ^2	2,2	$2(2,E)$	$-2.2242\ 10^{-2}$	$3.7815\ 10^{-2}$	$3.8153\ 10^{-2}$	10^2
	2,2	$2(0,A_1)$	$0.4066\ 10^{-2}$	$-5.2977\ 10^{-2}$	$-5.3605\ 10^{-2}$	
	4,4	$2(0,A_1)$	$0.1359\ 10^{-2}$	$4.7936\ 10^{-2}$	$4.7384\ 10^{-2}$	
	4,4	$2(2,E)$	$-0.6659\ 10^{-2}$	$5.9250\ 10^{-2}$	$5.8871\ 10^{-2}$	
	4,4	$2(2,F_2)$	$-1.5922\ 10^{-2}$	$-5.8197\ 10^{-2}$	$-5.7672\ 10^{-2}$	
	2,4	$2(2,F_2)$	$-2.061\ 10^{-2}$	$6.1\ 10^{-5}$	0	
λ^3	2,2	$3(3,A_2)$	$2.099\ 10^{-4}$	$13.715\ 10^{-4}$	$12.747\ 10^{-4}$	10^3
	4,4	$3(1,F_1)$	$-3.028\ 10^{-4}$	$-12.883\ 10^{-4}$	$-11.996\ 10^{-4}$	
	4,4	$3(3,F_1)$	$-1.363\ 10^{-4}$	$-10.266\ 10^{-4}$	$-9.734\ 10^{-4}$	
	2,4	$3(1,F_1)$	$0.478\ 10^{-4}$	$0.2\ 10^{-7}$	0	
	2,4	$3(3,F_1)$	$-1.327\ 10^{-4}$	$1.1\ 10^{-7}$	0	
	2,4	$3(3,F_2)$	$-1.144\ 10^{-4}$	$2.0\ 10^{-7}$	0	
λ^4	2,2	$4(0,A_1)$	0	$-2.36\ 10^{-6}$	$-4.42\ 10^{-6}$	10^4
	2,2	$4(4,A_1)$	0	$-1.505\ 10^{-5}$	$-1.274\ 10^{-5}$	
	2,2	$4(2,E)$	0	$1.177\ 10^{-5}$	$1.223\ 10^{-5}$	
	2,2	$4(4,E)$	0	$10.05\ 10^{-6}$	$9.35\ 10^{-6}$	
	4,4	$4(0,A_1)$	0	$1.52\ 10^{-6}$	$0.82\ 10^{-6}$	
	4,4	$4(4,A_1)$	0	$12.28\ 10^{-6}$	$9.55\ 10^{-6}$	
	4,4	$4(2,E)$	0	$1.501\ 10^{-5}$	$1.499\ 10^{-5}$	
	4,4	$4(4,E)$	0	$9.43\ 10^{-6}$	$2.08\ 10^{-6}$	
	4,4	$4(2,F_2)$	0	$4.15\ 10^{-6}$	$4.32\ 10^{-6}$	
	4,4	$4(4,F_2)$	0	$-2.64\ 10^{-6}$	$-2.87\ 10^{-6}$	

These numerical values of s generators enable us to calculate the transformed values of set I and to compare it with set II.

The computer realization of this procedure permits us to take into account less important terms in the transformed Hamiltonian and to use the least-squares approximation to find the numerical values of $s_{k,m}^{\Omega(K,\Gamma)}$. Nevertheless, this advanced treatment results in parameters of s generators which differ by no more than 10% from those listed in Eqn. (13) for $s_{2,4}^{1(1,F_1)}$ and $s_{2,4}^{2(2,F_2)}$. The difference in $s_{k,m}^{3(K,\Gamma)}$ may be more important.

Special attention must be paid to very large transformations when the multiple commutators become important. These terms result in nonlinear dependence on s parameters of the parametric variety of the Hamiltonians. The nonlinearity may be avoided by taking into account that the appropriate values of s parameters are approximately known. For example, the contribution from $S_{2,4}^{1(1,F_1)}$ to $U_{2,2}^{4(2,E)}$ has the form

$$is_{2,4}^{1(1,F_1)}\,[S_{2,4}^{1(1,F_1)}, \sum_{K,\Gamma} u_{2,4}^{3(K,\Gamma)} U_{2,4}^{3(K,\Gamma)}]_-$$

$$+ \frac{i^2}{2}(s_{2,4}^{1(1,F_1)})^2[S_{2,4}^{1(1,F_1)}, [S_{2,4}^{1(1,F_1)}, \sum_{m,K,\Gamma} u_{m,m}^{2(K,\Gamma)} U_{m,m}^{2(K,\Gamma)}]_-]_-$$

TABLE VII

Comparison of the Spectroscopic Parameters for ν_2, ν_4 Bands of $^{12}CH_4$ Obtained in Ref. (5) (Isolated and Resonance Band Models)

