

On the symmetry properties of non-rigid molecules A unified approach

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A unified, constructive approach to the symmetry properties of non-rigid molecules is outlined and the relation of the formalism to the permutation-inversion, isometric and isodynamic theories is discussed. The formulation of the molecular symmetry group as a semi-direct product is considered and isodynamic operations are defined as generalizations of the conventional Wigner vibrational symmetry operations.

1. INTRODUCTION

The application of group theory to the description of molecular structure and dynamics has long been recognized as an essential part of our understanding of these phenomena. It is therefore disturbing to find that there exist some significant differences of opinion concerning the symmetry properties of molecules, which involve both the fundamental interpretation of the various approaches adopted and the details of the implementation of group theory in particular instances.

On the specific question of the symmetry properties of non-rigid molecules (NRMs), it is well-known that several different theories have been proposed. This is, perhaps, not surprising given the immense variety of possible non-rigid behaviour. Indeed, if we think of the whole range of internal molecular dynamics, from the complete fluxionality expected, for example, in weakly-bound clusters of inert-gas atoms [1] to the small-amplitude nuclear vibrations in conventional quasi-rigid molecules, it is apparent that rival theories may have rather different domains of applicability, or may express essentially the same concepts in different ways. To date there have been three main theoretical approaches: the Longuet-Higgins permutation-inversion (PI) theory [2] (following Hougen's classic work [3-6] and supplemented by the Q -group approach of Dalton [7-10]), Altmann's isodynamic theory [11-13] and the more recent isometric theory of Günthard *et al.* [14-21]. Many applications of the PI theory are described in the review by Bunker [22] and the relation between the PI and isodynamic theories is discussed by Watson [23] and Altmann [12].

In this paper we outline a unified, constructive approach to the symmetry properties of a very large class of NRMs, those for which the dynamical picture introduced by Sayvetz [24] is appropriate. Thus, we imagine the nuclei to execute rapid, small-amplitude vibrations about an equilibrium configuration that is itself performing a slow, large-amplitude motion of some sort, in addition to undergoing overall rotation. The large-amplitude motion may involve a

rotation of one part of the molecule with respect to another, ring-puckering, inversion etc. A time-scale separation of internal and vibrational motions is therefore assumed in first approximation. Most detailed theoretical studies of NRMs are investigations of the properties of hamiltonians for systems of this type ; such work is complemented by the more general Q -group (induced representation) approach, where the dynamics of the internal motion is not treated explicitly (see also [25]). It should perhaps be emphasized that this conventional description of the molecule is taken for granted and we do not face the fundamental problem of the emergence of molecular structure as spontaneously-broken permutation-inversion symmetry [26, 27].

It is not our purpose to compare various theories directly ; we consider that in the absence of any additional interpretation they are founded upon distinct conceptual bases. Rather, we shall indicate how previous approaches can appear as particular aspects of a unified formalism, bearing in mind that a treatment of NRM symmetry in terms of any but the simplest of dynamical models [28] must necessarily be consistent with the PI theory, which utilizes only the fundamental symmetries of the complete molecular hamiltonian [2]. Very recently Günthard *et al.* have discussed the connection between the PI and Isometric theories in a similar spirit [20] and some of our conclusions are in accord with the results given in their paper. However, these authors work within the framework of the isometric theory and do not consider the isodynamic approach in any detail, so that a further discussion of these matters from another standpoint seems desirable. The work of Gilles and Philippot must also be mentioned in this connection [29]. It is unfortunate that many of the conclusions drawn from their penetrating formal analysis seem to be vitiated by a misinterpretation of the Eckart-Sayvetz conditions, as we show below.

No consideration will be given here to those particular problems of current interest concerning the symmetry properties of rigid molecules [6, 30-36]. However, we should like to note that the present work has been inspired by the detailed analysis of the Eckart frame concept given recently by Louck and Galbraith [34] and follows a comparison of different approaches to rigid-molecule symmetry [37]. The Eckart-Sayvetz constraints [24] (which generalize the Eckart conditions to certain non-rigid systems) are of particular importance in the theory, which may thus be regarded as an extension of the ideas of Louck and Galbraith.

2. THE SEMI-RIGID MOLECULAR MODEL

The *semi-rigid molecular model* (SRMM) is now introduced ([14] § 2.1). This is a geometrical object that represents the assumed equilibrium structure of the molecule (zero vibrational displacements) as it undergoes large-amplitude internal motion and should not be confused with the real molecule in motion (the dynamical molecular model, cf. § 4 and [34]). The SRMM defines the configurations about which a normal-mode analysis of nuclear motion is made and, as will be shown below, also determines the appropriate NRM symmetry group. It is a direct generalization of the *static molecular model* considered by Louck and Galbraith [34].

