Equivalent rotations associated with the permutation inversion group revisited: symmetry projection of the rovibrational functions of methane.

O. Álvarez-Bajo[1], **R. Lemus**[2], **M. Carvajal**[1], **and F. Pérez-Bernal**[1]

[1] Departamento de Física Aplicada, Facultad de Ciencias Experimentales,
Universidad de Huelva, 21071 Huelva, Spain.
[2] Instituto de Ciencias Nucleares, Universidad Nacional Autónoma de México,
Apartado Postal 70-543, 04510 México, DF, México.

Projection of rovibrational functions of methane.

Renato Lemus
Instituto de Ciencias Nucleares, UNAM
A. P. 70-543, Circuito Exterior, C. U. , 04510 Mexico, D. F. , Mexico
Tel.: +52-55-56224672
Fax: +52-55-56162233
e-mail: renato@nucleares.unam.mx

Abstract

In this work the analysis of the equivalent rotations from the permutation inversion group formalism is revisited. We emphasize that explicit knowledge of changes in the Euler angles are not required in order to determine the transformation that a given symmetry operation causes to the rotational functions when dealing with the permutation inversion group formalism. Indeed, matrix elements of the equivalent rotations are provided by a single Wigner's $\mathbf{D}^{(j)}(R)$ function. Taking advantage of this, we propose a symmetry projection approach to build the rovibrational functions of methane. This approach focus on the relevance of the isomorphism between permutations and equivalent rotations. In our method, symmetry adapted functions are obtained by simultaneous diagonalization of a set of commuting operators, whose representation is given in terms of direct products of Wigner's D functions and vibrational matrix representations provided by a local scheme. The proposed approach is general and permits to obtain in a systematic fashion an orthonormal set of symmetry-projected functions, with good total angular momentum, and carrying the irreducible representations of the molecular symmetry group.

Key words: Permutation-inversion group, equivalent rotations, ro-vibrational functions, symmetry projection, methane.

1. Introduction

With the advent of new spectroscopic techniques leading to significant advances in high resolution molecular spectroscopy [1], a demand of theoretical models has emerged to explain an impressive amount of experimental data [2]. In particular, it has been possible to identify the existence of multiple minima associated with nonrigid molecules [3, 4]. This possibility has stimulated the proposal of theoretical treatments aiming to describe the dynamics of large amplitude degrees of freedom.

Basically there are two possible frameworks to deal with non rigid molecules: the permutation inversion group (molecular symmetry group), which has its origins in the works of *H.C.Longuet-Higgins* [5] and *J.T.Hougen* [6, 7], and the Schrödinger supergroup formalism proposed by *S. Altmann* [8, 9]. The latter approach was recast by *Y.G. Smeyers* [10] to make both treatments equivalent. Both have advantages and disadvantages when dealing with nonrigid systems but, beyond their differences, the importance of the molecular symmetry (MS) group lies on two facts. On one hand, semirigid molecules are embedded in the formalism and, on the other hand rovibronic and nuclear spin degrees of freedom may be treated in a unified and clear fashion [11, 12, 13].

A remarkable feature of the molecular symmetry group elements is that they can be factorized into three mutually commuting operators, affecting the vibronic, rotational, and nuclear spin coordinates, respectively. This property facilitates the construction of symmetry adapted functions involving all the relevant degrees of freedom in a unified form. There are different approaches to accomplish this task, leading to different symmetry projection methods [14, 15, 16]. The present article focus in rovibrational functions. In this case a possible approach consists in symmetrizing the rotational and vibrational spaces separately and, later on, combining the resulting basis with coupling coefficients to construct symmetry-adapted rovibrational functions [17]. Following this scheme the first step is the projection of the rotational functions.

The rotational functions to be projected are, basically, the conjugate of Wigner's D functions, while the operators to be used correspond to rotations with respect to the molecule-fixed axis system. The projection can be done as long as the effect of the equivalent rotations over the rotational functions is known.

The usual properties of rotations are modified when acting on rotational functions, because rotational functions are expressed in the molecule-fixed axis system. This is commonly noted in changes in the commutation relations. In previous works the effect of equivalent rotations on rotational functions was obtained through the transformation of Euler angles under such rotations [11, 12, 18]. This is not necessary because, as it can be proved, the matrix elements correspond to Wigner's D functions. This fact has relevant implications, which is worth stressing.

The first part of our contribution consists in presenting the main properties of equivalent rotations from the point of view of representation theory. Although this material is part of the machinery of the well-known angular momentum theory [19, 20, 21], our point of view is somewhat different from the traditional one. We emphasize the connection with the molecular symmetry group. The second part of our work establishes an approach to obtain symmetry-adapted functions. Even in case of considering only the rotational subspace, this task is not trivial because, in the general case, there is multiplicity of representations appearing in the reduction of the (2J+1)-dimensional space. Our approach is based on the diagonalization of a set of commuting operators, as suggested by the eigenfunction method proposed by *Chen* [22]. The eigenfunction method, however, cannot be fully applied because of the intrinsic features of the rotational space and, consequently, an alternative approach is proposed.

Once we present in detail our approach for the projection of rotational functions, we incorporate the vibrational space in our treatment in order to obtain symmetry-adapted functions from the outset. The vibrational space is worked out in a local scheme, in terms of internal coordinates. Although this coordinate selection has the disadvantage of presenting spurious states [23], our approach permits their elimination in a systematic way.

The multiplicity of the irreducible representations (IRREPS) in the total space has both rotational and vibrational contributions. Both of them are removed by introducing commuting operators combined with traditional group theoretical techniques. An interesting feature of our method is that it takes into account anharmonic effects from the outset, associating anharmonic potentials with the local coordinates.

This paper is organized as follows. The properties of the equivalent rotations are revisited in §2, stressing those properties relevant for the symmetry projection. In §3 we apply the previous results to the symmetry projection of the rotational functions in the full $(2J+1)$-dimensional space. §4 is devoted to establish a six-dimensional representation subspace to simplify the projection for large J values. Vibrational degrees of freedom come into play in §5, its projection is carried out by simultaneous diagonalization of a set of operators chosen in accordance to the symmetry of the system. Finally, in §6 the summary and conclusions are presented.

2. Matrix elements of the equivalent rotations

In the case of semirigid molecules, the symmetry group of the molecule is identified with the molecular point group. On the other hand, for nonrigid molecules, the MS group represents an appropriate approach to describe the symmetry of the system, with the advantage that the semirigid case is embedded in the formalism [11]. The MS group is the subgroup of the complete nuclear permutation-inversion (CNPI) group obtained after the removal of unfeasible operations, and its elements, p, can be written in the form $p = v(p)\ \varphi(p)\ s(p)$, where $v(p)$ is an operation that produces the vibronic coordinates change caused by p, $\varphi(p)$ is an operation that affects rotational coordinates, and $s(p)$ is an operation that generates a nuclear spin permutation [11, 12]. Since the operations $v(p)$, $\varphi(p)$, and $s(p)$ act upon different subspaces, they commute with each other. For semirigid molecules a convenient basis to carry out the ro-vibrational description is the direct product $|\Psi_{rvs}\rangle = |\Phi_{vib}\rangle \otimes |\Phi_{rot}\rangle \otimes |\Phi_{ns}\rangle$. The vibrational functions $|\Phi_{vib}\rangle$ may be expressed in a local or a normal scheme. For nonrigid molecules, involving internal rotations for instance, additional functions should be added in order to incorporate the large amplitude degrees of freedom. With regard to rotations, the ket $|\Phi_{rot}\rangle$ that corresponds to symmetric top eigenfunctions is [19]

$$\Phi^{(rot)}_{Jkm}(\phi,\theta,\chi) = \langle\phi,\theta,\chi|J,k,m\rangle = \sqrt{\frac{(2J+1)}{8\pi^2}}\; D^{(J)*}_{mk}(\phi,\theta,\chi), \tag{1}$$

where $D^{(J)}_{mk}(\phi,\theta,\chi)$ are the well known Wigner's D functions. The explicit form of the nuclear spin part of the basis can be found in Ref. [11].

Hence, for semirigid molecules, a representation $\Delta^{(red)}(p)$ (in general reducible) is given in terms of the direct product

$$\Delta^{(red)}(p) = \Delta^{(red)}[v(p)] \otimes \Delta^{(red)}[\varphi(p)] \otimes \Delta^{(red)}[s(p)]. \tag{2}$$

We first discuss the representation obtained considering the rotational subspace, and its reduction to MS group IRREPS. The reducible representation $\Delta^{(red)}[\varphi(p)]$ is obtained with the action of equivalent rotations on the basis (1). Using Table 11.1 of Ref. [12], where the changes in Euler angles **are given** for a rotation ${R_z}^{\delta}$ about the z axis through the angle δ, and **for** a rotation ${R_\epsilon}^{\pi}$ of π radians about an axis in the xy plane that forms the angle ϵ with the x axis are given, the following results are derived [11]

$$\begin{aligned} \hat{R}_z{}^{\delta}|Jkm\rangle &= e^{i\delta k}\;|Jkm\rangle, & (3)\\ \hat{R}_\epsilon{}^{\pi}|Jkm\rangle &= (-1)^J e^{-2i\epsilon k}|J,-k,m\rangle. & (4) \end{aligned}$$

The approach followed to obtain () was possible because the transformation of the Euler angles was linear. Table 11.1 of Ref. [12] may be deduced either by geometrical arguments [12] or by pondering the transformation caused to the elements of the direction cosine matrix of the molecule-fixed (x,y,z) axis system in the space fixed (ξ,η,ζ) axis system [18]. For a general equivalent rotation this procedure becomes cumbersome. For example, in Ref. [18] it has been found the mapping between the original Euler angles (ϕ, θ, χ) and the transformed ones (ϕ', θ', χ') caused by the equivalent rotation $R_3(1,1,1)$. The solution of the resulting set of equations is not trivial, since it is not linear and, consequently, this method does not seem a practical alternative. It is thus compulsory to obtain the effect of a general rotation over Wigner's D functions without having to solve the set (1-5) in Ref. [18]. A possible way to bypass this problem consists in choosing as generators of the MS group some rotations and reflections whose effect over the Euler angles is linear [6], but we are not going to follow that route.

Let $R(\alpha, \beta, \gamma)$ be an equivalent rotation characterized by Euler angles (α, β, γ), referred to the molecule-fixed (x, y, z) system, with origin at the nuclear center of mass. There are two ways to apply this rotation, from **either** the active or the passive point of view **(see Appendix A for the discussion)**. Equivalent rotations are carried out about the molecule fixed axis, which move **the axis system** when the rotation is applied and consequently the passive point of view must be considered [11]. The effect of an equivalent rotation over the functions (1) is given by

$$\hat{R}(\alpha,\beta,\gamma)|Jkm\rangle = \sum_{k'=-J}^{J} D^{(J)}_{k,k'}(-\gamma,-\beta,-\alpha)\ |Jk'm\rangle = \sum_{k'=-J}^{J} D^{(J)*}_{k',k}(\alpha,\beta,\gamma)\ |Jk'm\rangle, \quad (5)$$

where clearly the argument $(-\gamma, -\beta, -\alpha)$ corresponds to the inverse of the rotation with Euler angles (α, β, γ). Proofs of this relation can be found in Refs. [7, 24]. In Appendix B we provide a different proof based on conjugation relations. The comparison of this result with the effect of a rotation $\hat{P}_R$ in the (ξ, η, ζ) parallel laboratory system over the same functions in the passive picture

$$\hat{P}_R(\alpha,\beta,\gamma)|Jkm\rangle = \sum_{m'=-J}^{J} D^{(J)}_{m'm}(-\gamma,-\beta,-\alpha)\ |Jkm'\rangle \sum_{m'=-J}^{J} D^{(J)*}_{m,m'}(\alpha,\beta,\gamma)\ |Jkm'\rangle, \quad (6)$$

cast light upon expression (5), since k is the projection of the angular momentum with respect to the rotated system, while m is the corresponding projection to the parallel laboratory system.

Using Eq. (5), the previous results () are reproduced in a straightforward way

$$\begin{aligned}
\hat{R}_z{}^{\delta}|Jkm\rangle &= \sum_{k'=-J}^{J} D^{(J)}_{kk'}(0,0,-\delta)\ |Jk'm\rangle = e^{i\delta k}\ |Jkm\rangle, \qquad (7)\\
\hat{R}_{\epsilon}{}^{\pi}|Jkm\rangle &= \sum_{k'=-J}^{J} D^{(J)*}_{k'k}(\epsilon-\frac{\pi}{4},\pi,-\epsilon+\frac{3\pi}{4})\ |Jk'm\rangle = (-1)^J e^{-2i\epsilon k}|J,-k,m\rangle
\end{aligned}$$

where we have used the properties of Wigner's D functions and the relation between the rotation angle ω and the polar angles $\{\Theta,\Phi\}$ that define a rotation axis and its corresponding Euler angles (α,β,γ), given in §1.4.4 of Ref.[21].