λ^n	$U_{k,m}^{\Omega(K,\Gamma)}$		Paremeters from (5) (resonance)	Transformed values	Parameters from (5) (isolated)
	k,m	$\Omega(K,\Gamma)$			
λ^0	2,2	0	2168.463	2168.463	2168.4616
	4,4	0	2270.299	2270.299	2270.306
λ^1	4,4	$1(1,F_1)$	-5.9765	-5.9215	-5.911
	2,4	$1(1,F_1)$	5.50	0.000	0
λ^2	2,2	$2(2,E)$	$-1.984\ 10^{-2}$	$3.816\ 10^{-2}$	$3.829\ 10^{-2}$
	2,2	$2(0,A_1)$	$0.235\ 10^{-2}$	$-5.371\ 10^{-2}$	$-5.380\ 10^{-2}$
	4,4	$2(0,A_1)$	$0.232\ 10^{-2}$	$4.810\ 10^{-2}$	$4.855\ 10^{-2}$
	4,4	$2(2,E)$	$-0.486\ 10^{-2}$	$5.995\ 10^{-2}$	$5.935\ 10^{-2}$
	4,4	$2(2,F_2)$	$-1.804\ 10^{-2}$	$-5.898\ 10^{-2}$	$-5.842\ 10^{-2}$
	2,4	$2(2,F_2)$	0	$-0.007\ 10^{-2}$	0
λ^3	2,2	$3(3,A_2)$	$6.87\ 10^{-4}$	$14.11\ 10^{-4}$	$12.18\ 10^{-4}$
	4,4	$3(1,F_1)$	$-7.00\ 10^{-4}$	$-13.28\ 10^{-4}$	$-11.77\ 10^{-4}$
	4,4	$3(3,F_1)$	$-5.13\ 10^{-4}$	$-11.07\ 10^{-4}$	$-9.81\ 10^{-4}$
	2,4	$3(1,F_1)$	0	$0.00\ 10^{-4}$	0
	2,4	$3(3,F_1)$	0	$0.00\ 10^{-4}$	0
	2,4	$3(3,F_2)$	0	$0.00\ 10^{-4}$	0
λ^4	2,2	$4(0,A_1)$	$2.3\ 10^{-6}$	$-3.5\ 10^{-6}$	$-4.9\ 10^{-6}$
	2,2	$4(4,A_1)$	$-7.4\ 10^{-6}$	$-1.60\ 10^{-5}$	$-1.26\ 10^{-5}$
	2,2	$4(2,E)$	$-1.1\ 10^{-6}$	$1.07\ 10^{-5}$	$1.29\ 10^{-5}$
	2,2	$4(4,E)$	$7.9\ 10^{-6}$	$13.3\ 10^{-6}$	$9.5\ 10^{-6}$
	4,4	$4(0,A_1)$	$-2.5\ 10^{-6}$	$2.3\ 10^{-6}$	$7.4\ 10^{-6}$
	4,4	$4(4,A_1)$	$5.2\ 10^{-6}$	$1.24\ 10^{-5}$	$1.04\ 10^{-5}$
	4,4	$4(2,E)$	$5.2\ 10^{-6}$	$2.20\ 10^{-5}$	$1.99\ 10^{-5}$
	4,4	$4(4,E)$	$-0.5\ 10^{-6}$	$-1.6\ 10^{-6}$	$-3.1\ 10^{-6}$
	4,4	$4(2,F_2)$	$4.5\ 10^{-6}$	$-0.4\ 10^{-6}$	$-1.0\ 10^{-6}$
	4,4	$4(4,F_2)$	$0.9\ 10^{-6}$	$-5.0\ 10^{-6}$	$-5.5\ 10^{-6}$

$$+\frac{i^3}{6}(s_{2,4}^{1(1,F_1)})^3[S_{2,4}^{1(1,F_1)}, [S_{2,4}^{1(1,F_1)}, [S_{2,4}^{1(1,F_1)}, u_{2,4}^{1(1,F_1)}U_{2,4}^{1(1,F_1)}]_-]_-]_-$$

$$+\frac{i^4}{24}(s_{2,4}^{1(1,F_1)})^4[S_{2,4}^{1(1,F_1)}, [S_{2,4}^{1(1,F_1)}, [S_{2,4}^{1(1,F_1)}, [S_{2,4}^{1(1,F_1)}, \sum_m u_{m,m}^0 U_{m,m}^0]_-]_-]_-]_-. \quad (14)$$

The corresponding numerical values obtained for the $^{12}CH_4$ spectroscopic parameters (*8*) are

$$-(1.645 + 1.809 - 11.153 + 2.819) \times 10^{-4} s_{2,4}^{1(1,F_1)}. \quad (15)$$

The order of terms identical to that in formulae (14) and the approximate value of $s_{2,4}^{1(1,F_1)}$ is used to eliminate the nonlinearity. The expression (15) shows that the multiple commutators become even more important than the ordinary ones.

IV. ν_2, ν_4 BANDS OF SiH_4

We choose the SiH_4 molecule to show the principles of the comparison of different sets of the spectroscopic parameters. Two treatments of the same experimental data

TABLE VIII

Characteristics of the Unitary Transformations Relating the Treatments of ν_2, ν_4 Bands of $^{12}CH_4$ Made in Refs. (*8*) and (*38*), and Ref. (*5*) (Isolated and Resonance Band Models)

N	k,m	$\Omega(K,\Gamma)$	$s_{k,m}^{\Omega(K,\Gamma)}$ parameters (8, 38)		$s_{k,m}^{\Omega(K,\Gamma)}$ parameters (5, 5)	
1	2,4	$1(1,F_1)$	2.5162	10^{-2}	2.4982	10^{-2}
2	2,4	$2(2,F_2)$	4.1724	10^{-4}	3.2390	10^{-4}
3	4,4	$3(3,F_2)$	3.709	10^{-7}	-1.6339	10^{-6}
4	2,4	$3(3,F_2)$	-5.593	10^{-7}	-8.372	10^{-7}
5	2,4	$3(3,F_1)$	-5.8458	10^{-6}	-4.5329	10^{-6}
6	2,4	$3(1,F_1)$	4.0578	10^{-6}	4.8962	10^{-6}

