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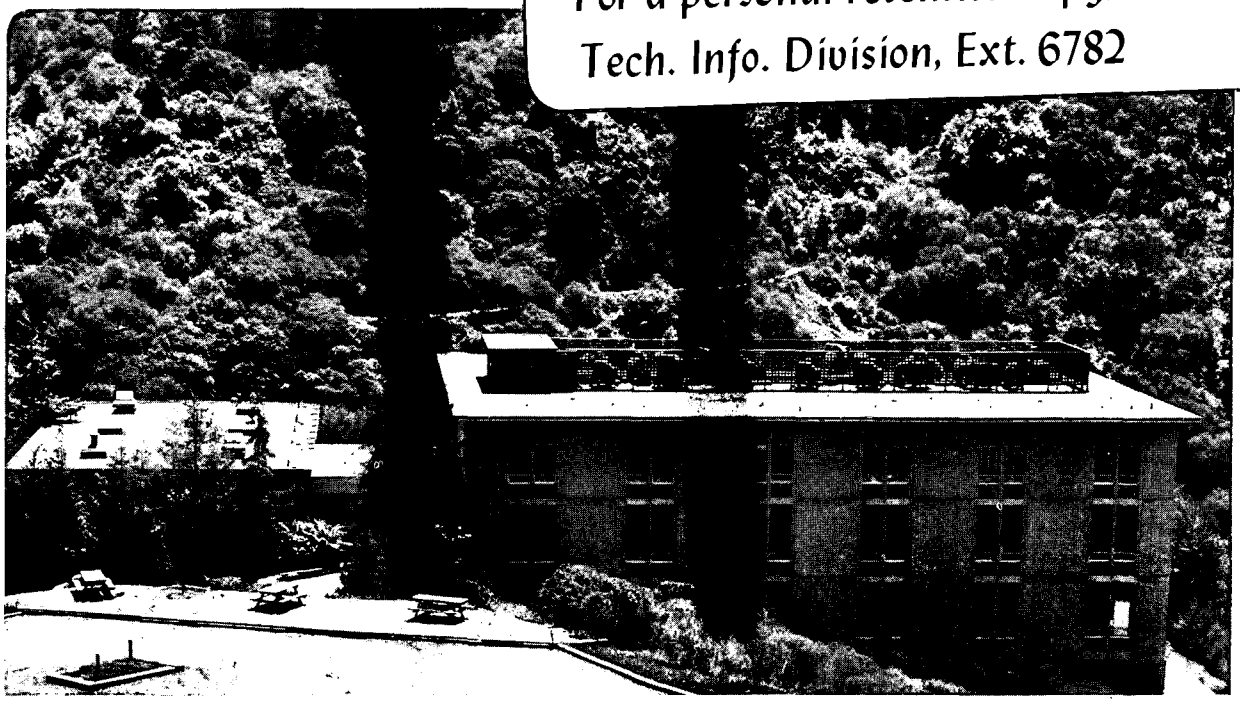

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Generating Functions for the Nuclear Spin Statistics of Non-rigid Molecules

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Abstract

Generating functions are developed for the nuclear spin species and nuclear spin statistical weights of non-rigid molecules as the trace of spin projection operators. These generating functions are obtained in terms of the GCCI's (Generalized Character Cycle Indices) of the PI groups of non-rigid molecules which are expressible as generalized wreath products. The GCCI's of generalized wreath products can be obtained in terms of the GCCI's of the composing groups. Thus the method developed here does not require the character table of the P group of non-rigid molecules. From these generating functions the nuclear spin statistical weights of the rovibronic levels and nuclear spin species of non-rigid molecules can be obtained easily. The method is illustrated with several examples of non-rigid molecules containing up to 3601989 nuclear spin functions. Application to molecular electric beam deflection studies of weakly bound complexes such as ammonia dimer is also discussed.

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1. Introduction

A molecule is said to be non-rigid if its electronic state has several potential minima separated by barriers. The symmetry groups of non-rigid molecules should contain permutations induced by not only rigid rotations but also torsions. Longuet-Higgins[1] formulated the symmetry groups of non-rigid molecules as Permutation-Inversion Groups. In order to obtain information on the intensity of the various allowed rovibronic transitions and the hyperfine structure of torsionally split rovibronic levels, it is necessary to obtain the nuclear spin statistical weights of the rovibronic levels and the nuclear spin species. The conventional method generally employed to obtain the nuclear spin statistical weights is to find the character of the nuclear spin functions under the non-rigid symmetry group and break it into irreducible components. The order of the PI (Permutation-Inversion) groups of non-rigid molecules increases exponentially with respect to the number of rotors. Further, the number of nuclear spin functions for a molecule containing b_1 nuclei with a_1 spin states, b_2 nuclei with a_2 spin states etc., is $a_1^{b_1} a_2^{b_2} \ldots\ldots$. Consequently, the conventional technique outlined above is quite difficult. Even for a simple non-rigid molecule such as triphenyl whose PI group is of order 32, there are 16,384 nuclear spin functions. Hence a systematic and general technique is warranted for the non-rigid molecules.

The statistical weights of the rotational levels of the rigid molecules in the rotational subgroup have been discussed by Placzek and Teller,[2] Wilson,[3-4] Schafer[5] and Mizushima.[6] Hougen[7] correlated these to the point groups of molecules. When the permutation inversion (PI) group of a molecule is not a direct product of the Permutation and Inversion groups, one has to use the PI group instead of the permutation group for obtaining the

nuclear spin statistical weights of the rovibronic levels. A review of several works related to the nuclear spin statistical weights can be found in the books by Herzberg[8] and more recently by Bunker.[9] Galbraith[10] obtained the nuclear spin statistical weights of molecules of the type XY_4, XY_5 and XY_6 belonging to T_d, D_{3h} and O_h symmetries, respectively, using the unitary group approach and Schur's theorem. Recently Weber[11-12] proposed a method for obtaining the characters of nuclear spin functions and hence the statistical weights of symmetry top molecules belonging to the D_{nd} and D_{nh} ($n \leqslant 6$) point groups. The present author[13] recently developed a general method for the nuclear spin species and nuclear spin statistical weights of any rigid molecule belonging to any point group.

In this paper we develop generating function techniques for the nuclear spin species and the nuclear spin statistical weights of non-rigid molecules. The method presented here for non-rigid molecules is different from the treatment of rigid molecules in that this method does not require the character tables of the symmetry groups of non-rigid molecules. This is a consequence of the fact that the symmetry groups of non-rigid molecules can be expressed as generalized wreath products.[14-15] Klemperer,[16] Read,[17] Robinson et al.[18] and Klein and Cowley[19] have used the wreath product groups for enumerating isomers and isomerization reactions of non-rigid molecules. Thus the generating functions for nuclear spin species of non-rigid molecules can be obtained in terms of the generalized character cycle indices of generalized wreath products which in turn are obtained by composing the generalized character cycle indices of the composing groups. Consequently, we need to know only the character tables of the symmetry group of the rigid frame and the torsional groups to obtain these generating functions provided the inversion operation is present in the PI group of

the molecule. If the inversion operation is not present in the PI group of the molecule then the generalized character cycle indices of the permutation group are obtained. Then one adds the inversion operations as additional terms in the generalized character cycle indices. In this case the characters which correspond to inversion operations are needed and they can be obtained using the well-known theorems on semi-direct product of two groups.[20] The generating functions developed here facilitate the computer generation of nuclear spin species and statistical weights as we will show in a future publication.

