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Reduced Effective Hamiltonians for Degenerate Vibrational States of Methane-Type Molecules[1]

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The ambiguity of effective Hamiltonians for the fundamental degenerate states of the methane-type molecules is studied. The transformations of these Hamiltonians to reduced forms which include only empirically determinable parameters are suggested. The set of parameters fitted by Champion and Pierre for the ν_4 band of CH_4 (*J. Mol. Spectrosc.* **79**, 225–280 (1980)) is found to be related to the set of parameters of Husson and Poussigue (*J. Phys.* **32**, 859–865 (1971)) by the unitary transformation of the effective Hamiltonian.

1. INTRODUCTION

The effective Hamiltonians are widely used in molecular spectroscopy for the interpretation of the vibration–rotation spectra. Their construction is an ambiguous procedure (*1, 2*) due to the existence of unitary transformations which change the effective Hamiltonian but do not change its eigenvalues. As a consequence of this ambiguity, it may happen that some parameters of effective Hamiltonians cannot be recovered from experimental data in a unique way. The type of admissible transformations which keeps the operator form of the effective Hamiltonian unaltered and the number of empirically determinable parameters strongly depend on the symmetry type of a molecule (asymmetric top, spherical top, and so on) and on the degeneracy of the vibrational state.

Up to now an elaborate treatment of the problem has been performed mostly for the cases of nondegenerate isolated (*3, 4*) or interacting (*5–7*) vibrational states. For asymmetric top molecules, Watson (*3*) has proposed to eliminate an ambiguity in a pure rotational effective Hamiltonian by the transformation to the so-called reduced Hamiltonian $\mathbf{H}^{\mathrm{red}}$. The latter includes only empirically determinable parameters and is used for this reason in most papers for a fit of experimental data. As was shown in Ref. (*4*), for nondegenerate vibrational states of spherical top molecules there are also "removable terms" in the effective rotational Hamiltonian. However, in this case the problem is not so urgent for practical applications as for asymmetric top molecules since the ambiguity appears (*4*) in very high orders of the expansion of $\mathbf{H}_{\mathrm{rot}}$ starting from the terms $\mathbf{J}^{12}$, which now are not yet available from the fit of experimental data. Reduced effective Hamiltonians for resonating states of asymmetric top molecules

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was recently introduced for Coriolis (*5, 7*) and anharmonic (*6, 7*) accidental resonances as well.

In Ref. (*8*) the ambiguity of spectroscopic parameters of spherical top molecules including the case of interacting E and F_2 states has been briefly considered. In the present paper we consider effective Hamiltonians for doubly and triply degenerate states of spherical top molecules in more detail. It is shown that the unitary transformations exist which change the values of the parameters associated with $\mathbf{q}^2\mathbf{J}^7$ terms (for E states) or with $\mathbf{q}^2\mathbf{J}^4$ terms (for F_2 states) but do not change the operator form of the effective Hamiltonians for T_d molecules. It means that the effective Hamiltonians which were derived by perturbation treatment using symmetry requirements contain more parameters than can be obtained from experimental data. Unlike the case of nondegenerate states, this type of ambiguity for triply degenerate states is of importance at present for interpretation of the experimental data. It appears to be the origin of the inconsistencies between the values of the spectroscopic parameters derived by different authors from the same experimental information. Some of the $\mathbf{q}^2\mathbf{J}^4$-type parameters by Husson and Poussigue (*10*) for the ν_4 state of $^{12}CH_4$ are essentially different from those of Champion and Pierre (*11*) but may be related by the considered unitary transformations.[2]

The reduced effective Hamiltonians which have the smaller number of adjustable parameters are suggested for the E and F_2 states of methane-type molecules.

2. EFFECTIVE HAMILTONIAN

We use the representation of the effective Hamiltonian in terms of irreducible tensor operators of T_d point group (*9*). The effective Hamiltonian for a degenerate vibrational state s may be written[3]

$$\mathcal{H} = \sum_{\Omega,K,n,\Gamma} t^{\Omega(K,n\Gamma)\Gamma_s\Gamma_s}_{s,s} \mathbf{T}^{\Omega(K,n\Gamma)\Gamma_s\Gamma_s}_{s,s} \qquad (1)$$

where

$$\mathbf{T}^{\Omega(K,n\Gamma)\Gamma_s\Gamma_s}_{s,s} = ({}^{(-1)^K}\mathbf{V}^{\Gamma_s\Gamma_s(\Gamma)}_{s,s} \times \mathbf{R}^{\Omega(K,n\Gamma)})^{A_1}. \qquad (2)$$

In this paper we restrict ourselves to the case of the states with one excited vibrational quantum like 0100, 0010, and 0001 in tetrahedral XY_4 molecules. A projector operator on one of this states will be denoted by the symbol $\mathbf{P}_1$.

We use the standard notations of Ref. (*9*). The rotational tensor $\mathbf{R}^{\Omega(K,n\Gamma)}$ introduced by Moret-Bailly (*13*) is a polynomial in J_x, J_y, J_z of degree Ω; the index K is the rank with respect to 0(3) group and Γ is the irreducible representation of the point symmetry group. The vibrational tensor ${}^{(-1)^K}\mathbf{V}^{\Gamma_s\Gamma_s(\Gamma)}_{s,s}$ is obtained by the coupling of the creation and annihilation operators $\mathbf{a}_s^+$ and $\mathbf{a}_s$. Explicit definition of this tensor has been given in Ref. (*11*). We use the following definition of tensor operator $\mathbf{T}^{\Omega(0,A_1)\Gamma\Gamma}$ according to Ref. (*11*):

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

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[2] It should be noted that in both papers the experimental data by Botineau (*12*) were used in the fits.