Mean square deviations from (38)

λ^n	(8)	transformed values	weight	(38)
λ^1	3.93	2.32 10^{-2}	1	0
λ^2	5.13 10^{-2}	4.54 10^{-4}	10^2	0
λ^3	6.15 10^{-4}	5.78 10^{-5}	10^3	0
λ^4	8.75 10^{-6}	2.69 10^{-6}	10^4	0
λ^1-λ^4	2.82	4.12 10^{-2}		0

Mean square deviations from (5, isolated)

λ^n	(5,resonance)	transformed values	weight	(5,isolated)
λ^1	3.89	7.42 10^{-3}	1	0
λ^2	4.90 10^{-2}	3.88 10^{-4}	10	0
λ^3	3.48 10^{-4}	1.12 10^{-4}	50	0
λ^4	8.38 10^{-6}	2.80 10^{-6}	10^3	0
λ^1- λ^4	1.15	4.41 10^{-3}		0

obtained by Johns *et al.* (*48*) are considered. These two treatments are based on different effective Hamiltonians. Gray *et al.* (*19*) used the effective Hamiltonian with 29 adjustable parameters and fixed parameters for the ground state. These 29 terms include all diagonal operators up to λ^4, some diagonal operators of order λ^5 and λ^6, and two nondiagonal operators (one of order λ and one of order λ^3). The corresponding set of spectroscopic parameters reproduces 645 lines with a mean square deviation of ~0.017 cm^{-1}. The effective Hamiltonian used by Pierre *et al.* (*20*) includes only 16 adjustable parameters and 6 fixed parameters for the ground state. All diagonal and nondiagonal operators up to λ^3 are considered. This set of spectroscopic parameters reproduces

TABLE IX

Characteristics[a] of the Unitary Transformations Relating the Treatments of ν_2, ν_4 Bands for $^{12}CH_4$ Made in Refs. (*8*) and (*6*); and in Refs. (*5*) and (*6*)

N	k,m	$\Omega(K,\Gamma)$	$s_{k,m}^{\Omega(K,\Gamma)}$ parameters for (8,6)	for (5,6)
1	2,4	$1(1,F_1)$	$-5.1669\ 10^{-5}$	$-3.4001\ 10^{-4}$
2	2,4	$2(2,F_2)$	$-4.0818\ 10^{-5}$	$-1.4658\ 10^{-4}$
3	4,4	$3(3,F_2)$	$2.0951\ 10^{-7}$	$0.8048\ 10^{-6}$
4	2,4	$3(3,F_2)$	$-3.8405\ 10^{-7}$	$-0.2630\ 10^{-6}$
5	2,4	$3(3,F_1)$	$-1.2964\ 10^{-7}$	$1.3222\ 10^{-6}$
6	2,4	$3(1,F_1)$	$-3.4067\ 10^{-7}$	$0.4780\ 10^{-6}$

Correlation matrix (5,6)

2	-0.03275				
3	0.00201	0.04632			
4	-0.00308	0.09070	-0.13342		
5	0.01218	-0.26249	-0.05305	0.04973	
6	0.00797	-0.24452	0.12260	-0.00132	0.10641

Mean square deviations from (6)

λ^n	(8)	transformed values	weight	(6)
λ^1	$9.72\ 10^{-3}$	$3.00\ 10^{-3}$	1	0
λ^2	$4.63\ 10^{-4}$	$2.32\ 10^{-4}$	20	0
λ^3	$1.36\ 10^{-4}$	$3.11\ 10^{-5}$	10^2	0
λ^4	$1.32\ 10^{-6}$	$4.02\ 10^{-7}$	10^4	0
$\lambda^1-\lambda^4$	$1.23\ 10^{-2}$	$3.87\ 10^{-3}$		0

Mean square deviations from (6)

λ^n	(5)	transformed values	weight	(6)
λ^1	$5.30\ 10^{-2}$	$5.65\ 10^{-4}$	1	0
λ^2	$2.23\ 10^{-3}$	$1.42\ 10^{-4}$	10^2	0
λ^3	$4.33\ 10^{-4}$	$1.43\ 10^{-5}$	10^3	0
λ^4	$5.20\ 10^{-6}$	$2.43\ 10^{-6}$	10^4	0
$\lambda^1-\lambda^4$	$2.47\ 10^{-1}$	$1.88\ 10^{-2}$		0

[a] (i) Parameters of the *S* generator; (ii) correlation matrix for *s* parameters; and (iii)–(iv) mean square deviations of the transformed parameters from Ref. (*6*) (neglecting the contribution from $u_{2,4}^{2(2,F_2)}$ parameters).