Formally, the SRMM is a set of triples

$$\mathcal{A} \equiv \{(\mathbf{a}^\alpha(\gamma), m_\alpha, z_\alpha) ; \alpha = 1, \dots, N\} \quad (1)$$

abbreviated to

$$\mathcal{A} = \{\mathbf{a}^\alpha(\gamma); \alpha = 1, \dots, N\} \quad (2)$$

defining N vectors $\mathbf{a}^\alpha(\gamma)$ as functions of a set of parameters denoted by the symbol γ (a representative point in the parameter domain Γ), where each vector $\mathbf{a}^\alpha(\gamma)$ is associated with a particle (nucleus) of mass m_α and charge z_α . Physically the parameters are torsional angles, angles of pucker etc., and have finite ranges [14]. We shall suppose that there are T ($\leq 3N - 6$) independent parameters, denoted by $\gamma = (\gamma_1, \dots, \gamma_t, \dots)$.

Two SRMM vectors $\mathbf{a}^\alpha(\gamma)$ and $\mathbf{a}^{\alpha'}(\gamma)$ are said to be associated with identical nuclei if

$$z_\alpha = z_{\alpha'} \quad \text{and} \quad m_\alpha = m_{\alpha'}. \quad (3)$$

This is an equivalence relation and partitions the set of SRMM vectors into subsets corresponding to identical nuclei [34].

It is convenient, but not essential [38], for the SRMM vectors to satisfy the centre of mass condition

$$\sum_{\alpha} m_{\alpha} \mathbf{a}^{\alpha}(\gamma) = \mathbf{0} \quad \forall \gamma \in \Gamma. \quad (4)$$

An arbitrary right-handed coordinate frame $\{\hat{\mathbf{e}}_i; i = x, y, z\}$ is set into the SRMM, which is then defined by the $3N$ components $\{a^\alpha(\gamma)_i; \alpha = 1 \dots N, i = x, y, z\}$, where

$$a^\alpha(\gamma)_i \equiv \hat{\mathbf{e}}_i \cdot \mathbf{a}^\alpha(\gamma) \quad \forall \alpha, \gamma. \quad (5)$$

The coordinate frame $\{\hat{\mathbf{e}}_i\}$ may be a principal axis system for a particular value of γ .

Consider now a transformation h of SRMM vectors, defined as an ordered pair (ρ, τ)

$$h \equiv (\rho, \tau): a^\alpha(\gamma)_i \rightarrow R(\rho)_{ij} a^\alpha(\tau^{-1} \gamma)_j. \quad (6)$$

(We adopt a summation convention for component indices i, j, \dots). Here ρ is a rotation-inversion ($\in O(3)$) of all vectors in the space \mathbb{E} spanned by the basis $\{\hat{\mathbf{e}}_i\}$

$$\rho: x_i \rightarrow R(\rho)_{ij} x_j \quad \forall \mathbf{x} \in \mathbb{E} \quad (7)$$

and τ is a mapping in parameter space

$$\forall \gamma \in \Gamma, \quad \tau: \gamma \rightarrow \tau \gamma \in \Gamma \quad (8)$$

corresponding, for example, to a change in torsional angles. The presence of the inverse operation τ^{-1} on the right-hand side of equation (6) should be noted; this is necessary to ensure the convenient result (12).

The identity transformation is denoted $h_0 = (\rho_0, \tau_0)$, where ρ_0 and τ_0 are the identity rotation and identity mapping of parameter space, respectively.

A transformation $h = (\rho, \tau)$ is termed a *symmetry operation of the SRMM* if it induces a permutation of the SRMM vectors associated with identical nuclei; that is, if

$$\forall \alpha, \quad h = (\rho, \tau): a^\alpha(\gamma)_i \rightarrow R(\rho)_{ij} a^\alpha(\tau^{-1} \gamma)_j \equiv \sum_{\beta} a^\beta(\gamma)_i S(h)_{\beta\alpha} \quad (9)$$

(cf. [34], equation (3.32 b)). The matrix $S(h)$ is an $N \times N$ permutation matrix, which permutes identical nuclei and so commutes with the mass matrix. The

set of all symmetry operations of the SRMM forms a group \mathbb{H} , which we call the *symmetry group of the SRMM*

$$\mathbb{H} \equiv \{h = (\rho, \tau) | h : a^\alpha(\gamma)_i \rightarrow \sum_\beta a^\beta(\gamma)_i S(h)_{\beta\alpha}\}. \quad (10)$$

The multiplication rule

$$h_2 \cdot h_1 = (\rho_2, \tau_2) \cdot (\rho_1, \tau_1) = (\rho_2 \rho_1, \tau_2 \tau_1) \quad (11)$$

is the simplest and most useful for elements of \mathbb{H} ; by definition the permutation matrices $\{S(h)\}$ form a representation of \mathbb{H}

$$S(h_2 h_1) = S(h_2) S(h_1). \quad (12)$$

We point out that $(\rho, \tau) \in \mathbb{H}$ does not necessarily imply that either (ρ, τ_0) or (ρ_0, τ) is an element of \mathbb{H} .