The expression (5) has important consequences in the relation between the product of permutations and the corresponding product of equivalent rotations, as the following theorem establishes

Theorem. The molecular symmetry group is isomorphic to the group of equivalent rotations

$$\varphi(p_1p_2) = \varphi(p_3) = \varphi(p_1)\varphi(p_2). \qquad (8)$$

The proof of this theorem is given in Appendix C. We should note that in the active picture we would have an anti-isomorphism **(see Appendix A), that turns out** the basis upon which *Chen* proposed the intrinsic group to establish the complete set of commuting operators of type III in the framework of discrete groups [22].

Equation (5) implies that tensors T^J_k in the molecule-fixed axis system transforms as

$$\hat{\mathcal{O}}_R T^J_k \hat{\mathcal{O}}_R^{-1} = \sum_{k'=-J}^{J} D^{(J)*}_{k'k}(\alpha,\beta,\gamma)\ T^J_{k'}, \qquad (9)$$

from which, after considering infinitesimal rotations, the anomalous commutations relations $[\hat{J}_j,\hat{J}_k] = -i\epsilon_{jkl}\hat{J}_l\ ;\ i,j,k = x,y,z$ are deduced [25]. Hence, if Eq. (5) is considered, it is not necessary to build a table of Euler angle changes in order to calculate the effect of equivalent rotations over the kets $|Jkm\rangle$. This advantage will be evident in next section, where we apply this result to the projection of rotational functions in the methane case.

3. Projection of methane rotational functions

In this section we establish an approach to carry out the projection of the rotational functions to IRREPS of the MS group $\mathcal{T}_d(M)$. To achieve this goal we follow the eigenfunction approach combined with an orthogonalization procedure when necessary.

According to the eigenfunction method [22], the first step consists in establishing an operator which is able to distinguish IRREPS of the MS group. This operator may be easily identified by constructing a λ's table using the formula [22]

$$\lambda_i^\nu = \frac{|K_i|\chi_i^{(\nu)*}}{n_\nu}, \tag{10}$$

where $|K_i|$ stands for the number of elements belonging to the i-th class, n_ν corresponds to the dimension of the ν-th IRREP, while $\chi_i^{(\nu)}$ is its character. We label IRREPS using ν, which is the eigenvalue of the CSCO-I, as explained below. Hence, from the character table of the $\mathcal{T}_d(M)$ group, given in Table A-14 of Ref.[11], we construct Table 1 displaying $\lambda_i^{(\nu)}$ values, with the following equivalence classes

$$K_1 = \{e\}; \quad K_2 = \{(\cdots)\}; \quad K_3 = \{(\cdot\cdot)(\cdot\cdot)\}; \quad K_4 = \{(\cdot\cdot\cdot\cdot)^*\}; \quad K_5 = \{(\cdot\cdot)^*\}. \tag{11}$$

The class K_5 distinguishes all the IRREPS. Consequently the diagonalization of the operator

$$\hat{C} \equiv K_5 = (12)^* + (13)^* + (14)^* + (23)^* + (24)^* + (34)^*, \tag{12}$$

in any representation space, provides eigenvectors $\psi_i^{(\nu)}$ carrying IRREPS of the MS group: $\hat{C}\psi_i^{(\nu)} = \nu\,\psi_i^{(\nu)}; \quad i = 1, \ldots, g_\nu$, where $\nu = \lambda_5^\nu$, g_ν is the degeneracy of the IRREP, and $g_\nu = n_\nu$ if there is no multiplicity of IRREPS.

It is clear that the operator (12) does not constitute a complete set of commuting operators: it does not distinguish between components of the IRREPS, for instance. Hence it is necessary to propose a canonical chain of groups to build a second operator. We may choose the chain

$$\mathcal{T}_d(M) \supset \mathcal{C}_{2v}, \tag{13}$$

where

$$\mathcal{C}_{2v} = \{e, (14)(23), (14)^*, (23)^*\}, \tag{14}$$

whose character table is displayed in Table 2. The subduction ${}^{\nu}\mathcal{T}_d(M) \downarrow \mathcal{C}_{2v}$ is $A_1 \to A_1, A_2 \to A_2, E \to A_1 \oplus A_2, F_1 \to A_2 \oplus B_1 \oplus B_2, F_2 \to A_1 \oplus B_1 \oplus B_2,$ where the canonical property becomes clear. In order to distinguish IRREPS of the subgroup $\mathcal{C}_{2v}$ two classes are needed. Indeed, the operator $\hat{C}(s)$ defined by

$$\hat{C}(s) = (14)^* + 3\,(23)^*, \tag{15}$$

when diagonalized, provides eigenvectors satisfying $\hat{C}(s)\,\phi_j^{(\mu)} = \mu\,\phi_j^{(\mu)}; \quad j = 1, \ldots, g_j,$ where μ labels the IRREPS of the $\mathcal{C}_{2v}$ subgroup. The eigenvalues μ are included in Table 2. The simultaneous diagonalization of the set of operators $\hat{C}_{II} = \{\hat{C}, \hat{C}(s)\}$ provides eigenvectors carrying IRREPS of $\mathcal{T}_d(M)$ and $\mathcal{C}_{2v}$:

$$\begin{pmatrix} \hat{C} \\ \hat{C}(s) \end{pmatrix} {}_{\kappa}\psi_{\mu}^{(\nu)} = \begin{pmatrix} \nu \\ \mu \end{pmatrix} {}_{\kappa}\psi_{\mu}^{(\nu)}, \tag{16}$$

where κ is a multiplicity label that takes into account that the same IRREP of the MS group could appear several times. In practice, the eigensystem (16) may be substituted by considering the linear combination $\hat{C}_{II} = \hat{C} + \alpha\,\hat{C}(s)$, where α is chosen to obtain different eigenvalues corresponding to $\zeta \equiv \nu + \alpha\mu$. The expected eigenvalues when α is taken to be $\alpha = 3$ are displayed in Table 3. With this selection all the eigenvalues are different and, consequently, the operator

$$\hat{C}_{II} = (12)^* + (13)^* + 4(14)^* + 10(23)^* + (24)^* + (34)^*, \tag{17}$$

constitutes a complete set of commuting operators of type II, with eigensystem $\hat{C}_{II}\,{}_{\kappa}\psi_{\mu}^{\nu} = \zeta\;{}_{\kappa}\psi_{\mu}^{\nu}; \quad \zeta = \nu + 3\mu$. The degeneracy manifested by the multiplicity index κ is still present. The treatment of this case is discussed later.

Let us now turn our attention back to the rotational space of functions (1). Each permutation-inversion element of the $\mathcal{T}_d(M)$ group has an associated equivalent rotation. All of them are displayed in Table 4. Taking into account Eq. (5) and the equivalent rotations associated with elements in Eq. (17), we obtain the matrix representation of the $\hat{C}_{II}$ operator:

$$\begin{aligned}\langle Jk'm|\hat{C}_{II}|Jkm\rangle &= D^{(J)*}_{k'k}(0,\frac{\pi}{2},\pi)+D^{(J)*}_{k'k}(\frac{\pi}{2},\frac{\pi}{2},\frac{\pi}{2})+4D^{(J)*}_{k'k}(0,\pi,\frac{\pi}{2})\\ &+ 10D^{(J)*}_{k'k}(\pi,\pi,\frac{\pi}{2})+D^{(J)*}_{k'k}(\frac{3\pi}{2},\frac{\pi}{2},\frac{3\pi}{2})+D^{(J)*}_{k'k}(\pi,\frac{\pi}{2},0), \quad (18)\end{aligned}$$

The diagonalization of this matrix representation of the $\hat{C}_{II}$ operator provides symmetry-adapted functions, displayed in Table 5 where only the reductions up to $J=4$ are given. The matrix elements of equivalent rotations in the symmetry-adapted basis

$$|\psi^{J:\Gamma}_{\gamma}\rangle=\sum_{k=-J}^{J}s^{J}_{k;\Gamma,\gamma}|Jkm\rangle \tag{19}$$

are given by

$$\langle\psi^{J:\Gamma}_{\gamma'}|\varphi(p)|\psi^{J:\Gamma}_{\gamma}\rangle=D^{(J:\Gamma)}_{\gamma',\gamma}[\varphi(p)] \tag{20}$$

for $p\in\mathcal{T}_d(M)$. Explicitly, the matrix elements take the form

$$D^{(J:\Gamma)}_{\gamma',\gamma}[\varphi(p)]=\sum_{k=-J}^{J}\sum_{k'=-J}^{J}s^{J*}_{k';\Gamma,\gamma'}s^{J}_{k;\Gamma,\gamma}D^{J*}_{k'k}(\alpha,\beta,\gamma), \tag{21}$$

where we have remarked the J-dependence of the matrices $\mathbf{D}^{(J:\Gamma)}[\varphi(p)]$. The matrices (20) form a representation. In fact

$$\mathbf{D}^{(J:\Gamma)}[\varphi(p_1)]\mathbf{D}^{(J:\Gamma)}[\varphi(p_2)]=\mathbf{D}^{(J:\Gamma)}[\varphi(p_1p_2)]. \tag{22}$$

When the same IRREP is generated from different J values the matrices are either equal or complex conjugate. In the latter case they turn out to be equivalent. Although this fact may be checked by computing the characters, this result is also expected because the IRREPS of $\mathcal{T}_d(M)$ are *integer representations* [14]. For example

$$\mathbf{D}^{(3;F_1)}(R)=\mathbf{S}\mathbf{D}^{(1;F_1)}(R)\mathbf{S}^{-1}. \tag{23}$$

where $\mathbf{S}$ is a diagonal matrix with elements $S_{11}=1, S_{22}=S^{*}_{33}=i$. The matrix $\mathbf{S}$ induces the change of basis

$$\left(\psi'^{(1;F_1)}_{A_2},\psi'^{(1;F_1)}_{B_1},\psi'^{(1;F_1)}_{B_2}\right)=\left(\psi^{(1;F_1)}_{A_2},\psi^{(1;F_1)}_{B_1},\psi^{(1;F_1)}_{B_2}\right)\mathbf{S}^{-1}, \tag{24}$$

which generates the representation equal to $\mathbf{D}^{(3;F_1)}(R)$. A similar approach applied to $\mathbf{D}^{(2;F_2)}$ leads to the same matrix transformation $\mathbf{S}$.

Following this approach we are able to obtain symmetry adapted basis generating the same representation. As it is well known, for $J \geq 5$ a multiplicity index appears; some IRREPS appear more than once. For instance, for $J = 5$ the following reduction is given $\mathbf{D}^{(5)}(\varphi(p)) \to E \oplus 2F_1 \oplus F_2$. In Table 6 we present the eigenvectors generated by the diagonalization of the matrix representation (18). As expected, degenerate eigenvectors are not in general orthogonal. In order to obtain an orthonormal set of functions generating the same representation we shall proceed as follows. We start considering the set of functions belonging to the first component of the representation, for instance, $\{{}_1\psi^{(5,F_1)}_{A_2}, {}_2\psi^{(5,F_1)}_{A_2}\}$. Since this set is not expected to be orthogonal we should proceed to apply a Gramm-Schmidt orthonormalization approach. In our example they turn out to be $\langle {}_1\psi^{(5,F_1)}_{A_2} | {}_2\psi^{(5,F_1)}_{A_2} \rangle = 0$. We now generate the rest of the components by means of the equation [14]

$$\sum_{R\in G} D^{(\Gamma)*}_{\beta\alpha}(R)\hat{\mathcal{O}}_R\, {}_\kappa\psi^{(J,\Gamma)}_\alpha = \frac{|G|}{n_\Gamma}\, {}_\kappa\psi^{(J,\Gamma)}_\beta. \tag{25}$$

Applying this relation to generate the rest of the components β, with $\beta \neq \alpha$, we are able to obtain orthogonal sets of functions, as the following theorem establishes

Theorem. In case of IRREP multiplicity, given the set $\{{}_{\kappa_1}\psi^{(J,\Gamma)}_\alpha, {}_{\kappa_2}\psi^{(J,\Gamma)}_\alpha\}$ *composed by the* α*-th component of the same IRREP* Γ *with* $\kappa_1 \neq \kappa_2$ *and the property* $\langle {}_{\kappa_1}\psi^{(J,\Gamma)}_\alpha | {}_{\kappa_2}\psi^{(J,\Gamma)}_\alpha \rangle = 0$*, the sets* $\{{}_{\kappa_1}\psi^{(J,\Gamma)}_\beta, {}_{\kappa_2}\psi^{(J,\Gamma)}_\beta;\quad \beta \neq \alpha\}$ *associated with the rest of the components and generated through Eq. (25), satisfy* $\langle {}_{\kappa_1}\psi^{(J,\Gamma)}_\beta | {}_{\kappa_2}\psi^{(J,\Gamma)}_\beta \rangle = 0$ *for* $\beta \not\alpha$.