[3] For a fit of experimental energies of an isolated vibrational state it is sufficient to consider effective Hamiltonian on a subspace $\mathbf{P}\mathcal{H}\mathbf{P}$ where $\mathbf{P}$ are associated projectors, whereas the operator (1) contributes to overtones as well.

The irreducible tensors included in the effective Hamiltonian for the first few degenerate vibrational states are listed in Table I. The parameters are given up to the rotational degree which possesses some ambiguity.

3. EFFECTIVE HAMILTONIAN AMBIGUITY

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

$$\tilde{\mathcal{H}} = \cdots \exp(i\mathcal{S})\mathcal{H}\exp(-i\mathcal{S}) \cdots \tag{3}$$

which change coefficients rather than the operators included in the effective Hamiltonian. The generators $\mathcal{S}$ of these unitary transformations must fulfill the following conditions:

$\mathcal{S}$ should be small,
$\mathcal{S}$ should be hermitian,
$\mathcal{S}$ should be imaginary (change the sign under the time reversal),
$\mathcal{S}$ should be totally symmetric under operation of symmetry group (T_d group for the problem considered).
$\mathcal{S}$ may be written as

$$\mathcal{S} = \sum_{\Omega,K,n,\Gamma} s_{s,s}^{\Omega(K,n\Gamma)\Gamma_s\Gamma_s} \mathbf{S}_{s,s}^{\Omega(K,n\Gamma)\Gamma_s\Gamma_s}$$

where

$$\mathbf{S}_{s,s}^{\Omega(K,n\Gamma)\Gamma_s\Gamma_s} = \left({}^{(-1)^{K-1}}\mathbf{V}_{s,s}^{\Gamma_s\Gamma_s(\Gamma)} \times \mathbf{R}^{\Omega(K,n\Gamma)}\right)^{A_1}. \tag{4}$$

The conditions mentioned above lead to some relations between the type of the vibrational operator ${}^{(-1)^{K-1}}\mathbf{V}_{s,s}^{\Gamma_s\Gamma_s(\Gamma)}$ and the rank K of the rotational tensor $\mathbf{R}^{\Omega(K,n\Gamma)}$ (see

TABLE I

Parameters of Effective Hamiltonians for First Excited States of Degenerate Vibrations
(The outlined parameters possess some ambiguity)

$\Gamma_s = E$		$\Gamma_s = F_2$	
$s = 2$		$s = 3,4$	
$\Omega(K,n\Gamma)$		$\Omega(K,n\Gamma)$	
$0(0,A_1)$	$6(0,A_1)$	$0(0,A_1)$	$4(0,A_1)$
$2(0,A_1)$	$6(2,E)$	$1(1,F_1)$	$4(4,A_1)$
$2(2,E)$	$6(4,A_1)$	$2(0,A_1)$	$4(2,E)$
$3(3,A_2)$	$6(4,E)$	$2(2,E)$	$4(2,F_2)$
$4(0,A_1)$	$6(6,A_1)$	$2(2,F_2)$	$4(4,E)$
$4(2,E)$	$6(6,E)$	$3(1,F_1)$	$4(4,F_2)$
$4(4,A_1)$	$7(3,A_2)$	$3(3,F_1)$	
$4(4,E)$	$7(7,A_2)$		
$5(3,A_2)$			

Table II). Table II enables one to find all independent parameters of the $\mathcal{S}$ generators. They are given in Table III up to sixth power in angular momentum.

It is well known that unitary transformations do not change the eigenvalues of a Hamiltonian. The transformed Hamiltonian may just as well be used as an effective one for the problem considered. Usually, the effective Hamiltonian is written in terms of power series expansion in angular momentum operators. Only a finite number of terms (up to the chosen order of magnitude) is taken into account. The unitary transformation may yield some contributions to the neglected terms but these contributions must be of the same order or smaller with respect to the neglected terms. Only such unitary transformations are admissible. The order of magnitude of the $\mathcal{S}$-generator terms must be chosen taking into account the above requirements. It should be noted that the transformation (3) with the generators (4) may generally change the form of the effective Hamiltonian due to the terms $\mathbf{T}_{ss,ss}^{\Omega(K,n\Gamma)\Gamma'\Gamma''}$, $\mathbf{T}_{sss,sss}^{\Omega(K,n\Gamma)\Gamma'\Gamma''}$, etc. in the transformed operator. In this paper, we do not take these terms into account since they do not contribute to the frequencies of the fundamental bands considered:

$$\mathbf{P}_1 \mathbf{T}_{ss,ss}^{\Omega(K,n\Gamma)\Gamma'\Gamma''} \mathbf{P}_1 = 0,$$

$$\mathbf{P}_1 \mathbf{T}_{sss,sss}^{\Omega(K,n\Gamma)\Gamma'\Gamma''} \mathbf{P}_1 = 0, \text{ etc.}$$

4. THE SCHEME OF THE REDUCTION

Let us now consider the transformation of the effective Hamiltonian to a reduced form. We apply the Hausdorff formula to Eq. (3):

