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CONTACT TRANSFORMATIONS IN TENSOR FORMALISM. EFFECTIVE HAMILTONIAN AND DIPOLE MOMENT FOR THE ν_2, ν_4 DYAD OF TETRAHEDRAL MOLECULES

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Abstract—Simultaneous unitary transformations of the effective Hamiltonian and the effective dipole moment are studied via an irreducible tensor formalism for the ν_2, ν_4 dyad of tetrahedral molecules. Large unitary transformations relating resonance and isolated band models are treated by taking into account the non-leading contributions and multiple commutators. The unitary equivalence of different parameter sets of the effective dipole moment is explicitly shown for the ν_2, ν_4 bands of $^{12}CH_4$.

1. INTRODUCTION

Analysis of modern, high-resolution vibration–rotation spectra and conversion of the rich experimental data into useful molecular information usually involves the use of rather complicated effective tensor operators. The construction of these operators for quasi-degenerate vibrational states of spherical top molecules requires extensive use of symmetry properties.[1] The parameters of the effective operators are phenomenological spectroscopic parameters defined by experimental data fitting.

An important property of the effective operators is the existence of a special class of unitary transformations relating those operators that reproduce a given set of energy levels to the same accuracy.[2,3] Study of the parametric family of effective operators is frequently called ambiguity analysis.

We write the unitary transformation $\mathbf{U}$ of any effective tensor operator $\mathbf{X}$ in the following form:

$$\begin{cases} \mathbf{U}^{A_1} = \exp(i\mathbf{S}^{A_1}), \quad \mathbf{S}^{A_1} = \sum_j s_j \mathbf{S}_j^{A_1}, \\ \mathbf{X}^G = \sum_k x_k \mathbf{X}_k^G, \qquad \tilde{\mathbf{X}}^G = \sum_k \tilde{x}_k \mathbf{X}_k^G, \\ \tilde{\mathbf{X}}^G = (\mathbf{U}^{A_1})^{-1}\mathbf{X}^G(\mathbf{U}^{A_1}) = \mathbf{X}^G + [i\mathbf{S}^{A_1}, \mathbf{X}^G]_-^G + \tfrac{1}{2}[i\mathbf{S}^{A_1}, [i\mathbf{S}^{A_1}, \mathbf{X}^G]_-^G]_-^G + \cdots. \end{cases} \tag{1}$$

The operator $\mathbf{X}$ is transformed into $\tilde{\mathbf{X}}$ with a new set of phenomenological parameters $\tilde{x}_k$ instead of x_k. The upper indices in Eq. (1) designate the irreducible representation of the molecular symmetry group. In the transformation of the effective Hamiltonian, both the $\mathbf{U}$ and $\mathbf{S}$ operators are totally symmetric with respect to the molecular symmetry group. The parameters s_j of the unitary transformation should be sufficiently small to preserve the classification of the terms of the transformed $\tilde{\mathbf{H}}$ in the order of the smallness parameter.[3]

Calculation of the unitary transformations (1) for highly symmetrical spherical-top molecules may be greatly simplified by using specially developed methods for rovibrational tensor commutator calculations based on a graphical technique for angular momentum recoupling, the symmetrized form of Wick's theorem,[4,5] and general reduction of the tensor products of the rotational operators.[6,7] We apply this technique to a study of the ambiguity problem.

The ambiguity analysis of the effective operators for the widely studied ν_2, ν_4 dyad of spherical tops is of great importance. The ν_2, ν_4 states can be adequately described using various effective

model operators. Both the models of isolated ν_2, ν_4 and that of resonance ν_2, ν_4 are possible. Parameters of corresponding effective operators are strictly different. The family of effective Hamiltonians for the ν_2, ν_4 dyad has been studied in detail, and the unitary equivalence of various model Hamiltonians demonstrated.[8-11] Here, we present the theoretical analysis of effective model dipole-moment operators[12,14] used for quantitative (within 1–3%) description of absolute intensities of rovibrational transitions of the ν_2, ν_4 bands.

The transformation from the initial dipole moment to the effective moment is produced by the same unitary operator as that relating the complete and the effective Hamiltonians.[12,13] If the effective Hamiltonian possesses some ambiguity due to a parametric family of unitary transformations, the same unitary transformation should be applied to the effective dipole moment operator. Thus, we discuss in Sec. 2 the unitary transformation of the effective Hamiltonian. The analysis of the effective dipole moment is given in Sec. 3. We demonstrate in Sec. 3 that the effective dipole-moment operators[14] are unitarily equivalent.