The proof of this theorem is given in the Appendix D. Following this approach we obtain the basis functions $\{{}_\kappa\zeta^{(J,\Gamma)}_\mu\}$ displayed in the lower half of Table 6. The two sets of functions $\{{}_1\zeta^{(\nu)}_\mu, {}_2\zeta^{(\nu)}_\mu\}$ are orthonormal, and the matrix elements of the equivalent rotation $\varphi(p)$ is identical to $\mathbf{D}^{(1;F_1)}[\varphi(p)]$ because this was the matrix representation used. This approach is general and may be used to the reduction of the representation $\mathbf{D}^{(J)}$ associated with any J.

The approach presented is useful if we intend to obtain the rovibrational functions by means of a coupling procedure using Clebsch-Gordan coefficients, since in this case the rotational as well as the vibrational functions must be built in a consistent way. Another possibility consists in obtaining the rovibrational functions in one step, following the eigenfunction method. Before discussing this point we take a closer look to the application of the eigenfunction method to the rotational space from the perspective of identifying invariant subspaces.

4. Reduction of the (2J+1)-dimensional space

In this section we shall identify the appropriate invariant subspace whose reduction is simple. The main purpose of this section is to ease the task of building a symmetry-adapted basis for large J values. As a first step to establish, if possible, a complete set of commuting operators, we start by identifying the equivalent rotations that leave the function $|Jkm\rangle$ invariant. From the result (5) and Table 4, we identify the cyclic subgroup $\mathcal{S}_4 = \{e, (14)(23), (1342)^*, (1243)^*\}$, as the set of transformations that leave the kets $|Jkm\rangle$ invariant up to a phase. Indeed, the associated equivalent rotations have $\beta = \gamma = 0$ and consequently $D^{J*}_{k'k}(\alpha, 0, 0) = \delta_{kk'} e^{ik\alpha}$. We may now expand the molecular group $\mathcal{T}_d(M)$ in left cosets of $\mathcal{S}_4$:

$$\mathcal{T}_d(M) = \sum_{\sigma=1}^{|\sigma|} s_\sigma \; \mathcal{S}_4; \qquad |\sigma| = \frac{|\mathcal{T}_d(M)|}{|\mathcal{S}_4|} = 6. \tag{26}$$

A possible set of representative elements is $\{s_\sigma\} \rightarrow \{e, (123), (132), (243), (234), (12)(34)\}$. The action of s_σ over a ket $|Jkm\rangle$ generates a representation space, which means that the set

$$|\phi_\sigma\rangle \equiv s_\sigma |Jkm\rangle; \quad \sigma = 1, \ldots, 6, \tag{27}$$

constitutes an invariant subspace under the elements of the group. This subspace spans a reducible representation $\mathbf{\Delta}^{(red)}(p)$ defined by

$$p \; |\phi_\sigma\rangle = \sum_{\sigma'=1}^{6} \Delta^{(red)}_{\sigma'\sigma}(p) \; |\phi_{\sigma'}\rangle; \qquad \forall p \in \mathcal{T}_d(M). \tag{28}$$

To obtain the explicit form of this reducible representation we first note that $p|\phi_\sigma\rangle = ps_\sigma|Jkm\rangle = s_{\sigma'}h_i|Jkm\rangle$ with $h_i \in \mathcal{S}_4$, since $ps_\sigma \in s_{\sigma'}\mathcal{S}_4$. In addition, from Table 4 we know that $h_i|Jkm\rangle = D_{kk}^{(J)*}(\alpha_i, 0, 0)|Jkm\rangle$, and consequently

$$p|\phi_\sigma\rangle = D_{kk}^{(J)*}(\alpha_i, 0, 0)s_{\sigma'}|Jkm\rangle = D_{kk}^{(J)*}(\alpha_i, 0, 0)|\phi_{\sigma'}\rangle. \tag{29}$$

Using this result we are able to obtain the matrix representation of any element p. In particular, if we want to know the IRREP contained in $\mathbf{\Delta}^{(red)}[\mathcal{T}_d(M)]$, we should calculate the characters. There is a contribution to the character when $ps_\sigma = s_\sigma h_i$, which means that $s_\sigma^{-1}ps_\sigma = h_i$. In other words, the character $\chi^{(red)}(p)$ vanishes unless p is in the same class as one of the elements of $\mathcal{S}_4$. We thus have for the non vanishing characters of the group $\mathcal{T}_d(M)$

$$\begin{aligned} \chi^{(red)}[(14)(23)] &= 2D_{kk}^{(J)*}(\pi, 0, 0) = (-1)^k, & (30) \\ \chi^{(red)}[(1423)^*] &= D_{kk}^{(J)*}(\pi/2, 0, 0) + D_{kk}^{(J)*}(3\pi/2, 0, 0) = (-i)^{-3k}(1 + (-1)^k). & (31) \end{aligned}$$

From these results we obtain the following reduction according to the parity of k:

$$\begin{array}{lllll} a) & k \text{ odd} & & & \\ & \mathbf{\Delta}^{(red)} & \rightarrow & F_1 \oplus F_2 & \\ b) & k = 2n & & & \\ & n \text{ even} & \mathbf{\Delta}^{(red)} & \rightarrow & A_1 \oplus E \oplus F_1 \\ & n \text{ odd} & \mathbf{\Delta}^{(red)} & \rightarrow & A_2 \oplus E \oplus F_2 \end{array} \tag{32}$$

We have obtained the remarkable result that the reducible representation is *simply reducible*. The space used to generate the representation $\Delta^{(red)}(p)$ in (28) constitute a non-orthogonal basis. Indeed the overlap is given by

$$g_{\sigma'\sigma} \equiv \langle s_{\sigma'}\phi_0|s_\sigma\phi_0\rangle = \langle\phi_0|s_{\sigma'}^{-1}s_\sigma\phi_0\rangle = \langle\phi_0|s_\rho\phi_0\rangle = D_{kk}^{(J)}(R_\rho), \tag{33}$$

where we have defined $|\phi_0\rangle \equiv |Jkm\rangle$.

Let us now consider the eigenvectors of the operator $\hat{C}_{II}$. The set $\hat{C}_{III}$ turns out to be unnecessary since the reducible representation is *simply* reducible. Let

$$|\psi_\alpha\rangle = \sum_{\sigma=1}^{6} c_{\sigma\alpha}|\phi_\sigma\rangle. \tag{34}$$

be an eigenvector of the operator $\hat{C}_{II}$:

$$\hat{C}_{II}|\psi_\alpha\rangle = \lambda_\alpha|\psi_\alpha\rangle. \tag{35}$$

If we substitute (34) into (35), and take into account the invariance of the subspace, we arrive at

$$\sum_{\sigma} c_{\sigma\alpha}\{\Delta_{m\sigma}(C_{II}) - \lambda_\alpha\delta_{m\sigma}\} = 0, \tag{36}$$

which has the same form as the usual eigenvalue equation in terms of an orthonormal basis **and it was obtained by multiplying the inverse of the overlap matrix**.

The matrix representation $\Delta(\hat{C}_{II})$ may be calculated and takes the explicit form

$$\Delta(\hat{C}_{II}) \quad = \quad \begin{pmatrix} 0 & e^{i\frac{3\pi}{2}k} & e^{i\frac{\pi}{2}k} & e^{i\frac{3\pi}{2}k} & e^{i\frac{\pi}{2}k} & 4e^{i\frac{3\pi}{2}k} + 10e^{i\frac{\pi}{2}k} \\ e^{i\frac{\pi}{2}k} & 0 & 4e^{i\frac{3\pi}{2}k} & z_k & 10e^{i\frac{\pi}{2}k} & e^{i\frac{\pi}{2}k} \\ e^{i\frac{3\pi}{2}k} & 4e^{i\frac{\pi}{2}k} & 0 & 10e^{i\frac{3\pi}{2}k} & z_k & e^{i\frac{\pi}{2}k} \\ e^{i\frac{\pi}{2}k} & z_k & 10e^{i\frac{\pi}{2}k} & 0 & 4e^{i\frac{3\pi}{2}k} & e^{i\frac{\pi}{2}k} \\ e^{i\frac{3\pi}{2}k} & 10e^{i\frac{3\pi}{2}k} & z_k & 4e^{i\frac{\pi}{2}k} & 0 & e^{i\frac{\pi}{2}k} \\ 4e^{i\frac{\pi}{2}k} + 10e^{i\frac{3\pi}{2}k} & e^{i\frac{3\pi}{2}k} & e^{i\frac{3\pi}{2}k} & e^{i\frac{3\pi}{2}k} & e^{i\frac{3\pi}{2}k} & 0 \end{pmatrix} \tag{37}$$

where we have defined $z_k \equiv e^{i\frac{\pi}{2}k} + e^{i\frac{3\pi}{2}k}$. The diagonalization of this matrix leads to the eigenvectors (34), which can be translated into the original basis $|Jkm\rangle$ through (27)

$$|\psi_\alpha\rangle = \sum_{k'} B_{k'\alpha}|Jk'm\rangle; \qquad B_{k'\alpha} = \sum_{\sigma=1}^{6} c_{\sigma\alpha}D^{(J)}_{kk'}[\phi(s_\sigma)]. \tag{38}$$

We should note that the representation matrix (37) does not depend on the angular momentum J. This dependence is given in the eigenvectors.

The sequence of steps to apply this approach is the following. First a k is chosen, which allows the eigensystem of $\hat{C}_{II}$ to be solved with eigenvalues associated with the appropriate reduction (32). The corresponding eigenvectors are obtained by calculating the coefficients $B_{k'\alpha}$ in (38). For the chosen k, some eigenvectors vanish, which means that the corresponding representation is not contained in the 6-dimensional subspace $\mathcal{L}_k$ characterized by k. Since there is no multiplicity of the IRREPS, the functions carrying the same representation in the original $2J+1$-dimensional space appear in different subspaces $\mathcal{L}_k$. But the subspaces $\mathcal{L}_k$ are not orthogonal $\langle\mathcal{L}_{k'}|\mathcal{L}_k\rangle \neq 0$, and consequently those functions are not expected to be orthogonal. Hence the same approach followed in the previous section must be applied in order to obtain a set of orthogonal functions carrying the same IRREP. The advantage of dealing with the subspace $\mathcal{L}_k$ instead of the $(2J+1)$-dimensional space is of course the dimension. For J large, this treatment is more efficient.

From this analysis we should remark that for the rotational space of spherical top molecules is not possible to generate orthogonal functions carrying the same IRREP according to the theory proposed by *Chen* [22]. A similar situation occurs when the vibrational space is incorporated in our analysis, as we next discuss.

5. Ro-vibrational functions

In this section we shall consider the rovibrational functions symmetrization. In compact form, these functions may be expressed as

$$|\Psi_{rv}^{\Gamma,\gamma}\rangle = [|\Phi_{rot}^{\Gamma_1}\rangle \times |\Phi_{vib}^{\Gamma_2}\rangle]_{\gamma}^{\Gamma}, \tag{39}$$

where the symbol × stands for coupling of the IRREPS Γ_1 and Γ_2 to Γ. Hence, according to (39), we may construct the functions $|\Phi_{rot}^{\Gamma_1,\gamma_1}\rangle$ and $|\Phi_{vib}^{\Gamma_2,\gamma_2}\rangle$ in an independent way to thereafter carry out the coupling. The rotational functions can be symmetry-projected using the approach presented in the previous sections. In the case of the vibrational functions, we may use a local or a normal scheme to construct the projected functions [26]. In any case, both projections have to be carried out using the same explicit **form** of the MS group IRREPS, in order to be able to use coupling coefficients later.

In the vibrational space, although the normal basis has the advantage of getting rid of spurious states in a straightforward way, a local scheme is a better option, even though the molecule is intended to be described in a normal basis. The advantages of the local scheme are the following [26]: a) it allows **you** easily generalize the vibrational description to any molecular system with a minimum input, b) the normal mode scheme is included as a particular case, c) the symmetry-adapted basis may be used with two possible interpretations: local harmonic or anharmonic (associated with Morse or Pöschl-Teller potentials) functions, and, finally, d) is the appropriate scheme to take advantage of the eigenfunction method of projection [26].