663 lines with a mean square deviation of ~0.014 cm^{-1}. Two sets of parameters reproduce the experimental data but the numerical values of the parameters are completely different. These numerical values from Refs. (*19*) and (*20*) recalculated in the same notation are given in Table III. To compare them we use the unitary transformation which minimizes the weighted mean square deviation between two sets of parameters. We try two choices of weights listed in columns (a) and (b). Choice (a) takes into account all diagonal and nondiagonal parameters. Choice (b) takes into account the nondiagonal parameters of orders λ, λ^2, λ^3 and diagonal parameters of order λ^4. The corresponding values of s parameters are given in Table IV. It must be noted that the correlations between the parameters of the S generator are absent for both kinds of weight factors. The s parameters obtained are satisfactory from the point of view of the order classification. To compare the transformed parameters of the treatment in Ref. (*19*) with the parameters of the treatment in Ref. (*20*) we use the weighted mean square deviation between these sets of the parameters. The corresponding values are given in Table IV for each order separately along with the total deviation. We illustrate the results of the least-squares procedure in Table V by com-

TABLE X

Comparison of the Spectroscopic Parameters for ν_2, ν_4 Bands of $^{12}CH_4$ Obtained in Refs. (*8*) and (*6*)[a]

λ^n	$U_{k,m}^{\Omega(K,\Gamma)}$ k,m $\Omega(K,\Gamma)$	Parameters from (8)	Transformed values	Parameters from (6)
λ^0	2,2 0	2168.4779	2168.4779	2168.4554
	4,4 0	2270.2952	2270.2952	2270.3039
λ^1	4,4 $1(1,F_1)$	−5.97396	−5.9739	−5.9778
	2,4 $1(1,F_1)$	5.5618	5.5733	5.5750
λ^2	2,2 $2(2,E)$	$-2.2242\ 10^{-2}$	$-2.293\ 10^{-2}$	$-2.314\ 10^{-2}$
	2,2 $2(0,A_1)$	$0.4066\ 10^{-2}$	$0.429\ 10^{-2}$	$0.403\ 10^{-2}$
	4,4 $2(0,A_1)$	$0.1359\ 10^{-2}$	$0.117\ 10^{-2}$	$0.091\ 10^{-2}$
	4,4 $2(2,E)$	$-0.6659\ 10^{-2}$	$-0.6934\ 10^{-2}$	$-0.6774\ 10^{-2}$
	4,4 $2(2,F_2)$	$-1.5922\ 10^{-2}$	$-1.5437\ 10^{-2}$	$-1.5694\ 10^{-2}$
	2,4 $2(2,F_2)$	$-2.0611\ 10^{-2}$	$-2.964\ 10^{-2}$	
λ^3	2,2 $3(3,A_2)$	$2.099\ 10^{-4}$	$0.176\ 10^{-4}$	$0.225\ 10^{-4}$
	4,4 $3(1,F_1)$	$-3.028\ 10^{-4}$	$-1.468\ 10^{-4}$	$-1.640\ 10^{-4}$
	4,4 $3(3,F_1)$	$-1.363\ 10^{-4}$	$0.184\ 10^{-4}$	$0.129\ 10^{-4}$
	2,4 $3(1,F_1)$	$0.478\ 10^{-4}$	$2.080\ 10^{-4}$	$1.936\ 10^{-4}$
	2,4 $3(3,F_1)$	$-1.328\ 10^{-4}$	$-0.294\ 10^{-4}$	$-0.285\ 10^{-4}$
	2,4 $3(3,F_2)$	$-1.144\ 10^{-4}$	$-0.901\ 10^{-4}$	$-1.626\ 10^{-4}$
λ^4	2,2 $4(0,A_1)$	0	$0.970\ 10^{-6}$	$0.497\ 10^{-6}$
	2,2 $4(4,A_1)$	0	$-0.055\ 10^{-6}$	$-0.528\ 10^{-6}$
	2,2 $4(2,E)$	0	$0.188\ 10^{-6}$	$-0.477\ 10^{-6}$
	2,2 $4(4,E)$	0	$-1.677\ 10^{-6}$	$-1.944\ 10^{-6}$
	4,4 $4(0,A_1)$	0	$-0.795\ 10^{-6}$	$-1.209\ 10^{-6}$
	4,4 $4(4,A_1)$	0	$0.045\ 10^{-6}$	$0.041\ 10^{-6}$
	4,4 $4(2,E)$	0	$-2.328\ 10^{-6}$	$-2.275\ 10^{-6}$
	4,4 $4(4,E)$	0	$1.951\ 10^{-6}$	$2.342\ 10^{-6}$
	4,4 $4(2,F_2)$	0	$0.143\ 10^{-6}$	$-0.424\ 10^{-6}$
	4,4 $4(4,F_2)$	0	$-0.654\ 10^{-6}$	$-0.737\ 10^{-6}$

[a] For the $u_{2,4}^{2(2,F_2)}$ parameter see the text.

parison of the initial and minimized differences obtained for weight factors (a). The general conclusion is: Two considered sets of parameters are in almost quantitative agreement except for $u_{4,4}^{4(4,F_2)}$. The utilization of only three additional nondiagonal parameters allows one to significantly reduce the numerical values of the diagonal λ^4 parameters.

V. ν_2, ν_4 BANDS OF CH_4: COMPARISON OF ISOLATED AND RESONANT BAND MODELS

Various treatments of ν_2, ν_4 bands of CH_4 may be divided into two classes due to the choice of the effective Hamiltonian. The model of isolated ν_2 and ν_4 states was used in Refs. (*5, 7, 38*). More recent studies take into account the resonance nondiagonal operators (*5, 6, 8*). In this section we compare the parameters obtained by the same authors for isolated and resonance band effective operators. The strong difference between parameters from different sets leads to large values of *s* parameters and consequently requires us to take into account the multiple commutators. Table VI shows the comparison of two treatments made in Dijon [Ref. (*8*) for the resonance band

TABLE XI

Comparison of the Spectroscopic Parameters for ν_2, ν_4 Bands of $^{12}CH_4$ Obtained in Refs. (*5*) and (*6*)[a]