It is sufficient for the validity of the simple rule (11) that the parametrization of the SRMM is chosen such that all the rotation-inversion operations ρ are fixed with respect to the coordinate frame $\{\hat{\mathbf{e}}_i\}$, independent of the particular point $\gamma = (\gamma_1, \dots, \gamma_t)$ in parameter space. This requirement was discussed by Gilles and Philippot [29], who showed that for some molecular models it is incompatible with the conditions

$$\epsilon_{ijk} \sum_\alpha m_\alpha \left(\frac{\partial a^\alpha(\gamma)_j}{\partial \gamma_t} \right) a^\alpha(\gamma)_k = 0 \quad \forall \gamma, \quad t = 1 \dots T. \quad (13)$$

(the vanishing of internal angular momentum expressed in our notation.) The equations (13) were identified (implicitly) by Gilles and Philippot as the Eckart-Sayvetz conditions; however, this is incorrect. Although the constraints (13) uncouple the internal motions and overall rotation of the molecule in zeroth approximation, this is a matter of convenience rather than necessity and we are in fact free to attempt to impose our condition on the SRMM parametrization. (Molecules for which difficulties cannot be avoided here are, for example, PF_5 and tetra-arylmethane. The symmetry of the latter system is described in [39]). The Eckart-Sayvetz constraints are discussed in § 4, where we consider the molecule in motion and present a rigorous definition of the perrotations of Gilles and Philippot.

In general, two or more elements of \mathbb{H} may correspond to the same permutation of SRMM vectors. If this is the case, then there exist one or more non-trivial elements of \mathbb{H} corresponding to the identity permutation of nuclei

$$\exists h = (\rho, \tau) \quad \text{with} \quad \rho \neq \rho_0 \quad \text{such that} \quad h \neq h_0 \quad \text{and} \quad S(h) = \mathbb{1}. \quad (14)$$

It should be noted that we only consider elements that have $\rho \neq \rho_0$. Those with $\rho = \rho_0$ are transformations (ρ_0, τ) corresponding to the identity permutation and acting only on the parameter space Γ ; in other words, they define the boundaries of Γ (for example, increase a torsional angle by 2π) and so do not appear in the group \mathbb{H} (all the h must be taken *modulo* these elements).

We shall refer to the operations defined by equation (14) as *Primitive period transformations* (PPTs) and it is shown below that they correspond to the primitive period internal isometric transformations introduced by Günthard *et al.* [20]. The characterization of PPTs *via* equation (14) enables us to obtain some useful results rather easily. Thus, the set of PPTs together with the identity element h_0 forms a subgroup of \mathbb{H} , as can be verified from the definition (14) and

equations (11) and (12). Moreover, using the representation property (12) of the permutation matrices, it follows that the subgroup of PPTs is in fact an invariant subgroup of \mathbb{H} . There is therefore a homomorphism from \mathbb{H} onto the group (denoted by \mathbb{H}^π) of distinct permutation matrices

$$\mathbb{H} \xrightarrow{\text{ho.}} \mathbb{H}^\pi, \quad (15)$$

where the PPTs form the kernel of the homomorphism. It should be stressed that the existence of PPTs depends upon our choice of SRMM parameters. For the reason mentioned above, for a molecule such as dimethylacetylene (which has two identical ends) it is necessary to adopt a parametrization that does not distinguish a top end from a frame end. It is well known that the resulting PPT is associated with the use of a double PI group in the description of the molecular vibrations [40-42].

The permutations that form the group \mathbb{H}^π are of course the feasible permutations of Longuet-Higgins. As pointed out by Günthard *et al.*, in any theory based upon the SRMM the feasibility of a permutation is determined directly by the hypothetical molecular model.