In the local scheme the vibrational basis of methane is given by

$$|V;\mathbf{v}\rangle \equiv |V;v_1,v_2,v_3,v_4,v_5,v_6,v_7,v_8,v_9,v_{10}\rangle, \tag{40}$$

where v_i is the number of quanta for the i-th oscillator, and $V = V_s + V_b$ is the total number of quanta, $V = \sum_i v_i$. We could proceed to project the local functions (40) to obtain

$$|V;\Phi_{vib}^{p,\Gamma_2,\gamma_2}\rangle = \sum_{\mathbf{v}} D_{\mathbf{v}}^{p,\Gamma_2,\gamma_2}|V;\mathbf{v}\rangle_p \tag{41}$$

where p stands for the partition [26]. This set of functions, however, contains the bending spurious mode. We can build approximate vibrational normal functions $|\nu_0;\nu_1\nu_2\nu_3^{\ell_3}\nu_4^{\ell_4}\rangle$ [27] introducing the change of basis [26]

$$|V;\nu_0\nu_1\nu_2\nu_3^{\ell_3}\nu_4^{\ell_4}\rangle_{\gamma_2}^{\Gamma_2} = \sum_p A_{\nu_0,\nu_1,\nu_2,\nu_3^{\ell_3},\nu_4^{\ell_4}}^{V,p}|V;\Phi_{vib}^{p,\Gamma_2,\gamma_2}\rangle. \tag{42}$$

The A coefficients in (42) are obtained diagonalizing the matrix representation of the number operators and the vibrational angular momentum in the symmetry-adapted basis of Eq. (41) [26]. The label ν_0 corresponds to the A_1 spurious bending mode. Hence the physical space is identified by setting $\nu_0 = 0$ in (42).

Let us now turn our attention to the projection of the rovibrational space. To this end we shall consider the simplified operator $p = \varphi(p)v(p)$, where the spin permutation is **not incorporated**. The approach that we follow is general, but in order to illustrate the procedure followed to eliminate spurious states, we consider as an example the rovibrational space composed by rotational functions and vibrational states with one quantum in the bending modes $V = V_b = 1$.

In general our starting point is the basis

$$\{|Jkm\rangle \otimes |V;\mathbf{v}\rangle\}, \tag{43}$$

which in the considered particular case

$$\{|Jkm\rangle \otimes |1; v_5 v_6 v_7 v_8 v_9 v_{10}\rangle\}. \tag{44}$$

For the sake of brevity we introduce the following notation for the vibrational subspace

$$|i\rangle = |1; 0 \dots v_i \dots 0\rangle; \quad v_i = 1 \tag{45}$$

The action of a permutation operator p on the direct product

$$|Jkm\rangle \otimes |i\rangle \ ; \quad i = 5, \dots, 10, \tag{46}$$

is given by

$$p\{|Jkm\rangle \otimes |i\rangle\} = \sum_{k',j} \Delta^{(red)}_{k'j;ki}(p)\{|Jk'm\rangle \otimes |j\rangle\}, \tag{47}$$

where

$$\Delta^{(red)}_{k'j;ki}(p) = D^{(J)}_{kk'}[\varphi(p)^{-1}] \ \Delta^{(vib)}_{ji}[v(p)]. \tag{48}$$

Therefore, the matrix representation of an element $p \in \mathcal{T}_d(M)$ is given by the direct product

$$\boldsymbol{\Delta}^{(red)}(p) = D^{(J)*}[\varphi(p)] \ \otimes \Delta^{(vib)}[v(p)]. \tag{49}$$

This result implies that the representation of the operator $\hat{C}_{II}$ is obtained in terms of a sum of direct products. For $J = 1$ the dimension of the space (46) is 18, with reduction

$$\boldsymbol{\Delta}^{(red)}(p) \quad \rightarrow \quad A_2 \oplus E \oplus 3F_1 \oplus 2F_2. \tag{50}$$

The corresponding symmetry adapted functions are provided by the eigenvectors of $\hat{C}_{II}$ in the representation of the basis (46). In (50) several multiplicities appear. In this case, however, the approach followed in §3 to distinguish the eigenvectors is not enough, because in addition to the necessity of obtaining a set of orthogonal function carrying the same IRREP, the spurious states must be identified and eliminated.

In order to break the degeneracy in the $\hat{C}_{II}$ eigensystem, we propose to introduce a new set of operators to obtain a complete set of commuting operators. To this end we define tensors constructed in terms of linear combinations of local bosonic operators $a_i^\dagger$, associated with internal coordinates. For the stretching space we have

$$\begin{aligned} T_s^{\dagger A_1} &= \frac{1}{2}(a_1^\dagger + a_2^\dagger + a_3^\dagger + a_4^\dagger), & (51) \\ T_s^{\dagger F_2,A_1} &= \frac{1}{2}(a_1^\dagger - a_2^\dagger - a_3^\dagger + a_4^\dagger), & (52) \\ T_s^{\dagger F_2,B_1} &= -\frac{1}{\sqrt{2}}(a_2^\dagger - a_3^\dagger), & (53) \\ T_s^{\dagger F_2,B_2} &= -\frac{1}{\sqrt{2}}(a_1^\dagger - a_4^\dagger), & (54) \end{aligned}$$

where the coefficients are the same used to build symmetry-adapted local coordinates. In a similar way, for the bending space

$$\begin{aligned} T_b^{\dagger A_1} &= \frac{1}{\sqrt{6}}(a_5^\dagger + a_6^\dagger + a_7^\dagger + a_8^\dagger + a_9^\dagger + a_{10}^\dagger), & (55) \\ T_b^{\dagger E,A_1} &= \frac{1}{2\sqrt{3}}(-a_5^\dagger - a_6^\dagger + 2a_7^\dagger - a_8^\dagger - a_9^\dagger + 2a_{10}^\dagger), & (56) \\ T_b^{\dagger E,A_2} &= \frac{1}{2}(a_5^\dagger - a_6^\dagger - a_8^\dagger + a_9^\dagger), & (57) \\ T_b^{\dagger F_2,A_1} &= -\frac{1}{\sqrt{2}}(-a_7^\dagger + a_{10}^\dagger), & (58) \\ T_b^{\dagger F_2,B_1} &= \frac{1}{\sqrt{2}}(-a_5^\dagger - a_6^\dagger + a_8^\dagger + a_9^\dagger), & (59) \\ T_b^{\dagger F_2,B_2} &= \frac{1}{\sqrt{2}}(-a_5^\dagger + a_6^\dagger - a_8^\dagger + a_9^\dagger). & (60) \end{aligned}$$

We now proceed to construct the number operators

$$\begin{aligned} \hat{\nu}_0 &= [\hat{T}_b^{\dagger A_1} \times \hat{T}_b^{A_1}]^{A_1} = \frac{1}{6}(\hat{X}_b + \hat{Y}_b + \hat{Z}_b), & (61) \\ \hat{\nu}_1 &= [\hat{T}_s^{\dagger A_1} \times \hat{T}_s^{A_1}]^{A_1} = \frac{1}{4}(\hat{X}_s + \hat{Y}_s), & (62) \\ \hat{\nu}_2 &= \sqrt{2}][\hat{T}_b^{\dagger E} \times \hat{T}_b^{E}]^{A_1} = \frac{1}{3}(\hat{X}_b + \hat{Z}_b) - \frac{1}{6}\hat{Y}_b, & (63) \end{aligned}$$

$$\begin{aligned}\hat{\hat{\nu}}_3 &= \sqrt{3}[\hat{T}_s^{\dagger F_2} \times \hat{T}_s^{F_2}]^{A_1} = \frac{1}{4}(3\hat{X}_s - \hat{Y}_s), & (64)\\ \hat{\hat{\nu}}_4 &= \sqrt{3}[\hat{T}_b^{\dagger F_2} \times \hat{T}_b^{F_2}]^{A_1} = \frac{1}{2}(\hat{X}_b - \hat{Z}_b), & (65)\end{aligned}$$

where the symbol × stands for tensorial coupling, and we have introduced the definitions

$$\begin{aligned}\hat{X}_s &= \sum_{i=1}^{4} a_i^\dagger a_i, & (66)\\ \hat{Y}_s &= \sum_{i<j=1}^{4} (a_i^\dagger a_j + a_j^\dagger a_i), & (67)\\ \hat{X}_b &= \sum_{i=5}^{10} a_i^\dagger a_i, & (68)\\ \hat{Y}_b &= (a_5^\dagger a_8 + a_5^\dagger a_6 + a_5^\dagger a_{10} + a_5^\dagger a_7 + a_8^\dagger a_{10} + a_8^\dagger a_7 + a_8^\dagger a_9 + a_6^\dagger a_{10} \\ &+ a_6^\dagger a_7 + a_6^\dagger a_9 + a_{10}^\dagger a_9 + a_7^\dagger a_9 + H.c.), & (69)\\ \hat{Z}_b &= (a_5^\dagger a_9 + a_6^\dagger a_8 + a_7^\dagger a_{10} + H.c.), & (70)\end{aligned}$$

where H.c. stands for Hermitian conjugate.

Simultaneous diagonalization of C_{II} and the operators () breaks the degeneracy in (50), as we proceed to explain. After having diagonalized the CSCO-II, the eigenvectors take the general form

$$|_q\Psi_{\Gamma\gamma}^{JmV}\rangle = \sum_{k=-J}^{J} \sum_{\mathbf{v}} s_{k\mathbf{v};q\Gamma\gamma}^{JmV} |Jkm\rangle \otimes |V;\mathbf{v}\rangle, \qquad (71)$$

where $\{JmV\}$ characterize the representation space and q is the multiplicity index. The number operators only connect states with different multiplicity label q because they are invariant and preserve the number of quanta. Hence, for a number operator $\hat{\hat{\nu}}_\zeta$ we have

$$\langle_{q'}\Psi_{\Gamma\gamma}^{JmV}|\hat{\hat{\nu}}_\zeta|_q\Psi_{\Gamma\gamma}^{JmV}\rangle = \sum_{k',\mathbf{v}'} \sum_{k,\mathbf{v}} s_{k'\mathbf{v}';q'\Gamma\gamma}^{JmV*} \langle Jk'm| \otimes \langle V;\mathbf{v}'|\hat{\hat{\nu}}_\zeta|Jkm\rangle \otimes |V;\mathbf{v}\rangle s_{k\mathbf{v};q\Gamma\gamma}^{JmV}. \qquad (72)$$

If we now use the extension of the operator $\hat{\hat{\nu}}_\zeta$ given by $\hat{1} \otimes \hat{\hat{\nu}}_\zeta$, the matrix defined by

$$\mathbf{M} = ||\langle_{q'}\Psi_{\Gamma\gamma}^{JmV}|\hat{\hat{\nu}}_\zeta|_q\Psi_{\Gamma\gamma}^{JmV}\rangle|| \qquad (73)$$

takes the form

$$\mathbf{M} = \mathbf{S}^{\dagger}\{\mathbf{1}^{(J)} \otimes \mathbf{C}\}\mathbf{S}, \tag{74}$$

where

$$\mathbf{S} = ||s^{JmV}_{k\mathbf{v};q\Gamma\gamma}||; \qquad \mathbf{1}^{(J)} = \delta_{k'k}; \qquad \mathbf{C} = ||\langle V;\mathbf{v}'|\hat{\nu}_{\zeta}|V;\mathbf{v}\rangle||. \tag{75}$$

The matrix $\mathbf{1}^{(J)}$ is the $(2J+1)$-dimensional identity matrix. Let us now suppose that the transformation (42) is known. In this case, the matrix $\mathbf{C}$ can be expressed as

$$\mathbf{C} = \mathbf{A}^{\dagger}\ \Lambda\ \mathbf{A}, \tag{76}$$

where Λ is a diagonal matrix whose elements are given by the eigenvalues of the equation

$$\hat{\nu}_{\zeta}|V;\nu_0;\nu_1\nu_2\nu_3^{\ell_3}\nu_4^{\ell_4}\rangle^{\Gamma}_{\gamma} = \nu_{\zeta}|V;\nu_0;\nu_1\nu_2\nu_3^{\ell_3}\nu_4^{\ell_4}\rangle^{\Gamma}_{\gamma}. \tag{77}$$