TABLE II

Relations between the Type of the Vibrational Operator ${}^{(-1)^{K-1}}\mathbf{V}_{s,s}^{\Gamma_s\Gamma_s(\Gamma)}$ and the rank K of the Rotational Operator $\mathbf{R}^{\Omega(K,n\Gamma)}$ in $\mathbf{S}_{s,s}^{\Omega(K,n\Gamma)\Gamma_s\Gamma_s}$

$\Gamma_s = E$ $s = 2$	$\Gamma_s = F_2$ $s = 3,4$
K - even	
${}^{(-1)}V_{2,2}^{EE(A_2)}$	${}^{(-1)}V_{s,s}^{F_2F_2(F_1)}$
K - odd	
$V_{2,2}^{EE(A_1)}$	$V_{s,s}^{F_2F_2(A_1)}$
$V_{2,2}^{EE(E)}$	$V_{s,s}^{F_2F_2(E)}$
	$V_{s,s}^{F_2F_2(F_2)}$

TABLE III

Independent Parameters of $\mathscr{S}$ Generator up to Sixth Power in Angular Momentum

$\Gamma_s = E$ $s = 2$	$\Gamma_s = F_2$ $s = 3,4$
$\Omega(K,n\Gamma)$	$\Omega(K,n\Gamma)$
5 (5,E)	3 (3,F_2)
6 (6,A_2)	4 (4,F_1)
	5 (3,F_2)
	5 (5,E)
	5 (5,F_2)
	6 (4,F_1)
	6 (6,F_1)

$$\tilde{\mathscr{H}} = \mathscr{H} + [i\mathscr{S}, \mathscr{H}] + \frac{1}{2!}[i\mathscr{S}, [i\mathscr{S}, \mathscr{H}]] + \cdots . \tag{5}$$

The main contributions to the parameters of the $\tilde{\mathscr{H}}$ may be written as

$$\tilde{t} = t + \sum_i c_i s_i t_i \tag{6}$$

where c_i are the coefficients arising from the commutator calculation, t_i are the Hamiltonian parameters, and s_i are the free parameters of the $\mathscr{S}$ generator.

The relation (6) shows that the ambiguity in the effective Hamiltonian parameters is due to the existence of free s parameters in $\mathscr{S}$ generators.

To calculate the coefficients in Eq. (6) it is sufficient to consider the single commutator $[i\mathscr{S}, \mathscr{H}]$, which is given by

$$\begin{aligned} &Z[(\mathbf{V}^{\Gamma} \times \mathbf{R}^{\Omega(K,n\Gamma)})^{A_1}, (\mathbf{V}^{\Gamma'} \times \mathbf{R}^{\Omega'(K',n'\Gamma')})^{A_1}] \\ &\quad = \frac{1}{2} Z \sum_x \sqrt{\frac{[x]}{[\Gamma][\Gamma']}} \{[\mathbf{V}^{\Gamma}, \mathbf{V}^{\Gamma'}]^x_- \times [\mathbf{R}^{\Omega(K,n\Gamma)}, \mathbf{R}^{\Omega'(K',n'\Gamma')}]^x_+\}^{A_1} \\ &\quad + \frac{1}{2} Z \sum_x \sqrt{\frac{[x]}{[\Gamma][\Gamma']}} \{[\mathbf{V}^{\Gamma}, \mathbf{V}^{\Gamma'}]^x_+ \times [\mathbf{R}^{\Omega(K,n\Gamma)}, \mathbf{R}^{\Omega'(K',n'\Gamma')}]^x_-\}^{A_1}, \end{aligned} \tag{7}$$

$$Z = is^{\Omega(K,n\Gamma)} t^{\Omega'(K',n'\Gamma')}.$$

The definition of the tensor commutator and the details of the calculation of the rotation and vibration commutators and anticommutators are discussed in the Appendix. If one of the $(\mathbf{V} \times \mathbf{R})$ operators in Eq. (7) is a purely rotational one, the vibrational commutators in Eq. (7) are to be omitted.

The commutator of $\mathbf{S}^{5(5,E)EE}_{2,2}$ generator with the $\mathbf{T}^{2(2,E)EE}_{2,2}$ term of the Hamiltonian is the first nonzero one for the doubly degenerate vibrational E state. The commutator

$[\mathbf{S}_{s,s}^{3(3,F_2)F_2F_2}, \mathbf{T}_{s,s}^{1(1,F_1)F_2F_2}]$ ($s = 3, 4$) is the first nonzero one for the triply degenerate vibrational F_2 states.

Let us now consider the orders of magnitude. The terms of the initial Hamiltonians have the following correspondence between the order of magnitude and the power of the vibrational and rotational operators

$$t_0^{\Omega}\mathbf{R}^{\Omega} \sim \lambda^{\Omega-2}\omega, \qquad t^{\Omega}\mathbf{R}^{\Omega} \sim \lambda^{\Omega}\omega \qquad \text{for} \qquad J \sim \lambda^{-1}. \tag{8}$$

So, the order of magnitude of terms in Eq. (7) is

$$\begin{aligned} s^{\Omega}t^{\Omega'}\{[\mathbf{V}^{\Gamma}, \mathbf{V}^{\Gamma'}]_-^x \times [\mathbf{R}^{\Omega}, \mathbf{R}^{\Omega'}]_+^x\}^{A_1} &\sim s^{\Omega}t^{\Omega'}\mathbf{R}^{\Omega+\Omega'}, \\ s^{\Omega}t^{\Omega'}\{[\mathbf{V}^{\Gamma}, \mathbf{V}^{\Gamma'}]_+^x \times [\mathbf{R}^{\Omega}, \mathbf{R}^{\Omega'}]_-^x\}^{A_1} &\sim s^{\Omega}t^{\Omega'}\mathbf{R}^{\Omega+\Omega'-1}. \end{aligned} \tag{9}$$