It should be noted that we use in the present work the tensor operators $\mathbf{U}_{k,m}^{\Omega(K,G)}$, which were introduced in Ref. 10 and differ from $\mathbf{T}_{k,m}^{\Omega(K,G)}$, as defined by Champion,[1] by neglecting some numerical factors. Relations between the corresponding parameters u and t are given in detail in Ref. 10.

2. TRANSFORMATION OF THE EFFECTIVE MODEL HAMILTONIAN FOR THE ν_2, ν_4 DYAD

Use of the unitary transformations (1) requires the calculation of rovibrational commutators. The basic commutators are those of $[i\mathbf{S}, \mathbf{H}]$ type. These are calculated in Ref. 10 for the effective Hamiltonian of the ν_2, ν_4 dyad. Table II of Ref. 10 enables us to include all contributions to the transformed Hamiltonian $\tilde{\mathbf{H}}$ for operators of orders λ^1–λ^3, as well as the main contributions for the diagonal operators of order λ^4. At the same time, we may easily construct contributions from multiple commutators.

In the present paper, we limit ourselves to two important terms of the generator of the unitary transformation[9,10]

$$\mathbf{S}^{A_1} = s_{2,4}^{1(1,F_1)}\mathbf{S}_{2,4}^{1(1,F_1)} + s_{2,4}^{2(2,F_2)}\mathbf{S}_{2,4}^{2(2,F_2)}. \tag{2}$$

Parameters of the generator (2) are mainly due to the difference between the transformed and the initial parameters of the ν_2, ν_4 Coriolis coupling.[10] The value of the $s_{2,4}^{1(1,F_1)}$ parameter may be calculated (with an accuracy of about 1%) from the relation

$$\tilde{u}_{2,4}^{1(1,F_1)} - u_{2,4}^{1(1,F_1)} = -s_{2,4}^{1(1,F_1)}(\Delta + 6^{-1/2}u_{4,4}^{1(1,F_1)})$$

$$\Delta = 2^{-1/2}u_{2,2}^{0(0,A_1)} - 3^{-1/2}u_{4,4}^{0(0,A_1)} = \nu_2 - \nu_4. \tag{3}$$

Analysis of the main contributions to the operator $\mathbf{U}_{2,4}^{2(2,F_2)}$ allows us to write similar expressions for the second parameter of the generator. This procedure requires the calculation of the following commutators:

$$[is_{2,4}^{1(1,F_1)}\mathbf{S}_{2,4}^{1(1,F_1)}, u_{4,4}^{1(1,F_1)}\mathbf{U}_{4,4}^{1(1,F_1)}]_- + \left[is_{2,4}^{2(2,F_2)}\mathbf{S}_{2,4}^{2(2,F_2)}, \sum_{k=2,4} u_{k,k}^{0(0,A_1)}\mathbf{U}_{k,k}^{0(0,A_1)}\right]_-, \tag{4}$$

which leads to the expression

$$\tilde{u}_{2,4}^{2(2,F_2)} - u_{2,4}^{2(2,F_2)} = \Delta s_{2,4}^{2(2,F_2)} + (1/2)u_{4,4}^{1(1,F_1)}s_{2,4}^{1(1,F_1)}. \tag{5}$$

We determine from Eqs. (3, 5) the parameters of the generator (2) and describe the family of effective Hamiltonians with an accuracy up to λ^3–λ^4.

To investigate the variation of the diagonal λ^1–λ^3 parameters, we calculate the commutator[9-11]

$$[i\mathbf{S}_{2,4}^{1(1,F_1)}, \mathbf{U}_{2,4}^{1(1,F_1)}]_-. \tag{6}$$

Due to the large value of $\Delta \sim 100$–$200\,\mathrm{cm}^{-1}$, the resonance parameters are negligibly influenced by the nonleading contributions and contributions from multiple commutators. On the other hand,

taking into account these contributions to the diagonal parameters enables us to describe some important qualitative features of the parameter variation rather than simply increase the accuracy of calculation.[10] In particular, the variation of the diagonal Coriolis interaction parameter $u_{4,4}^{1(1,F_1)}$ is completely caused by the nonleading contribution from the commutator (6). Nonleading contributions are formed from terms of the general rovibrational commutators [see Eq. (7) of Ref. 7 and Appendices in Refs. 7–9] that include the commutators of the rotational operators. The nonleading contribution to the operator $\mathbf{U}_{4,4}^{1(1,F_1)}$ derived from the commutator (6) leads to the following relation:

$$\tilde{u}_{4,4}^{1(1,F_1)} - u_{4,4}^{1(1,F_1)} = (2/3)^{1/2} u_{2,4}^{1(1,F_1)} s_{2,4}^{1(1,F_1)}. \tag{7}$$