This treatment is completely general. We now come back to the suggested example, considering the subspace (44) with $J=1$ and $V_b=1$. In this case the $\mathbf{A}$ matrix can be built from the symmetry adapted tensors

$$\mathbf{A}^{-1} = \begin{pmatrix} \frac{1}{\sqrt{6}} & -\frac{1}{2\sqrt{3}} & \frac{1}{2} & 0 & -\frac{1}{2} & -\frac{1}{2} \\ \frac{1}{\sqrt{6}} & -\frac{1}{2\sqrt{3}} & -\frac{1}{2} & 0 & -\frac{1}{2} & \frac{1}{2} \\ \frac{1}{\sqrt{6}} & \frac{1}{\sqrt{3}} & 0 & -\frac{1}{\sqrt{2}} & 0 & 0 \\ \frac{1}{\sqrt{6}} & -\frac{1}{2\sqrt{3}} & -\frac{1}{2} & 0 & \frac{1}{2} & -\frac{1}{2} \\ \frac{1}{\sqrt{6}} & -\frac{1}{2\sqrt{3}} & \frac{1}{2} & 0 & \frac{1}{2} & \frac{1}{2} \\ \frac{1}{\sqrt{6}} & \frac{1}{\sqrt{3}} & 0 & \frac{1}{\sqrt{2}} & 0 & 0 \end{pmatrix}, \tag{78}$$

where the local basis has been taken in consecutive order, and the normal basis order corresponds to the appearance of the bending tensors in (). In practice, it is more convenient to consider a unique operator $\hat{\mathcal{N}} = 10000\hat{\nu}_0 + 1000\hat{\nu}_1 + 100\hat{\nu}_2 + 10\hat{\nu}_3 + \hat{\nu}_4$ instead of diagonalizing each operator $\hat{\nu}_{\zeta}$. In this way the $\hat{\mathcal{N}}$ eigenvalues provide normal labels in a straightforward way. Hence, the $\mathbf{\Lambda}$ matrix takes the form

$$\Lambda = \begin{pmatrix} 10000 & 0 & 0 & 0 & 0 & 0 \\ 0 & 100 & 0 & 0 & 0 & 0 \\ 0 & 0 & 100 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix}, \tag{79}$$

and selecting the subspace of functions spanning the A_2 component of the representation F_1, the substitution of the corresponding matrices into (74), leads to the matrix

$$\mathbf{M}^{(F_1,A_2)} = \begin{pmatrix} 3110.36 & 307.77 - 1975.14i & 4085.70 + 790.96i \\ 307.77 + 1975.14i & 1392.81 & -151.05 + 2681.92i \\ 4085.7 - 790.96i & -151.05 - 2681.92i & 5597.83 \end{pmatrix}, \tag{80}$$

whose diagonalization provides symmetry-adapted rovibrational functions displayed in the lower half of **Table 7**. With the number of quanta labels (eigenvalues of the number operators isomorphic to normal quantum numbers), the spurious states identification is immediate: all states with $\nu_0 \neq 0$ should be eliminated. In this example it was not necessary to diagonalize the square of the vibrational angular momentum operators

$$\begin{aligned} \hat{\ell}_2^{A_2} &= -i\sqrt{2}[\hat{T}_b^{\dagger E} \times \hat{T}_b^{E}]^{A_2} \\ \hat{\ell}_3^{F_1,\gamma} &= i\sqrt{2}[\hat{T}_s^{\dagger F_2} \times \hat{T}_s^{F_2}]^{F_1}_{\gamma} \\ \hat{\ell}_4^{F_1,\gamma} &= i\sqrt{2}[\hat{T}_b^{\dagger F_2} \times \hat{T}_b^{F_2}]^{F_1}_{\gamma}, \end{aligned}$$

where $\gamma = A_2, B_1, B_2$. If necessary, they may be incorporated to the set of operators to be diagonalized to distinguish degenerate states. Following this approach we obtain the physical states

$$\big|_{0;0100}\zeta^{1m1}_{F_1,\gamma'}\big\rangle; \qquad \big|_{0;0100}\zeta^{1m1}_{F_2,\gamma''}\big\rangle, \tag{81}$$

$$\big|_{0;0001}\zeta^{1m1}_{A_2}\big\rangle; \qquad \big|_{0;0001}\zeta^{1m1}_{E,\gamma}\big\rangle; \qquad \big|_{0;0001}\zeta^{1m1}_{F_1,\gamma'}\big\rangle; \qquad \big|_{0;0001}\zeta^{1m1}_{F_2,\gamma''}\big\rangle \tag{82}$$

where

$$\gamma = A_1, A_2; \quad \gamma' = A_2, B_1, B_2; \quad \gamma'' = A_1, B_1, B_2. \tag{83}$$

The rovibrational Hamiltonian commutes, in addition to the elements of $\mathcal{T}_d(M)$, with the components of the angular momentum $\mathbf{R}$, which in our case is given by [28]

$$\hat{\mathbf{R}} = \hat{\mathbf{J}} - (\hat{\ell}_s + \hat{\ell}_b), \tag{84}$$

The formula for the coupled wave functions in the case of angular momentum substraction is the same as the addition formula with the exception that the eigenfunctions $\phi_{\ell m}$ of the vector $\ell = (\ell_3 + \ell_4)$ are replaced by their complex conjugate, where $\phi^*_{\ell m} = (-1)^m \phi_{\ell -m}$. The eigenvalues of $\hat{R}^2$ are $R(R+1)$. We should thus consider also the diagonalization of the operator

$$\hat{R}^2 = \hat{J}^2 + \hat{\ell}^2 - 2\hat{\mathbf{J}} \cdot \hat{\ell}, \tag{85}$$

involving functions of the same IRREP, angular momentum J and total vibrational angular momentum ℓ. In our particular example we have states with $\ell = 0$, given by (81), which implies that $R = 1$, and states with $\ell = 1$, given by (82), corresponding to $R = 0, 1, 2$, in accordance with the angular momentum rules. The states are eigenstates of $\hat{R}^2$ as follows

$$\left|{}_{0;0001}\zeta^{1m1}_{A_2}\right\rangle^{R=0}; \quad \left|{}_{0;0001}\zeta^{1m1}_{E,\gamma}\right\rangle^{R=2}; \quad \left|{}_{0;0001}\zeta^{1m1}_{F_1,\gamma'}\right\rangle^{R=1}; \quad \left|{}_{0;0001}\zeta^{1m1}_{F_2,\gamma''}\right\rangle^{R=2}. \tag{86}$$

In general, we may first proceed to diagonalize the operator

$$\ell^2 = \ell_3^2 + \ell_4^2 + 2\ \ell_3 \cdot \ell_4, \tag{87}$$

and later on continue diagonalizing (85) following an approach similar to the one used to obtain (74). In this case, however, the transformation properties of J are needed. Projecting the operators $\hat{J}_i$, using (9), we obtain

$$T^{(1)}_{F_1,A_2} = J_0; \quad T^{(1)}_{F_1,B_1} = \frac{1}{\sqrt{2}}(J_{+1} + iJ_{-1}); \quad T^{(1)}_{F_1,B_2} = \frac{1}{\sqrt{2}}(J_{+1} - iJ_{-1}), \tag{88}$$

which enable us to carry out the dot product with ℓ:

$$\mathbf{J}\cdot\ell = \sqrt{3}[J\times\ell]^{A_1}, \tag{89}$$

with

$$\hat{J}_{\pm}|Jkm\rangle = \sqrt{(j\pm k)(j\mp k+1)}|J,k\mp 1,m\rangle. \tag{90}$$

We have thus presented an approach that has the remarkable property that given the matrix elements of number operators, angular momentum operators, and symmetry operations involved in the CSCO-II in the vibrational space, the symmetrization of the rovibrational functions can be obtained in a relatively simple way through the incorporation of the Wigner's D matrices associated with equivalent rotations. This approach, although simple, is expected to involve matrices of large dimensions for large J values and high number of quantum V. In order to explore a treatment for high V, an approach associated with the identification of smaller invariant subspaces should be followed, in a similar form to the method presented in §4. Let us consider the intrinsic function

$$|\phi_0\rangle = |Jkm\rangle\otimes|V;\mathbf{v}\rangle. \tag{91}$$

There is no permutation $p\in\mathcal{T}_d(M)$ that leaves this function invariant. Consequently the action of every element p_σ over the ket $|\phi_0\rangle$ generates a 24-dimensional representation space $p_\sigma|\phi_0\rangle\equiv|\phi_\sigma\rangle$, and then

$$p\;|\phi_\sigma\rangle = \sum_{\sigma'=1}^{24}\Delta^{(red)}_{\sigma'\sigma}(p)\;|\phi_{\sigma'}\rangle;\qquad \forall p\in\mathcal{T}_d(M), \tag{92}$$

where we suppose to consider the same element ordering than in Table 4. Again the matrix $\Delta^{(red)}(p)$ is J-independent and corresponds to the regular representation. In this case we can follow the standard approach to establish a CSCO-III, as explained in Ref. [22]. The new operator is provided by the chain $\overline{\mathcal{T}}_d(M)\supset\overline{\mathcal{C}}_{2v}$, which together with (13) permits to establish the following CSCO-III

$$\text{CSCO-III} = \{C, C(s), \overline{C}(s)\}, \tag{93}$$

where C is given by (12), $C(s)$ by (15) and $\overline{C}(s) = (\overline{14})^* + 3(\overline{23})^*$. It should be remembered that the action of a permutation $\bar{p}$ over a ket $|\phi_\sigma\rangle$ is given by

$$\bar{p}|\phi_\sigma\rangle = \bar{p}p_\sigma|\phi_0\rangle = p_\sigma p|\phi_0\rangle. \tag{94}$$

The simultaneous diagonalization of the set of operators (93) can be substituted by the unique diagonalization of the operator $\hat{C}_{III} \equiv \hat{C} + 3\hat{C}(s) + 5\overline{C}(s)$. The action of this operator on the representation space takes the form

$$\hat{C}_{III}\ |\phi_\sigma\rangle = \sum_{\sigma'=1}^{24} \Delta^{(red)}_{\sigma'\sigma}(C_{III})\ |\phi_{\sigma'}\rangle. \tag{95}$$

The diagonalization of this matrix provides the eigenvectors with the general form

$$|\psi_\zeta\rangle = \sum_{\sigma=1}^{24} C^{(rv)}_{\sigma,\zeta}\ |\phi_\sigma\rangle, \tag{96}$$

which can be translated into the original basis to obtain

$$|\psi_\zeta\rangle = \sum_{k'}\sum_{\mathbf{v}'} B^{(rv)}_{k'\mathbf{v}';\zeta}|Jk'm\rangle \otimes |V;\mathbf{v}'\rangle. \tag{97}$$

where

$$B^{(rv)}_{k'\mathbf{v}';\zeta} = \sum_{\sigma=1}^{24} C^{(rv)}_{\sigma,\zeta} D^{(J)}_{kk'}[\varphi(p_\sigma)^{-1}]\Delta^{(vib)}_{\mathbf{v}'\mathbf{v}}[v(p_\sigma)]. \tag{98}$$

The procedure to follow is similar to the one presented in §4. First an intrinsic function is chosen by selecting k and $\mathbf{v}$ in Eq. (91). These labels are used to generate the coefficients (98), once the vibrational representation $\Delta^{(vib)}[v(p_\sigma)]$ is constructed. Again, for a given set of values $(k, \mathbf{v})$, some eigenvectors may vanish, which means that the corresponding IRREP is not contained in the reduction. In contrast to the previous case of pure rotations, IRREPS multiplicity may appear in the space $\mathcal{L}_{k\mathbf{v}}$. In this case the eigenvectors are expected to be orthogonal. However, additional functions carrying the same IRREP must be projected through another space $\mathcal{L}_{k'\mathbf{v}'}$, which are not orthogonal $\langle\mathcal{L}_{k\mathbf{v}}|\mathcal{L}_{k'\mathbf{v}'}\rangle \neq 0$. More labels are provided by the diagonalization of the set of number operators and vibrational angular momentum operators, following the same approach previously described.

As mentioned before, the resulting eigenfunctions are given in terms of local functions, which may be translated into anharmonic oscillators, a feature that may be used to take into account anharmonicities from the outset.

6. Summary and conclusions

In this work some relations involving the equivalent rotations associated with the permutation-inversion group have been analyzed. In particular, the matrix elements of equivalent rotations were deduced following a novel method, different to the ones found in the literature. The isomorphism between permutations and equivalent rotations has been also proved, a remarkable property taken into account in the projection of rotational and rovibrational functions.

Rotational functions are projected to IRREPS of the molecular symmetry group $\mathcal{T}_d(M)$ using the eigenfunction method, which is based on the diagonalization of a complete set of commuting operators (CSCO) in the representation space. The CSCO of type II, which distinguishes IRREPS as well as their corresponding components, was built in terms of a linear combination of Wigner's D functions. Since in this process degeneracy persists for $J > 4$, an approach to orthogonalize the degenerate functions carrying the same IRREP was presented. This is a compulsory task if coupling coefficients are used to construct the rovibrational functions. An attempt to define a CSCO-III was unsuccessful, due to the fact that the invariant subspaces are simply reducible and not orthogonal. However, the identification of the six-dimensional invariant spaces allows us to accomplish the projection in a more efficient way, although at the end an orthogonalization approach should be carried out.

The incorporation of the vibrational degrees of freedom has also been presented. It has been shown that the projection of the rovibrational space is given in terms of direct products of Wigner's D functions and representation matrices involving the vibrational space. It has been also established a procedure to eliminate spurious sates that are intrinsic to spherical top molecules when described in terms of internal coordinates. In particular the bending space of one quanta was studied in detail in order to exemplify our approach to eliminate the spurious modes as well as to introduce the invariance under the **R angular momentum**. In our method the diagonalization of the Hamiltonian may be viewed as the last step in the accomplishment of establishing the complete set of commuting operators of the system.

The attractive feature of our approach is that the projection of the rovibrational functions is relatively simple, provided that one has a code to deal with the vibrational degrees of freedom. In addition, the projected functions are given in a local scheme, a fact that allows to consider local potentials as anharmonic potentials (Morse, for instance). This fact may represent an interesting alternative to the approaches based on tensorial formalisms where a normal mode basis is used from the beginning [29]. Although this approach has been applied to methane, it should be stressed that the method is general. Besides, this procedure may help to build in a systematic manner the interactions of the molecular Hamiltonian in phenomenological fashion either in the algebraic or phase space.