λ^n	$U_{k,m}^{\Omega(K,\Gamma)}$ k,m	$\Omega(K,\Gamma)$	Parameters from (5)	Transformed values	Parameters from (6)
λ^0	2,2	0	2168.463	2168.463	2168.4554
	4,4	0	2270.299	2270.299	2270.3039
λ^1	4,4	$1(1,F_1)$	-5.9765	-5.9770	-5.9778
	2,4	$1(1,F_1)$	5.50	5.575	5.575
λ^2	2,2	$2(2,E)$	$-1.984\ 10^{-2}$	$-2.299\ 10^{-2}$	$-2.314\ 10^{-2}$
	2,2	$2(0,A_1)$	$0.235\ 10^{-2}$	$0.388\ 10^{-2}$	$0.402\ 10^{-2}$
	4,4	$2(0,A_1)$	$0.233\ 10^{-2}$	$0.108\ 10^{-2}$	$0.091\ 10^{-2}$
	4,4	$2(2,E)$	$-0.486\ 10^{-2}$	$-0.667\ 10^{-2}$	$-0.677\ 10^{-2}$
	4,4	$2(2,F_2)$	$-1.803\ 10^{-2}$	$-1.583\ 10^{-2}$	$-1.569\ 10^{-2}$
	2,4	$2(2,F_2)$	0	$-3.197\ 10^{-2}$	
λ^3	2,2	$3(3,A_2)$	$6.875\ 10^{-4}$	$0.251\ 10^{-4}$	$0.225\ 10^{-4}$
	4,4	$3(1,F_1)$	$-7.000\ 10^{-4}$	$-1.393\ 10^{-4}$	$-1.639\ 10^{-4}$
	4,4	$3(3,F_1)$	$-5.134\ 10^{-4}$	$-0.008\ 10^{-4}$	$0.130\ 10^{-4}$
	2,4	$3(1,F_1)$	0	$2.002\ 10^{-4}$	$1.935\ 10^{-4}$
	2,4	$3(3,F_1)$	0	$-0.255\ 10^{-4}$	$-0.285\ 10^{-4}$
	2,4	$3(3,F_2)$	0	$-1.432\ 10^{-4}$	$-1.626\ 10^{-4}$
λ^4	2,2	$4(0,A_1)$	$2.30\ 10^{-6}$	$-1.25\ 10^{-6}$	$0.49\ 10^{-6}$
	2,2	$4(4,A_1)$	$-7.41\ 10^{-6}$	$1.10\ 10^{-6}$	$-0.53\ 10^{-6}$
	2,2	$4(2,E)$	$-1.15\ 10^{-6}$	$-1.55\ 10^{-6}$	$-0.48\ 10^{-6}$
	2,2	$4(4,E)$	$7.99\ 10^{-6}$	$1.95\ 10^{-6}$	$-1.94\ 10^{-6}$
	4,4	$4(0,A_1)$	$-2.57\ 10^{-6}$	$0.31\ 10^{-6}$	$-1.21\ 10^{-6}$
	4,4	$4(4,A_1)$	$5.26\ 10^{-6}$	$-0.64\ 10^{-6}$	$0.04\ 10^{-6}$
	4,4	$4(2,E)$	$5.23\ 10^{-6}$	$-0.35\ 10^{-6}$	$-2.27\ 10^{-6}$
	4,4	$4(4,E)$	$-0.56\ 10^{-6}$	$0.27\ 10^{-6}$	$2.34\ 10^{-6}$
	4,4	$4(2,F_2)$	$4.57\ 10^{-6}$	$1.17\ 10^{-6}$	$-0.42\ 10^{-6}$
	4,4	$4(4,F_2)$	$0.91\ 10^{-6}$	$4.17\ 10^{-6}$	$-0.73\ 10^{-6}$

[a] For the $u_{2,4}^{2(2,F_2)}$ parameter see the text.

model; Ref. (*38*) for the isolated band model]. Table VII includes two treatments made in Reading [Ref. (*5*) for isolated and resonance models]. We use as the initial set the parameters in each case that include nonzero interaction parameters. The numerical values of *s* parameters and the corresponding mean square deviations of the spectroscopic parameters are listed in Table VIII. The results of the transformations show that the parameters of order λ, λ^2, and λ^3 may be put in a quantitative agreement by the proper choice of the unitary transformation.

The difference in the parameters of λ^4 order becomes smaller after such a transformation. It should be noted that we have used only the main contributions to λ^4 parameters and the nonleading contributions may become important (about 10%). Thus the results obtained show the explicit equivalence between isolated and resonance models for ν_2, ν_4 states of CH_4. The inclusion of nondiagonal parameters again significantly reduces the numerical values of λ^4 diagonal parameters.

VI. ν_2, ν_4 BANDS OF CH_4: COMPARISON OF DIFFERENT RESONANCE TREATMENTS

We consider in this section the model treatments (*5, 6, 8*) which all include the interaction operator $U^{1(1,F_1)}_{2,4}$ with nearly the same coefficient. So the difference in parameters of order λ^2 in Refs. (*5, 6, 8*) is not large. The present results may be considered as an extension of the comparison of treatments made in Refs. (*34, 37*). We consider three pairs of treatments. The comparison of the spectroscopic parameters from Refs. (*6*) and (*8*) is given in Tables IX and X. The comparison of the parameters from Refs. (*6*) and (*5*) is presented in Tables IX and XI. Finally, the comparison of the parameters from Refs. (*5*) and *8*) is given in Tables XII and XIII.