If the unitary transformation (1) is sufficiently large, the variations $\tilde{u}_{k,k}^{\Omega(K,G)} - u_{k,k}^{\Omega(K,G)}$ are essentially nonlinear due to large contributions from the multiple commutators. The most important multiple commutator for the λ^1–λ^2 parameters is

$$\frac{1}{2}\left[is_{2,4}^{1(1,F_1)} \mathbf{S}_{2,4}^{1(1,F_1)}, \left[is_{2,4}^{1(1,F_1)} \mathbf{S}_{2,4}^{1(1,F_1)}, \sum_{k=2,4} u_{k,k}^{0(0,A_1)} \mathbf{U}_{k,k}^{0(0,A_1)} \right]_- \right]_- = -(\Delta/2)(s_{2,4}^{1(1,F_1)})^2 [i\mathbf{S}_{2,4}^{1(1,F_1)}, \mathbf{U}_{2,4}^{1(1,F_1)}]_-. \tag{8}$$

Taking into account the double commutator (8), we describe properly the whole region of the $u_{4,4}^{1(1,F_1)}$ parameter variation

$$\tilde{u}_{4,4}^{1(1,F_1)} - u_{4,4}^{1(1,F_1)} = (2/3)^{1/2} u_{2,4}^{1(1,F_1)} s_{2,4}^{1(1,F_1)} - (\Delta/2)(2/3)^{1/2} (s_{2,4}^{1(1,F_1)})^2. \tag{9}$$

To verify Eq. (9), we use the analysis of the experimental data for the ν_2, ν_4 dyad of CH_4 given in Tables II and III of Ref. 11. The single interaction parameter $u_{2,4}^{1(1,F_1)}$ was used in these treatments and it was fixed at different values in a wide interval, thus giving interesting information about the parametric family of the effective Hamiltonians. Starting from the effective Hamiltonian for the isolated band model [$u_{2,4}^{1(1,F_1)} = 0$], we obtain from Eqs. (3, 9)

$$\begin{aligned} \tilde{u}_{4,4}^{1(1,F_1)} &= u_{4,4}^{1(1,F_1)} - (\Delta 6^{1/2})^{-1} (u_{2,4}^{1(1,F_1)})^2, \\ \tilde{t}_{4,4}^{1(1,F_1)} &= t_{4,4}^{1(1,F_1)} + (3\,\Delta 2^{1/2})^{-1} (t_{2,4}^{1(1,F_1)})^2. \end{aligned} \tag{10}$$

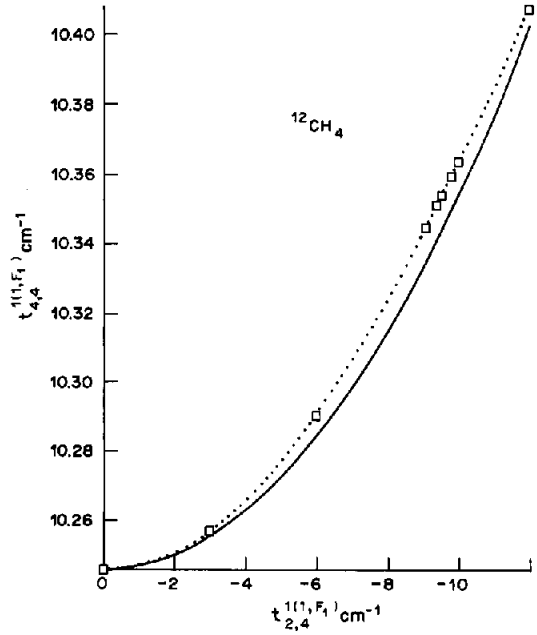

Fig. 1. Variation of $t_{4,4}^{1(1,F_1)}$ under transition from the isolated ν_2, ν_4 band model to the resonance ν_2, ν_4 model. The points are the values from Ref. 11. The solid line presents calculations from Eq. (10). The dotted line refers to empirical data.