Acknowledgments.

This work has partially **been** supported by CONACyT, México. This work has also been partially supported by the Spanish MEC and by European regional development funds (FEDER) under project CPAN-Ingenio (CSD2007-00042), and by the Junta de Andalucía (projects P07-FQM-02962 and P07-FQM-03014).

Appendix A.

In this Appendix we prove that both expressions $\hat{P}_R\psi(\mathbf{r}) = \psi(R^{-1}\mathbf{r})$ **for the active point of view** and $\hat{P}_R\psi(\mathbf{r}) = \psi(R\mathbf{r})$ **for the passive transformations** are equally valid and establish their differences. Let R an element of the group with associated operator $\hat{P}_R$. The operator is defined by its action over the basis vectors $|\mathbf{r}\rangle$. In the active point of view we have:

$$\hat{P}_R|\mathbf{r}\rangle = |R\mathbf{r}\rangle; \qquad \langle\mathbf{r}|\hat{P}_R^\dagger = \langle R\mathbf{r}|. \tag{99}$$

Consider now an arbitrary ket $|\psi\rangle$ with $\hat{P}_R|\psi\rangle = |\psi'\rangle$. We are interested in obtaining $\langle\mathbf{r}|\psi'\rangle = \langle\mathbf{r}|\hat{P}_R|\psi\rangle$. To this end we have to find $\langle\mathbf{r}|\hat{P}_R$. Introducing the unitary property of the operators $\hat{P}_R^\dagger\hat{P}_R = 1$, we have

$$\hat{P}_R^\dagger\hat{P}_R|\mathbf{r}\rangle = \hat{P}_R^\dagger|R\mathbf{r}\rangle = |\mathbf{r}\rangle; \qquad \langle\mathbf{r}|\hat{P}_R = \langle R^{-1}\mathbf{r}| \tag{100}$$

where we have taken into account (99). This result allows us to obtain the transformed ket in terms of the original one in the coordinate representation

$$\langle\mathbf{r}|\psi'\rangle = \langle\mathbf{r}|\hat{P}_R|\psi\rangle = \langle R^{-1}\mathbf{r}|\psi\rangle = \psi(R^{-1}\mathbf{r}), \tag{101}$$

which corresponds to $\hat{P}_R\psi(\mathbf{r}) = \psi(R^{-1}\mathbf{r})$. We stress that this expression may be established as the invariance principle of scalar functions $\langle\mathbf{r}'|\psi'\rangle = \langle\mathbf{r}|\psi\rangle$. Applying this result we can prove the isomorphism $\hat{P}_R\hat{P}_S = \hat{P}_{RS}$ [14]. Given this isomorphism is crucial to note that given the basis $\{\psi_i(\mathbf{r}); \quad i = 1\ldots n\}$ the matrices involved in

$$\hat{P}_R\psi_i(\mathbf{r}) = \sum_{j=1}^{n} D_{ji}(R)\psi_j(\mathbf{r}), \tag{102}$$

constitute a vectorial representation of the group, *e.g.*; $\mathbf{D}(R)\mathbf{D}(S) = \mathbf{D}(RS)$.

Let us now consider the case $\hat{P}_R\psi(\mathbf{r}) = \psi(R\mathbf{r})$ **for the passive point of view**. We proceed just changing the definition of the action of the operator over the basis to reflect the pasive point of view

$$\hat{P}_R|\mathbf{r}\rangle = |R^{-1}\mathbf{r}\rangle; \qquad \langle\mathbf{r}|\hat{P}_R^\dagger = \langle R^{-1}\mathbf{r}|. \tag{103}$$

Using the unitary property (100) we have that $\langle\mathbf{r}|\hat{P}_R = \langle R\mathbf{r}|$, which allow us to obtain

$$\langle\mathbf{r}|\hat{P}_R|\psi\rangle = \langle R\mathbf{r}|\psi\rangle = \psi(R\mathbf{r}). \tag{104}$$

Following the **traditional** representation theory the passive point of view (104) leads to the anti-isomorphism $\hat{P}_R\hat{P}_S = \hat{P}_{SR}$ [9, 14]. This fact explain the preference for the active picture. In the framework of permutation invertion group, however, the elements S, R correspond to elements of the molecular symmetry group with two possibilities to define their effect over the functions. The permutations may be carried out either the coordinates, denoted with p_S, or over the nuclei, denoted with π_S. It can be shown that p_S is consistent with the anti-isomorphism.

A remarkable property of these pictures is that they satisfy the property $p_S = \pi_S^{-1}$ [22]. Hence if we identify R with p_R in $\hat{P}_R \hat{P}_S = \hat{P}_{SR}$ we indeed have an anti-isomorphism **for the passive transformations** $\hat{P}_{p_R} \hat{P}_{p_S} = \hat{P}_{p_{SR}}$, but considering π_s we have that $\hat{P}_{\pi_R} \hat{P}_{\pi_S} = \hat{P}_{p_R^{-1}} \hat{P}_{p_S^{-1}} = \hat{P}_{p_S^{-1} p_R^{-1}} = \hat{P}_{(p_R p_S)^{-1}} = \hat{P}_{\pi_{RS}}$, which correspond to an isomorphism [1]. An additional consequence of choosing the operators π_S is that now the set of functions $\{\psi_i(\mathbf{r}); \quad i = 1 \ldots n\}$ generate the matrix representation through [11]

$$\begin{aligned} \hat{P}_{\pi_R} \psi_i(\mathbf{r}) &= \sum_{j=1}^{n} D_{ij}(\pi_R) \psi_j(\mathbf{r}), \\ &= \sum_{j=1}^{n} D_{ij}(p_R^{-1}) \psi_j(\mathbf{r}), \end{aligned} \tag{105}$$

instead of (102), as long as we are dealing with functions $\psi_i(\mathbf{r})$ involving coordinates of nuclei.

Appendix B.

In this Appendix we obtain the effect of an equivalent rotation $R(\alpha, \beta, \gamma)$, characterized by the (α, β, γ) Euler angles, over the rotational functions (1). Equivalent rotations are referred to the molecule-fixed (x, y, z) system , with origin at the nuclear center of mass. At first glance this task is not obvious due to the fact that equivalent rotations and rotational functions are referred to different systems of reference: the molecule-fixed (x, y, z) system and the space-fixed (ξ, η, ζ) system, parallel to the

---

[1] With the effect of the permutation-inversion group over the **coordinates of the** nuclei, the active point of view provides a anti-isomorphism for the representations.

laboratory. Explicitly, the rotation operator is given by [20]

$$\hat{R}(\alpha,\beta,\gamma) = e^{-i\alpha\hat{J}_z} e^{-i\beta\hat{J}_y} e^{-i\gamma\hat{J}_z}, \tag{106}$$

where the operators $\{\hat{J}_x, \hat{J}_y, \hat{J}_z\}$ are the angular momentum components with respect to the molecule-fixed axis system.

In order to apply the rotation $\hat{R}(\alpha,\beta,\gamma)$, it is necessary to carry out a successive set of transformations in order to express equivalent rotations in the rotational functions reference system. To this end we note the following identities

$$\begin{aligned} e^{-i\alpha\hat{J}_z} &= e^{-i\theta\hat{J}_{y'}} e^{-i\alpha\hat{J}_\zeta} e^{i\theta\hat{J}_{y'}} && (107) \\ e^{-iA\hat{J}_{y'}} &= e^{-i\phi\hat{J}_\zeta} e^{-iA\hat{J}_\eta} e^{i\phi\hat{J}_\zeta} && (108) \\ e^{-iB\hat{J}_y} &= e^{-i\chi\hat{J}_z} e^{-iB\hat{J}_{y'}} e^{i\chi\hat{J}_z}, && (109) \end{aligned}$$

where A and B stand for arbitrary angles, y' corresponds to the intermediate axis according to the three rotations associated to the Euler angles, and $\{\hat{J}_\xi, \hat{J}_\eta, \hat{J}_\zeta\}$ are the corresponding angular momentum operators associated with the (ξ,η,ζ) system. The substitution of () into the equivalent rotation (106) leads to the expression

$$\hat{R}(\alpha,\beta,\gamma) = e^{-i\phi\hat{J}_\zeta} e^{-i\theta\hat{J}_\eta} e^{-i(\alpha+\chi)\hat{J}_\zeta} e^{-i\beta\hat{J}_\eta} e^{-i(\gamma-\chi)\hat{J}_\zeta} e^{i\theta\hat{J}_\eta} e^{i\phi\hat{J}_\zeta}, \tag{110}$$

which can now be applied to the rotational functions.

In accordance to (1), we shall be interested in the result of applying a rotation $\hat{P}_R$, referred to the (ξ,η,ζ) system, to the functions $D^{(J)*}_{mk}(S)$. Following the standard approach we have, **in the active point of view** [20, 22]

$$\hat{P}_R D^{(J)*}_{mk}(S) = D^{(J)*}_{mk}(R^{-1}S) = \sum_{m'=-J}^{J} D^{(J)}_{m'm}(R)\, D^{(J)*}_{m'k}(S), \tag{111}$$

where we have taken into account the unitary property of the representations. Hence we may now take the operator (110) over the rotational functions applying successively the equation (111). After some simplifications we arrive to the simple expression

$$\hat{R}(\alpha,\beta,\gamma)|Jkm\rangle = \sum_{k'=-J}^{J} D^{(J)}_{kk'}(\alpha,\beta,\gamma)\ |Jk'm\rangle, \tag{112}$$

which can be found in Refs.[7, 24], for instance, but using different arguments in their proofs. In the case of equivalent rotations the passive picture is taken, and consequently the inverse of the rotations has to be considered. This explains the expression (5).

Appendix C.

Theorem:*The molecular symmetry group is isomorphic to the group of equivalent rotations.*

Proof: Let p_1, p_2 and $p_3 = p_1 p_2$ be elements of the molecular symmetry group, $\mathcal{G}(M)$, and $\{\varphi(p_i) \equiv R_i; \quad i = 1, 2, 3\}$ their corresponding equivalent rotations. Let us now use (5) to apply the successive rotations $\varphi(p_1)\varphi(p_2)$ over the rotational function

$$\begin{aligned}\varphi(p_1)\varphi(p_2)|Jkm\rangle &= \sum_{k''}\{\sum_{k'} D^{(J)}_{kk'}(R_2^{-1})D^{(J)}_{k'k''}(R_1^{-1})\}|Jk''m\rangle \\ &= \sum_{k''} D^{(J)}_{kk''}((R_1R_2)^{-1})|Jk''m\rangle. \qquad (113)\end{aligned}$$

On the other hand

$$\varphi(p_3)|Jkm\rangle = \varphi(p_1p_2)|Jkm\rangle = \sum_{k''} D^{(J)}_{kk''}(R_3^{-1})|Jk''m\rangle. \qquad (114)$$

The comparison of the latter equation with (113) proves the isomorphism

$$\varphi(p_1p_2) = \varphi(p_3) = \varphi(p_1)\varphi(p_2). \qquad (115)$$

Appendix D.

Theorem. In case of IRREP multiplicity, given the set $\{{}_{\kappa_1}\psi^{(J,\Gamma)}_\alpha, {}_{\kappa_2}\psi^{(J,\Gamma)}_\alpha\}$ *composed by the* α*-th component of the same IRREP* Γ *with* $\kappa_1 \neq \kappa 2$ *and the property* $\langle {}_{\kappa_1}\psi^{(J,\Gamma)}_\alpha | {}_{\kappa_2}\psi^{(J,\Gamma)}_\alpha\rangle = 0$*, the sets* $\{{}_{\kappa_1}\psi^{(J,\Gamma)}_\beta, {}_{\kappa_2}\psi^{(J,\Gamma)}_\beta; \quad \beta \neq \alpha\}$ *associated with the rest of the components and generated through Eq. (25), satisfy* $\langle {}_{\kappa_1}\psi^{(J,\Gamma)}_\beta | {}_{\kappa_2}\psi^{(J,\Gamma)}_\beta\rangle = 0$ *for* $\beta \not\alpha$.

