

SYMMETRY OF NON-RIGID MOLECULES

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I. INTRODUCTION

At the present time the conventional concept of molecular structure is based on the Born-Oppenheimer approximation. Molecular structure is commonly understood as relative nuclear configurations which may be considered as stable in the sense of certain criteria. Many structures may be characterized by a continuous set of nuclear configurations (NCs) which deviate only infinitesimally from each other. For such quasi-rigid molecules (sometimes called rigid molecules) the covering symmetry group (point group) of the equilibrium structure (r_e -structure) is the relevant symmetry group for many problems in molecular research. This group was applied first to problems in stereochemistry in the second half of the last century [1,2] and formed the basis of extended applications to molecular dynamics since 1930, developed first by Wigner [3].

In recent years experimental and theoretical investigation of the dynamics of non-rigid molecules, i.e. molecules with internal coordinates varying over finite domains has attracted increasing attention. Therefore a symmetry concept for such molecules is required which should have a range of application in molecular dynamics and stereochemistry comparable to the covering group of rigid molecules.

Attempts to construct symmetries of non-rigid molecules have first been made by Hougen [4], Longuet-Higgins [5] and Altmann [6]. These approaches base on the symmetries of the Hamiltonian of a system of nuclei and electrons. In particular Longuet-Higgins defines the molecular symmetry group as a subgroup of the "complete group of permutations of the positions and spins of identical nuclei and simultaneous inversion of the positions of all particles in the centre of mass". This subgroup may be constructed by means of the intuitive concept of feasibility, which states that a permutation or permutation-inversion corresponds to a feasible operation if it corresponds to a path on the electronic energy surface involving points of low potential energy. Though this concept has been applied to a number of specific examples it lacks well defined mathematical tools for determination of transformation properties of energy operators, multipole operators and functions of the dynamical coordinates.

Recently Bauder et al. [7] developed a new symmetry concept of non-rigid molecules, which will be presented here. It has been motivated by the desire to find a method, which starts from the geometrical

description of nuclear configurations and replaces the feasibility concept by rigorous mathematical definitions. This new symmetry group is based on the concept of isometry of NGs and therefore is a natural generalization of the concept of covering symmetry of rigid point sets to non-rigid point sets. It allows determination of the transformation properties of operators and functions by the methods used generally in applications of group theory to physical problems in strict analogy to the treatment of quasi-rigid molecules within the framework of the covering symmetry group [8]. In addition, the isometric group gives a necessary and sufficient symmetry criterion for the chirality of non-rigid molecules [9] and a method for enumeration and classification of conformational isomers.

In this paper the construction of the isometric group of non-rigid molecules will be presented and the relation between isometric groups and the Longuet-Higgins group will be discussed (section 2). Applications of isometric groups to the rotation-internal nuclear motion problem, the transformation properties of irreducible tensor operators and derivation of multipole selection rules of non-rigid molecules will be discussed in section 3.

II. THE ISOMETRIC GROUP OF NON-RIGID MOLECULES

2.1 Approximation of a non-rigid molecule by a semi-rigid model

For any molecule containing K nuclei there is associated a nuclear configuration $NC\{\vec{X}_k(\xi), Z_k, M_k\}$ defined by the position vectors \vec{X}_k the charges Z_k and the masses M_k . Use of centre of mass coordinates and Eulerian angles for a dynamical description of the K mass point system leaves $3K-6$ internal coordinates $\xi_1, \xi_2, \dots, \xi_{3K-6}$ for the relative configuration of the system, which are invariant under translations and overall-rotations. Examples for internal coordinates are bond lengths, bond angles, dihedral angles a.s.o. The nuclear coordinate vectors \vec{X}_k referred to appropriately chosen molecule fixed axis depend on these internal coordinates only. The frame system \vec{e}^f is defined w.r.t. its orientation to the laboratory fixed system \vec{e}^l by

$$\vec{e}^f = \vec{e}^l D(\epsilon) \quad (1)$$

where ϵ stands for the Eulerian angles α, β, γ and $D(\epsilon)$ is the rotation matrix characterized by the three Eulerian angles.

For most non-rigid molecules only a few structural parameters ξ vary over finite domains, all other internal degrees of freedom being infinitesimal. To such a non-rigid molecule may be associated a semi-rigid model (SRM) defined by these $1, 2, 3, \dots, f \ll 3K-6$ finite internal coordinates, while all other coordinates are kept constant. These SRMs play the same role for non-rigid molecules as the r_e -structure plays for quasi-rigid molecules. The isometric groups of a non-rigid molecule and its associated SRM are isomorphic. SRMs may be characterized by the covering symmetries of their rigid parts usually termed frame, inverter a.s.o. and the finite internal coordinates ξ which measure the relative positions of the rigid parts. Figure 1 shows two examples of non-rigid molecules.

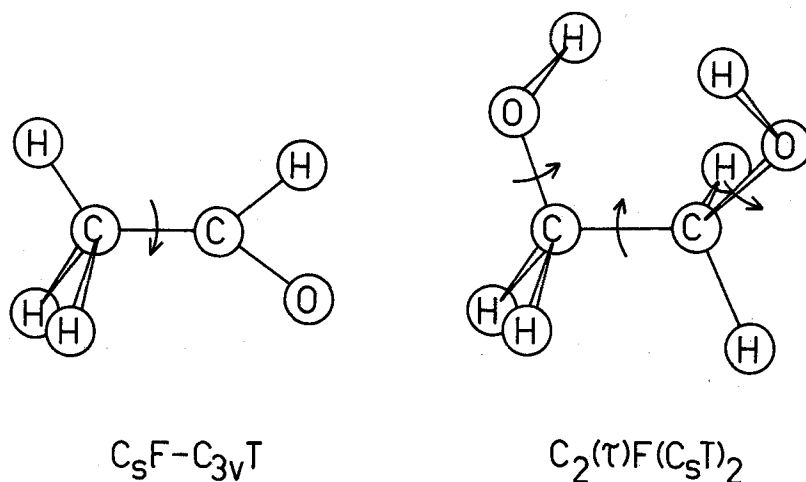


Fig. 1. Acetaldehyd and ethylene glycol semi-rigid models. The arrows indicate internal-rotational degrees of freedom.

Acetaldehyd (CH_3CHO) may be described by a SRM of the type $C_sF-C_{3v}T$ with one finite internal coordinate (rotation around the CC bond) consisting of a CCHO frame of covering symmetry C_s and a CH_3 top of covering symmetry C_{3v} . To the second non-rigid molecule in this figure, ethylene glycol (CH_2OH-CH_2OH), is associated the SRM $C_2(\tau)F(C_sT)_2$, a model with three finite internal coordinates (rotation around the two CO bonds and the CC bond), which consists of a OCH_2-CH_2O frame of covering symmetry C_2 and two equivalent OH tops of covering symmetry C_s .