We can choose s^{Ω} in such a way that $s^{\Omega}t^{\Omega'} \sim t^{\Omega+\Omega'}$. Then the rotational commutator in Eq. (9) gives only small correction to $t^{\Omega+\Omega'-1}$ parameter, because $s^{\Omega}t^{\Omega'}/t^{\Omega+\Omega'-1} \sim t^{\Omega+\Omega'}/t^{\Omega+\Omega'-1} \sim \lambda^2$. It is impossible to take s^{Ω} so large that $s^{\Omega}t^{\Omega'} \sim t^{\Omega+\Omega'-1}$ because the contribution of the rotational anticommutator to the Hamiltonian term $s^{\Omega}t^{\Omega'}\mathbf{R}^{\Omega+\Omega'}$ in Eq. (9) becomes greater than the term $t^{\Omega+\Omega'-1}\mathbf{R}^{\Omega+\Omega'-1}$ arising in smaller order of perturbation theory

$$\frac{t^{\Omega+\Omega'-1}\mathbf{R}^{\Omega+\Omega'-1}}{s^{\Omega}t^{\Omega'}\mathbf{R}^{\Omega+\Omega'}} \sim \frac{\mathbf{R}^{\Omega+\Omega'-1}}{\mathbf{R}^{\Omega+\Omega'}} \sim \lambda.$$

It should be noted also that the commutators of **S** generators with diagonal terms $t_0^{\Omega(K,A_1)}\mathbf{T}_0^{\Omega(K,A_1)}$ of the Hamiltonian do not change the order of magnitude in the expansion of the transformed Hamiltonian. It is sufficient to consider the first nonzero commutator

$$s^{\Omega}t_0^{4(4,A_1)}[\mathbf{S}^{\Omega}, \mathbf{T}_0^{4(4,A_1)}]_- \sim s^{\Omega}t_0^{4(4,A_1)}\mathbf{R}^{\Omega+3}.$$

s^{Ω} is chosen to satisfy $s^{\Omega}t^{\Omega'} \sim t^{\Omega+\Omega'}$, therefore, we have

$$\frac{s^{\Omega}t_0^{4(4,A_1)}}{t^{\Omega+3}} \sim \frac{t^{\Omega+\Omega'}t_0^{4(4,A_1)}}{t^{\Omega'}t^{\Omega+3}} \sim \frac{\lambda^{2(\Omega+\Omega')}\lambda^6}{\lambda^{2\Omega'}\lambda^{2(\Omega+3)}} \sim 1.$$

So the contribution $s^{\Omega}t_0^{4(4,A_1)}\mathbf{R}^{\Omega+3}$ from the commutator considered and the corresponding term $t^{\Omega+3}\mathbf{R}^{\Omega+3}$ of the Hamiltonian have the same order of magnitude.

The following scheme of reduction may be proposed taking into account the order of magnitude analysis carried out above.

By the appropriate choice of the free s parameters in Eq. (6) one may eliminate (or fix to a given value) some parameters in the transformed Hamiltonian. To derive Eq. (6) explicitly, it is sufficient to consider only vibrational commutator term in Eq. (7) if both **S** and **T** operators in commutator are vibration–rotation ones. The term with rotational commutator becomes important if one of the operators **S** or **T** is purely rotational.

5. REDUCTION OF THE EFFECTIVE HAMILTONIAN FOR VIBRATIONAL *E* STATE

According to the scheme considered, the existence of the free parameter $s_{2,2}^{5(5,E)EE}$ in the generator $\mathcal{S}$ (Table III) results in the ambiguity of the parameters $t_{2,2}^{7(3,A_2)EE}$ and $t_{2,2}^{7(7,A_2)EE}$. The following commutator is responsible for the variation of this parameter:

$$[is_{2,2}^{5(5,E)EE}\mathbf{S}_{2,2}^{5(5,E)EE}, t_{2,2}^{2(2,E)EE}\mathbf{T}_{2,2}^{2(2,E)EE}]. \tag{10}$$

Straightforward calculation of the commutator (10) yields the following relation between parameters of the initial and transformed Hamiltonians:

$$\tilde{t}_{2,2}^{7(3,A_2)EE} = t_{2,2}^{7(3,A_2)EE} + \frac{2}{11}\sqrt{\frac{5}{3}}\,Z,$$

$$\tilde{t}_{2,2}^{7(7,A_2)EE} = t_{2,2}^{7(7,A_2)EE} + \sqrt{\frac{15}{154}}\,Z,$$

$$Z = s_{2,2}^{5(5,E)EE} t_{2,2}^{2(2,E)EE}. \tag{11}$$

Equations (11) include one free parameter $s_{2,2}^{5(5,E)EE}$. So only one parameter, rather than two, is independent among the $\mathbf{q}^2\mathbf{J}^7$ terms of the effective Hamiltonian. To eliminate the ambiguity we may fix one of these parameters to zero or to another given value, for example, to the value derived by perturbation calculation.