Table 1. The family of effective Hamiltonians for the dyad ν_2, ν_4 of $^{12}CH_4$ according to Ref. 11. The table shows the variation of the parameter $t_{4,4}^{1(1,F_1)}$ and of invariant combinations under transition from the isolated ν_2, ν_4 model to the resonance model.

Parameter	Values of spectroscopic parameters in cm^{-1}						
$t_{2,4}^{1(1,F_1)}$	0.*	-3.*	-6.*	-9.1*	-9.52*	-10.*	-12.*
$t_{4,4}^{1(1,F_1)}$	10.2459	10.2571	10.2901	10.3445	10.3533	10.3634	10.4073
Eq.(10)	10.2459	10.2554	10.2840	10.3336	10.3418	10.3518	10.3984

Invariant	Values of invariant combinations in 10^{-1} cm^{-1}							maximum deviation
I_1'	-1.089	-1.083	-1.047	-1.026	-1.020	-1.013	-0.977	10%
I_4'	0.899	0.891	0.855	0.834	0.828	0.821	0.786	12%
Eq.(11)	0.0422	0.0424	0.0426	0.0427	0.0427	0.0426	0.0424	1%

Equation (10) is compared with data from Ref. 11 in Fig. 1 and in Table 1. It follows clearly that Eqs. (3) and (9) provide a quantitative description of the $u_{4,4}^{1(1,F_1)}$ variation.

The same approach but based on calculation of the double commutator (8) enables us to analyse the parametric family of the diagonal q^2J^2-operators. Equations (33) and (15) of Ref. 11 follow directly from the commutator (8). We may now introduce the coefficient $C_1^{1(1,F_1)} = 2^{1/2}/3$ in addition to those of Ref. 11 in order to characterize the variation of the $t_{4,4}^{1(1,F_1)}$ parameter.

Another example demonstrating the importance of nonleading contributions is the construction of invariant combinations of the spectroscopic parameters.[11,15] If only leading contributions are taken into account for the derivation of an invariant combination,[11] the resulting combination may vary within 10% as the result of a unitary transformation. Invariant combinations which take into account the nonleading contributions are generally rather complicated, except for the following combination of scalar parameters:[15]

$$I = (2/3)^{1/2}u_{2,2}^{2(0,A_1)} + u_{4,4}^{2(0,A_1)} = -(\alpha_2/2 + 3\alpha_4/4). \tag{11}$$

Using the notation of Sec. VII of Ref. 11, the invariant (11) has the form $I = -(2/9)(I_1' + I_4')$. As may be seen from Table 1, the proposed invariant combination (11), in contrast to I_1', I_4' etc., remains practically invariable under unitary transformations.

3. UNITARY TRANSFORMATION OF THE EFFECTIVE DIPOLE MOMENT OPERATOR FOR THE ν_2, ν_4 DYAD

Construction of the effective dipole-moment operator for the ν_2, ν_4 dyad of tetrahedral molecules is considered in Ref. 14 in detail. To simplify the tensor calculations, we use in this article the parameters $m_q^{\Omega(K,G)}$, which are defined as coefficients before corresponding tensor operators without any additional factors:

$$\mathbf{M}^{(F_2)} = \sum m_q^{\Omega(K,G)}\mathbf{M}_q^{\Omega(K,G)}; \quad \mathbf{M}_q^{\Omega(K,G)} = ({}^s a_q^{(G_q)}\mathbf{R}^{\Omega(K,G)})^{F_2}, \tag{12}$$

where $q = 2,4$; $s = (-)^K$ $^{\oplus}\mathbf{A} = \mathbf{A} + \mathbf{A}^+$ $^{\ominus}\mathbf{A} = i(\mathbf{A} - \mathbf{A}^+)$.