TABLE XII

Characteristics[a] of the Unitary Transformation Relating the Treatments of ν_2, ν_4 Bands for $^{12}CH_4$ Made in Refs. (*8*) and (*5*)

N	k,m Ω(K,Γ)	$s^{\Omega(K,\Gamma)}_{k,m}$ parameters for (8, 5)
1	2,4 $1(1,F_1)$	$3.0529\ 10^{-4}$
2	2,4 $2(2,F_2)$	$9.6386\ 10^{-5}$
3	4,4 $3(3,F_2)$	$-7.8258\ 10^{-7}$
4	2,4 $3(3,F_2)$	$1.5777\ 10^{-7}$
5	2,4 $3(3,F_1)$	$-1.3704\ 10^{-6}$
6	2,4 $3(1,F_1)$	$-6.9586\ 10^{-7}$

	Mean square deviations from (5)			
λ^n	(8)	transformed values	weight	(5)
λ^1	$4.37\ 10^{-2}$	$8.05\ 10^{-3}$	1	0
λ^2	$8.58\ 10^{-3}$	$2.35\ 10^{-4}$	2 10	0
λ^3	$3.06\ 10^{-4}$	$2.09\ 10^{-5}$	$2\ 10^2$	0
λ^4	$4.57\ 10^{-6}$	$1.86\ 10^{-6}$	$2\ 10^3$	0
$\lambda^1-\lambda^4$	$9.21\ 10^{-2}$	$4.59\ 10^{-3}$		0

[a] (i) Parameters of the *S* generator, and (ii) mean square deviations of the transformed parameters from Ref. (*5*).

The results of the comparisons of the spectroscopic sets from Refs. (*5*) and (*8*) (see Tables XII and XIII) are similar to the results obtained in Section IV for SiH_4. The traditional difference in the effective Hamiltonians used in Dijon and Reading (see Sect. IV for the SiH_4 example) results in strong disagreement in λ^3 and λ^4 parameters. Otherwise the extended model Hamiltonian used by Robiette (*6*) includes all operators taken into account by Pierre *et al.* (*8*) and all diagonal operators of order λ^4 also. This significantly increases the accuracy of the model. It should be noted that the numerical values of λ^4 parameters for CH_4 even after inclusion of all nondiagonal operators of order λ, λ^2, λ^3 do not become smaller than $\sim 0.5 \times 10^{-6}$ cm^{-1}, which correspond to the energy contribution for $J = 10$ equal to $\sim 5 \times 10^{-3}$ cm^{-1} and limit the accuracy of the model (*8*).

The comparison of the spectroscopic parameters obtained in Refs. (*8*) and (*6*) and in Refs. (*5*) and (*6*) is complicated due to the unclear relation between d_{24} used in Ref. (*6*) and $u_{2,4}^{2(2,F_2)}$. The parameters $u_{2,4}^{1(1,F_1)}$ for these treatments are very close and the main contribution to λ^2 and diagonal λ^3 parameters are defined (up to $\sim 1\%$) by the $S_{2,4}^{2(2,F_2)}$ generator. The corresponding parameter $s_{2,4}^{2(2,F_2)}$ may be determined from the expression similar to (12) by the difference $\tilde{u}_{2,4}^{2(2,F_2)} - u_{2,4}^{2(2,F_2)}$ and must satisfy five in-

TABLE XIII

Comparison of the Spectroscopic Parameters for ν_2, ν_4 Bands of $^{12}CH_4$ Obtained in Refs. (*8*) and (*5*)

λ^n	$U_{k,m}^{\Omega(K,\Gamma)}$ k,m	Ω(K,Γ)	Parameters from (8)	Transformed values	Parameters from (5)
λ^0	2,2	0	2168.4779	2168.4779	2168.463
	4,4	0	2270.2952	2270.2952	2270.299
λ^1	4,4	$1(1,F_1)$	-5.97396	-5.9667	-5.9765
	2,4	$1(1,F_1)$	5.5618	5.4942	5.50
λ^2	2,2	$2(2,E)$	$-2.2242\ 10^{-2}$	$-1.976\ 10^{-2}$	$-1.984\ 10^{-2}$
	2,2	$2(0,A_1)$	$0.4066\ 10^{-2}$	$0.268\ 10^{-2}$	$0.235\ 10^{-2}$
	4,4	$2(0,A_1)$	$0.1359\ 10^{-2}$	$0.249\ 10^{-2}$	$0.233\ 10^{-2}$
	4,4	$2(2,E)$	$-0.6659\ 10^{-2}$	$-0.501\ 10^{-2}$	$-0.486\ 10^{-2}$
	4,4	$2(2,F_2)$	$-1.5922\ 10^{-2}$	$-1.766\ 10^{-2}$	$-1.804\ 10^{-2}$
	2,4	$2(2,F_2)$	$-2.0611\ 10^{-2}$	$0.015\ 10^{-2}$	0
λ^3	2,2	$3(3,A_2)$	$2.099\ 10^{-4}$	$6.55\ 10^{-4}$	$6.875\ 10^{-4}$
	4,4	$3(1,F_1)$	$-3.028\ 10^{-4}$	$-6.81\ 10^{-4}$	$-7.00\ 10^{-4}$
	4,4	$3(3,F_1)$	$-1.363\ 10^{-4}$	$-4.84\ 10^{-4}$	$-5.13\ 10^{-4}$
	2,4	$3(1,F_1)$	$0.478\ 10^{-4}$	$-0.014\ 10^{-4}$	0
	2,4	$3(3,F_1)$	$-1.328\ 10^{-4}$	$0.002\ 10^{-4}$	0
	2,4	$3(3,F_2)$	$-1.144\ 10^{-4}$	$0.193\ 10^{-4}$	0
λ^4	2,2	$4(0,A_1)$	0	$3.69\ 10^{-6}$	$2.30\ 10^{-6}$
	2,2	$4(4,A_1)$	0	$-6.75\ 10^{-6}$	$-7.41\ 10^{-6}$
	2,2	$4(2,E)$	0	$0.51\ 10^{-6}$	$-1.15\ 10^{-6}$
	2,2	$4(4,E)$	0	$4.89\ 10^{-6}$	$7.99\ 10^{-6}$
	4,4	$4(0,A_1)$	0	$-3.02\ 10^{-6}$	$-2.57\ 10^{-6}$
	4,4	$4(4,A_1)$	0	$5.51\ 10^{-6}$	$5.26\ 10^{-6}$
	4,4	$4(2,E)$	0	$3.91\ 10^{-6}$	$5.23\ 10^{-6}$
	4,4	$4(4,E)$	0	$0.57\ 10^{-6}$	$-0.55\ 10^{-6}$
	4,4	$4(2,F_2)$	0	$3.45\ 10^{-6}$	$4.57\ 10^{-6}$
	4,4	$4(4,F_2)$	0	$-3.63\ 10^{-6}$	$0.91\ 10^{-6}$