If one has two equivalent sets of the parameters $\{t_{2,2}^{7(K,A_2)EE}\}$ and $\{\tilde{t}_{2,2}^{7(K,A_2)EE}\}$, it is evident from Eqs. (11) that the parameter $s_{2,2}^{5(5,E)EE}$ of unitary transformation (4) which connects the associated Hamiltonians $\mathscr{H}$ and $\tilde{\mathscr{H}}$ has the form

$$s_{2,2}^{5(5,E)EE} = \frac{11}{2}\sqrt{\frac{3}{5}}\,\frac{\tilde{t}_{2,2}^{7(3,A_2)EE} - t_{2,2}^{7(3,A_2)EE}}{t_{2,2}^{2(2,E)EE}}. \tag{12}$$

By eliminating the free parameter $s_{2,2}^{5(5,E)EE}$ from Eq. (11) we immediately obtain the linear relationship between the parameters $\tilde{t}_{2,2}^{7(7,A_2)EE}$ and $\tilde{t}_{2,2}^{7(3,A_2)EE}$:

$$\tilde{t}_{2,2}^{7(7,A_2)EE} = t_{2,2}^{7(7,A_2)EE} + \frac{3\sqrt{11}}{2\sqrt{14}}\left(\tilde{t}_{2,2}^{7(3,A_2)EE} - t_{2,2}^{7(3,A_2)EE}\right). \tag{13}$$

So, the reduced Hamiltonian for vibrational E state includes only one independent parameter associated with seventh power rotational operators.

6. REDUCTION OF THE EFFECTIVE HAMILTONIAN FOR A VIBRATIONAL F_2 STATE ($s = 3, 4$)

The existence of the free parameter $s_{s,s}^{3(3,F_2)F_2F_2}$ in $\mathscr{S}$ generator (Table III) results in an ambiguity of $t_{s,s}^{4(K,\Gamma)F_2F_2}$ ($\Gamma \neq A_1$) parameters. The change of these parameters is due to the commutator

$$[is_{s,s}^{3(3,F_2)F_2F_2}\mathbf{S}_{s,s}^{3(3,F_2)F_2F_2},\ t_{s,s}^{1(1,F_1)F_2F_2}\mathbf{T}_{s,s}^{1(1,F_1)F_2F_2}]. \tag{14}$$

The calculation of the expression (14) yields the following relations between the parameters of the initial and transformed operators:

$$\tilde{t}_{s,s}^{4(2,E)F_2F_2} = t_{s,s}^{4(2,E)F_2F_2} - \frac{\sqrt{2}}{7}\,Y,$$

$$\tilde{t}_{s,s}^{4(4,E)F_2F_2} = t_{s,s}^{4(4,E)F_2F_2} + \sqrt{\frac{2}{21}}\,Y,$$

$$\tilde{t}_{s,s}^{4(2,F_2)F_2F_2} = t_{s,s}^{4(2,F_2)F_2F_2} + \frac{\sqrt{2}}{7}\,Y,$$

$$\tilde{t}_{s,s}^{4(4,F_2)F_2F_2} = t_{s,s}^{4(4,F_2)F_2F_2} + \frac{1}{2}\sqrt{\frac{3}{14}}\,Y,$$

$$Y = s_{s,s}^{3(3,F_2)F_2F_2}\,t_{s,s}^{1(1,F_1)F_2F_2}. \tag{15}$$

There is only one free parameter $s_{s,s}^{3(3,F_2)F_2F_2}$ in Eqs. (15). Consequently, there are three rather than four independent parameters $t_{s,s}^{4(K,\Gamma)F_2F_2}$ ($\Gamma \neq A_1$). To obtain the reduced Hamiltonian it is necessary to fix one of these parameters to zero or to any given constant.

Analogously to the case of E vibrational state, if one has two equivalent sets of the parameters $\{t_{s,s}^{4(K,\Gamma)F_2F_2}\}$ and $\{\tilde{t}_{s,s}^{4(K,\Gamma)F_2F_2}\}$ ($\Gamma \neq A_1$) one can obtain from Eqs. (15) the parameter $s_{s,s}^{3(3,F_2)F_2F_2}$ of unitary transformation (3) which connects the associated Hamiltonians $\mathscr{H}$ and $\tilde{\mathscr{H}}$. The expression for this parameter has the form

$$s_{s,s}^{3(3,F_2)F_2F_2} = \frac{7}{\sqrt{2}}\,\frac{\tilde{t}_{s,s}^{4(2,F_2)F_2F_2} - t_{s,s}^{4(2,F_2)F_2F_2}}{t_{s,s}^{1(1,F_1)F_2F_2}}. \tag{16}$$

By eliminating the free parameter $s_{s,s}^{3(3,F_2)F_2F_2}$ from Eqs. (15) we derive the relationships among the parameters of the transformed Hamiltonian

$$\tilde{t}_{s,s}^{4(2,E)F_2F_2} = t_{s,s}^{4(2,E)F_2F_2} - (\tilde{t}_{s,s}^{4(2,F_2)F_2F_2} - t_{s,s}^{4(2,F_2)F_2F_2}),$$

$$\tilde{t}_{s,s}^{4(4,E)F_2F_2} = t_{s,s}^{4(4,E)F_2F_2} + \sqrt{\frac{7}{3}}\,(\tilde{t}_{s,s}^{4(2,F_2)F_2F_2} - t_{s,s}^{4(2,F_2)F_2F_2}),$$

$$\tilde{t}_{s,s}^{4(4,F_2)F_2F_2} = t_{s,s}^{4(4,F_2)F_2F_2} + \frac{\sqrt{21}}{4}\,(\tilde{t}_{s,s}^{4(2,F_2)F_2F_2} - t_{s,s}^{4(2,F_2)F_2F_2}). \tag{17}$$