This paper uses the concepts outlined in an earlier paper[13] where a method is developed for the nuclear spin statistics of rigid molecules. The present author[21-22] introduced operator methods in combinatorial applications to chemical problems. Even though this paper itself contains preliminaries and definitions, a more detailed account of these can be found in the text books.[23-28] This paper uses a theorem of Williamson[29-30] with which GCCI's of generalized wreath products are obtained. Further we use another theorem of Williamson[33] for abelian characters, recently generalized by Merris[34] for nonabelian characters.

2. Generating Function Techniques

A. Definition and Preliminaries

Let G be a permutation group acting on a set Ω. Let the set Ω be partitioned into mutually disjoint sets $Y_1, Y_2, \ldots . Y_t$. Further assume that any $g \varepsilon G$ permutes elements in Ω such that it does not permute elements of different Y sets. Let $H_1, H_2, \ldots, H_t$ be t permutation groups. Then the generalized wreath product $G[H_1, H_2, \ldots, H_t]$ is defined as[15] the set $\{(g; \pi_1, \pi_2, \ldots, \pi_t)/g \varepsilon G, \pi_i : Y_i \rightarrow H_i\}$, with

$$(g;\ \pi_1,\ \pi_2,\ldots,\pi_t)(g';\ \pi_1',\ \pi_2',\ldots,\pi_t') = (gg';\ \pi_1\ \pi_{1g}',\ \pi_2\ \pi_{2g}',\ldots,\pi_t\ \pi_{tg}')$$

where

$$\pi_{ig}'(j) = \pi_i'(g^{-1}j),$$

with $j,\ g^{-1}\ j\ \varepsilon\ Y_i$. The symmetry group of any non-rigid molecule which exhibits internal rotation can be expressed as a generalized wreath product $G[H_1,\ H_2,\ldots,H_t]$ with G being the PI group of the rigid nuclear frame work and $H_1,\ H_2,\ldots,H_t$ being the permutation groups representing internal rotations in the molecule. To illustrate, consider the non-rigid ethane molecule. The rotational subgroup of this molecule is $C_2[C_3]$. C_2 acts on the rigid framework and C_3 is the group which corresponds to three-fold internal rotation. The set Ω contains the two carbon atoms. In this case there is just one Y-set Y_1 containing the two carbon atoms. Any element in $C_2[C_3]$ can be denoted by $(g;\pi)$ with $g\varepsilon C_2$ and $\pi:Y_1 \to H = C_3$. For example, one such element is shown below.

$$g = c_2\ \varepsilon\ C_2$$

$$\pi(1) = c_3\ \varepsilon\ C_3$$

$$\pi(2) = c_3^2\ \varepsilon\ C_3$$

Equivalently, rotate the three hydrogen atoms on carbon 1 by $2\pi/3$ in the anticlockwise direction, rotate the three hydrogen atoms on carbon 2 by $4\pi/3$ in the anticlockwise direction and then switch the carbon atoms, which in turn switches the hydrogen atoms. If one denotes the hydrogen atoms on carbon 1 by 1,2 and 3 and the hydrogen atoms on carbon 2 by 4, 5 and 6 then the result of this operation can be seen to be the permutation (163425).

The representation theory of generalized wreath product groups has been outlined in detail in reference 15. In this paper we shall review briefly the important concepts in this representation theory since this is needed for the present paper.

Let m_i denote the number of elements in Y_i. Let $H_i^{m_i}$ denote the m_i-fold direct product of m_i copies of the group H_i. Then $G[H_1, H_2,\ldots H_t]$ is isomorphic to $(H_1^{m_i} \times H_2^{m_2} \times\ldots\times H_t^{m_t})$. G' with

$$G' = \{(g;\ e_1,\ e_2,\ldots,e_t)/g\varepsilon G,\ e_i(j) = {}^1H_i\}$$

${}^1H_i$ is the identity of the group H_i. Since $H_1^{m_1} \times H_2^{m_2} \times\ldots\times H_t^{m_t}$ is a direct product, the irreducible representations of this group are given by $\Gamma = F_1^{m_1*} \# F_2^{m_2*} \#\ldots\# F_t^{m_t*}$, where $\#$ denotes the outer tensor product and $F_i^{m_i*}$ is the outer product $F_{i1} \# F_{i2} \#\ldots\# F_{in_i}$ with F_{ij} being an irreducible representation of the group H_i. For a definition of the outer tensor product, see reference 25 or Messaih.[31] The representation matrices of outer tensor products are given by Kronecker products. For a Γ of the above form, the inertia group which corresponds to this Γ is defined as

$$G_\Gamma[H_1, H_2,\ldots,H_t] = \{(g;\ \pi_1,\ \pi_2,\ldots\pi_t)/\Gamma^{(g;\pi_1,\pi_2,\ldots,\pi_t)} \sim \Gamma\}$$

with

$$\Gamma^{(g;\pi_1,\pi_2,\ldots\pi_t)} = \Gamma(g;\ \pi_1,\ \pi_2,\ldots,\pi_t)^{-1}(e;\ \pi_1',\ \pi_2',\ldots,\pi_t')(g;\ \pi_1,\ \pi_2,\ldots\pi_t).$$

Equivalently, the inertia group consists of those elements which leave Γ invariant. The group $G_\Gamma\ [H_1, H_2,\ldots,H_t]$, by definition, has the permutation representation $(H_1^{m_1} \times H_2^{m_2} \times\ldots\times H_t^{m_t})$. G_Γ'. The group G_Γ' is known as the inertia factor of the representation Γ. If the representation matrices of $F_1^{m_1*} \# F_2^{m_2*} \#\ldots\# F_t^{m_t*}$ $(e;\ \pi_1,\ \pi_2,\ldots,\pi_t)$ are known it is possible to find the

representation matrices of $F_1^{m_1^*} \# F_2^{m_2^*} \#\ldots\# F_t^{m_t^*}$ $(g; \pi_1, \pi_2,\ldots,\pi_t)$ by a suitable permutation of the columns of the former as described in reference 15. The tilde symbol is used to denote a suitable permutation of the columns of the representation matrices of $F_1^{m_1^*} \# F_2^{m_2^*} \#\ldots\# F_t^{m_t^*}$. If F' is an irreducible representation of G_{Γ}, the irreducible representations of $G[H_1, H_2,\ldots,H_t]$ are given by $(\#_i \widetilde{F_i^{m_i^*}} \otimes F') \uparrow G[H_1, H_2,\ldots,H_t]$, where the arrow stands for an induced representation. The concept of induced representation has been extensively reviewed by Altmann[20] and Coleman[32]. For several detailed illustrative examples, see reference 15.