Our development of the theory shows clearly the basis for the isometric approach to the symmetry group of the SRMM. It can be seen from equations (6) and (9) that a transformation of the internal parameters of the form

$$\tau : a^\alpha(\gamma)_i \rightarrow a^\alpha(\tau^{-1} \gamma)_i, \quad (16)$$

where $(\rho, \tau) \in \mathbb{H}$ for some ρ , merely permutes the elements of the distance set Δ , where

$$\Delta \equiv \{ | \mathbf{a}^\alpha(\gamma) - \mathbf{a}^{\alpha'}(\gamma) | ; \alpha > \alpha' = 1, \dots, N \} \quad (17)$$

and is therefore called an *internal isometric transformation*. The group of all distinct internal isometric transformations is denoted \mathcal{F} (following the notation of [20])

$$\mathcal{F} \equiv \{ \tau \mid (\rho, \tau) \in \mathbb{H} \}. \quad (18)$$

There is, in general, a homomorphism from \mathbb{H} onto the Internal Isometric group \mathcal{F}

$$\mathbb{H} \xrightarrow{\text{ho.}} \mathcal{F}. \quad (19)$$

It is thus apparent that a determination of the internal isometric group does not completely specify the symmetry of the SRMM (in particular, when the SRMM has any point (covering) symmetry for arbitrary γ). Günthard *et al.* define the *complete isometric group* \mathcal{H} as an abstract product of the point group \mathbb{G}^P of the SRMM (cf. § 3) with the group \mathcal{F}

$$\mathcal{H} \equiv \mathbb{G}^P \cdot \mathcal{F} \quad (20)$$

and have concluded from a study of various representations of \mathcal{H} that it is, in some abstract sense, a semi-direct product [20].

The group \mathbb{H} is a complete characterization of the symmetry of the SRMM and must be determined by a process of exhaustion based upon a study of the transformations (9). We note also that it is a direct generalization to NRM of the point symmetry group for rigid molecules and that our formalism parallels the treatment of the molecular point group given by Louck and Galbraith. The

definition of a group multiplication rule such as (11) means that the elements of \mathbb{H} can be manipulated simply and directly, a fact which is of considerable importance when determining whether or not the group has any significant internal structure. The possible construction of \mathbb{H} as a semi-direct product is a problem that is discussed in the next section.

We now show that the PPTs defined above correspond to the primitive period internal isometric transformations of [20]. For, if $h = (\rho, \tau)$ is a PPT according to equation (14), then

$$a^\alpha(\tau^{-1} \gamma)_i = \tilde{R}(\rho)_{ij} a^\alpha(\gamma)_j \quad (21)$$

so that for all α, α'

$$|a^\alpha(\tau^{-1} \gamma) - a^{\alpha'}(\tau^{-1} \gamma)| = |a^\alpha(\gamma) - a^{\alpha'}(\gamma)| \quad (22 a)$$

with

$$a^\alpha(\tau^{-1} \gamma) \neq a^{\alpha'}(\gamma) \quad \forall \alpha. \quad (22 b)$$

These are precisely the conditions that define primitive period internal isometric transformations.

3. INTRINSIC OPERATIONS AND COVERING SYMMETRY

Even for only moderately complicated SRMMs, the associated symmetry group can be very large. It is therefore important to make full use of any internal structure that \mathbb{H} may possess, when obtaining its irreducible representations and character table. Such a consideration has motivated several formulations of NRM symmetry groups as semi-direct products, including those of Altmann [11–13], Woodman [43], and Günthard *et al.* [14, 20, 21]. We now consider the problem briefly.

First, we note that, given the validity of the rule (11), \mathbb{H} has *two* invariant subgroups, the *intrinsic group* and the *point group*. The intrinsic group \mathbb{G}^I is the subgroup of \mathbb{H} consisting of all *intrinsic operations* of the SRMM (cf. [13]). These are transformations acting only upon the internal parameter space Γ , so that the rotational part of the operation is the identity ρ_0

$$\mathbb{G}^I \equiv \{(\rho, \tau) \in \mathbb{H} \mid \rho = \rho_0\}. \quad (23)$$

Physically the intrinsic operations correspond to internal transformations such as the rotation of a methyl group about a bond. The point group \mathbb{G}^P is simply defined by the covering (point) symmetry of the SRMM for arbitrary γ . The covering operations do not act upon the parameter space Γ

$$\mathbb{G}^P \equiv \{(\rho, \tau) \in \mathbb{H} \mid \tau = \tau_0\}. \quad (24)$$

Using the multiplication rule (11), it is trivial to establish that both \mathbb{G}^I and \mathbb{G}^P are invariant subgroups of \mathbb{H} . The elements of \mathbb{G}^I and \mathbb{G}^P commute; we can therefore form the direct product $\mathbb{G}^I \otimes \mathbb{G}^P$, which is also an invariant subgroup of \mathbb{H}

$$\mathbb{H} \supset \mathbb{G}^I \otimes \mathbb{G}^P. \quad (25)$$

The factor group \mathcal{K} is defined

$$\mathcal{K} \equiv \mathbb{H} / (\mathbb{G}^I \otimes \mathbb{G}^P). \quad (26)$$