The transformation considered may explain the essential difference between the parameters for the ν_4 band of methane given by Champion and Pierre (*11*) and by Husson and Poussique (*10*) (Table IV). Let us choose the parameter $s_{4,4}^{3(3,F_2)F_2F_2}$ of the generator in such a way that it transforms the value $t_{4,4}^{4(2,F_2)F_2F_2} = 7.49 \times 10^{-6}\ \mathrm{cm}^{-1}$ (*11*) to the value of $\tilde{t}_{4,4}^{4(2,F_2)F_2F_2} = 2.75 \times 10^{-6}\ \mathrm{cm}^{-1}$ (*10*), i.e., we make the transformation (3) with the generator

$$\mathscr{S} = 2.2912 \times 10^{-6}(\mathbf{V}_{4,4}^{F_2F_2(F_2)} \times \mathbf{R}^{3(3,F_2)})^{A_1}. \tag{18}$$

Under such transformation the parameters given in Ref. (*11*) are transformed to new values close to that given in Ref. (*10*) (Table IV). This transformation proves the "unitary equivalence" of Champion–Pierre parameters (*11*) and Husson–Poussique parameters (*10*).

7. DISCUSSION

The conclusion is that the parameters associated with the $\mathbf{q}^2\mathbf{J}^4$-type diagonal coupling terms in the effective Hamiltonian for F_2 states of T_d molecules are not constants for a given molecule and for a given vibrational state.[4] They are the functions of one free parameter as follows from Eqs. (15) or (17).

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[4] It is convenient here to distinguish between "diagonal coupling parameters" $t_{s,s}^{4(K,\Gamma)F_2F_2}$ ($\Gamma \neq A_1$) and the parameters $t_{s,s}^{4(K,A_1)F_2F_2}$ which are constants in fact and describe the vibrational dependence of D_0 and D_t quartic terms.

TABLE IV

Demonstration of Unitary Equivalence of Champion–Pierre (*11*) and Husson–Poussigue (*10*) Parameters for the ν_4 Band of Methane

$\Omega(K,n\Gamma)$ cm^{-1}	Champion and Pierre (1980)	Unitary transformed parameters	Husson and Poussigue (1971)
$0(0,A_1)$	310.735		1310.745
$1(1,F_1)$	10.2394		10.240
$2(0,A_1)$	5.177957		5.17679
$2(2,E)\times10^2$	8.3257		8.35
$2(2,F_2)\times10^2$	- 9.9891		- 10.05
$3(1,F_1)\times10^3$	2.0779		2.065
$3(3,F_1)\times10^3$	1.6861		1.75
$4(0,A_1)\times10^4$	- 1.08334		- 1.006
$4(4,A_1)\times10^6$	4.30		4.22
$4(2,E)\times10^6$	21.21	25.95	26.4
$4(2,F_2)\times10^6$	7.49	2.75	2.75
$4(4,E)\times10^6$	2.95	- 4.29	- 4.28
$4(4,F_2)\times10^6$	- 4.98	-10.41	- 10.45

This is not a special feature of Champion's formalism. Quite analogously the transformations (12) and (16) may be carried out within the formalism of Moret-Bailly (*13*) or within the formalism of Robiette *et al.* (*14*). The corresponding equations for the ψ, σ, τ, η parameters of Moret-Bailly (*13*) or for G_{220}, G_{224}, G_{244}, G_{246} parameters of Robiette *et al.* (*14*) can be derived by changing the notation in Eqs. (15) and (17) with the use of Table IV, Ref. (*11*).

In any formalism there are an infinite number of different sets of this four diagonal coupling $\mathbf{q}^2\mathbf{J}^4$-type parameter, which provide the same eigenvalues of an effective Hamiltonian. The set of Husson–Poussique parameters (*10*) and the set of Champion–Pierre parameters (*11*) correspond to different effective Hamiltonians which differ by their eigenfunctions. These sets of eigenfunctions are related by the transformations (3) and (4) with the generator (18).

This kind of ambiguity may be avoided if one uses the reduced effective Hamiltonian as illustrated in Table V. The reduced effective Hamiltonian for the F_2 vibrational state contains only three adjustable $\mathbf{q}^2\mathbf{J}^4$-type diagonal coupling parameters instead of four adjustable parameters in an unreduced Hamiltonian.

APPENDIX

The definition of the tensor *commutator* and *anticommutator*

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

TABLE V

Comparison of the q^2J^4-type Diagonal Coupling Parameters in Unreduced (Refs. (*10*, *11*)) and Reduced Effective Hamiltonians for the 0001 state of the CH_4 Molecule.