Comparison of Eq. (12) and of the tensor operators introduced by Loete[12,14] leads to the following relation betweem $m_q^{\Omega(K,G)}$ and the $\mu_{0,q}^{\Omega(K,G)(F_2)}$ parameters of Refs. 12, 14:

$$m_q^{\Omega(K,G)} = [G_q]^{-1/2}\mu_{0,q}^{\Omega(K,G)}. \tag{13}$$

To reproduce the experimental intensity data for the ν_2, ν_4 bands, Loete et al[14] use only three parameters for the effective dipole moment in the resonance-band treatment, whereas seven parameters of orders λ^0–λ^2 are introduced for the isolated-band model to take into account the mixing of the ν_2 and ν_4 states properly. Ambiguity of these parameters is due to the possibility of a unitary transformation with the generator (2).[16,17]

The unitary transformation of the effective dipole moment operator differs slightly from that of the effective Hamiltonian due to dipole-moment symmetry properties. The effective dipole moment is not totally symmetric in the molecule-fixed frame. For tetrahedral molecules, it has F_2-type symmetry. Therefore, the general expression for the irreducible tensor commutators is more complicated, viz.

$$\begin{aligned}[\mathbf{M}^{(G)}, \mathbf{S}^{(A_1)}]_-^G &= [(\mathbf{V}^{G_v}\mathbf{R}^{G_r})^G, (\mathbf{V}^{G_s}\mathbf{R}^{G_s})^{A_1}]_-^G \\ &= \tfrac{1}{2}(-)^{G_v+G_r+G}[G_s]^{-1/2}\sum_{G',G''}(-)^{G''}([G'][G''])^{1/2}\begin{pmatrix} G' & G'' & G \\ G_r & G_v & G_s \end{pmatrix} \\ &\quad\times([\mathbf{V}^{G_v}, \mathbf{V}^{G_s}]_-^{G'}[\mathbf{R}^{G_r}, \mathbf{R}^{G_s}]_+^{G''} + [\mathbf{V}^{G_v}, \mathbf{V}^{G_s}]_+^{G'}[\mathbf{R}^{G_r}, \mathbf{R}^{G_s}]_-^{G''})^G. \end{aligned} \tag{14}$$

A brief derivation of Eq. (14) is given in the Appendix. We use Eq. (14) to calculate the rovibrational commutator of the tensor operators, i.e.

$$[\mathbf{M}^{(G)}, \mathbf{S}^{(A_1)}]_-^G = [\mathbf{M}_q^{\Omega_r(K_r,G_r)}, \mathbf{S}_{p,t}^{\Omega_s(K_s,G_s)}]_-^G. \tag{15}$$

The vibrational part of the commutator (15) is

$$\begin{aligned}[\mathbf{a}_q^{(G_q)}, (\mathbf{a}_p^{+(G_p)}\mathbf{a}_t^{(G_t)})^{G_s}]_\pm^{G'} &= \delta_{qp}\delta_{G'G_t}[G_s]^{1/2}[G_t]^{-1/2}(-)^{G_p+G_s+G_t}\mathbf{a}_t^{(G_t)}(G_sG_pG_t) + \cdots, \\ [\mathbf{a}_q^{+(G_q)}, (\mathbf{a}_p^{+(G_p)}\mathbf{a}_t^{(G_t)})^{G_s}]_\pm^{G'} &= \pm\delta_{qp}\delta_{G'G_p}[G_s]^{1/2}[G_p]^{-1/2}\mathbf{a}_p^{+(G_p)}(G_sG_pG_t) + \cdots, \end{aligned} \tag{16}$$

where $(G_1G_2G_3)$ is the $3G$-triangle symbol that equals 1 if the G_1, G_2, G_3 satisfy the triangle condition and is zero otherwise. We write in Eq. (16) explicitly only the terms that are necessary for a description of the unitary transformation in the ν_2, ν_4 block: $q, p, t = 2, 4$. Calculation of the rotational commutator $[\mathbf{R}^{\Omega_r(K_r,G_r)}, \mathbf{R}^{\Omega_s(K_s,G_s)}]_\pm^{G''}$ is explained in detail in Appendix of Ref. 7. All rovibrational commutators necessary for a study of the effective dipole moment up to λ^2 terms are given in Table 2.