Now, in general it is *not* possible to find a set of coset representatives of $\mathbb{G}^I \otimes \mathbb{G}^P$ which closes to form a group (denoted \mathbb{K}) isomorphic with the factor

group \mathcal{K} . If, however, this is possible, then the group \mathbb{H} can be written as a *semi-direct product* [13]

$$\mathbb{H} = (\mathbb{G}^I \otimes \mathbb{G}^P) \triangleleft \mathbb{K}, \quad (27)$$

which may be rearranged to

$$\mathbb{H} = \mathbb{G}^I \triangleleft (\mathbb{G}^P \triangleleft \mathbb{K}) \quad (28)$$

or

$$\mathbb{H} = \mathbb{G}^P \triangleleft (\mathbb{G}^I \triangleleft \mathbb{K}). \quad (29)$$

Here, both \mathbb{K} and $(\mathbb{G}^P \triangleleft \mathbb{K})$ are isomorphic with point groups. The particular group structure (28) corresponds to the most recent version of Altmann's theory [13] and to the reduction given by Woodman for the symmetry groups of certain NRMs [43]. The group structure (29) corresponds to the abstract semi-direct product structure for the complete isometric group \mathcal{H} proposed by Günthard *et al.* [20], with

$$\mathcal{H} \stackrel{\text{iso}}{=} \mathbb{G}^I \triangleleft \mathbb{K}. \quad (30)$$

We define the *extended intrinsic group* $\tilde{\mathbb{G}}^I$ as the subgroup of \mathbb{H} consisting of all transformations (ρ, τ) with either $\rho = \rho_0$ or $\rho = i$, the inversion operation. This definition is only useful provided that the point group \mathbb{G}^P does not itself contain the inversion

$$\tilde{\mathbb{G}}^I \equiv \{(\rho, \tau) \in \mathbb{H} \mid \rho = \rho_0 \text{ or } \rho = i; (i, \tau_0) \notin \mathbb{G}^P\}. \quad (31)$$

Since the inversion i commutes with all rotation-inversions ρ , $\tilde{\mathbb{G}}^I$ is an invariant subgroup of \mathbb{H}

$$\mathbb{H} \triangleright \tilde{\mathbb{G}}^I \quad (32)$$

and we can still form a direct product $\tilde{\mathbb{G}}^I \otimes \mathbb{G}^P$, so that

$$\mathbb{H} \triangleright (\tilde{\mathbb{G}}^I \otimes \mathbb{G}^P). \quad (33)$$

The appropriate factor group is denoted $\tilde{\mathcal{K}}$

$$\tilde{\mathcal{K}} \equiv \mathbb{H} / (\tilde{\mathbb{G}}^I \otimes \mathbb{G}^P). \quad (34)$$

The point of this is that while it might be impossible to form the group \mathbb{K} isomorphic with \mathcal{K} , and thereby to write \mathbb{H} as the semi-direct product (28) or (29), it may well be possible to find a group $\tilde{\mathbb{K}}$ that is isomorphic with $\tilde{\mathcal{K}}$ (note that $\tilde{\mathcal{K}}$ is smaller than \mathcal{K}). The group \mathbb{H} can then be written as a semi-direct product

$$\mathbb{H} = \tilde{\mathbb{G}}^I \otimes \mathbb{G}^P \triangleleft \tilde{\mathbb{K}} \quad (35)$$

$$= \tilde{\mathbb{G}}^I \triangleleft (\mathbb{G}^P \triangleleft \tilde{\mathbb{K}}) \quad (36)$$

$$= \mathbb{G}^P \triangleleft (\tilde{\mathbb{G}}^I \triangleleft \tilde{\mathbb{K}}). \quad (37)$$

It can be seen from equation (37) that the introduction of the extended intrinsic group corresponds to an alternative breakdown of the group \mathcal{H} as a semi-direct product. As an example [37], we note that the NRM $\text{BF}_2\text{-BF}_2$ [44] has a SRMM for which it is necessary to invoke an Extended Intrinsic group $\tilde{\mathbb{G}}^I$. In this

case, the group \mathbb{H} is (cf. equation (35))

$$\mathbb{H} = (C_{2n} \otimes D_2) \otimes C_s \quad (38)$$

$$\stackrel{\text{iso}}{=} G_{16}^\dagger. \quad (39)$$

(NB. The group C_s of order two is *not* generated by a PPT.)