Proof. According to the theorem we have to prove that

$$\langle {}_{\kappa_1}\psi^{(\Gamma)}_\beta | {}_{\kappa_2}\psi^{(\Gamma)}_\beta\rangle = \langle \sum_{R\in G} D^{(\Gamma)*}_{\beta\alpha}(R)\hat{\mathcal{O}}_{R\kappa_1}\psi^{(\Gamma)}_\alpha | \sum_{S\in G} D^{(\Gamma)*}_{\beta\alpha}(S)\hat{\mathcal{O}}_{S\kappa_2}\psi^{(\Gamma)}_\alpha\rangle = 0, \qquad (116)$$

where for the sake of brevity we have removed the angular momentum J label. Expanding the rhs of (116) we have

$$\langle_{\kappa_1}\psi_\beta^{(\Gamma)}|_{\kappa_2}\psi_\beta^{(\Gamma)}\rangle = \sum_{R\in G}\sum_{S\in G} D_{\beta\alpha}^{(\Gamma)}(R) D_{\beta\alpha}^{(\Gamma)*}(S)\langle\hat{\mathcal{O}}_{R\kappa_1}\psi_\alpha^{(\Gamma)}|\hat{\mathcal{O}}_{S\kappa_2}\psi_\alpha^{(\Gamma)}\rangle. \tag{117}$$

The last factor of the sum has the form

$$\langle\hat{\mathcal{O}}_{R\kappa_1}\psi_\alpha^{(\Gamma)}|\hat{\mathcal{O}}_{S\kappa_2}\psi_\alpha^{(\Gamma)}\rangle = \langle_{\kappa_1}\psi_\alpha^{(\Gamma)}|\hat{\mathcal{O}}_R^\dagger\hat{\mathcal{O}}_{S\kappa_2}\psi_\alpha^{(\Gamma)}\rangle = \langle_{\kappa_1}\psi_\alpha^{(\Gamma)}|\hat{\mathcal{O}}_{T\kappa_2}\psi_\alpha^{(\Gamma)}\rangle, \tag{118}$$

with $T = R^{-1}S$, given the isomorphism in the passive point of view (see Appendix A). But

$$\langle_{\kappa_1}\psi_\alpha^{(\Gamma)}|\hat{\mathcal{O}}_{T\kappa_2}\psi_\alpha^{(\Gamma)}\rangle = \sum_\gamma D_{\alpha\gamma}^{(\Gamma)}(T^{-1})\langle_{\kappa_1}\psi_\alpha^{(\Gamma)}|_{\kappa_2}\psi_\gamma^{(\Gamma)}\rangle = 0, \tag{119}$$

because of the orthogonality of functions carrying different components, as well as the initial condition $\langle_{\kappa_1}\psi_\alpha^{(\Gamma)}|_{\kappa_2}\psi_\alpha^{(\Gamma)}\rangle = 0$. This proves the theorem.

References

[1] J.M. Hollas, *High Resolution Spectroscopy*, John Wiley & Sons, New York, 1998.

[2] P.Jensen and P.Bunker editors, *Computational Molecular Spectroscopy*, , John Wiley & Sons, New York, 2000.

[3] H.J. Wörner, X. Qian, and F. Merkt, *J.Chem.Phys.* **126**, 144305 (2007).

[4] M. Carvajal, F.W. Willaert, J. Demaison, and I. Kleiner, *J.Mol.Spectrosc.* **246**, 158-166 (2007).

[5] H.C. Longuet-Higgins, *Mol. Phys.* **6**, 445 (1963).

[6] J.T. Hougen *J.Chem.Phys.* **37**, 1433 (1962).

[7] J.T. Hougen *J.Chem.Phys.***39**,358 (1963).

[8] S. Altmann, Proc. Roy.Soc. 1967 *Mol.Phys.*, **A298** 184.

[9] S.Altmann, *Induced reprentations in crystals and molecules*, Academic Press, London, 1977.

[10] Y.G.Smeyers, *Introduction to group theory for nonrigid molecules*, Advances in Quantum Chemistry, Vol. 24, 1992.

[11] P.R.Bunker and P.Jensen *Molecular Symmetry and Spectroscopy*, 1998, NRC Research Press, Ottawa, Canada.

[12] P.R.Bunker and P.Jensen *Fundamentals of Molecular Symmetry*, 2005.Institute of Physics. Series in Chemical Physics.

[13] D.Papousek, and M.R.Aliev, *Molecular Vibrational-Rotational Spectra.* Elsevier, Amsterdam,1982.

[14] M.Hammermesh *Group Theory and its applications to physical problems*, 1962, DoverPublications, Inc., New York.

[15] S.K.Kim *Group Theoretical Methods and Applications to Molecules and Crystals*, 1962, DoverPublications, Inc., New York.

[16] P.H.Butler, A.M.Ford and M.F.Reid , *J.Phys.B:At.Mol.Phys.*, **16** 967-974 (1983).

[17] A.Nikitin, J.P. Champion and V.G. Tyuterev, *J.Mol.Spectrosc.*, **182** 72-84 (1997).

[18] P.R.Bunker and P.Jensen , *Mol.Phys.*, **97** 255-264 (1999).

[19] E.P.Wigner, *Group Theory and its applications to the quantum mechanics of atomic spectra*, 1959, Academic Press, New York.

[20] M.E.Rose, *Elementary Theory of Angular Momentum*, Dover Publications, INC. New York. 1957.

[21] D.A.Varshalovich, A.N. Moskalev and V.K.Khersonskii, *Quantum Theory of Angular Momentum*. World Scientific,1989.

[22] J.Q. Chen, *Group Representation Theory for Physicists*, World Scientific, 1989.

[23] A. Frank, R. Lemus, F. Pérez-Bernal, and R. Bijker, *J.Mol.Spectrosc.*, **196** 329-334 (1999).

[24] William G. Harter, *Principles of Symmetry, Dynamics and Spectroscopy*, John Wiley & Sons, INC. 1993.

[25] Richard N. Zare , *Angular Momentum: Understanding Spatial Aspects in Chemistry and Physics* , John Wiley & Sons, INC. 1988.

[26] R. Lemus, *Mol.Phys.*, **101** 2511-2528 (2003).

[27] G.H. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules*, Krieger Publishing Company, Malabar, Florida, 1991.

[28] K.T. Hecht, *J.Mol.Spectrosc.*, **5** 355-389 (1960).

[29] V. Boudon *et al.*, *J. Mol. Spectrosc.* **228**, 620-634 (2004).

Table 1 λ_i^ν table for the $\mathcal{T}_d(M)$ MS group defined by (10).

$\mathcal{T}_d(M)$	K_1	K_2	K_3	K_4	K_5
A_1	1	8	3	6	6
A_2	1	8	3	-6	-6
E	1	-4	3	0	0
F_1	1	0	-1	2	-2
F_2	1	0	-1	-2	2

Table 2 Character table of the group $\mathcal{C}_{2v}$ **and eigenvalues** μ **of** $\hat{C}(s)$ **operator (15)**.

$\mathcal{C}_{2v}$	e	$(14)(23)$	$(14)^*$	$(23)^*$	μ
A_1	1	1	1	1	4
A_2	1	1	-1	-1	-4
B_1	1	-1	1	-1	-2
B_2	1	-1	-1	1	2

Table 3 Eigenvalues of the complete set of commuting operators of type II.

${}^{\nu}\mathcal{T}_d(M)$	ν	${}^{\mu}\mathcal{C}_{2v}$	μ	ζ
A_1	6	A_1	4	18
A_2	−6	A_2	−4	−18
E	0	A_1	4	12
E	0	A_2	−4	−12
F_1	−2	A_2	−4	−14
F_1	−2	B_1	−2	−8
F_1	−2	B_2	2	4
F_2	2	A_1	4	14
F_2	2	B_1	−2	−4
F_2	2	B_2	2	8

Table 4. Elements of the molecular symmetry group $\mathcal{T}_d(M)$ and their equivalent rotations in terms of the Euler angles (α, β, γ).

Element of $\mathcal{T}_d(M)$ p	Equivalent rotation $\phi(p) \to (\alpha, \beta, \gamma)$	Point operation $v(p)$	Spin permutation p_n
E	(0,0,0)	E	p_0
$(12)^*$	$(0, \frac{\pi}{2}, \pi)$	$\sigma_d^{(6)}$	p_{12}
$(13)^*$	$(\frac{\pi}{2}, \frac{\pi}{2}, \frac{\pi}{2})$	$\sigma_d^{(3)}$	p_{13}
$(14)^*$	$(0, \pi, \frac{\pi}{2})$	$\sigma_d^{(2)}$	p_{14}
$(23)^*$	$(\pi, \pi, \frac{\pi}{2})$	$\sigma_d^{(1)}$	p_{23}
$(24)^*$	$(\frac{3\pi}{2}, \frac{\pi}{2}, \frac{3\pi}{2})$	$\sigma_d^{(4)}$	p_{24}
$(34)^*$	$(\pi, \frac{\pi}{2}, 0)$	$\sigma_d^{(5)}$	p_{34}
(123)	$(\frac{3\pi}{2}, \frac{\pi}{2}, 0)$	$C_3^{(4)}$	$p_{(132)}$
(132)	$(\pi, \frac{\pi}{2}, \frac{3\pi}{2})$	$C_3^{(4)2}$	$p_{(123)}$
(243)	$(\frac{\pi}{2}, \frac{\pi}{2}, \pi)$	$C_3^{(1)}$	$p_{(234)}$
(234)	$(0, \frac{\pi}{2}, \frac{\pi}{2})$	$C_3^{(1)2}$	$p_{(243)}$
(134)	$(\frac{3\pi}{2}, \frac{\pi}{2}, \pi)$	$C_3^{(2)}$	$p_{(143)}$
(143)	$(0, \frac{\pi}{2}, \frac{3\pi}{2})$	$C_3^{(2)2}$	$p_{(134)}$
(142)	$(\frac{\pi}{2}, \frac{\pi}{2}, 0)$	$C_3^{(3)}$	$p_{(124)}$
(124)	$(\pi, \frac{\pi}{2}, \frac{\pi}{2})$	$C_3^{(3)2}$	$p_{(142)}$
(12)(34)	$(0, \pi, 0)$	$C_2^{(y)}$	$p_{(12)(34)}$
(13)(24)	$(\frac{\pi}{2}, \pi, \frac{3\pi}{2})$	$C_2^{(x)}$	$p_{(13)(24)}$
(14)(23)	$(\pi, 0, 0)$	$C_2^{(z)}$	$p_{(14)(23)}$
$(1342)^*$	$(\frac{3\pi}{2}, 0, 0)$	$S_4^{(z)3}$	$p_{(1342)}$
$(1243)^*$	$(\frac{\pi}{2}, 0, 0)$	$S_4^{(z)}$	$p_{(1243)}$
$(1324)^*$	$(0, \frac{\pi}{2}, 0)$	$S_4^{(y)}$	$p_{(1324)}$
$(1423)^*$	$(0, \frac{3\pi}{2}, 0)$	$S_4^{(y)3}$	$p_{(1423)}$
$(1432)^*$	$(\frac{\pi}{2}, \frac{3\pi}{2}, \frac{3\pi}{2})$	$S_4^{(x)3}$	$p_{(1432)}$
$(1234)^*$	$(\frac{\pi}{2}, \frac{\pi}{2}, \frac{3\pi}{2})$	$S_4^{(x)}$	$p_{(1234)}$

Table 5. Symmetry adapted functions up to $J = 4$. The states $|J, -k, m\rangle$ are denoted by $|J\bar{k}m\rangle$