Let D be the set of nuclei of the same kind and R be the set of possible spin states of the nuclei in the set D. For example, if one considers the non-rigid hydrazine molecule D is the set of 4 hydrogen nuclei and R is the set of two spin states. The nitrogen nuclei will be treated as a separate D set. In this paper we will consider each kind of nuclei as a separate D set and obtain the spin species of each kind of nuclei separately. Then the overall nuclear spin species is obtained as a direct product of different kinds of nuclear spin species. The symmetry group of the non-rigid hydrazine molecule is given by the wreath product $C_{2v}[C_2]$[14]. In this example, the PI group is a direct product of P and I groups and thus the nuclear spin statistics can be treated either in P or in PI groups. The group $C_{2v}[C_2]$ acts on the set D in that it permutes the nuclei in D. Consider the set F of maps from D to R. Each such map in F is a spin function. An example of such a map for hydrazine is shown below.

$$f_1(1) = \underset{\sim}{\beta}$$

$$f_1(2) = \underset{\sim}{\alpha}$$

$$f_1(3) = \underset{\sim}{\alpha}$$

$$f_1(4) = \underset{\sim}{\beta}.$$

The PI group which acts on D also acts on F by the recipe shown below. $\tau(f(i)) = f(\tau^{-1} i)$ for every $i \varepsilon D$, $\tau \varepsilon G[H_1, H_2, \ldots, H_t]$. To illustrate, consider τ as (1324) $\varepsilon C_{2v}[C_3]$. Since τ^{-1} = (1423), the action of τ on the map f_1 is shown below.

$$\tau f_1(1) = f_1(\tau^{-1} 1) = f_1(4) = \underset{\sim}{\beta}$$
$$\tau f_1(2) = f_1(\tau^{-1} 2) = f_1(3) = \underset{\sim}{\alpha}$$
$$\tau f_1(3) = f_1(\tau^{-1} 3) = f_1(1) = \underset{\sim}{\beta}$$
$$\tau f_1(4) = f_1(\tau^{-1} 4) = f_1(2) = \underset{\sim}{\alpha}.$$

Consequently, (1324) acts on $\underset{\sim}{\beta}\ \underset{\sim}{\alpha}\ \underset{\sim}{\alpha}\ \underset{\sim}{\beta}$ to produce the spin function $\underset{\sim}{\beta}\ \underset{\sim}{\alpha}\ \underset{\sim}{\beta}\ \underset{\sim}{\alpha}$.

In order to book-keep the number of various possible spin states in a spin function let us introduce the concept of weight of an element r in the set R. To each $r \varepsilon R$ assign a weight w(r), which is just a formal symbol used to differentiate the various spin states in the set R. For example, we may assign a weight α to the spin state $\underset{\sim}{\alpha}$, and a weight β to the spin state $\underset{\sim}{\beta}$ for the spin 1/2 problem. Then define the weight of any function $f \varepsilon F$ as the products of the weights of the images of f. In symbols, the weight of f, W(f) is given by

$$W(f) = \prod_{d \varepsilon D} w(f(d))$$

To illustrate, consider the map f_1 used as an illustrative example above. The weight of this map is $\alpha^2\beta^2$ since its image contains $2\underset{\sim}{\alpha}$'s and $2\underset{\sim}{\beta}$'s and the weight of $\underset{\sim}{\alpha}$ is α and that of $\underset{\sim}{\beta}$ is β.

B. Spin Projection Operators of PI Groups

Let us denote the PI group of a non-rigid molecule, $G[H_1, H_2, \ldots, H_t]$, by simply H. Let V be a vector space of dimension $|R|$, the number of elements in the set R. For example, V is a 3-dimensional

vector space for the spin 1 problem. Let V^d be the d-fold tensor product[31] of d copies of the vector space V. Symbolically,

$$V^d = \bigotimes_{d\epsilon D} V.$$

Let $e_1, e_2, \ldots, e_{|R|}$ be a basis for the vector space V. Then to each $f\epsilon F$, we can assign an e_f defined as follows.

$$e_f = e_{f(1)} \otimes e_{f(2)} \otimes \ldots\ldots \otimes e_{f(d)}$$

e_f is a tensor in the space V^d. The set of tensors $S = \{e_f : f\epsilon F\}$ forms a basis for V^d. For any $h\epsilon H$, define an operator P(h) by its action on e_f shown below.

$$P(h)e_f = e_{hf} = e_{f(h^{-1}1)} \otimes e_{f(h^{-1}2)} \otimes \ldots \otimes e_{f(h^{-1}d)}.$$

Thus P(h) is a permutation operator relative to the basis S, since it permutes the tensors in S by way of the action of g on f. Let $h \to \chi(h)$ be the character of an irreducible representation Γ in H. Williamson,[33] in his general theorem for any group considered χ to be the character of one dimensional representations. However, Merris[34] generalized this result to irreducible representations of any dimension. Define an operator T_H^χ as follows.

$$T_H^\chi = \frac{1}{|H|} \sum_{h\epsilon H} \chi(h)\ P(h)$$

T_H^χ is easily shown to be an idempotent operator, i.e., $(T_H^\chi)^2 = T_H^\chi$. Equivalently, T_H^χ is a projection operator in the space V^d.

The projection operator T_H^χ projects all spin functions from D to R which transform according to the irreducible representation whose character is χ. However, if one wishes to project spin functions according to their total spin quantum number then one needs to consider a subspace of V^d in

in which only functions having the same total spin quantum number are projected. For this purpose consider the subspace V_x^d of V^d spanned by all the tensors that have the same weight x. That is, V_x^d is spanned by the set $S_x = \{e_f : W(f) = x\}$. All the spin functions in the space S_x will have the same total spin quantum number. Let the restrictions of the operators T_H^χ and P(h) to the subspace V_x^d be $T_H^{\chi,x}$ and $P_x(h)$, respectively. $T_H^{\chi,x}$ is a spin projector of spin functions with the same weight x. For example, if we consider all spin functions of the type $\underset{\sim}{\alpha}\,\underset{\sim}{\beta}\,\underset{\sim}{\beta}\,\underset{\sim}{\beta}$, $\underset{\sim}{\beta}\,\underset{\sim}{\alpha}\,\underset{\sim}{\beta}\,\underset{\sim}{\beta}$ etc., which have the same weight $\alpha\beta^3 = x$, then $T_H^{\chi,x}$ projects only those spin functions that have $3\underset{\sim}{\beta}$'s and $1\underset{\sim}{\alpha}$. Define a weighted permutation operator $P_W(h)$ and a weighted projector $T_G^{\chi,W}$ as follows.

$$P_W(h) = \bigoplus_x xP_x(h)$$

$$T_H^{\chi,W} = \bigoplus_x xT_H^{\chi,x}$$

where $\oplus$ denotes a finite direct sum. A definition of finite direct sum can be found in Hamermesh[25]; x's vary over all the functions. In a matrix representation of $P_W(h)$, trace of $P_W(h)$, tr $P_W(h)$ is

$$\text{tr } P_W(h) = \sum_f^{(h)} W(f),$$

where the sum is taken over all $f \in F$ such that hf = f. To illustrate, if we consider the protons of hydrazine molecule with $R = \{\underset{\sim}{\alpha}, \underset{\sim}{\beta}\}$ and h = (12) then

$$\text{tr } P_W(h) = \alpha^4 + 2\alpha^3\beta + 2\alpha^2\beta^2 + 2\alpha\beta^3 + \beta^4.$$

(This is because by the action of h=(12), $\underset{\sim}{\alpha}\,\underset{\sim}{\alpha}\,\underset{\sim}{\alpha}\,\underset{\sim}{\alpha}$, $\underset{\sim}{\alpha}\,\underset{\sim}{\alpha}\,\underset{\sim}{\beta}\,\underset{\sim}{\alpha}$, $\underset{\sim}{\alpha}\,\underset{\sim}{\alpha}\,\underset{\sim}{\alpha}\,\underset{\sim}{\beta}$, $\underset{\sim}{\alpha}\,\underset{\sim}{\alpha}\,\underset{\sim}{\beta}\,\underset{\sim}{\beta}$, $\underset{\sim}{\beta}\,\underset{\sim}{\beta}\,\underset{\sim}{\alpha}\,\underset{\sim}{\alpha}$, $\underset{\sim}{\beta}\,\underset{\sim}{\beta}\,\underset{\sim}{\alpha}\,\underset{\sim}{\beta}$, $\underset{\sim}{\beta}\,\underset{\sim}{\beta}\,\underset{\sim}{\beta}\,\underset{\sim}{\alpha}$ and $\underset{\sim}{\beta}\,\underset{\sim}{\beta}\,\underset{\sim}{\beta}\,\underset{\sim}{\beta}$ are left invariant. Hence, tr $P_W(h)$ is the sum of the weights of the functions that are invariant

under the action of h). In this formulation Williamson[33] and later Merris[34] proved the following theorem.