Fitted parameters of an unreduced Hamiltonian	Husson and Poussigue (1971)	Champion and Pierre (1980)
$t^{4(2,F_2)}$	2.75	7.49
$t^{4(2,E)}$	26.4	21.21
$t^{4(4,E)}$	-4.28	2.95
$t^{4(4,F_2)}$	-10.45	-4.98

Reduction

$\mathscr{H} \longrightarrow \tilde{\mathscr{H}}$

Recalculated parameters of the reduced Hamiltonian	$s^{3\,(3,F_2)F_2F_2}_{4,4} = -1.33 \times 10^{-6}$	$s^{3\,(3,F_2)F_2F_2}_{4,4} = -3.62 \times 10^{-6}$
$\tilde{t}^{4(2,F_2)}$	0	0
$\tilde{t}^{4(2,E)}$	29.15	28.70
$\tilde{t}^{4(4,E)}$	-8.48	-8.49
$\tilde{t}^{4(4,F_2)}$	-13.60	-13.56

Note. In the table we omit some indices assuming $t^{4(K,\Gamma)} \equiv t^{4(K,\Gamma)F_2F_2}_{4,4}$. The units of t parameters are 10^{-6} cm^{-1}. The version of the reduction is chosen with the term $(\mathbf{a}_4^+ \times \mathbf{a}_4)^{F_2} \times \mathbf{R}^{4(2,F_2)}$ removed from the Hamiltonian. The recalculation to the reduced Hamiltonian was done by the use of Eq. (17) where the parameter $\tilde{t}^{4(2,F_2)F_2F_2}_{4,4}$ was fixed to zero.

The factor $(-1)^{\Gamma+\Gamma_1+\Gamma_2}$ in this equation is due to the definition of product of tensorial operators

$$(A^{\Gamma_1} \times A^{\Gamma_2})^{\Gamma}_{\sigma} = [\Gamma]^{1/2} \sum_{\sigma_1\sigma_2} F^{\Gamma_1\Gamma_2\Gamma}_{\sigma_1\sigma_2\sigma} A^{\Gamma_1}_{\sigma_1} A^{\Gamma_2}_{\sigma_2}$$

and properties of vector-coupling coefficients F adapted to the tetrahedral symmetry (Ref. (*13*))

$$F^{\Gamma_2\Gamma_1\Gamma}_{\sigma_2\sigma_1\sigma} = (-1)^{\Gamma_1+\Gamma_2+\Gamma} F^{\Gamma_1\Gamma_2\Gamma}_{\sigma_1\sigma_2\sigma}.$$

Here $(-1)^{\Gamma} = 1$ when $\Gamma = A_1, E, F_2$ and $(-1)^{\Gamma} = -1$ when $\Gamma = A_2, F_1$. $[\Gamma]$ is the dimension of the Γ representation of the T_d group.

Calculation of the Commutators and Anticommutators of Rotational Tensor Operators

The calculation of the rotational commutators and anticommutators is done by the transformation of the product of rotational operators to standard operators (15, 16):

$$[\mathbf{R}^{\Omega_1(J_1,t_1\Gamma_1)}, \mathbf{R}^{\Omega_2(J_2,t_2\Gamma_2)}]_{\pm}^{x} = \frac{1}{\sqrt{[x]}} \sum_{t_3 J_3} \sum_{\delta} (1 \pm (-1)^{J_1+J_2+J_3}) \\ \times (-1)^{J_3}\sqrt{2J_3+1}\,K^{J_1J_2J_3}_{t_1\Gamma_1 t_2\Gamma_2 t_3 x}((J_1J_2|\}\delta J_3))\mathbf{R}^{\Omega_1+\Omega_2-\delta(J_3,t_3 x)}$$

This formula includes isoscalar coefficients $K^{J_1J_2J_3}_{t_1\Gamma_1t_2\Gamma_2t_3x}$ tabulated, for example, in Ref. (*9*) and genealogical coefficients $((J_1J_2|\}\delta J_3))$.

The genealogical coefficients $((J_1J_2|\}\delta J_3))$ were introduced by one of the authors (*15*, *16*) in order to express the tensor product of any number of standard operator $\mathbf{R}^{\Omega(K)}$ in terms of standard ones. The standard operators $\mathbf{R}^{\Omega(K)}$ introduced by Moret-Bailly (*13*) are defined by the relation

$$\mathbf{R}^{\Omega(K)} = [(\mathbf{R}^{1(1)} \times \mathbf{R}^{1(1)})^0 \times \cdots \times (\mathbf{R}^{1(1)} \times \mathbf{R}^{1(1)})^0 \times \underbrace{\mathbf{R}^{1(1)} \times \cdots \times \mathbf{R}^{1(1)}}_{K}]^{(K)}$$

where $\mathbf{R}^{1(1)}_{\alpha} = 2\mathbf{J}_{\alpha}$. The recoupling procedure enables one to express any tensor product of $\mathbf{R}^{\Omega(K)}$ in terms of the standard operators

$$[\mathbf{R}^{\Omega_1(J_1)} \times \mathbf{R}^{\Omega_2(J_2)}]^{J}_{p} = \sum_{\Omega} ((\Omega_1J_1, \Omega_2J_2|\}\Omega J))\mathbf{R}^{\Omega(J)}_{p}.$$

The result does not depend on the basis used. So the index p may correspond to spherical basis or to any subgroup symmetry adapted basis. The symbol $((\Omega_1J_1, \Omega_2J_2|\}\Omega J))$ may be written as $((\Omega_1J_1, \Omega_2J_2|\}\Omega_1 + \Omega_2 - \delta, J))$ and it is defined only when $\Omega_1 \geqslant J_1$, $\Omega_2 \geqslant J_2$, $\Omega \equiv \Omega_1 + \Omega_2 - \delta \geqslant J$, $\delta \geqslant 0$. This symbol is completely defined by the indexes J_1, J_2, J, and δ. So the indexes Ω_1, Ω_2 may be dropped:

$$((\Omega_1J_1, \Omega_2J_2|\}\Omega_1 + \Omega_2 - \delta, J)) \equiv ((J_1J_2|\}\delta J)).$$

The coefficient $((J_1J_2|\}\delta J))$ is symmetrical with respect to interchange of J_1 and J_2:

$$((J_1J_2|\}\delta J)) = ((J_2J_1|\}\delta J)).$$

Another property of this symbol is $((J_1J_2|\}\delta J)) \neq 0$ only when $|J_1 - J_2| \leqslant J \leqslant |J_1 + J_2|$.