J	IRREP	eigenvalue	name	eigenvector
	(Γ, γ)	ζ		
0	A_1	18	$\psi^{(0:A_1)}$	$\|000\rangle$
1	(F_1, A_2)	-14	$\psi_{A_2}^{(1:F_1)}$	$\|10m\rangle$
	(F_1, B_1)	-8	$\psi_{B_1}^{(1:F_1)}$	$\frac{1}{\sqrt{2}}\{-i\|11m\rangle + \|1\bar{1}m\rangle\}$
	(F_1, B_2)	4	$\psi_{B_2}^{(1:F_1)}$	$\frac{1}{\sqrt{2}}\{\ \ i\|11m\rangle + \|1\bar{1}m\rangle\}$
2	(E, A_1)	12	$\psi_{A_1}^{(2:E)}$	$\|20m\rangle$
	(E, A_2)	-12	$\psi_{A_2}^{(2:E)}$	$\frac{1}{\sqrt{2}}\{\|22m\rangle + \|2\bar{2}m\rangle\}$
2	(F_2, A_1)	14	$\psi_{A_1}^{(2:F_2)}$	$\frac{1}{\sqrt{2}}\{-\ \|22m\rangle + \|2\bar{2}m\rangle\}$
	(F_2, B_1)	-4	$\psi_{B_1}^{(2:F_2)}$	$\frac{1}{\sqrt{2}}\{\ \ i\|21m\rangle + \|2\bar{1}m\rangle\}$
	(F_2, B_2)	8	$\psi_{B_2}^{(2:F_2)}$	$\frac{1}{\sqrt{2}}\{-i\|21m\rangle + \|2\bar{1}m\rangle\}$
3	A_2	-18	$\psi^{(3:A_2)}$	$\frac{1}{\sqrt{2}}\{-\|32m\rangle + \|3\bar{2}m\rangle\}$
3	(F_1, A_2)	-14	$\psi_{A_2}^{(3:F_1)}$	$\|30m\rangle$
	(F_1, B_1)	-8	$\psi_{B_1}^{(3:F_1)}$	$\frac{1}{4}\{\ \ i\sqrt{5}\|33m\rangle + \sqrt{3}\|31m\rangle + i\sqrt{3}\|3\bar{2}m\rangle + \sqrt{5}\|3\bar{3}m\rangle\}$
	(F_1, B_2)	4	$\psi_{B_2}^{(3:F_1)}$	$\frac{1}{4}\{-i\sqrt{5}\|33m\rangle + \sqrt{3}\|31m\rangle - i\sqrt{3}\|3\bar{2}m\rangle + \sqrt{5}\|3\bar{3}m\rangle\}$
3	(F_2, A_1)	14	$\psi_{A_1}^{(3:F_2)}$	$-\frac{1}{\sqrt{2}}\{\|32m\rangle + \|3\bar{2}m\rangle\}$
	(F_2, B_1)	-4	$\psi_{B_1}^{(3:F_2)}$	$\frac{1}{4}\{\ \ i\sqrt{3}\|33m\rangle - \sqrt{5}\|31m\rangle - i\sqrt{5}\|3\bar{2}m\rangle + \sqrt{3}\|3\bar{3}m\rangle\}$
	(F_2, B_2)	8	$\psi_{B_2}^{(3:F_2)}$	$\frac{1}{4}\{-i\sqrt{3}\|33m\rangle - \sqrt{5}\|31m\rangle + i\sqrt{5}\|3\bar{2}m\rangle + \sqrt{3}\|3\bar{3}m\rangle\}$
4	A_1	18	$\psi^{(4;A_1)}$	$\frac{1}{2\sqrt{3}}\{\sqrt{5}\|44m\rangle + \sqrt{14}\|40m\rangle + \sqrt{5}\|4\bar{4}m\rangle\}$
4	(E, A_1)	12	$\psi_{A_1}^{(4:E)}$	$\frac{1}{2\sqrt{3}}\{\sqrt{7}\|44m\rangle - \sqrt{10}\|40m\rangle + \sqrt{7}\|4\bar{4}m\rangle\}$
	(E, A_2)	-12	$\psi_{A_2}^{(4:E)}$	$\frac{1}{\sqrt{2}}\{\|42m\rangle + \|4\bar{2}m\rangle\}$
4	(F_1, A_2)	-14	$\psi_{A_2}^{(4:F_1)}$	$-\frac{1}{\sqrt{2}}\{-\|44m\rangle + \|4\bar{4}m\rangle\}$
	(F_1, B_1)	-8	$\psi_{B_1}^{(4:F_1)}$	$\frac{1}{4}\{-i\|43m\rangle + \sqrt{7}\|41m\rangle - i\sqrt{7}\|4\bar{1}m\rangle + \|4\bar{3}m\rangle\}$
	(F_1, B_2)	4	$\psi_{B_2}^{(4:F_1)}$	$\frac{1}{4}\{i\|43m\rangle + \sqrt{7}\|41m\rangle + i\sqrt{7}\|4\bar{1}m\rangle + \|4\bar{3}m\rangle\}$
4	(F_2, A_1)	14	$\psi_{A_1}^{(4:F_2)}$	$\frac{1}{\sqrt{2}}\{-\|42m\rangle + \|4\bar{2}m\rangle\}$
	(F_2, B_1)	-4	$\psi_{B_1}^{(4:F_2)}$	$\frac{1}{4}\{-i\sqrt{7}\|43m\rangle - \|41m\rangle + i\|4\bar{1}m\rangle + \sqrt{7}\|4\bar{3}m\rangle\}$
	(F_2, B_2)	8	$\psi_{B_1}^{(4:F_2)}$	$\frac{1}{4}\{i\sqrt{7}\|43m\rangle - \|41m\rangle - i\|4\bar{1}m\rangle + \sqrt{7}\|4\bar{3}m\rangle\}$

Table 6. Symmetry projection to F_1 for $J = 5$. The states $|J, -k, m\rangle$ are denoted by $|J\bar{k}m\rangle$. The first set is provided by the diagonalization of the matrix representation (18). The second set was obtained by means of (25).

J	IRREP (Γ, γ)	eigenvalue ζ	name	eigenvector
5	(F_1, A_2)	-14	${}_1\psi^{(5:F_1)}_{A_2}$	$\vert 50m\rangle$
	(F_1, A_2)	-14	${}_2\psi^{(5:F_1)}_{A_2}$	$\frac{1}{\sqrt{2}}\{\vert 54m\rangle + \vert 5\bar{4}m\rangle\}$
	(F_1, B_1)	-8	${}_1\psi^{(5:F_1)}_{B_1}$	$\sqrt{\frac{7}{29}}\{-i\vert 55m\rangle - i\sqrt{\frac{15}{14}}\vert 51m\rangle + \sqrt{\frac{15}{14}}\vert 5\bar{1}m\rangle + \vert 5\bar{5}m\rangle\}$
	(F_1, B_1)	-8	${}_2\psi^{(5:F_1)}_{B_1}$	$\sqrt{\frac{7}{17}}\{i\vert 53m\rangle - \sqrt{\frac{3}{14}}\vert 51m\rangle - i\sqrt{\frac{3}{14}}\vert 5\bar{1}m\rangle + \vert 5\bar{3}m\rangle\}$
	(F_1, B_2)	4	${}_1\psi^{(5:F_1)}_{B_2}$	$\sqrt{\frac{7}{29}}\{i\vert 55m\rangle + i\sqrt{\frac{15}{14}}\vert 51m\rangle + \sqrt{\frac{15}{14}}\vert 5\bar{1}m\rangle + \vert 5\bar{5}m\rangle\}$
	(F_1, B_2)	4	${}_2\psi^{(5:F_1)}_{B_2}$	$\sqrt{\frac{7}{17}}\{-i\vert 53m\rangle - \sqrt{\frac{3}{14}}\vert 51m\rangle + i\sqrt{\frac{3}{14}}\vert 5\bar{1}m\rangle + \vert 5\bar{3}m\rangle\}$
5	(F_1, A_2)	-14	${}_1\zeta^{(5:F_1)}_{A_2}$	$\vert 50m\rangle$
	(F_1, B_1)	-8	${}_1\zeta^{(5:F_1)}_{B_1}$	$\frac{3\sqrt{7}}{16}\{-i\vert 55m\rangle + \frac{\sqrt{5}}{3}\vert 53m\rangle - i\sqrt{\frac{10}{21}}\vert 51m\rangle + \sqrt{\frac{10}{21}}\vert 5\bar{1}m\rangle - i\frac{\sqrt{5}}{3}\vert 5\bar{3}m\rangle + \vert 5\bar{5}m\rangle\}$
	(F_1, B_2)	4	${}_1\zeta^{(5:F_1)}_{B_2}$	$\frac{3\sqrt{7}}{16}\{\quad i\vert 55m\rangle + \frac{\sqrt{5}}{3}\vert 53m\rangle + i\sqrt{\frac{10}{21}}\vert 51m\rangle + \sqrt{\frac{10}{21}}\vert 5\bar{1}m\rangle + i\frac{\sqrt{5}}{3}\vert 5\bar{3}m\rangle + \vert 5\bar{5}m\rangle\}$
5	(F_1, A_2)	-14	${}_2\zeta^{(5:F_1)}_{A_2}$	$\frac{1}{\sqrt{2}}\{\vert 54m\rangle + \vert 5\bar{4}m\rangle\}$
	(F_1, B_1)	-8	${}_2\zeta^{(5:F_1)}_{B_1}$	$\frac{\sqrt{5}}{16}\{-i\vert 55m\rangle - \frac{9}{\sqrt{5}}\vert 53m\rangle - i\sqrt{\frac{42}{5}}\vert 51m\rangle + \sqrt{\frac{42}{5}}\vert 5\bar{1}m\rangle + i\frac{9}{\sqrt{5}}\vert 5\bar{3}m\rangle + \vert 5\bar{5}m\rangle\}$
	(F_1, B_2)	4	${}_2\zeta^{(5:F_1)}_{B_2}$	$\frac{\sqrt{5}}{16}\{\quad i\vert 55m\rangle - \frac{9}{\sqrt{5}}\vert 53m\rangle + i\sqrt{\frac{42}{5}}\vert 51m\rangle + \sqrt{\frac{42}{5}}\vert 5\bar{1}m\rangle - i\frac{9}{\sqrt{5}}\vert 5\bar{3}m\rangle + \vert 5\bar{5}m\rangle\}$

Table 7. Eigenvectors provided by the diagonalization of the operator C_{II} in the rovibrational subspace (44) using the result (49). Only the reduction corresponding to the three-dimensional subspace (F_1, A_2) is presented. In the lower part of the table, the functions $|_{\nu_0;\nu_1\nu_2\nu_3\nu_4}\zeta^{1m1}_{F_1,A_2}\rangle$ obtained diagonalizing the number operators in the basis $|_i\Psi^{1m1}_{F_1,A_2}\rangle$ can be found. The eigenvector$|_{1;0000}\zeta^{1m1}_{F_1,A_2}\rangle$ is clearly identified as a spurious state.

	$\lvert_1\Psi^{1m1}_{F_1,A_2}\rangle$	$\lvert_2\Psi^{1m1}_{F_1,A_2}\rangle$	$\lvert_3\Psi^{1m1}_{F_1,A_2}\rangle$	basis
	$0.2631 + 0.0571i$	$-0.0978 - 0.0320i$	$-0.2020 - 0.0328i$	$\lvert 11m\rangle \otimes \lvert 5\rangle$
	$0.0571 - 0.2631i$	$-0.0320 + 0.0978i$	$-0.0328 + 0.2020i$	$\lvert 11m\rangle \otimes \lvert 6\rangle$
	0	0	0	$\lvert 11m\rangle \otimes \lvert 7\rangle$
	$-0.0571 + 0.2631i$	$0.0320 - 0.0978i$	$0.0328 - 0.2020i$	$\lvert 11m\rangle \otimes \lvert 8\rangle$
	$-0.2631 - 0.0571i$	$0.0978 + 0.0320i$	$0.2020 + 0.0328i$	$\lvert 11m\rangle \otimes \lvert 9\rangle$
	0	0	0	$\lvert 11m\rangle \otimes \lvert 10\rangle$
	$0.1265 + 0.1848i$	$-0.1609 - 0.1345i$	$0.2694 + 0.2884i$	$\lvert 10m\rangle \otimes \lvert 5\rangle$
	$0.1265 + 0.1848i$	$-0.1609 - 0.1345i$	$0.2694 + 0.2884i$	$\lvert 10m\rangle \otimes \lvert 6\rangle$
	$0.3306 - 0.0174i$	$0.6033 - 0.0742i$	$0.1391 + 0.0381i$	$\lvert 10m\rangle \otimes \lvert 7\rangle$
	$0.1265 + 0.1848i$	$-0.1609 - 0.1345i$	$0.2694 + 0.2884i$	$\lvert 10m\rangle \otimes \lvert 8\rangle$
	$0.1265 + 0.1848i$	$-0.1609 - 0.1345i$	$0.2694 + 0.2884i$	$\lvert 10m\rangle \otimes \lvert 9\rangle$
	$0.3306 - 0.0174i$	$0.6033 - 0.0742i$	$0.1391 + 0.0381i$	$\lvert 10m\rangle \otimes \lvert 10\rangle$
	$-0.2631 - 0.0571i$	$0.0978 + 0.0320i$	$0.2020 + 0.0328i$	$\lvert 1\bar{1}m\rangle \otimes \lvert 5\rangle$
	$0.0571 - 0.2631i$	$-0.0320 + 0.0978i$	$-0.0328 + 0.2020i$	$\lvert 1\bar{1}m\rangle \otimes \lvert 6\rangle$
	0	0	0	$\lvert 1\bar{1}m\rangle \otimes \lvert 7\rangle$
	$-0.0571 + 0.2631i$	$0.0320 - 0.0978i$	$0.0328 - 0.2020i$	$\lvert 1\bar{1}m\rangle \otimes \lvert 8\rangle$
	$0.2631 + 0.0571i$	$-0.0978 - 0.0320i$	$-0.2020 - 0.0328i$	$\lvert 1\bar{1}m\rangle \otimes \lvert 9\rangle$
	0	0	0	$\lvert 1\bar{1}m\rangle \otimes \lvert 10\rangle$
$\lvert_{1;0000}\zeta^{1m1}_{F_1,A_2}\rangle$	$0.5462 + 0.1072i$	$-0.0181 + 0.3620i$	0.7474	
$\lvert_{0;0100}\zeta^{1m1}_{F_1,A_2}\rangle$	$-0.0982 + 0.3168i$	$0.4694 + 0.7505i$	-0.3258	
$\lvert_{0;0001}\zeta^{1m1}_{F_1,A_2}\rangle$	$0.7605 - 0.0399i$	$-0.2877 + 0.0450i$	-0.5789	

Figure Captions

Figure 1. Coordinate system chosen and location of the symmetry elements to describe the methane molecule.