Theorem 1: $$T_H^{\chi,W} = \frac{1}{|H|} \sum_{h\epsilon H} \chi(h)\ P_W(h).$$

Thus, $$\text{tr}\ T_H^{\chi,W} = \frac{1}{|H|} \sum_{h\epsilon H} \chi(h)\ \text{tr}\ P_W(h) = \frac{1}{|H|} \sum_{h\epsilon H} \chi(h) \sum_{f}^{(h)} W(f).$$

The implication of this theorem is that the weighted spin projection operator is the same as the projection operator with permutation operator replaced by the corresponding weighted permutation operator. Trace of the weighted spin projector is the generator of the irreducible representations contained in the set of spin functions and the nuclear spin species.

C. Generalized Character Cycle Indices (GCCI)

In this section we introduce group structures called generalized character cycle indices, hereafter abbreviated as GCCI, which are potentially useful in expressing Williamson's theorem outlined in Sec 2B in a form suitable for applications. We also obtain the GCCI's of generalized wreath products $G[H_1, H_2,\ldots,H_t)$, which are generators of nuclear spin species and nuclear spin statistical weights in terms of GCCI's of G, H_1, H_2,.... and H_t. Consequently, it is not necessary to know the character table of the PI groups of non-rigid molecules in order to obtain the nuclear spin species.

Define the generalized character cycle index (GCCI) of a group H, corresponding to the character χ of an irreducible representation Γ of H as

$$P_H^{\chi} = \frac{1}{|H|} \sum_{h\epsilon H} \chi(h)\ x_1^{b_1} x_2^{b_2} \ldots x_n^{b_n}$$

where $x_1^{b_1} x_2^{b_2} \ldots x_n^{b_n}$ is a representation of a typical permutation $h\epsilon H$, which has b_1 cycles of length 1, b_2 cycles of length 2, etc.

Equivalently, the cycle type of $h \in H$ is $(b_1, b_2, \ldots, b_n)$. For example, the permutation (12)(34) of the PI group of hydrazine has the cycle representation x_2^2 since it has 2 cycles of length 2. Similarly the permutation (1324) of the same group has the cycle representation x_4^1 (1 cycle of length 4), etc. The GCCI which corresponds to character χ is just the sum of the product of cycle representations of elements in H and the corresponding character. For example, the character of the B_1^+ representation of the P group of hydrazine and the corresponding GCCI are shown below.

	(1)(2)(3)(4)	(12)	(12)(34)	(14)(23)	(1324)
	1	2	1	2	2
B_1^+	1	1	1	-1	-1

$$P_{C_2[C_2]}^{B_1^+} = \frac{1}{8}\left(x_1^4 + 2x_1^2x_2 - x_2^2 - 2x_4\right)$$

The use of GCCI as generators of nuclear spin species is discussed in Section 2D. In this section we proceed to obtain the GCCI's of generalized wreath product $G[H_1, H_2, \ldots, H_t]$ in terms of GCCI's of G, H_1, H_2,... and H_t.

We need the concept of inertia group and inertia factor that we introduced in the earlier section for obtaining the GCCI's of $G[H_1, H_2, \ldots, H_t]$ in terms of the GCCI's of G, H_1, H_2,..., H_t. Let the inertia group of a representation $F^* = F_1^{m_1*} \# F_2^{m_2*} \# \ldots \# F_t^{m_t*}$ be $G_{F^*}[H_1, H_2, \ldots, H_t]$ and let G'_{F^*} be the corresponding inertia factor. By definition, GCCI of G'_{F^*} corresponding to the character χ, is

$$P^{\chi}_{G'_{F*}} = \frac{1}{|G'_{F*}|} \sum_{g \in G'_{F*}} \prod_i \prod_j \chi(g)\ \chi_{ij}^{C_{ij}(g)},$$

where $C_{ij}(g)$ is the number of j-cycles of $g \in G_{F*}$ in the set Y_i. The GCCI of G'_{F*} takes the above form because g permutes elements only within a set Y_i as one can recall from Section 2B. Hence $x_1^{b_1} x_2^{b_2} \ldots x_t^{b_t}$ can be recast in a convenient form shown above. Recall that $F_i^{m_i*}$ is the m_i-fold outer product of the same irreducible representation F_i. Let λ_k be the character of F_i. Define the GCCI, $Z_i^{\lambda_k}$ to be

$$Z_i^{\lambda_k} = \frac{1}{|H_i|} \sum_{h \in H_i} \lambda_k(h)\ x_1^{b_1} x_2^{b_2} \ldots$$

where $x_1^{b_1} x_2^{b_2} \ldots$ has the same meaning as in the definition of any GCCI. Define $Z_{ij}^{\lambda_k}$ by the following substitution.

$$Z_{ij}^{\lambda_k} = Z_i^{\lambda_k}(x_\ell \rightarrow x_{\ell j})$$

where the subscripts on the x variables are the products. If we denote an irreducible representation of $G[H_1, H_2, \ldots, H_t]$ by $\Gamma = (\#_i F_i^{m_i*} \times F')\uparrow G[H_1, H_2, \ldots, H_t]$ then a GCCI of $G[H_1, H_2, \ldots, H_t]$ which corresponds to the character of Γ, denoted by P^{Γ} $(G[H_1, H_2, \ldots, H_t]$ is given by

$$P^{\Gamma}(G[H_1, H_2, \ldots, H_t]) = P^{\chi}_{G'_{F*}}(x_{ij} \rightarrow Z_{ij}^{\lambda_k})$$

if this j-cycle in Y_i is constituted by j copies of the representation whose character is λ_k. For all the irreducible representations, this result can be proved by a method similar to the one used by Williamson[29-30] for wreath products. In particular, when Γ is an induced representation this result also follows from a lemma of Foulkes[35] which relates the GCCI of an induced representation to the GCCI of the inducing representation. The

substitution outlined above is reminiscent of plethysms of S-functions outlined in Read's paper[36].

A special case of this substitution for the identity representation was used and illustrated with examples by the present author[14,37-39] in isomer enumeration and NMR.