Table 2. The commutators $[i\mathbf{S}, \mathbf{M}]$ of the effective dipole moment and the generator of the unitary transformation for the ν_2, ν_4 block.

n	M / S	$\mathbf{S}_{2,4}^{1(1,F_1)}$	$\mathbf{S}_{2,4}^{2(2,F_2)}$
0†	$\mathbf{M}_4^{0(0,A_1)}$	$(3^{-\frac{1}{2}})\mathbf{M}_2^{1(1,F_1)}$	$-(3^{-\frac{1}{2}})\mathbf{M}_2^{2(2,F_2)}$
1	$\mathbf{M}_4^{1(1,F_1)}$	$-(6^{-\frac{1}{2}})\mathbf{M}_2^{1(1,F_1)} + (1/2)\mathbf{M}_2^{2(2,F_2)}$	
1	$\mathbf{M}_2^{1(1,F_1)}$	$(6^{-\frac{1}{2}})\mathbf{M}_4^{1(1,F_1)} + (1/3)\mathbf{M}_4^{2(0,A_1)} + (2^{\frac{1}{2}}/3)\mathbf{M}_4^{2(2,E)} - (3^{-\frac{1}{2}}/2)\mathbf{M}_4^{2(2,F_2)}$	

†Commutators in this row possess a trivial rotational part and are equivalent to that of Ref. 16.

Table 3. Unitary transformation of the effective dipole moment for the ν_2, ν_4 dyad, including terms up to λ^2; $Z = (3^{-1/2})m_4^{\Omega(A_1)} - (6^{-1/2})m_4^{1(1,F_1)}$.

n	$\mathbf{M}_q^{\Omega(K,G)}$ q $\Omega(K,G)$	contributions to $\tilde{m}_q^{\Omega(K,G)} - m_q^{\Omega(K,G)}$ from	
		$i[S,M]_-$	$(i^2/2)[S,[S,M]_-]_-$
0	4 $0(0,A_1)$	not transformed	
1	4 $1(1,F_1)$	$s_{2,4}^{1(1,F_1)}\, m_2^{1(1,F_1)}\,(6^{-\frac{1}{2}})$	$(s_{2,4}^{1(1,F_1)})^2 Z(6^{-\frac{1}{2}}/2)$
1	2 $1(1,F_1)$	$s_{2,4}^{1(1,F_1)}\, Z$	$(s_{2,4}^{1(1,F_1)})^2 m_2^{1(1,F_1)}\,(-1/12)$
2	4 $2(0,A_1)$	$s_{2,4}^{1(1,F_1)}\, m_2^{1(1,F_1)}\,(1/3)$	$(s_{2,4}^{1(1,F_1)})^2 Z(1/6)$
2	4 $2(2,E)$	$s_{2,4}^{1(1,F_1)}\, m_2^{1(1,F_1)}\,(2^{\frac{1}{2}}/3)$	$(s_{2,4}^{1(1,F_1)})^2 Z(2^{\frac{1}{2}}/6)$
2	4 $2(2,F_2)$	$s_{2,4}^{1(1,F_1)}\, m_2^{1(1,F_1)}\,(-3^{-\frac{1}{2}}/2)$	$(s_{2,4}^{1(1,F_1)})^2 Z(-3^{-\frac{1}{2}}/4)$
2	2 $2(2,F_2)$	$s_{2,4}^{1(1,F_1)}\, m_4^{1(1,F_1)}\,(1/2) - s_{2,4}^{2(2,F_2)}\, m_4^{0(0,A_1)}\,(3^{-\frac{1}{2}})$	$(s_{2,4}^{1(1,F_1)})^2 m_2^{1(1,F_1)}\,(6^{-\frac{1}{2}}/4)$

To describe the variation of the effective dipole-moment parameters properly under large unitary transformations from an isolated to a resonance model, multiple commutators must be taken into account. The most important of these is the double commutator with the operator $\mathbf{S}_{2,4}^{1(1,F_1)}$. The contributions from single and double commutators are listed in Table 3, which was obtained by using Table 2.

To verify the theoretical expressions, we compare the two effective dipole-moment operators of Ref. 14. We use the values of the S-generator parameters obtained in Ref. 10 for transformation from the resonance-band model[18] to the isolated-band model.[1] These values are typical for the transformation considered [see Table VIII of Ref. 10]. Without any adjustable parameters, we have transformed the resonance-band dipole moment to the isolated-band model using Table 3. Parameters of the operator obtained are given in the central column of Table 4. These are in reasonable agreement with that of the isolated-band model of Ref. 14, except for $m_4^{1(1,F_1)}$. The $m_4^{1(1,F_1)}$ variation under a unitary transformation is due to nonleading contributions only, which is of the same order as the variation of the λ^2 parameters. Therefore, the disagreement is probably caused by a very limited number of adjustable parameters in the resonance model of Ref. 14. Consequently, as follows from Table 4, the effective dipole moments for the resonance and the isolated band models are in essence unitary equivalents.