It is apparent that a knowledge of $\mathbb{G}^I(\tilde{\mathbb{G}}^I)$, \mathbb{G}^P , and $\mathbb{K}(\tilde{\mathbb{K}})$ enables us to use systematic methods (described, for example, by Altmann [13]) that are available for the construction of the irreducible representations and character table of the group \mathbb{H} .

4. THE MOLECULE IN MOTION

We now turn to the dynamical problem of the nuclear motion in a molecule having a specified SRMM. The crucial point is that each element of the symmetry group of the SRMM induces a well-defined transformation of molecular (Born–Oppenheimer) variables, the net result of which is a feasible permutation of nuclear position vectors. The permutation itself is determined by the transformation (9). We thus arrive, as indeed we should, at the familiar PI theory (with a reservation concerning the inversion, see below).

Let R_i^α be the components of the position vector of nucleus α , referred to the laboratory coordinate frame $\{\hat{\mathbf{i}}_i\}$. In terms of molecular variables, the components R_i^α are (cf. [3, 6]):

$$R_i^\alpha = R_i + C_{ij}(a^\alpha(\gamma)_j + d_j^\alpha) \quad (40)$$

with R_i = the laboratory-fixed components of the nuclear centre of mass vector and $C_{ij} \equiv \{\hat{\mathbf{i}}_i \cdot \hat{\mathbf{f}}_j\}$ the direction cosine matrix specifying the orientation of the Eckart frame $\{\hat{\mathbf{f}}_i\}$ with respect to the laboratory frame. It is conventional to introduce a set of three independent rotational coordinates for the molecule, such as the Euler angles. Following Louck, however, we note that it is useful for clarity in formal manipulations to avoid any explicit parametrization and to work directly with the elements of the matrix C [45]. We shall actually take $C \in O(3)$ (that is $\det. C = +1$ or -1 [36]). The $\{\gamma\}$ are dynamical variables for internal motion, in obvious 1 : 1 correspondence with the SRMM parameters, $a^\alpha(\gamma)_i$ is the i th component with respect to the Eckart frame of the notional equilibrium position of nucleus α (a function of the variables γ as determined by the SRMM) and d_i^α is the i th component with respect to the Eckart frame of the displacement vector of nucleus α . Also, the components of the position vector of electron e , referred to the Eckart frame, are denoted r_i^e .

As there are T ($\leq 3N-6$) independent parameters γ_t , the $3N$ components $\{d_i^\alpha\}$ satisfy $T+6$ constraints (linear in the displacements) [24, 46]:

$$\text{centre of mass} \quad \sum_{\alpha} m_{\alpha} d_i^{\alpha} = 0 \quad i = x, y, z; \quad (41 a)$$

$$\text{Eckart} \quad \epsilon_{ijk} \sum_{\alpha} m_{\alpha} a^{\alpha}(\gamma)_j d_k^{\alpha} = 0 \quad i = x, y, z; \quad (41 b)$$

$$\text{Sayvetz} \quad \sum m_{\alpha} \left(\frac{\partial a^{\alpha}(\gamma)_i}{\partial \gamma_t} \right) d_i^{\alpha} = 0 \quad t = 1 \dots T. \quad (41 c)$$

The conditions (41 *c*) uncouple the nuclear vibrations and large-amplitude internal motions in first approximation.

Each element $h = (\rho, \tau) \in \mathbb{H}$ induces the following transformation of molecular variables (cf. [34])

$$h : C \rightarrow C\tilde{R}(\rho) \quad (42 a)$$

$$h : a^\alpha(\gamma)_i \rightarrow \mathcal{L}_h \cdot a^\alpha(\gamma)_i \equiv \sum_\beta S(h)_{\alpha\beta} R(\rho)_{ij} a^\beta(\gamma)_j \quad (42 b)$$

$$h : d_i^\alpha \rightarrow \mathcal{L}_h \cdot d_i^\alpha \equiv \sum_\beta S(h)_{\alpha\beta} R(\rho)_{ij} d_j^\beta \quad (42 c)$$

$$h : R_i \rightarrow R_i \quad (42 d)$$

$$h : r_i^\epsilon \rightarrow R(\rho)_{ij} r_j^\epsilon. \quad (42 e)$$

These transformations generalize those given for rigid molecules by Hougen [3, 4, 6] and Louck and Galbraith [34], and are a realization of the group \mathbb{H} , which is identified as the *NRM symmetry group*.

We should be careful to distinguish between the transformations (9), which are mappings in the space E spanned by the SRMM coordinate frame, and the induced transformations (42 *b*), which are mappings in real space spanned by $\{\hat{\mathbf{f}}_i\}$ or $\{\hat{\mathbf{l}}_i\}$.