Let us now illustrate the above result with hydrazine. Since the PI group of the non-rigid hydrazine molecule is a direct product of the P and I groups, the nuclear spin statistics can be described in either groups. The P group of hydrazine is given by $S_2[S_2]$, whose structure was studied in great details by the present author.[15] (cf. Table II of ref. 15). The irreducible representations of $S_2[S_2]$ are $\Gamma_1 = [2] \# [2] \otimes [2]'$, $\Gamma_2 = [2] \# [2] \otimes [1^2]'$, $\Gamma_3 = [2] \# [1^2] \uparrow S_2[S_2]$, $\Gamma_4 = [1^2] \# [1^2]' \otimes [2]'$ and $\Gamma_5 = [1^2] \#]1^2] \otimes [1^2]'$, where [2] is the identity representation and $[1^2]$ is the alternating representation of S_2. The inertia factors which correspond to $[2] \# [2]$, $[2] \# [1^2]$ and $[1^2] \# [1^2]$ are S_2', S_1' and S_2', where S_1' is the group containing only the identity. The P^{χ}_{G',F^*} for various χ and G'_{F^*} are shown below.

$$P^{[2]'}_{S_2'} = \frac{1}{2}(x_{11}^2 + x_{12})$$

$$P^{[1^2]'}_{S_2'} = \frac{1}{2}(x_{11}^2 - x_{12})$$

$$P^{[1]'}_{S_1'} = x_{11}^2$$

The various $Z_i^{\lambda_k}$'s and $Z_{ij}^{\lambda_k}$'s are shown below.

$$Z_1^{[2]} = \frac{1}{2}(x_1^2 + x_2); \quad Z_1^{[1^2]} = \frac{1}{2}(x_1^2 - x_2)$$

$$Z_{11}^{[2]} = Z_1^{[2]};\ Z_{12}^{[2]} = \frac{1}{2}\,(x_2^2 + x_4)$$

$$Z_{11}^{[1^2]} = Z_1^{[1^2]};\ Z_{12}^{[1^2]} = \frac{1}{2}\,(x_2^2 - x_4).$$

Hence,

$$P^{\Gamma_1}(S_2[S_2]) = P_{S_2'}^{[2]'}(x_{ij} \to Z_{ij}^{[2]}) = \frac{1}{2}\,[\{\tfrac{1}{2}(x_1^2 + x_2)\}^2 + \frac{1}{2}\,(x_2^2 + x_4)]$$

$$= \frac{1}{8}\,(x_1^4 + 2x_1^2x_2 + 3x_2^2 + 2x_4).$$

This is what one directly also obtains using the character table of the P group of hydrazine. However, the above expression was obtained with this method without the knowledge of the character table of the P group of hydrazine. Similarly,

$$P^{\Gamma_2}(S_2[S_2]) = P_{S_2'}^{[1^2]'}(x_{ij} \to Z_{ij}^{[2]})$$

$$= \frac{1}{2}\,[\{\frac{1}{2}\,(x_1^2 + x_2)\}^2 - \frac{1}{2}\,(x_2^2 + x_4)]$$

$$= \frac{1}{8}\,(x_1^4 + 2x_1^2x_2 - x_2^2 - 2x_4).$$

Since the inertia factor of the third representation is the group containing only the identity we have to replace one x_{11} by $Z_{11}^{[2]}$ and for the other by $Z_{11}^{[1^2]}$. Thus

$$P^{\Gamma_3}(S_2[S_2]) = \frac{1}{2}\,(x_1^2 + x_2) \cdot \frac{1}{2}\,(x_1^2 - x_2) = \frac{1}{8}\,(2x_1^4 - 2x_2^2).$$

The last two GCCI's are obtained with the substitution similar to that in Γ_1 and Γ_2. They are shown below.

$$P^{\Gamma_4}(S_2[S_2]) = P_{S_2'}^{[2]'}(x_{ij} \to Z_{ij}^{[1^2]}) = \frac{1}{2}\,[\{\tfrac{1}{2}(x_1^2 - x_2)\}^2 + \frac{1}{2}\,(x_2^2 - x_4)]$$

$$= \frac{1}{8}\,(x_1^4 - 2x_1^2x_2 + 3x_2^2 - 2x_4)$$

$$P^{\Gamma_5}(S_2[S_2]) = P^{[1^2]'}_{S_2'}(x_{ij} \to Z^{[1^2]}_{ij}) = \frac{1}{2}\left[\{\frac{1}{2}(x_1^2 - x_2)\}^2 - \frac{1}{2}(x_2^2 - x_4)\right]$$

$$= \frac{1}{8}(x_1^4 - 2x_1^2x_2 - x_2^2 + 2x_4).$$

D. Generators of Nuclear Spin Species

The GCCI's introduced in Sec 2C are the generators of nuclear spin species. Theorem 1 introduced in Sec 2B can be expressed in a convenient form in terms of the GCCI's. With a little algebric manipulation, similar to the one in reference 24 it can be shown that Theorem 1 takes the following form.

$$\text{tr } T_h^{\chi,W} = P_H^{\chi}(x_k \to \sum_{r\epsilon R} (w(r))^k).$$

The coefficient of a typical term $w_1^{b_1}w_2^{b_2}\ldots$ in tr $T_H^{\chi,W}$ gives the frequency of occurrence of the irreducible representation Γ whose character is χ in the set of spin functions with the same weight $w_1^{b_1}w_2^{b_2}\ldots$. For example if we set χ to the character of B_1^+ representation of the PI group of hydrazine, then the coefficient of $\alpha^2\beta^2$ in the polynomial obtained by replacing every x_k by $\alpha^k + \beta^k$ in the corresponding GCCI gives the number of B_1^+ representation in the set of spin functions that have 2α's and 2β's.

We now illustrate the above procedure with hydrazine. All the GCCI's of the PI group of hydrazine were obtained in Sec 2C. Let us identify the irreducible representations Γ_1, Γ_2, Γ_3, Γ_4 and Γ_5 by the species A_1, B_1, E, B_2 and A_2. Then

$$G.F.^{A_1} = P^{\Gamma_1}_{S_2[S_2]}(x_k \to \alpha^k + \beta^k) = \frac{1}{8}\left[(\alpha+\beta)^4 + 2(\alpha+\beta)^2(\alpha^2+\beta^2) + 3(\alpha^2+\beta^2)^2\right.$$

$$\left. + 2(\alpha^4+\beta^4)\right] = \alpha^4 + \alpha^3\beta + 2\alpha^2\beta^2 + \alpha\beta^3 + \beta^4.$$

Thus, spin function containing all $\underset{\sim}{\alpha}$'s has one A_1 representation, spin functions containing $3\underset{\sim}{\alpha}$'s and 1β have one A_1 representation, spin functions

containing 2α's and 2β's contain $2A_1$ representations, and so on. The coefficient of a typical term $\alpha^{a_1}\beta^{b_1}$ in this generating function corresponds to the total spin quantum number $m_z = (a_1-b_1)/2$ since α represents $m_z = 1/2$ and β represents $m_z = -1/2$. Consequently, if one arranges the spin species according to their m_z values as given by the above generating function, they separate into spin multiplets with m_z varying from -S to S. For example, from G.F.^{A_1}, we obtain the nuclear spin species which correspond to A_1 representation as $^5A_1$ and $^1A_1$. The G.F.'s corresponding to the other irreducible representations obtained in a similar manner are shown below.