dependent equations for the parameters $u_{2,2}^{2(2,E)}$ and $u_{4,4}^{2(2,F_2)}$ from λ^2 terms and for the parameters $u_{2,2}^{3(3,A_2)}$, $u_{4,4}^{3(1,F_1)}$, $u_{4,4}^{3(3,F_1)}$ from λ^3 terms. Unfortunately the numerical value of the parameter $s_{2,4}^{2(2,F_2)}$ obtained from $u_{2,4}^{2(2,F_2)} = (\sqrt{3}/2\sqrt{2})d_{24} = 1.494 \times 10^{-2}$ (see Table I) does not satisfy any of these equations for the comparison of the parameters from Refs. (*8*) and (*6*) or for comparisons from Refs. (*5*) and (*6*). We believe that the commutator relations listed in Table II were sufficiently verified analytically and by the numerical examples listed earlier. We therefore exclude the $u_{2,4}^{2(2,F_2)}$ parameter on the stage of the determination of the $s_{2,4}^{2(2,F_2)}$ generator parameter and use the least-squares approximation with zero weight for the $u_{2,4}^{2(2,F_2)}$ parameter. The absence of the correlation between s parameters (see Table IX) verifies such a procedure. We obtain the quantitative agreement between almost all parameters of λ^2 and λ^3 orders (see Tables X and XI). The predicted value of the parameter $u_{2,4}^{2(2,F_2)}$ for the treatment in Ref. (*6*) resulting from the comparison with Ref. (*8*) is -2.971×10^{-2} cm^{-1} and the value from the comparison with Ref. (*5*) is -3.345×10^{-2} cm^{-1}. These values are in complete disagreement with the value 1.49×10^{-2} cm^{-1} which corresponds to the coefficient d_{24} indicated in Ref. (*6*). We suppose that the definition of the corresponding operator in Ref. (*6*) has to include an additional numerical factor. This factor probably equals -2 in accordance to Champion's belief (*49*).

VII. ν_2, ν_4 BANDS OF CD_4

The treatments in Refs. (*15*) and (*16*) for CD_4 realized in Reading and Dijon are similar to the SiH_4 case (Sect. IV) except for the additional exclusion of the λ^3 non-

TABLE XIV

Characteristics[a] of the Unitary Transformation Relating the Treatments of ν_2, ν_4 Bands for $^{12}CD_4$ Made in Refs. (*16*) and (*15*)

N	k,m Ω(K,Γ)	$s_{k,m}^{\Omega(K,\Gamma)}$ parameters for (16, 15)
1	2,4 $1(1,F_1)$	-1.52514 10^{-4}
2	2,4 $2(2,F_2)$	1.01127 10^{-4}
3	4,4 $3(3,F_2)$	-9.8648 10^{-7}
4	2,4 $3(3,F_2)$	6.6718 10^{-7}
5	2,4 $3(3,F_1)$	-5.0422 10^{-7}
6	2,4 $3(1,F_1)$	-3.9681 10^{-7}

Mean square deviations from (15)

λ^n	(16)	transformed values	weight	(15)
λ^1	1.06 10^{-2} $(1.34$ $10^{-3})$	4.24 10^{-4}	1	0
λ^2	4.00 10^{-3} $(3.32$ $10^{-4})$	1.03 10^{-4}	10	0
λ^3	1.67 10^{-4}	6.43 10^{-6}	500	0
λ^4	1.71 10^{-6}	9.13 10^{-7}	2500	0
$\lambda^1-\lambda^4$	4.65 10^{-2} $(4.37$ $10^{-2})$	2.24 10^{-3}		0

[a] (i) Parameters of the S generator, and (ii) mean square deviations of the transformed parameters from Ref. (*15*) (values in parentheses correspond to diagonal parameters only).

diagonal parameter R_{24}^{01} in Ref. (*15*). The small difference in $u_{2,4}^{1(1,F_1)}$ parameters gives nearly the same values of the diagonal λ^2 parameters. As a result, the unitary transformed Hamiltonian is slightly influenced by the $s_{2,4}^{1(1,F_1)}$ parameter of the S generator. The transformation made in Ref. (*16*) took into account only this $s_{2,4}^{1(1,F_1)}$ parameter [see the transformation from fit *a* to fit *b* in Table IV of Ref. (*16*)]. In Tables XIV and XV we give the results of the complete unitary transformation for all λ^1–λ^4 parameters included in Refs. (*15*) and (*16*). Good agreement is obtained for all parameters except for $u_{4,4}^{4(4,E)}$ from λ^4.