2.2 The isometric group of a semi-rigid model

The isometric group of a SRM will be constructed from two subgroups

- (i) the internal isometric group $\mathcal{F}(\xi)$
- (ii) the covering group $\mathcal{G}(\xi)$

Since the overwhelming majority of non-rigid molecules may be described by a SRM whose covering group is the improper group C_1 , the internal isometric group \mathcal{F} will be treated first.

2.2.1 The internal isometric group $\mathcal{F}(\xi)$

The construction of the internal isometric group is based on the isometric mappings of the graph $\mathcal{N} = \{P(\Pi_k(Z_k, M_k)), K(d_{kk'})\}$ consisting of the set P of vertices Π_k (the nuclei) valued by charge Z_k and mass M_k , and the set K of edges valued by the internuclear distances $d_{kk'}$. In general, an internuclear distance $d_{kk'}$ depends on the internal coordinates

$$d_{kk'}(\xi_1, \xi_2, \dots, \xi_f) = |\vec{X}_k(\xi) - \vec{X}_{k'}(\xi)|. \quad (2)$$

If it is possible to find substitutions of the internal coordinates

$$\xi' = F(\xi) \quad (3)$$

which map the sets P and K of the graph \mathcal{N} onto themselves conserving valuations of both the vertices and the edges, we call the substitutions isometric and the two NCs $NC\{\vec{X}_k(F^{-1}(\xi))\}$ and $NC\{\vec{X}_k(\xi)\}$ isometric NCs, i.e. both have equal distance sets. The interrelation between the distance sets of the two isometric NCs may be considered as a mapping of the set of distances onto itself and can be expressed as a linear transformation

$$\hat{P}_F\{\widetilde{d_{kk'}}(\xi)\} = \{\widetilde{d_{kk'}}(\xi)\} \cdot \Gamma^{(\mathcal{N}\mathcal{G})}(F) \quad (4)$$

where the operator \hat{P}_F is associated with the substitution (3) and $\Gamma^{(\mathcal{N}\mathcal{G})}(F)$ is a permutation matrix.

The isometric substitutions may often be written as linear homogeneous or inhomogeneous transformations

$$\begin{pmatrix} \xi' \\ 1 \end{pmatrix} = \mathcal{A}(F) \begin{pmatrix} \xi \\ 1 \end{pmatrix}, \quad \mathcal{A}(F) = \begin{bmatrix} A(F) & a(F) \\ \tilde{O} & 1 \end{bmatrix} \quad (5)$$

The set of isometric substitution $\mathcal{A}(F)$ and the set of permutation ma-

trices $\Gamma^{(\mathcal{N}\mathcal{E})}(\mathbb{F})$ form two isomorphic groups which we call the internal isometric group $\mathcal{F}(\xi)$

$$\mathcal{A}\{\mathcal{F}\} \stackrel{\text{i.s.}}{=} \Gamma^{(\mathcal{N}\mathcal{E})}\{\mathcal{F}\} \stackrel{\text{i.s.}}{=} \mathcal{F}(\xi) \quad (6)$$

In order to get the transformation properties of the dynamical variables of the rotation-internal nuclear motion problem under the isometric substitutions, the representations of \mathcal{F} on the nuclear coordinate vectors and the Eulerian angles have to be derived. The operators $\hat{P}_{\mathbb{F}}$, $\mathbb{F} \in \mathcal{F}$, applied to the substrate $\{\tilde{X}_k(\xi)\}$, i.e. to the nuclear coordinate vectors referred to the frame system written as a row vector induce linear transformations

$$\hat{P}_{\mathbb{F}}\{\tilde{X}_k(\xi)\} = \{\tilde{X}_k(\xi)\} \Pi(\mathbb{F}) \boxtimes \Gamma^{(3)}(\mathbb{F}) = \{\tilde{X}_k(\xi)\} \Gamma^{(\text{NCF})}(\mathbb{F}) \quad (7)$$

where $\Pi(\mathbb{F})$ denotes a permutation matrix of dimension K and $\Gamma^{(3)}(\mathbb{F})$ a properly or improperly orthogonal 3×3 matrix. The set of matrices $\Gamma^{(\text{NCF})}(\mathbb{F})$ will furtheron be denoted by

$$\Gamma^{(\text{NCF})}\{\mathcal{F}\} := \{\Pi(\mathbb{F}) \boxtimes \Gamma^{(3)}(\mathbb{F}) \mid \forall \mathbb{F} \in \mathcal{F}(\xi)\}, \quad (8)$$

the index f indicating reference to the frame system. This form of the representation $\Gamma^{(\text{NCF})}$ reflects the fact that isometric NCs are either properly or improperly congruent (up to permutations of identical nuclei). That means, we can superimpose a NC on any isometric NC by a proper or improper rotation $\Gamma^{(3)}(\mathbb{F})$. The permutative part $\Pi(\mathbb{F})$ describes the associated permutation of identical nuclei. As in the case of the distance set, ordering of the position vectors in subsets of nuclei equivalent w.r.t. \mathcal{F} results in a decomposition of this representation to a direct sum.

The set

$$\Gamma^{(3)}\{\mathcal{X}\} := \{\Gamma^{(3)}(\mathbb{F}) \mid \forall \mathbb{F} \in \mathcal{F}(\xi)\} \quad (9)$$

consisting of all different rotational parts $\Gamma^{(3)}(\mathbb{F})$ of the representation $\Gamma^{(\text{NCF})}\{\mathcal{F}\}$ form a representation of \mathcal{F} by a finite group of orthogonal matrices in \mathcal{R}_3 and is therefore identical with one of the molecular point symmetry groups (subgroup of $O(3)$). $\Gamma^{(3)}\{\mathcal{X}\}$ plays an important role in most applications of isometric groups. It pictures the set of all orthogonal matrices which map a reference NC onto all possible isometric NCs. In general the group theoretical relation between $\Gamma^{(\text{NCF})}\{\mathcal{F}\}$ and $\Gamma^{(3)}\{\mathcal{X}\}$ is a homomorphism. Concerning the structure of $\Gamma^{(3)}\{\mathcal{X}\}$, the following two cases will prove important:

case a: $\Gamma^{(3)}\{\mathcal{K}\}$ is properly orthogonal

$$|\Gamma^{(3)}(K)| = 1, \quad \forall K \in \mathcal{K} \quad (10)$$

case b: $\Gamma^{(3)}\{\mathcal{K}\}$ is improperly orthogonal. Then $\Gamma^{(3)}\{\mathcal{K}\}$ may be decomposed according to

$$\begin{aligned} \Gamma^{(3)}\{\mathcal{K}\} &:= \Gamma^{(3)}\{\mathcal{K}^+\} \cup \Gamma^{(3)}(T) \Gamma^{(3)}\{\mathcal{K}^+\}, \\ \text{where } \Gamma^{(3)}\{\mathcal{K}^+\} &:= \{\Gamma^{(3)}(K) | K \in \mathcal{K}, |\Gamma^{(3)}(K)| = +1\} \\ \text{and } |\Gamma^{(3)}(T)| &= -1 \end{aligned} \quad (11)$$