$$\text{G.F.}^{B_1} = \frac{1}{8}\left[(\alpha+\beta)^4 + 2(\alpha+\beta)^2(\alpha^2+\beta^2) - (\alpha^2+\beta^2)^2 - 2(\alpha^4+\beta^4)\right] = \alpha^3\beta + \alpha^2\beta^2 + \alpha\beta^3$$

$$\text{G.F.}^{E} = \frac{1}{8}\left[2(\alpha+\beta)^4 - 2(\alpha^2+\beta^2)^2\right] = \alpha^3\beta + \alpha^2\beta^2 + \alpha\beta^3$$

$$\text{G.F.}^{B_2} = \frac{1}{8}\left[(\alpha+\beta)^4 - 2(\alpha+\beta)^2(\alpha^2+\beta^2) + 3(\alpha^2+\beta^2)^2 - 2(\alpha^4+\beta^4)\right] = \alpha^2\beta^2$$

$$\text{G.F.}^{A_2} = \frac{1}{8}\left[(\alpha+\beta)^4 - 2(\alpha+\beta)^2(\alpha^2+\beta^2) - (\alpha^2+\beta^2)^2 + 2(\alpha^4+\beta^4)\right] = 0.$$

Thus, we obtain the proton nuclear spin species of the non-rigid hydrazine molecule to be $^5A_1$, $^1A_1$, $^3B_1$, ^3E, and $^1B_2$. If one includes the inversion operations these spin species carry the additional + label. These species are in agreement with the results of Longuet-Higgins[1] for hydrazine. However, these spin species were obtained without enumerating all the nuclear spin functions and obtaining the character of each block of spin functions with the same m_z value and then breaking each block into irreducible representations. With our method all that we needed was the set of GCCI's of PI group from which generating functions and the nuclear spin functions were obtained immediately. Even the character table of the PI group of hydrazine was not needed since GCCI's were obtained without knowing the character table

of the PI group of hydrazine. However, to obtain GCCI's, we need the character tables of the P group of the rigid nuclear structure and the torsional groups.

Let us now give a non-trivial example. Consider the molecule Boron trimethyl $B(CH_3)_3$. This molecule was used by Longuet-Higgins[1] to illustrate how rapidly the order of the PI group of non-rigid molecules increases. He did not obtain the nuclear spin species or the nuclear spin statistical weights of the rovibronic levels of this molecule. We will now illustrate the power and use of the above procedure with this molecule. The PI group of this molecule is the wreath product $D_{3h}[C_3]$ or $D_3[C_3]\Lambda I$, where the symbol Λ has been used to denote a semi-direct product. This is an example of a molecule whose PI group is not a direct product of P and I groups. We will first obtain the GCCI's of the P group ($D_3[C_3]$) of this molecule and then add the additional terms arising from the I group. The GCCI's of the group D_3 and C_3 are shown in tables 1 and 2, respectively. The irreducible representation of $D_3[C_3]$, their GCCI's obtained using the GCCI's of D_3 and C_3 are shown in Table 3. When the inversion operations are included, the irreducible representations A_1, A_2, E_1 and I_7 double; the other GCCI's remain the same. The GCCI's of the PI group of $B(CH_3)_3$ are shown in Table 4.

We will now obtain the nuclear spin species of $^{11}B(^{12}CD_3)_3$ using these GCCI's, where D denotes the deuterium isotope of hydrogen. The total number of nuclear spin functions in this molecule is $4.3^9 = 78,732$. Let us first find the deuterium spin species and then multiply the Boron spin species by a Clebsch-Gordan series. Let us denote the three nuclear spin states of D by $\underset{\sim}{\lambda}$, $\underset{\sim}{\mu}$ and $\underset{\sim}{\nu}$. Let the weights associated with these 3 states be λ, μ and ν, which stand for spin states with nuclear spin = -1, 0 and 1, respectively. Then if one replaces every x_k in the GCCI which corresponds

to the irreducible representation Γ by $\lambda^k + \mu^k + \nu^k$, one obtains the generating function for nuclear spin species, corresponding to Γ. To illustrate, given below is the expression obtained by replacing every χ_k in the GCCI of the irreducible representation I_3 of the PI group of $B(CD_3)_3$ by $\lambda^k + \mu^k + \nu^k$.

$$\text{G.F.}^{I_3} = \text{GCCI}^{I_3}(x_k \to \lambda^k + \mu^k + \nu^k)$$

$$= \frac{1}{324}\,[6(\lambda+\mu+\nu)^9 - 24(\lambda^3+\mu^3+\nu^3)^3 + 18(\lambda+\mu+\nu)^6$$

$$\times\ (\lambda^3+\mu^3+\nu^3) + 18(\lambda+\mu+\nu)^3\ (\lambda^2+\mu^2+\nu^2)^3$$

$$+ 36(\lambda+\mu+\nu)^3(\lambda^6+\mu^6+\nu^6) - 18(\lambda^2+\mu^2+\nu^2)^3\ (\lambda^3+\mu^3+\nu^3)$$

$$- 36(\lambda^3+\mu^3+\nu^3)(\lambda^6+\mu^6+\nu^6)]$$

$$= \lambda^8\mu+2\lambda^7\mu^2+3\lambda^6\mu^3+4\lambda^5\mu^4+4\lambda^4\mu^5+3\lambda^3\mu^6+2\lambda^2\mu^7+\lambda\mu^8+\lambda^8\nu+4\lambda^7\mu\nu+9\lambda^6\mu^2\nu$$

$$+ 14\lambda^5\mu^3\nu+16\lambda^4\mu^4\nu+14\lambda^3\mu^5\nu+9\lambda^2\mu^6\nu+4\lambda\mu^7\nu+\mu^8\nu+2\lambda^7\nu^2+9\lambda^6\mu\nu^2+20\lambda^5\mu^2\nu^2$$

$$+ 29\lambda^4\mu^3\nu^2+29\lambda^3\mu^4\nu^2+20\lambda^2\mu^5\nu^2+9\lambda\mu^6\nu^2+2\mu^7\nu^2+3\lambda^6\nu^3 14\lambda^5\mu\nu^3+29\lambda^4\mu^2\nu^3$$

$$+ 36\lambda^3\mu^3\nu^3+29\lambda^2\mu^4\nu^3+14\lambda\mu^5\nu^3+3\mu^6\nu^3+4\lambda^5\nu^4+16\lambda^4\mu\nu^4+29\lambda^3\mu^2\nu^4+29\lambda^2\mu^3\nu^4$$

$$+ 16\lambda\mu^4\nu^4+4\mu^5\nu^4+4\lambda^4\nu^5+14\lambda^3\mu\nu^5+20\lambda^2\mu^2\nu^5+14\lambda\mu^3\nu^5+4\mu^4\nu^5+3\lambda^3\nu^6+9\lambda^2\mu\nu^6$$

$$+ 9\lambda\mu^2\nu^6+3\mu^3\nu^6+2\lambda^2\nu^7+4\lambda\mu\nu^7+2\mu^2\nu^7+\lambda\nu^8+\mu\nu^8.$$