It follows from (40) and (42) that $h \in \mathbb{H}$ induces an overall permutation $S(h)$ of the nuclear position vectors $\{\mathbf{R}^\alpha\}$

$$h : \mathbf{R}^\alpha \rightarrow \sum_\beta S(h)_{\alpha\beta} \mathbf{R}^\beta \quad \alpha = 1 \dots N \quad (43 a)$$

$$h : C_{ij} r_j^\epsilon \rightarrow C_{ij} r_j^\epsilon. \quad (43 b)$$

Such a relabelling of the nuclear position vectors (and spins) is a symmetry operation of the complete molecular hamiltonian, which should, following Gilles and Philippot, be regarded as a change in the rule of association between SRMM vectors and nuclear positions in space [29]. As mentioned above, when \mathbb{H} possesses PPTs there is a homomorphism from \mathbb{H} onto the group of distinct permutations \mathbb{H}^τ .

The transformations (42) leave invariant the dynamical constraints (41), so that we can interpret (42 *b*) as a change in internal coordinate :

$$h : a^\alpha(\gamma)_i \rightarrow a^\alpha(\gamma')_i \quad (44)$$

with

$$\gamma' = \tau\gamma. \quad (45)$$

We therefore write the induced action of h as the mapping (cf. [34] equation (6.16), also [20] equation (5.4))

$$h : (C, \gamma, d_i^\alpha, r_i^\epsilon) \rightarrow (C\tilde{R}(\rho), \tau\gamma, \mathcal{L}_h \cdot d_i^\alpha, R(\rho)_{ij} r_j^\epsilon). \quad (46)$$

In this form, the coordinate transformations can be used to classify tensor operators and wavefunctions (rotational, internal motion, vibrational and electronic) in the NRM symmetry group \mathbb{H} . In particular, (42 *c*) provides a reducible vibrational representation (external coordinates, not necessarily a representation obtained using various sets of internal coordinates [22]).

The operations (42 *a*) define the equivalent rotations of Longuet-Higgins, which are specified with respect to the Eckart frame $\{\hat{\mathbf{f}}_i\}$ and are elements of the group $O'(3)$ of Louck and Galbraith. It should be remarked that this

conclusion is contrary to the interpretation of PI theory given in [34], but seems to be implicit in Hougen's original work (cf. [3], equations (8) and (9)). If it is stipulated that $\det(C) = +1$ only (that is $C \in SO(3)$), then the appropriate transformation of rotational variables is

$$h : C \rightarrow (\det R(\rho)) C \tilde{R}(\rho) \quad (42 a')$$

and the permutation $S(h)$ becomes a permutation-inversion when $\det R(\rho) = -1$ (all transformations (42 a') are thus continuously connected with the identity). The introduction of permutation-inversions enables us to distinguish between the identity h_0 and a given PPT when the equivalent rotation associated with the PPT is improper. In this case, the PI group is an extension of \mathbb{H}^π by the inversion operation E^* , where inversion affects only the rotational coordinates [30, 31]. However, use of a consistent scheme for determining the behaviour of rotational wave functions under improper rotations, such as that proposed recently by Harter and Patterson ([36], see also [35, 37]) allows us to deal solely with the group of feasible permutations \mathbb{H}^π (the IRs of which define the 'soul' of the molecule [36]).

When all interactions between molecular degrees of freedom are taken into account, the rotorvibronic product wave function must be classified in \mathbb{H}^π . Allowed irreducible representations of \mathbb{H} are those that are totally symmetric under the PPTs, which are all equivalent to the identity permutation of nuclear labels. The Pauli principle is then simply implemented as a restriction on the IRs of \mathbb{H}^π spanned by the product of the rotorvibronic and nuclear spin functions.

Isodynamic operations are now defined. Consider once again the transformation

$$\mathcal{L}_h \cdot a^\alpha(\gamma)_i = \sum_{\beta} S(h)_{\alpha\beta} R(\rho)_{ij} a^\beta(\gamma)_j \quad (47 a)$$

$$= a^\alpha(\tau\gamma)_i \quad (47 b)$$

and

$$\mathcal{L}_h \cdot d_i^\alpha = \sum_{\beta} S(h)_{\alpha\beta} R(\rho)_{ij} d_j^\beta. \quad (48)$$

Generalizing the arguments of Louck and Galbraith to include the possibility of large-amplitude internal motion, it is found that the operations (47) and (48) leave the orientation of the Eckart-Sayvetz frame unchanged. Therefore, we can consider the molecule-fixed operations $\{\mathcal{L}_h; h \in \mathbb{H}\}$ independently of the associated transformations of rotational variables. We shall use the generic term *isodynamic operation* to describe transformations of this type.