We present another form of the utilization of Table 3. We may study the dependence of the $m_q^{\Omega(K,G)}$ parameters on $u_{2,4}^{1(1,F_1)}$, which is easily obtained from Eqs. (3, 5) and Table 3. The results are given in Fig. 2, with the isolated-band parameters taken as the initial values. It should be noted that the effective parameters of the ν_4 band ($m_4^{\Omega(K,G)}$) behave quite differently from those of the ν_2 band ($m_2^{\Omega(K,G)}$). The $m_4^{\Omega(K,G)}$ parameters resemble the diagonal parameters of the Hamiltonian $u_{q,q}^{\Omega(K,G)}$, whereas the $m_2^{\Omega(K,G)}$ parameters resemble the nondiagonal interaction parameters $u_{q,p}^{\Omega(K,G)}$.

Table 4. Comparative analysis of parameters for the effective dipole moment for the ν_2, ν_4 bands of $^{12}CH_4$.

n	$M_q^{\Omega(K,G)}$ q $\Omega(K,G)$	resonance model from Ref.14	transformed values †	isolated model from Ref.14	D
0	4 0(0,A_1)	0.56216(57)	0.56216	0.56216(86)	10^{-1}
1	4 1(1,F_1)	-0.1778(63)	-0.1749	-0.1478(75)	10^{-3}
	2 1(1,F_1)	-0.1336(21)	0.684	0.658(10)	
2	4 2(0,A_1)	0‡	0.23	0.25(3)	10^{-5}
	4 2(2,E)	0‡	0.32	0.30(3)	
	4 2(2,F_2)	0‡	-0.20	-0.31(3)	
	2 2(2,F_2)	0‡	-1.58	-1.60(8)	

†Parameters of S-generator are taken from Table VIII of Ref. 10.
‡Fixed at zero value in Ref. 14.

Finally, Table 3 allows us to construct several simple invariant combinations of the effective dipole-moment parameters. These are:

$$I_4^1 = m_4^{2(0,A_1)} - 2^{-1/2} m_4^{2(2,E)},$$
$$I_4^2 = (1/2) m_4^{2(0,A_1)} + 3^{-1/2} m_4^{2(2,F_2)},$$
$$I_4^3 = (1/2) m_4^{2(2,E)} + (2/3)^{1/2} m_4^{2(2,F_2)}. \tag{17}$$

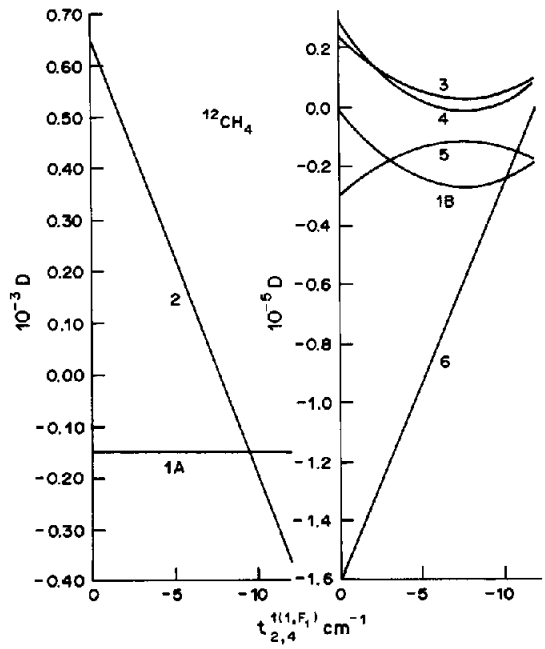

Fig. 2. Variation of the effective dipole-moment parameters of orders λ^1 (left-hand side) and λ^2 (right-hand side) under unitary transformation for the ν_2, ν_4 dyad of $^{12}CH_4$. The parameters are denoted by numbers as follows: (1A) $m_4^{1(1,F_1)}$, (1B) $\tilde{m}_4^{1(1,F_1)} - m_4^{1(1,F_1)}$, (2) $m_2^{1(1,F_1)}$, (3) $m_4^{2(0,A_1)}$, (4) $m_4^{2(2,E)}$, (5) $m_4^{2(2,F_2)}$, (6) $m_2^{2(2,F_2)}$.