A table of $((J_1J_2|\}\delta J))$ coefficients for small J_1 values is given in (15). The genealogical coefficients with $\delta = 0$, 1 are sufficient to calculate the main contributions to rotational commutators and anticommutators. For these coefficients general formulae may be given[5]:

$$((J_1J_2|\}0, J_1 + J_2 - 2\Delta)) = \left[\frac{3^{\Delta}(2\Delta - 1)!!J_1!(2J_1 - 2\Delta + 1)!!J_2!}{\Delta!(J_1 - \Delta)!(2J_1 - 1)!!(J_2 - \Delta)!(2J_2 - 1)!!} \\ \times \frac{(J_2 - 2\Delta - 1)!!(J_1 + J_2 - \Delta)!(2J_1 + 2J_2 - 4\Delta + 1)!!}{(J_1 + J_2 - 2\Delta)!(2J_1 + 2J_2 - 2\Delta + 1)!!}\right]^{1/2},$$

$$((J_1J_2|\}1, J_1 + J_2 - 1 - 2\Delta)) = -\left[\frac{3^{\Delta}(2\Delta + 1)!!J_1!(2J_1 - 2\Delta - 1)!!}{\Delta!(J_1 - \Delta - 1)!(2J_1 - 1)!!(J_2 - \Delta - 1)!} \\ \times \frac{J_2!(2J_2 - 2\Delta - 1)!!(J_1 + J_2 - \Delta)!(2J_1 + 2J_2 - 4\Delta - 1)!!}{(2J_2 - 1)!!(J_1 + J_2 - 2\Delta - 1)!(2J_1 + 2J_2 - 2\Delta - 1)!!}\right]^{1/2}.$$

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[5] We assume here that $(-1)!! \equiv 1$.

Thus the scheme of the rotational (anti)commutator calculation is completely defined. We give here the list of the rotational anticommutators used in the present work.

$$[\mathbf{R}^{3(3,F_2)}, \mathbf{R}^{1(1,F_1)}]_{+}^{4(2,E)} = \frac{3\sqrt{6}}{7}\,\mathbf{R}^{4(2,E)},$$

$$[\mathbf{R}^{3(3,F_2)}, \mathbf{R}^{1(1,F_1)}]_{+}^{4(2,F_2)} = \frac{6\sqrt{2}}{7}\,\mathbf{R}^{4(2,F_2)},$$

$$[\mathbf{R}^{3(3,F_2)}, \mathbf{R}^{1(1,F_1)}]_{+}^{4(4,E)} = -3\,\sqrt{\frac{2}{7}}\,\mathbf{R}^{4(4,E)},$$

$$[\mathbf{R}^{3(3,F_2)}, \mathbf{R}^{1(1,F_1)}]_{+}^{4(4,F_2)} = \frac{3\sqrt{3}}{\sqrt{14}}\,\mathbf{R}^{4(4,F_2)},$$

$$[\mathbf{R}^{5(5,E)}, \mathbf{R}^{2(2,E)}]_{+}^{7(3,A_2)} = \frac{8\sqrt{5}}{11\sqrt{3}}\,\mathbf{R}^{7(3,A_2)},$$

$$[\mathbf{R}^{5(5,E)}, \mathbf{R}^{2(2,E)}]_{+}^{7(7,A_2)} = \frac{2\sqrt{30}}{\sqrt{77}}\,\mathbf{R}^{7(7,A_2)}.$$

Calculation of the Commutators of Vibrational Tensor Operators

To calculate the vibrational commutators used in the present work one may take the formula

$$[(\mathbf{a}_i^{+} \times \mathbf{a}_i)^{\Gamma_1}, (\mathbf{a}_i^{+} \times \mathbf{a}_i)^{\Gamma_2}]_{-}^{\Gamma} = \{(-1)^{\Gamma} - (-1)^{\Gamma_1+\Gamma_2}\}\begin{Bmatrix}\Gamma_1 & \Gamma_2 & \Gamma \\ \Gamma_i & \Gamma_i & \Gamma_i\end{Bmatrix}\sqrt{[\Gamma_1][\Gamma_2]}(\mathbf{a}_i^{+} \times \mathbf{a}_i)^{\Gamma}$$

where $\begin{Bmatrix}\Gamma_1 & \Gamma_2 & \Gamma \\ \Gamma_i & \Gamma_i & \Gamma_i\end{Bmatrix}$ is the 6Γ symbol for the T_d group. From this formula one immediately obtains the vibrational commutators

$$[\mathbf{V}_{2,2}^{EE(E)}, \mathbf{V}_{2,2}^{EE(E)}]_{-}^{A_2} = -2\,{}^{(-1)}\mathbf{V}_{2,2}^{EE(A_2)},$$

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

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

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