The coefficient of a typical term $\lambda^{a_1}\mu^{a_2}\nu^{a_3}$ in the G.F.$^{\Gamma}$ gives the number of irreducible representations Γ in the set of nuclear spin functions containing $a_1\underset{\sim}{\lambda}$ states, $a_2\underset{\sim}{\mu}$ states and $a_3\underset{\sim}{\nu}$ states. Thus, this coefficient corresponds to the number of spin functions transforming as Γ with the total spin quantum number equal to $a_3 - a_1$. When we group the species Γ as generated by G.F.$^{\Gamma}$, they separate into multiplets with their total spin

varying from -S to S. For example, when we group the coefficients in the generating function corresponding I_3 in accordance to the total spin quantum number, we obtain $^{17}I_3(1)$, $^{15}I_3(2)$, $^{13}I_3(4)$, $^{11}I_3(8)$, $^{9}I_3(12)$, $^{7}I_3(15)$, $^{5}I_3(17)$, $^{3}I_3(13)$ and $^{1}I_3(4)$ as the nuclear spin species. The numbers in the parentheses indicate the frequency of occurrence of the corresponding spin species. In this manner all the nuclear spin species can just be read-off from the generating functions. Generating functions thus obtained for the D species of $B(CD_3)_3$ are shown in Table 5. In that table the various terms appearing in the generating functions are shown in the first row. The coefficients in the generating functions for all the irreducible representations are shown in the subsequent rows. For example, from this table one infers that the coefficient of $\lambda^4\mu^4\nu$ which corresponds to the A_1 species is 6. The nuclear spin species thus obtained from these generating functions are shown in Table 6. Since the nuclear spin of ^{11}B is 3/2 and this nucleus is the center of the molecule, the nuclear spin species of ^{11}B is $^{4}A_1$. The overall nuclear spin species of this molecule is the direct product of the boron and the deuterium spin species. A typical direct product of the species $D_i^{s_1}$ and $D_j^{s_2}$, $D_i^{s_1} \otimes D_j^{s_2}$, decomposes into a Clebsch-Gordan series[25]

$$D_i^{s_1} \otimes D_j^{s_2} = \sum_k \sum_{S=|s_1-s_2|}^{s_1+s_2} D_k^S$$

where

$$D_i \otimes D_j = \sum_k D_k,$$

the direct sum of irreducible representations D_k's contained in $D_i \otimes D_j$.

To illustrate the 9 $^7E_1$ deuterium species and the $^4A_1$ boron species give

$$^7E_1 \otimes {}^4A_1 = {}^{10}E_1 + {}^8E_1 + {}^6E_1 + {}^4E_1.$$

Thus from this combination alone we obtain the overall species to be $^{10}E_1(9)$, $^8E_1(9)$, $^6E_1(9)$ and $^4E_1(9)$. In Table 7 we show the overall nuclear spin species of $B(CD_3)_3$. The process can be repeated to obtain the nuclear spin species of the molecule $B^{11}(C^{13}D_3)_3$, for which one also needs the carbon species. The carbon species can be easily obtained by obtaining the GCCI's corresponding to the carbon nuclei.

If one denotes the nuclear spin states of ^{13}C by $\underset{\sim}{\alpha}$ and $\underset{\sim}{\beta}$ with the weights α and β, and replace every x_k by $\alpha^k + \beta^k$ in the corresponding GCCI's, one obtains the G.F.'s of carbon species. It can be seen that the resulting species are $^4A_1$ and $^2E_1$. One then takes the direct product of carbon, boron and deuterium species to obtain the overall species. For the sake of comparison in Table 8 we give the proton spin species of $B(CH_3)_3$ obtained using the GCCI's in Table 4. In this case every x_k in the GCCI's is replaced by $\alpha^k + \beta^k$ where α and β are the weights associated with the two spin state $\underset{\sim}{\alpha}$ and $\underset{\sim}{\beta}$ of protons.

To illustrate the elegance of this procedure we consider yet another non-rigid molecule, namely, triphenyl which contains 14 protons and 18 carbon atoms. This molecule was considered as an illustrative example in reference 15, where the character table of its symmetry group was also obtained. For details of the character table of its PI group the readers are referred to reference 15. Table 9 shows the GCCI's corresponding to hydrogen nuclei present in this molecule. Note that the GCCI's which

correspond to $A_1^{"+}$ and $B_1^{"+}$, and, $A_2^{"+}$ and $B_2^{"+}$ are identical. Thus it is enough if one generates the nuclear spin species of one of the two irreducible representations. In Table 10 we have the deuterium species of the non-rigid triphenyl molecule, $C_{18}D_{14}$.

3. The Statistical Weights of Rovibronic Levels from Generating Functions

The nuclear spin statistical weights of the rovibronic levels of non-rigid molecules can also be obtained using the GCCI's. If one is interested in the statistical weights of rovibronic levels instead of the possible nuclear spin species, it is possible to obtain them directly from GCCI's. Evidently, the number of times an irreducible representation Γ occurs in Γ^{spin}, the reducible representation of all nuclear spin functions, is given by the sum of the coefficients of all the terms in the corresponding nuclear spin generating function. For example, the number of times the A_1 representation appears in the set of deuterium spin functions of $B(CD_3)_3$ is the sum of the coefficients in the row corresponding to A_1 in Table 5 which is 230. The sum of the coefficients in any generating function is obtained by setting all the weights to unity in the generating function. This is tantamount to replacing every x_k in P_H^{χ} by $\sum_{r\varepsilon R} (w(r))^k = |R|$, since $w(r) = 1$ for all $r\varepsilon R$. Thus the number of times the irreducible representation Γ whose character is χ appears in Γ^{spin} is given by

$$\text{Corollary 1: } N(\Gamma) = P_H^{\chi}(\chi_k \rightarrow |R|).$$

Let us now illustrate corollary 1 with several examples. We start with $B(CD_3)_3$. The GCCI's of this molecule are in Table 4. The number of A_1 representations in Γ_D^{spin} is obtained by replacing every x_k in $P_G^{A_1}$ by 3 since the number of possible nuclear spin states of D is 3. Consequently,

$$N(A_1) = \frac{1}{324}\,(3^9 + 26.3^3 + 6.3^6.3 + 12.3^3.3^2 + 36.3 + 36.3^3.3^3 + 18.3^3.3$$
$$+ 18.3^3.3 + 90.3.3. + 27.3.3^4 + 54.3.3.3) = 230$$

Similary,

$$N(I_1) = \frac{1}{324}\,(6.3^9 + 12.3^3 - 18.3^3.3^2 + 18.3^3.3^3 - 18.3^3.3 + 36.3^3.3$$
$$- 36.3.3) = 396.$$

In this manner when one computes $N(\Gamma)$ for all Γ's of the PI group of $B(CD_3)_3$, one obtains

$$\Gamma_D^{spin} = 230\ A_1 + 45A_2 + 56A_3 + 120A_4 + 340E_1 + 100E_2 + 120E_3 + 56E_4 + 168G$$
$$+ 396I_1 + 308I_2 + 528I_3 + 440I_4 + 288I_5 + 224I_6 + 388I_7 + 316I_8$$

We arrive at the same result by adding the multiplicity times the frequency of occurrence of deuterium spin species in Table 6. Since ^{11}B nuclear spin functions span the representation $4A_1$, the overall spin species Γ^{spin}, is given by

$$\Gamma^{spin} = \Gamma_D^{spin} \otimes \Gamma_B^{spin} = 920A_1 + 180A_2 + 224A_3 + 480A_4 + 1360E_1 + 400E_2$$
$$+ 480E_3 + 224E_4 + 672G + 1584I_1 + 1232I_2 + 2112I_3 + 1760I_4$$
$$+ 1152I_5 + 896I_6 + 1552I_7 + 1264I_8.$$

To obtain the nuclear spin statistical weight of a rovibronic level transforming as Γ^{rve} representation, one stipulates that $\Gamma^{rve} \otimes \Gamma^{spin}$ should contain Γ^{int}, where Γ^{int} is the symmetry species of the total internal wavefunction. By Pauli exclusion principle Γ^{int} must be antisymmetric with respect to <u>permutations alone</u> for Fermions. For Bosons Γ^{int} must be symmetric with respect to permutations alone. Note that there is no restriction placed on inversion operations. Since deuterium nuclei are Bosons Γ^{int} can be A_1 or A_3. Γ^{spin} for $^{11}B(^{12}CD_3)_3$ has already been found. Thus, for example, the nuclear spin statistical

weight of the rovibronic level A_2 is 660 since $180A_2$ and $480A_4$ of Γ^{spin} contain Γ^{int} in the direct product $\Gamma^{spin} \otimes \Gamma^{rve}$. This way one obtains the nuclear spin statistical weights of all the rovibronic levels and they are shown below in parenthesis.