The isodynamic operations form a group \mathbb{I}

$$\mathbb{I} \equiv \{\mathcal{L}_h; h \in \mathbb{H}\}, \quad (49)$$

which is isomorphic with \mathbb{H} , the symmetry group of the SRMM. To prove this, we note that the multiplication rule

$$\begin{aligned} (\mathcal{L}_{h_2} \cdot \mathcal{L}_{h_1}) \cdot d_i^\alpha &= \mathcal{L}_{h_2} \cdot \left(\sum_{\beta} S(h_1)_{\alpha\beta} R(\rho_1)_{ij} d_j^\beta \right) \\ &= \sum_{\beta'} S(h_2)_{\alpha\beta'} R(\rho_2)_{ij'} \left(\sum_{\beta} S(h_1)_{\beta'\beta} R(\rho_1)_{j'\beta} d_j^\beta \right) \\ &= \sum_{\beta} S(h_2 h_1)_{\alpha\beta} R(\rho_2 \rho_1)_{ij} d_j^\beta \\ &= \mathcal{L}_{h_2 h_1} \cdot d_i^\alpha \end{aligned} \quad (50)$$

ensures that there is at least a homomorphism from \mathbb{H} onto \mathbb{I} , which will be an isomorphism if \mathcal{L}_h and $\mathcal{L}_{h'}$ are distinct operations when $h \neq h'$. However, as the transformation \mathcal{L}_h involves both the rotation $R(\rho)$ and the permutation $S(h)$ associated with $h = (\rho, \tau)$; if two different elements $h \neq h' \in \mathbb{H}$ induce identical isodynamic operations they can differ only by a factor $(\rho_0, \tau'') \in \mathbb{H}$ that corresponds to the identity permutation of nuclei. As noted earlier, transformations of this type merely serve to define the boundaries of the parameter space and all symmetry elements $h \in \mathbb{H}$ must be specified *modulo* such operations. The transformations h and h' are therefore identical, contrary to the original assumption, and the group \mathbb{I} is indeed isomorphic with \mathbb{H}

$$\mathbb{H} \stackrel{\text{iso}}{=} \mathbb{I}. \quad (51)$$

The isodynamic operations that we have defined are symmetry operations of the vibration/internal-motion hamiltonian, where interactions with rotation are ignored (as we have suppressed the restorative rotations (42 a)). It is thus clear that they are a generalization of the conventional Wigner vibrational symmetry operations to NRMs [34, 47–49] (vibronic interactions can be included easily using the transformation of electronic variables (42 e)). Examination of the transformations (47, 48) in particular cases [37] shows that they are identical with the isodynamic operations introduced on intuitive grounds by Altmann.

It should also be noted that our isodynamic operations have the form of the perrotations of molecule-fixed variables introduced by Gilles and Philippot [29]; we therefore take these to be rigorously defined by equations (47) and (48), together with the equivalent rotations (42 a).

Finally, for a rigid molecule the parameter space Γ consists of a single point, and the SRMM becomes the *static molecular model*. The formalism that we have presented then reduces to that of Louck and Galbraith.

5. SUMMARY

In this paper we have outlined a unified approach to the symmetry of non-rigid molecules (NRMs), based explicitly upon the hypothetical semi-rigid molecular Model (SRMM). The significance of previous theories, namely the permutation-inversion, isodynamic and isometric theories, has been discussed in relation to our formalism. The symmetry group of the SRMM, which we call \mathbb{H} , is identified as the NRM symmetry group and the transformations of molecular variables induced by the elements of \mathbb{H} result in feasible permutations of nuclei. The extreme generality of the Longuet-Higgins permutation-inversion theory means that some of its applications fall outside the scope of our discussion; however, we have been concerned with a class of NRMs for which a constructive approach to the notion of feasibility is possible. The formulation of the NRM symmetry group as a semi-direct product has been examined, and a unified framework provided for the previous treatments of Altmann, Woodman and Günthard *et al.* Isodynamic operations have been defined as straightforward generalizations of the conventional Wigner vibrational symmetry operations and it is indicated that the isodynamic theory suppresses the equivalent rotations by viewing induced transformations of molecular variables from the Eckart frame. Our isodynamic operations have been identified with the perrotations of Gilles and Philippot.

The full implications of our analysis will be developed in a forthcoming paper. Subjects to be treated include : application of the formalism to specific molecules and more detailed comparison with previous approaches ; classification of SRMM symmetry groups and correlation with rigid-molecule geometries ; the development of selection rules etc. on the basis of semi-direct product structure.

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