4. CONCLUSIONS

In order to perform the analysis of effective rovibrational operators a calculation technique based on an irreducible tensor formalism[4–10] was used. We have demonstrated the high efficiency of this technique for highly symmetrical, spherical-top molecules. The effective Hamiltonian and dipole moment for the ν_2, ν_4 dyad have been studied in detail using simultaneous unitary transformations. The unitary equivalence of the effective dipole-moment operators[14] for a model of the resonance bands ν_2, ν_4 and for that of the isolated bands ν_2, ν_4 of the $^{12}CH_4$ molecule is shown. The irreducible tensor calculation technique used in the present paper has other important applications.

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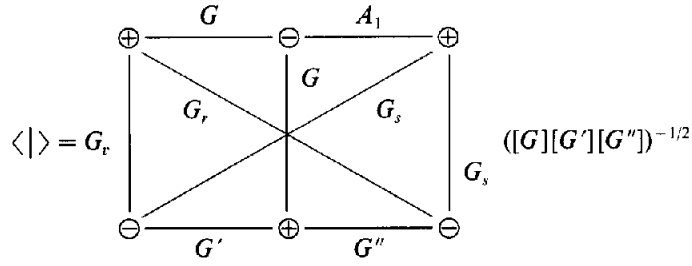
APPENDIX

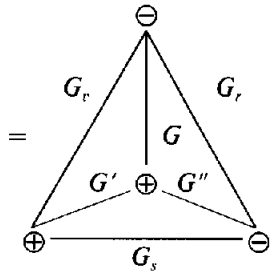
Calculation of Rovibrational Commutators

The formulae (14) for the general rovibrational commutator are based on the usual recoupling formulae

$$[(\mathbf{V}^{G_r}\mathbf{R}^{G_r})^{G}(\mathbf{V}^{G_s}\mathbf{R}^{G_s})^{A_1}]^{G} = \sum_{G',G''} \langle [(G_rG_r)G(G_sG_s)A_1]G | [(G_rG_s)G'(G_rG_s)G'']G \rangle \times [(\mathbf{V}^{G'}\mathbf{V}^{G_s})^{G''}(\mathbf{R}^{G_r}\mathbf{R}^{G_s})^{G''}]^{G}. \quad \text{(A1)}$$

The corresponding Clebsch–Gordan coefficient may be easily evaluated by using the following graphical technique:





$$= \frac{([G'][G''])^{1/2}}{[G_s]^{1/2}} = (-)^{G_v+G_s+G+G''} \frac{([G'][G''])^{1/2}}{[G_s]^{1/2}} \begin{pmatrix} G' & G'' & G \\ G_r & G_v & G_s \end{pmatrix}. \quad \text{(A2)}$$

Equation (14) follows immediately by substituting Eq. (A1) for the definition of the irreducible tensor commutator, i.e.

$$[(\mathbf{V}^{G_r}\mathbf{R}^{G_r})^G, (\mathbf{V}^{G_s}\mathbf{R}^{G_s})^{A_1}]^G_- = [(\mathbf{V}^{G_v}\mathbf{R}^{G_r})^G(\mathbf{V}^{G_s}\mathbf{R}^{G_s})^{A_1}]^G - (-)^{G+G+A_1}[(\mathbf{V}^{G_s}\mathbf{R}^{G_s})^{A_1}(\mathbf{V}^{G_v}\mathbf{R}^{G_r})^G]^G,$$

where $(-)^{G+G+A_1} = 1$.

The tensorial rovibrational commutator may be reduced to rotational and vibrational commutators of the general form

$$[(\mathbf{V}^{G_1}\mathbf{R}^{G_2})^{G_{12}}, (\mathbf{V}^{G_3}\mathbf{R}^{G_4})^{G_{34}}]^G_- = \frac{1}{2}\sum_{X,Y}([G_{12}][G_{34}][X][Y])^{1/2} \begin{pmatrix} G_1 & G_2 & G_{12} \\ G_3 & G_4 & G_{34} \\ X & Y & G \end{pmatrix}$$

$$\times \{[\mathbf{V}^{G_1}, \mathbf{V}^{G_3}]^X_+[\mathbf{R}^{G_2}, \mathbf{R}^{G_4}]^Y_- + [\mathbf{V}^{G_1}, \mathbf{V}^{G_3}]^X_-[\mathbf{R}^{G_2}, \mathbf{R}^{G_4}]^Y_+\}. \quad \text{(A3)}$$

Equation (A3) may be simplified to Eq. (14) by setting $G_{34} = A_1$.