Therefore, for all case b SRMs the relation holds

$$\Gamma^{(3)}\{\mathcal{K}\} \stackrel{\text{ho}}{=} \mathcal{V}_2 \quad (12)$$

In order to derive the transformations of the Eulerian angles under isometric substitutions, we have to write every improperly orthogonal matrix $\Gamma^{(3)}(F)$ in the form

$$\Gamma^{(3)}(F) = Z \cdot R(F) \quad (13)$$

where $Z = -1^{(3)}$ denotes the inversion and $R(F)$ a properly orthogonal matrix. Since the Eulerian angles are unaffected under the inversion, the set of all different matrices $R(F)$ together with all elements of $\Gamma^{(3)}\{\mathcal{K}^+\}$ form a representation $\Delta^{(3)}\{\mathcal{K}\}$ required for the derivation of the transformations of α , β and γ under $\mathcal{F}(\xi)$. For this representation, the following relations hold:

$$\text{case a: } \Delta^{(3)}\{\mathcal{K}\} \equiv \Gamma^{(3)}\{\mathcal{K}\}$$

$$\begin{aligned} \text{case b: } \Delta^{(3)}\{\mathcal{K}\} &\equiv \Gamma^{(3)}\{\mathcal{K}^+\} \text{ if } Z \in \Gamma^{(3)}(T) \Gamma^{(3)}\{\mathcal{K}^+\} \\ \Delta^{(3)}\{\mathcal{K}\} &\stackrel{\text{is}}{=} \Gamma^{(3)}\{\mathcal{K}\} \text{ if } Z \notin \Gamma^{(3)}(T) \Gamma^{(3)}\{\mathcal{K}^+\} \end{aligned} \quad (14)$$

$\Delta^{(3)}\{\mathcal{K}\}$ is always identical with a finite subgroup of $SO(3)$. By means of eq. (1) and the elements of $\Delta^{(3)}\{\mathcal{K}\}$ the transformations of the Eulerian angles may be derived as follows:

$$\tilde{\mathbf{e}} f' = \tilde{\mathbf{e}} f \tilde{\Gamma}^{(3)}(F) = \tilde{\mathbf{e}} \mathbf{t} D(\boldsymbol{\epsilon}) \tilde{\Gamma}^{(3)}(F) = \tilde{\mathbf{e}} \mathbf{t} D(\boldsymbol{\epsilon}') |\Gamma^{(3)}(F)| \quad (15)$$

Hence by eq. (13)

$$\begin{aligned} D(\boldsymbol{\epsilon}') &= D(\boldsymbol{\epsilon}) \tilde{R}(F) \text{ if } |\Gamma^{(3)}(F)| = -1 \\ D(\boldsymbol{\epsilon}') &= D(\boldsymbol{\epsilon}) \tilde{\Gamma}^{(3)}(F) \text{ if } |\Gamma^{(3)}(F)| = +1 \end{aligned} \quad (16)$$

The eqs. (16) define transformations of the Eulerian angles

$$\boldsymbol{\epsilon}' = \boldsymbol{\epsilon}'(\boldsymbol{\epsilon}, F) \quad (17)$$

which in most practical cases are linear inhomogeneous

$$\begin{pmatrix} \epsilon' \\ 1 \end{pmatrix} = \mathcal{B}(F) \begin{pmatrix} \epsilon \\ 1 \end{pmatrix}, \quad \mathcal{B}(F) = \begin{pmatrix} B(F) & b(F) \\ 0 & 1 \end{pmatrix} \quad (18)$$

The proper set of the matrices $\mathcal{B}(F)$

$$\mathcal{B}\{\mathcal{F}\} := \{\mathcal{B}(F) \mid \forall F \in \mathcal{F}(\xi)\} \quad (19)$$

forms a group isomorphic to $\Delta^{(3)}\{\mathcal{K}\}$.

By direct summation of the matrices $\mathcal{B}(F)$ and $\mathcal{A}(F)$ we get the important matrix $\Gamma(F)$ which in the case where both the transformations of the Eulerian angles ϵ and the internal coordinates ξ are linear inhomogeneous takes the form

$$\Gamma(F) = \begin{bmatrix} B(F) & 0 & b(F) \\ 0 & A(F) & a(F) \\ 0 & 0 & 1 \end{bmatrix}, \quad \forall F \in \mathcal{F}(\xi). \quad (20)$$

The innermost circle of figure 2 shows the most important group theoretical relations among the representations of the internal isometric group \mathcal{F} on the various substrates. The homomorphism of $\Gamma\{\mathcal{F}\}$ onto $\Gamma^{(3)}\{\mathcal{K}\}$ implies that for all case b SRMs $\Gamma\{\mathcal{F}\}$ is homomorphic onto \mathcal{V}_2 .

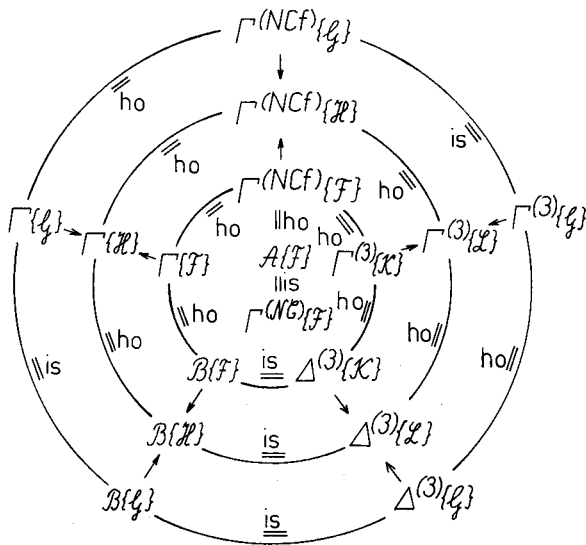


Fig. 2. Group theoretical interrelations between representations of the isometric group.

Tables 1 and 2 show a number of examples of semi-rigid models and their isometric groups ($\mathcal{G}(\xi) \stackrel{iS}{=} C_1$).