VIII. CONCLUSIONS

The transformations of different sets of spectroscopic parameters explicitly show their equivalence and indicate the most important differences. We demonstrate that the recently developed algebraic technique for the irreducible tensor operator transformation (*34–37, 39, 40*) is very effective for the theoretical investigations in vibration–rotation spectroscopy. The results obtained are essential for further solution of the

TABLE XV

Comparison of the Spectroscopic Parameters for ν_2, ν_4 Bands of $^{12}CD_4$ Obtained in Refs. (*16*) and (*15*)

λ^n	$U_{k,m}^{\Omega(K,\Gamma)}$		Parameters from (16)	Reduced values	Parameters from (15)	weight
	k,m	Ω(K,Γ)				
λ^0	2,2	0	1543.8429	1543.8429	1543.836	0
	4,4	0	1728.3752	1728.3752	1728.372	
λ^1	4,4	$1(1,F_1)$	-2.21835	-2.2191	-2.2197	1
	2,4	$1(1,F_1)$	3.060	3.075	3.075	
λ^2	2,2	$2(2,E)$	$-7.061\ 10^{-3}$	$-6.828\ 10^{-3}$	$-6.87\ 10^{-3}$	10
	2,2	$2(0,A_1)$	$0.389\ 10^{-3}$	$0.772\ 10^{-3}$	$0.85\ 10^{-3}$	
	4,4	$2(0,A_1)$	$-0.136\ 10^{-3}$	$-0.448\ 10^{-3}$	$-0.35\ 10^{-3}$	
	4,4	$2(2,E)$	$-2.624\ 10^{-3}$	$-3.048\ 10^{-3}$	$-2.98\ 10^{-3}$	
	4,4	$2(2,F_2)$	$-6.070\ 10^{-3}$	$-6.229\ 10^{-3}$	$-6.43\ 10^{-3}$	
	2,4	$2(2,F_2)$	$-9.78\ 10^{-3}$	$-0.04\ 10^{-3}$	0	
λ^3	2,2	$3(3,A_2)$	$1.66\ 10^{-5}$	$2.739\ 10^{-4}$	$2.859\ 10^{-4}$	10^2
	4,4	$3(1,F_1)$	$-3.85\ 10^{-5}$	$-2.524\ 10^{-4}$	$-2.614\ 10^{-4}$	10^2
	4,4	$3(3,F_1)$	$-0.68\ 10^{-5}$	$-2.097\ 10^{-4}$	$-2.145\ 10^{-4}$	10^2
	2,4	$3(1,F_1)$	$3.98\ 10^{-5}$	$-0.01\ 10^{-5}$	0	$5\cdot10^2$
	2,4	$3(3,F_1)$	$-0.79\ 10^{-5}$	$-0.03\ 10^{-5}$	0	10^3
	2,4	$3(3,F_2)$	$0.94\ 10^{-5}$	$0.02\ 10^{-5}$	0	10^3
λ^4	2,2	$4(0,A_1)$	0	$1.49\ 10^{-6}$	$1.56\ 10^{-6}$	$2.5\cdot10^3$
	2,2	$4(4,A_1)$	0	$-2.50\ 10^{-6}$	$-2.36\ 10^{-6}$	
	2,2	$4(2,E)$	0	$-0.85\ 10^{-6}$	$-0.77\ 10^{-6}$	
	2,2	$4(4,E)$	0	$3.15\ 10^{-6}$	$3.26\ 10^{-6}$	
	4,4	$4(0,A_1)$	0	$-1.34\ 10^{-6}$	$-0.83\ 10^{-6}$	
	4,4	$4(4,A_1)$	0	$2.06\ 10^{-6}$	$1.80\ 10^{-6}$	
	4,4	$4(2,E)$	0	$1.88\ 10^{-6}$	$1.12\ 10^{-6}$	
	4,4	$4(4,E)$	0	$-0.75\ 10^{-6}$	$-0.33\ 10^{-6}$	
	4,4	$4(2,F_2)$	0	$4.67\ 10^{-6}$	$2.12\ 10^{-6}$	
	4,4	$4(4,F_2)$	0	$-0.31\ 10^{-6}$	$0.53\ 10^{-6}$	

inverse vibrational problem and for the description of higher excited rovibrational states. The construction of the spectroscopic parameters for isotopically substituted molecules and for series of similar molecules is of special interest. Further developments must include the comparison of the intensities along with the comparison of the spectral parameters, i.e., the consideration of the corresponding transformation of the transition operator. The natural extension of the present work is the comparative analysis of the spectroscopic parameters for other vibrational bands and polyads. Comparison of ν_1, ν_3 resonance models for SiH_4 and GeH_4 have been done by the present authors up to λ^4 (*41*). For the isolated ν_4 state the study made earlier up to λ^4 (*35*) is generalized up to λ^6 (*42*) taking into account the most recent experimental data. Natural extension is to consider the spectroscopic parameters for the pentad treatments (*10, 11*).

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