2.2.2 Primitive period isometric transformations

If the distances $d_{kk'}(\xi)$ possess a primitive period p w.r.t. the internal coordinates ξ , i.e.

$$d_{kk'}(\xi+p) = d_{kk'}(\xi) , \quad \forall k, k' \in [1, K],$$

the ξ 's have to be taken modulo their respective primitive periods. Thus, isometric transformations of the type

$$\begin{pmatrix} \xi' \\ 1 \end{pmatrix} = \begin{pmatrix} 1^{(f)} & p \\ \tilde{0} & 1 \end{pmatrix} \begin{pmatrix} \xi \\ 1 \end{pmatrix} = \mathcal{A}(F_p) \begin{pmatrix} \xi \\ 1 \end{pmatrix} \quad (21)$$

are not included in $\mathcal{F}(\xi)$ since the relative NCs $\text{RNC}\{\tilde{X}_k(\xi+p)\}$ and $\text{RNC}\{\tilde{X}_k(\xi)\}$ are identical and $\Gamma^{(\mathcal{N}^{\mathcal{C}})}(F) = 1$. However, in all those applications where the orientation of the NC w.r.t. both the frame and laboratory coordinate system is relevant primitive period isometric transformations have to be included as non trivial symmetry operations in $\mathcal{F}(\xi)$ if the rotational part $\Gamma^{(3)}(F_p)$ in the representation of F_p on the nuclear coordinate vectors expressed w.r.t. the frame system is a nontrivial element of $SO(3)$

$$\begin{aligned} \hat{P}_P \{ \tilde{X}_k(\xi) \} &= \{ \tilde{X}_k(\xi-p) \} = \{ \tilde{X}_k(\xi) \} 1^{(K)} \otimes \Gamma^{(3)}(F_p) \\ \Gamma^{(3)}(F_p) &\in SO(3) , \quad \Gamma^{(3)}(F_p) \neq 1^{(3)} \end{aligned} \quad (22)$$

In all these cases

$$\Gamma(F_p) = \begin{bmatrix} B(F_p) & 0 & b(F_p) \\ 0 & 1^{(f)} & p \\ 0 & 0 & 1 \end{bmatrix} \neq 1^{(f+4)} \quad (23)$$

The occurrence of primitive period transformations is closely related to the choice of the internal coordinates and the molecule fixed axis. The group of all internal isometric transformations including F_p will be denoted by $\tilde{\mathcal{F}}(\xi)$. It should be emphasized that the group $\mathcal{F}_P(\xi)$ and its representations are relevant and sufficient for all problems which are completely defined by the relative NCs of a SRM. All other applications require use of the group $\tilde{\mathcal{F}}(\xi)$.

TABLE 1 Isometric Groups of Semirigid Models $\mathcal{G}(\xi) = C_1^b$, $f = 1$ ^a

System	type of int. motion	covering symmetry		symmetry groups			typical molecule	
		frame	top/invertor	$\Gamma^{(3)}\{\mathcal{L}\}$	$\mathcal{F}(\xi)$	$\mathcal{K}(\xi)$		$\overline{\mathcal{F}}\{\hat{H}\}$
$C_s F-C_{3v} T$	int. rotation	C_s	C_{3v}	C_s	ϑ_3	ϑ_3	ϑ_3	CH ₃ CHO
$C_s F-C_{2v} T$	int. rotation	C_s	C_{2v}	C_s	\mathcal{U}_4	\mathcal{U}_4	\mathcal{U}_4	CH ₂ :CHNO ₂
$C_s F-C_s T$	int. rotation	C_s	C_s	C_s	\mathcal{U}_2	\mathcal{U}_2	\mathcal{U}_2	CH ₂ :CHCHO
$C_{2v} F-C_{3v} T$	int. rotation	C_{2v}	C_{3v}	C_{2v}	ϑ_6	ϑ_6	$\vartheta_6[E, T]^c$	CH ₃ NO ₂
$C_s F-C_s I$	inversion	C_s	C_s	C_s	\mathcal{U}_2	\mathcal{U}_2	\mathcal{U}_2	CHONHD
$C_s F-C_{2v} I$	inversion	C_s	C_{2v}	C_s	\mathcal{U}_2	\mathcal{U}_2	\mathcal{U}_2	$\overline{CH_2CR_2NH}$

^a number of finite degrees of freedom

^b covering group for arbitrary values of ξ

^c T commutes with all other elements

TABLE 2 Isometric Groups of Semirigid Molecules $\mathcal{G}(\xi) = C_1^b$, $f \geq 2$ a

f ^a	system	type of motion ^c	covering symmetry			symmetry groups			typical molecule
			frame	top 1	top 2/ inverter	$\Gamma(3)$ { \mathcal{L} }	$\mathcal{F}(\xi)$	$\mathcal{H}(\xi)$	
2	$C_{2V}(C_{3V})_2$	RIR	C_{2V}	C_{3V}	C_{3V}	C_{2V}	\mathcal{F}_{36}	\mathcal{H}_{36}	CH_3COCH_3
2	$C_S(C_{3V})(C_{3V})'$	RIR	C_S	C_{3V}	C_{3V}	C_S	\mathcal{F}_{18}	\mathcal{H}_{18}	$CH_3CH:NCH_3$
2	$C_S(C_{3V})(C_{2V})$	RIR	C_S	C_{3V}	C_{2V}	C_S	\mathcal{F}_6	\mathcal{H}_6	$CH_3CH_2NO_2$
2	$C_S(C_{3V})(C_S)$	RIR	C_S	C_{3V}	C_S	C_S	\mathcal{F}_3	\mathcal{H}_3	CH_3CH_2CHO
2	$C_{2V}(C_{2V})_2$	RIR	C_{2V}	C_{2V}	C_{2V}	C_{2V}	$\mathcal{F}_{16} = \mathcal{F}_4[E, T]^d$	\mathcal{H}_{16}	$CH_2(NO_2)_2$
2	$C_S(C_{2V})(C_{2V})'$	RIR	C_S	C_{2V}	C_{2V}	C_S	$\mathcal{A}(2, 2, 2)$	$\mathcal{A}(2, 2, 2)$	$NO_2CH:CFNO_2$
2	$C_S(C_{2V})(C_S)$	RIR	C_S	C_{2V}	C_S	C_S	\mathcal{U}_4	\mathcal{U}_4	$NO_2CH_2CH_2F$
2	$C_{2V}(C_S)_2$	RIR	C_{2V}	C_S	C_S	C_{2V}	\mathcal{U}_4	\mathcal{U}_4	$O(CHO)_2$
2	$C_S(C_S)(C_S)$	RIR	C_S	C_S	C_S	C_S	\mathcal{U}_2	\mathcal{U}_2	CH_2FCH_2CHO
2	$C_{2V}(C_{3V})(C_{2V})$	RIRINV	C_{2V}	C_{3V}	C_{2V}	C_{2V}	\mathcal{F}_6	\mathcal{H}_6	CH_3NH_2
3	$C_2(\tau)F(C_S)_2$	RIR	$C_2(\tau)$	C_S	C_S	$C_{2V}(C_{2h})$	\mathcal{U}_4	\mathcal{U}_4	CH_2OHCH_2OH

^a number of finite degrees of freedom

^c RIR = rotation-internalrotation, INV = inversion

^b covering group for arbitrary values of ξ

^d T commutes with all other elements

2.2.3 The covering group $\mathcal{G}(\xi)$ and the full isometric group $\mathcal{H}(\xi)$

Besides internal symmetry SRMs may have covering symmetry in the sense that nontrivial covering operations exist for NCs with arbitrarily chosen but fixed values of the internal coordinates. It is obvious that these covering operations also involve mappings of the graph \mathcal{N} (defined in section 2.2.1) onto itself and therefore are again isometries of $\text{NC}\{\tilde{\mathbf{X}}_k(\xi), Z_k, M_k\}$. Since a covering operation may always be written either as a permutation or as a rotation, there exist two versions for the representation of $\mathcal{G}(\xi)$ on the nuclear coordinate vectors

$$\begin{aligned} \hat{P}_G\{\tilde{\mathbf{X}}_k(\xi)\} &= \{\tilde{\mathbf{X}}_k(\xi)\} \Pi(G) \boxtimes \mathbf{1}^{(3)} \\ \hat{P}_G\{\tilde{\mathbf{X}}_k(\xi)\} &= \{\tilde{\mathbf{X}}_k(\xi)\} \mathbf{1}^{(K)} \boxtimes \Gamma^{(3)}(G) \end{aligned} \quad (24)$$

These matrices $\Gamma^{(\text{NCf})}(G)$ may always be written either as a direct product of a K -dimensional permutation matrix $\Pi(G)$ and the unit matrix, or as a direct product of a K -dimensional unit matrix and a three-dimensional orthogonal matrix $\Gamma^{(3)}(G)$.

The outermost circle of figure 2 shows the representations induced by the covering group \mathcal{G} . They are arranged in strict analogy to those of the internal isometric group \mathcal{F} on the innermost circle, the analogy being based on the substrates on which the representations are generated.

The two groups $\mathcal{F}(\xi)$ and $\mathcal{G}(\xi)$ generate an abstract group $\mathcal{H}(\xi)$, the full isometric group. The representations of $\mathcal{H}(\xi)$ on each substrate may be generated from the corresponding pairs of groups using the usual group extension procedures, e.g. the two matrix groups $\Gamma^{(\text{NCf})}\{\mathcal{F}\}$ and $\Gamma^{(\text{NCf})}\{\mathcal{G}\}$ generate a matrix group $\Gamma^{(\text{NCf})}\{\mathcal{H}\}$, or $\Gamma^{(3)}\{\mathcal{F}\}$ and $\Gamma^{(3)}\{\mathcal{G}\}$ generate $\Gamma^{(3)}\{\mathcal{H}\}$ a.s.o. as symbolized in figure 2. It should be remarked that a complicated indeterminateness of the representation $\Gamma^{(\text{NCf})}\{\mathcal{H}\}$ results if $\mathcal{G}(\xi)$ is a non-trivial group [8], which is caused by the indeterminateness of $\Gamma^{(\text{NCf})}\{\mathcal{G}\}$ (eq. (24)). However, it may be shown that all possible forms of the representations $\Gamma^{(3)}\{\mathcal{L}\}$, $\Delta^{(3)}\{\mathcal{L}\}$ and $\Gamma\{\mathcal{H}\}$, which play a key role for applications, are automorphic. In all problems where primitive period isometric transformations are relevant (cf. section 2.2.2) the full isometric group $\mathcal{H}(\xi)$ has to be generated from the two subgroups $\mathcal{F}(\xi)$ and $\mathcal{G}(\xi)$.

Table 3 shows the isometric groups of a number of SRMs with proper group $\mathcal{G}(\xi)$.

2.3 Relation of the isometric group to the permutation-inversion group of non-rigid molecules

An interrelation between the isometric group and the permutation-inversion group of non-rigid molecules introduced by Longuet-Higgins [5] is obtained if the isometric transformations are applied to the nuclear coordinate vectors referred to the laboratory coordinate system \vec{e}^L . A one to one correspondence between these two groups may be established only for SRMs with improper covering group $\mathcal{G}(\xi) \stackrel{!}{=} C_1$. For the sake of brevity the discussion will be restricted to this case.

The relation between the components of the nuclear position vectors referred to the frame and laboratory system is given by

$$\{\tilde{X}_k^L(\epsilon, \xi)\} = \{\tilde{X}_k(\xi)\} 1^{(K)} \boxtimes R(\epsilon) \quad (25)$$

Using a general transformation formula for rotation group coefficients, we find for any $F \in \mathcal{F}$

$$\begin{aligned} \hat{P}_F \{\tilde{X}_k^L(\epsilon, \xi)\} &= \hat{P}_F \{\tilde{X}_k(\xi)\} 1^{(K)} \boxtimes R(\epsilon) \\ &= \{\tilde{X}_k(\xi)\} \Pi(F) \boxtimes \Gamma^{(3)}(F) 1^{(K)} \boxtimes \tilde{R}(F) R(\epsilon) \\ &= \{\tilde{X}_k^L(\epsilon, \xi)\} \Pi(F) \boxtimes 1^{(3)} |\Gamma^{(3)}(F)| = \{\tilde{X}_k^L(\epsilon, \xi)\} \Gamma^{(NCl)}(F) \end{aligned} \quad (26)$$

Therefore if $\Gamma^{(3)}(F)$ is properly orthogonal the isometric transformation F induces on the substrate $\{\tilde{X}_k^L\}$ a permutation of the coordinate vectors of a set of equivalent nuclei. If $\Gamma^{(3)}(F)$ is improperly orthogonal ($|\Gamma^{(3)}(F)| = -1$), F induces a permutation and an inversion of the coordinate vectors of a set of equivalent nuclei. Hence, the representation matrix $\Gamma^{(NCl)}(F)$ may be considered as the analog of a Longuet-Higgins permutation-inversion operation.

It should be pointed out, however, that in general the group \mathcal{F} (internal isometric group including primitive period transformations) is only homomorphic onto the Longuet-Higgins group. This homomorphism arises from the fact that, by virtue of eq. (22), primitive period operations are represented in the Longuet-Higgins group by the identity

$$\Gamma^{(NCl)}(F_p) = 1^{(K)} \boxtimes 1^{(3)} \quad (27)$$

TABLE 3 Isometric Groups of Semirigid Molecules

$\mathcal{G}(\xi)$ b proper, $f = 1$ a

System	type of int. motion	symmetry groups				fixed points	typical molecule
		$\mathcal{F}(\xi)$	$\mathcal{G}(\xi)$	$\mathcal{H}(\xi)$	$\Gamma^{(3)}\{\mathcal{L}\}$		
$D_{\infty h}(C_{2v}T)_2$	int. rot.	$\phi_2 \stackrel{is}{=} U_4$	D_2	$\phi_4 [E, T]^c$	D_{4h}	D_{2h}, D_{2d}	$(C_6H_5)_2$
$C_{2v}F-C_{2v}T$	int. rot.	$\phi_2 \stackrel{is}{=} U_4$	C_2	$\mathcal{A}(2, 2, 2)$	C_{2v}	C_{2v}	$C_6H_5NO_2$
$D_{\infty h}(C_sT)_2$	int. rot.	U_2	C_2	U_4	$C_{2v}(C_{2h})$	C_{2v}, C_{2h}	CHOCHO
$C_{2v}F-C_{2v}I$	inversion	U_2	C_s	U_4	C_{2v}	C_{2v}	$\overline{CH_2CH_2NH}$
$C_{3v}I$	inversion	U_2	C_{3v}	ϕ_6	D_{3h}	D_{3h}	NH_3
$(XY_2)_4$	puckering	U_2	D_{2d}	$\phi_4 [E, T]^c$	D_{4h}	D_{4h}	$\overline{CH_2CH_2CH_2CH_2}$

a number of finite degrees of freedom

b covering group for arbitrary values of ξ

c T commutes with all other elements

This fact explains why in some applications to non-rigid molecules an extension of the Longuet-Higgins group had to be made [10,11].

III. APPLICATIONS OF ISOMETRIC GROUPS TO THE ROTATION-LARGE AMPLITUDE INTERNAL MOTION PROBLEM OF SEMI-RIGID MODELS

3.1 Symmetry group of the rotation-internal nuclear motion problem of a semi-rigid model

The non-relativistic hamiltonian of a system of K nuclei and N electrons, usually expressed within the framework of the Born-Oppenheimer approximation by

- (i) centre of mass coordinates
- (ii) Eulerian angles for molecule fixed coordinate systems
- (iii) internal coordinates for relative NCs
- (iv) Cartesian coordinates of electrons w.r.t. molecule fixed coordinate systems

is decomposed into parts defining the translational problem, the rotation-internal motion problem of the nuclei and the electronic problem. Concerning the rotation-internal nuclear motion problem of a semi-rigid model, the energy function may classically be written in the form

$$T + V = \frac{1}{2} (\tilde{\omega} \tilde{\xi}) (g_{mn}(\xi)) \begin{pmatrix} \omega \\ \xi \end{pmatrix} + V(\xi) . \quad (28)$$

ω denotes the angular velocities referred to the centre of mass frame coordinate system and the $\dot{\xi}$'s the time derivatives of the internal coordinates. The potential $V(\xi)$ may be identified with the electronic energy function. Expressing the angular velocities by Eulerian angles and their time derivatives [12]

$$\omega = E(\epsilon) \dot{\epsilon} \quad (29)$$

the total energy may be transformed into the usual hamiltonian form

$$H = \frac{1}{2} (\tilde{P} \tilde{p}_{\xi}) (g^{mn}(\xi)) \begin{pmatrix} P \\ p_{\xi} \end{pmatrix} + V(\xi) \quad (30)$$

where the total angular momentum components are to be expressed by the Eulerian dynamical variables

$$\tilde{P} = \tilde{p}_{\epsilon} E^{-1}(\epsilon) \quad (31)$$

Concerning the symmetry group of the Hamiltonian (30), the following important theorem holds: The full isometric group $\bar{\mathcal{K}}(\xi)$ is a proper or improper subgroup of the symmetry group $\bar{\mathcal{G}}\{\hat{H}\}$ of the rotation internal motion Hamiltonian \hat{H}

$$\hat{P}_H \hat{H} \hat{P}_H^{-1} = \hat{H} \quad , \quad \forall H \in \bar{\mathcal{K}}(\xi). \quad (32)$$

$\bar{\mathcal{G}}\{\hat{H}\}$ represents the set of all operations applied to the frame system leaving \hat{H} symmetric and is in most cases isomorphic to $\bar{\mathcal{K}}(\xi)$, but nevertheless there are cases for which $\bar{\mathcal{K}}$ is a proper subgroup of $\bar{\mathcal{G}}\{\hat{H}\}$ [8].

Besides the isometric group, this Hamiltonian is symmetric w.r.t. transformations of the laboratory system

$$\vec{e}^{\prime} = \vec{e}^{\prime} R^{\prime} \quad , \quad R^{\prime} \in SO(3)^{\prime} \quad (33)$$

$$\hat{P}_{R^{\prime}} \hat{H} \hat{P}_{R^{\prime}}^{-1} = \hat{H} \quad (34)$$

Since the operators \hat{P}_H and $\hat{P}_{R^{\prime}}$ commute pairwise \hat{H} is symmetric w.r.t. $\bar{\mathcal{G}}\{\hat{H}\}$

$$\bar{\mathcal{G}}\{\hat{H}\} = SO(3)^{\prime} \boxtimes \bar{\mathcal{G}}\{\hat{H}\} \quad , \quad \bar{\mathcal{G}}\{\hat{H}\} \supseteq \bar{\mathcal{K}}(\xi) \quad (35)$$

The isometric group may therefore be used for the construction of symmetrized basis functions required for solution of the energy eigenvalue problem. The characteristic solutions of the eigenvalue problem

$$\hat{H}\psi = E\psi \quad (36)$$

may be denoted by $\psi_{JM}^{(j)}_{\mu N}(\epsilon, \xi)$, where the first two indices stand for representation and row of the group $SO(3)$ and the third and fourth index for representation and row of $\bar{\mathcal{K}}(\xi)$. For further discussion, $\bar{\mathcal{G}}\{\hat{H}\}$ will be assumed to be isomorphic to $\bar{\mathcal{K}}(\xi)$.

3.2 Irreducible tensors and selection rules of SRMs

The isometric group allows a systematic treatment and compact presentation of multipole selection rules of non-rigid molecules in a manner strictly analogous to the familiar group theoretical treatment of quasi-rigid molecules [3, 13]. First a set of general transformation formulae for tensor operators associated with SRMs will be presented. These then serve as a mathematical tool for the formulation of Wigner-Eckart theorems for matrix elements of irreducible tensor operators and selection rules for transitions induced by them. The discussion will be restricted to irreducible tensor operators (\hat{A}_{SG}) of rank s

which transform w.r.t. transformations of the frame system cogrediently to the irreducible components of the n th Kronecker power $X(\xi)^{f_{\text{sn}}}$ of $X(\xi)^f = \sum_{\kappa} X_{\kappa}^f(\xi)$, i.e. the sum over a set of equivalent nuclei. The most important tensor operators of this type are

- (i) the electric and magnetic dipole operators ($\hat{M}^{(e)f}(\xi)$) and ($\hat{M}^{(m)f}(\xi)$), both of rank 1 but parity $p = +$ and $p = -$, respectively
- (ii) the electric quadrupole and polarization operators ($\hat{A}_{20}^f(\xi)$), both of rank 2 and parity $p = +$.

The relation between the components of an irreducible tensor operator in the laboratory and frame system is given by

$$(\hat{A}_{SO}^l(\epsilon, \xi)) = D^{(s+)}(\epsilon)^\dagger (\hat{A}_{SO}^f(\xi)) \quad (37)$$

the $+$ denoting an even irreducible representation of $O(3)$. For tensor operators expressed w.r.t. the frame system, the following fundamental transformation formula may be derived from the Born-Oppenheimer theory [8] (p denotes the parity of \hat{A}):

$$\hat{P}_H (\hat{A}_{SO}^f) \hat{P}_H^{-1} = D^{(sp)}(H)^\dagger (\hat{A}_{SO}^f(\xi)), \quad \forall H \in \bar{\mathcal{H}}(\xi) \quad (38)$$

From the theory of the rotation group the following two formulae may be derived

$$\hat{P}_{R^l} D^{(s)}(\epsilon) = D^{(s)}(\epsilon) D^{(s)}(R^l), \quad \forall R^l \in SO(3)^l \quad (39)$$

$$\hat{P}_H D^{(s)}(\epsilon) = D^{(s)}(H)^\dagger D^{(s)}(\epsilon), \quad \forall H \in \bar{\mathcal{H}}(\xi) \quad (39')$$

Using eqs. (37), (38) and (39), we obtain for the transformation of an irreducible tensor w.r.t. the laboratory system

$$\begin{aligned} \hat{P}_{R^l} \hat{P}_H (\hat{A}_{SO}^l(\epsilon, \xi)) \hat{P}_H^{-1} \hat{P}_{R^l}^{-1} &= D^{(s+)}(R^l)^\dagger D^{(s+)}(\epsilon)^\dagger D^{(s+)}(H) D^{(sp)}(H)^\dagger (\hat{A}_{SO}^f(\xi)) \\ &= \begin{cases} D^{(s+)}(R^l)^\dagger (\hat{A}_{SO}^l(\epsilon, \xi)) & \text{if } p = + \quad (\text{even}) \\ |\Gamma(3)(H)| D^{(s+)}(R^l)^\dagger (\hat{A}_{SO}^l(\epsilon, \xi)) & \text{if } p = - \quad (\text{odd}) \end{cases} \quad (40) \end{aligned}$$

Therefore, for the electric and magnetic dipole moment operators the following transformation formulae hold

$$\hat{P}_{R^L} \hat{P}_H (\hat{M}_\sigma^{(e)l}(\epsilon, \xi)) \hat{P}_H^{-1} \hat{P}_{R^L}^{-1} = |\Gamma^{(3)}(H)| D^{(1+)}(R^L)^\dagger (\hat{M}_\sigma^{(e)l}(\epsilon, \xi)) \quad (41)$$

$$\hat{P}_{R^L} \hat{P}_H (\hat{M}_\sigma^{(m)l}(\epsilon, \xi)) \hat{P}_H^{-1} \hat{P}_{R^L}^{-1} = D^{(1+)}(R^L)^\dagger (\hat{M}_\sigma^{(m)l}(\epsilon, \xi)) \quad (41')$$

For the sake of brevity the discussion of selection rules will be restricted to dipole selection rules. Using the transformation formula (41), one finds by the usual Wigner-Eckart technique for

$$(\psi_{\overline{JM}\Gamma}(\bar{j})_{\bar{\mu}\bar{N}}(\epsilon, \xi), \hat{M}^{(e)l}(\epsilon, \xi) \psi_{JM\Gamma}(j)_{\mu N}(\epsilon, \xi))$$

the following electric dipole selection rules:

$$SO(3) : \Delta J = 0, \pm 1 \quad J = 0 \leftrightarrow J = 0 \quad (42)$$

$\overline{\mathcal{H}}(\xi)$: the selection rules may be expressed by the quantity

$$\Theta_{\bar{\mu}\mu}(\bar{j}j) = \frac{1}{\hbar} \sum_{\overline{\mathcal{H}}} \Gamma_{\bar{\mu}\bar{\mu}}(\bar{j})^* (H) \Gamma_{\mu'\mu}(j)(H) |\Gamma^{(3)}(H)| \quad (43)$$

which holds for all three (cartesian or spherical) components of $(\hat{M}^{(e)l})$.

The quantity (43) may be specified further for case a and b SRMs (cf. section 2.2.1).

case a: $|\Gamma^{(3)}(H)| = +1$, $\forall H \in \overline{\mathcal{H}}(\xi)$

$$\text{therefore } \Theta_{\bar{\mu}\mu}(\bar{j}j) = \frac{1}{\hbar} \delta_{\bar{j}j} \delta_{\bar{\mu}, \mu'} \delta_{\bar{\mu}\mu} \quad (44)$$

Hence the electric dipole selection rule reads

$$\Gamma(j) \leftrightarrow \Gamma(\bar{j}), \quad \mu \leftrightarrow \bar{\mu} \quad (45)$$

The symbol $\delta_{\bar{\mu}, \mu'}$ does not express a selection rule since $\bar{\mu}'$ and μ' are summation indices.

case b: the group $\Gamma^{(3)}\{\overline{\mathcal{H}}\}$ is improperly orthogonal and therefore the isometric group $\overline{\mathcal{H}}$ has a normal subgroup $\overline{\mathcal{H}}^+$ of index 2

$$\overline{\mathcal{H}} = \overline{\mathcal{H}}^+ \cup_S \overline{\mathcal{H}}^+ \quad (46)$$

Hence

$$\Theta_{\bar{\mu}\mu}(\bar{j}j) = \frac{1}{\hbar} \left\{ \sum_{\overline{\mathcal{H}}^+} \Gamma_{\bar{\mu}\bar{\mu}}(\bar{j})^* (H) \Gamma_{\mu'\mu}(j)(H) - \sum_{\overline{\mathcal{H}}^+} \Gamma_{\bar{\mu}\bar{\mu}}(\bar{j})^* (SH) \Gamma_{\mu'\mu}(j)(SH) \right\} \quad (47)$$

In the special case where

$$SH = HS, \quad S^2 = E, \quad \forall H \in \overline{\mathcal{H}}^+$$

the irreducible representations of $\overline{\mathcal{K}}$ occur in pairs of associated representations $\Gamma^{(j+)}$, $\Gamma^{(j-)}$ for which

$$\begin{aligned}\Gamma^{(jP)}(H) &= \Gamma^{(j)}(H) \\ \Gamma^{(jP)}(SH) &= (P) \Gamma^{(j)}(H), \quad H \in \overline{\mathcal{K}}^+\end{aligned}\quad (48)$$

Consequently

$$\Theta_{\mu\mu}^{(\bar{j}j)} = \frac{1}{2\ell_j} [1 - (\bar{P})(P)] \delta_{\bar{j}j} \delta_{\mu^-\mu^+} \delta_{\mu\mu^+}\quad (49)$$

Therefore,

$$\Gamma^{(j)} \leftrightarrow \Gamma^{(j)}, \quad \mu \leftrightarrow \mu, \quad (50)$$

but the upper and lower state must have different parity p .

For the magnetic dipole selection rules one finds the following simple selection rules for all SRMs (case a and case b)

$$\begin{aligned}SO(3) : \Delta J &= 0, \pm 1 \quad J = 0 \leftrightarrow J = 0 \\ \overline{\mathcal{K}}(\xi) : \Theta_{\mu\mu}^{(\bar{j}j)} &= \frac{1}{h} \sum_{\overline{\mathcal{K}}} \Gamma_{\mu^-\mu^+}^{(\bar{j})^*}(H) \Gamma_{\mu^-\mu^+}^{(j)}(H)\end{aligned}$$

Hence

$$\Gamma^{(j)} \leftrightarrow \Gamma^{(j)}, \quad \mu \leftrightarrow \mu \quad (51)$$

holds for all three components of the magnetic dipole moment.

For a number of typical SRMs electric and magnetic dipole moment selection rules are given in Tables 4 and 5.

TABLE 4 Selection Rules of Dipole Transitions of SRMs

f = 1

System/ example	$\mathcal{H}(\xi)$	dipole selection rules	
		electric	magnetic
$C_s F-C_{3v} T$ CH_3CHO	\mathcal{V}_3	$\Gamma(o+) \leftrightarrow \Gamma(o-)$ $\Gamma(1) \leftrightarrow \Gamma(1)$	$\Gamma(j) \leftrightarrow \Gamma(j)$
$C_s F-C_{2v} T$ $CH_2:CHNO_2$	$\mathcal{V}_2 \stackrel{is}{=} \mathcal{V}_4$	$\Gamma(1) \leftrightarrow \Gamma(2)$ $\Gamma(3) \leftrightarrow \Gamma(4)$	$\Gamma(j) \leftrightarrow \Gamma(j)$
$C_s F-C_s T$ $CH_2:CHCHO$	\mathcal{V}_2	$\Gamma(o+) \leftrightarrow \Gamma(o-)$	$\Gamma(j) \leftrightarrow \Gamma(j)$
$C_s F-C_{2v} I$ $\overline{CH_2}CR_2NH$	\mathcal{V}_2	$\Gamma(o+) \leftrightarrow \Gamma(o-)$	$\Gamma(j) \leftrightarrow \Gamma(j)$
$C_{2v} F-C_{2v} I$ $\overline{CH_2}CH_2NH$	\mathcal{V}_4	$\Gamma(1) \leftrightarrow \Gamma(2)$ $\Gamma(3) \leftrightarrow \Gamma(4)$	$\Gamma(j) \leftrightarrow \Gamma(j)$
$D_{\infty h} F(C_s T)_2$ $CHOCHO$	\mathcal{V}_4	$\Gamma(1) \leftrightarrow \Gamma(2)$ $\Gamma(3) \leftrightarrow \Gamma(4)$	$\Gamma(j) \leftrightarrow \Gamma(j)$
$C_{2v} F-C_{2v} T$ $C_6H_5NO_2$	$A(2,2,2)$	$\Gamma(j+) \leftrightarrow \Gamma(j-)$	$\Gamma(jp) \leftrightarrow \Gamma(jp)$

TABLE 5 Selection Rules of Dipole Transitions of SRMs

$$g(\xi) = C_1, f \geq 2$$

f	system/ example	$\mathcal{H}(\xi)$	dipole section rules	
			electric	magnetic
2	$C_s F(C_{3v} T)(C_{3v} T)'$ <chem>CH3CH:NCH3</chem>	g_{18}	$\Gamma^{(oo+)} \leftrightarrow \Gamma^{(oo-)}$ $\Gamma^{(MN)} \leftrightarrow \Gamma^{(MN)}$	$\Gamma^{(j)} \leftrightarrow \Gamma^{(j)}$
2	$C_s F(C_{3v} T)(C_{2v} T)$ <chem>CH3CH2NO2</chem>	ν_6	$\Gamma^{(o+)} \leftrightarrow \Gamma^{(o-)}$ $\Gamma^{(3+)} \leftrightarrow \Gamma^{(3-)}$ $\Gamma^{(1)} \leftrightarrow \Gamma^{(1)}$ $\Gamma^{(2)} \leftrightarrow \Gamma^{(2)}$	$\Gamma^{(j)} \leftrightarrow \Gamma^{(j)}$
2	$C_{2v} F(C_{3v} T)(C_{2v} I)$ <chem>CH3NH2</chem>	ν_6	$\Gamma^{(o+)} \leftrightarrow \Gamma^{(o-)}$ $\Gamma^{(3+)} \leftrightarrow \Gamma^{(3-)}$ $\Gamma^{(1)} \leftrightarrow \Gamma^{(1)}$ $\Gamma^{(2)} \leftrightarrow \Gamma^{(2)}$	$\Gamma^{(j)} \leftrightarrow \Gamma^{(j)}$
2	$C_s F(C_{2v} T)(C_{2v} T)'$ <chem>NO2CH:CFNO2</chem>	$\mathcal{A}(2,2,2)$	$\Gamma^{(j+)} \leftrightarrow \Gamma^{(j-)}$	$\Gamma^{(jp)} \leftrightarrow \Gamma^{(jp)}$
2	$C_{2v} F(C_{2v} T)_2$ <chem>CH2(NO2)2</chem>	$\nu_4 \{E, T\}$	$\Gamma^{(o++)} \leftrightarrow \Gamma^{(o+-)}$ $\Gamma^{(o-+)} \leftrightarrow \Gamma^{(o--)}$ $\Gamma^{(2++)} \leftrightarrow \Gamma^{(2+-)}$ $\Gamma^{(2-+)} \leftrightarrow \Gamma^{(2--)}$ $\Gamma^{(1+)} \leftrightarrow \Gamma^{(1-)}$	$\Gamma^{(j)} \leftrightarrow \Gamma^{(j)}$
2	$C_{2v} F(C_s T)_2$ <chem>O(CHO)2</chem>	ν_4	$\Gamma^{(1)} \leftrightarrow \Gamma^{(2)}$ $\Gamma^{(3)} \leftrightarrow \Gamma^{(4)}$	$\Gamma^{(j)} \leftrightarrow \Gamma^{(j)}$
2	$C_s F(C_s T)(C_s T)'$ <chem>CH2FCH2CHO</chem>	ν_2	$\Gamma^{(o+)} \leftrightarrow \Gamma^{(o-)}$	$\Gamma^{(j)} \leftrightarrow \Gamma^{(j)}$
3	$C_2(\tau)F(C_s T)_2$ <chem>CH2OHCH2OH</chem>	ν_4	$\Gamma^{(1)} \leftrightarrow \Gamma^{(2)}$ $\Gamma^{(3)} \leftrightarrow \Gamma^{(4)}$	$\Gamma^{(j)} \leftrightarrow \Gamma^{(j)}$

IV. REMARKS

The foregoing discussion should have made clear that the isometric group allows applications to physical and geometrical problems of nonrigid molecules by the same methods as the covering group does for quasirigid molecules. Among such application the problem of the chirality of nonrigid molecules might be mentioned, which finds a satisfactory solution within the isometric group frame work [9]. Further applications concern the treatment of the Stark effect [14] and molecular beam deflection experiments of nonrigid molecules and kinetics of chemical exchange processes and statistical thermodynamics of molecules with large amplitude internal motion, hyperfine interactions within nonrigid molecules.

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