$A_1(1144)$, $A_2(660)$, $A_3(1144)$, $A_4(660)$, $E_1(2720)$, $E_2(800)$, $E_3(960)$, $E_4(448)$, $G(1344)$, $I_1(3168)$, $I_2(2464)$, $I_3 4224)$, $I_4(3520)$, $I_5(2304)$, $I_6(1792)$, $I_7(3104)$, $I_8(2528)$.

For ^{12}C-triphenyl, $^{12}C_{18}D_{14}$, Γ^{spin}, obtained using Corollary 1 is shown below.

$$\Gamma_D^{spin} = 410670\ A_1'^{+} + 409455\ B_1'^{+} + 261954\ A_2'^{+} + 262926\ B_2'^{+} + 328050\ A_1''^{+} + 328050\ B_1''^{+} + 209952\ A_2''^{+} + 209952\ B_2''^{+} + 656100\ E'^{+} + 524880\ E''^{+}.$$

Since D nuclei are Bosons Γ^{int} can be $A_1'^{+}$ or $A_1'^{-}$. Since the PI group of this molecule is a direct product of P and I groups, the statistical weights are unaffected by $\pm$ labels. The statistical weights thus obtained are shown below.

$A_1'^{\pm}(410670)$, $B_1'^{\pm}(409455)$, $A_2'^{\pm}(261954)$, $B_2'^{\pm}(262926)$, $A_1''^{\pm}(328050)$, $B_1''^{\pm}(328050)$, $A_2''^{\pm}(209952)$, $B_2''^{\pm}(209952)$, $E'^{\pm}(656100)$, $E''^{\pm}(524880)$.

4. Application to Molecular Beam Experiments

Muenter and co-workers[40] have been carrying out molecular electric beam deflection and electric resonance experiments to derive structural information of weakly bound complexes such as $(H_2O)_2$, HF·HCl, HF·ClF, ammonia polymers, etc. These authors also formulated the PI group of these weakly bound polymers which are reminiscent of non-rigid molecules. In fact, all the P groups of these polymer complexes can be represented by wreath product groups. The inversion operations are either incorporated

as a semi-direct product to the P group or as a direct product depending on if the inversion operation is present in the molecule. One of the problems these authors are considering is an attempt to interpret the microwave spectra of these compounds in order to understand its structure. To interpret the microwave spectra one needs the statistical weights of the rovibronic levels. In this section we shall illustrate our method with an ammonia dimer (Structure I of Fig. 1 in reference 40a). The PI group of this molecule is $S_2[S_3] \times I$ where S_n denotes the complete permutation group containing n! elements and I is the inversion group. This is an example where the PI group is a direct product of P and I groups. The GCCI's which correspond to protons of this molecule are shown in Table 11. Note that the notation for the symmetry species we follow here is that of reference 15 (cf. Table 4). In this special case where the P group is a wreath product of 2 symmetric groups, the GCCI's are the plethysms of S-functions (or Schur functions); for a detailed discussion of S-functions see Read[36] or Littlewood,[41] or the paper of the author.[22] From these GCCI's the generating functions for the proton species can be obtained immediately. The proton species of this molecule are shown in Table 12. The ^{14}N nuclei span the species $6A_1^+ + 3A_2^+$. Thus Γ^{spin} for this molecule is given by

$$\Gamma_H^{spin} \times \Gamma_{^{14}N}^{spin} = 78\ A_1^+ + 66\ A_2^+ + 21\ G_1^+ + 15\ G_2^+ + 72\ G_3^+$$

Since ^{14}N nuclei are Bosons and protons are Fermions Γ^{int} can be A_3^+ or A_3^-. Thus one obtains the following statistical weights of the rovibronic levels.

$$A_1^{\pm}(0),\ A_2^{\pm}(0),\ A_3^{\pm}(78),\ A_4^{\pm}(66),\ E^{\pm}(0),\ G_1^{\pm}(15),\ G_2^{\pm}(21),\ G_3^{\pm}(0),\ G_4^{\pm}(72).$$

As one can see the statistical weights for the G species that we obtain are one fourth of the statistical weights reported by Odutola et al.[40a]

(cf. Table II of their paper). The statistical weights reported by these authors are multiplied by the dimension of the irreducible representation.[42] It will be interesting to see how the statistical weights alter if one replaces protons by deuterium nuclei in this molecule. The deuterium species are shown in Table 13. Using Corollary 1 it can also be directly inferred that Γ_D^{spin} is given as follows.

$$\Gamma_D^{spin} = 55A_1^+ + 45A_2^+ + A_4^+ + 10E^+ + 36G_1^+ + 28G_2^+ + 80G_3^+ + 8G_4^+$$

Hence the overall spin species is

$$\Gamma^{spin} = \Gamma_D^{spin} \otimes \Gamma_N^{spin} = 465A_1^+ + 435A_2^+ + 3A_3^+ + 6A_4^+ + 90E^+ + 300G_1^+ + 276G_2^+ + 720G_3^+ + 72G_4^+.$$

Since both ^{14}N and D are Bosons the overall species can be $A_1^{\pm}$. Thus the statistical weights are

$$A_1^{\pm}(465),\ A_2^{\pm}(435),\ A_3^{\pm}(3),\ A_4^{\pm}(6),\ E^{\pm}(90),\ G_1^{\pm}(300),\ G_2^{\pm}(276),\ G_3^{\pm}(120),\ G_4^{\pm}(72).$$

Eight of the levels which were forbidden by Pauli exclusion principle have become allowed up on replacement of H nuclei by D nuclei.

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Table 1. The GCCI's of the Group D_3

Irreducible Representation	$6 \cdot P_G^x$
$A_1 = [3]$	$x_1^3 + 2x_3 + 3x_1x_2$
$A_2 = [1^3]$	$x_1^3 + 2x_3 - 3x_1x_2$
$E = [2,1]$	$2x_1^3 - 2x_3$

Table 2. The GCCI's of the Cyclic Group C_3

Irreducible Representation	$3 \cdot P_G^x$
A_1	$x_1^3 + 2x_3$
$E \begin{cases} \gamma_1 \\ \gamma_2 \end{cases}$	$\begin{cases} x_1^3 - x_3 \\ x_1^3 - x_3 \end{cases}$ or $2x_1^3 - 2x_3$

Table 3. The GCCI's of $D_3[C_3]$, the P group of $B(CH_3)_3$

Irreducible Representation	$162\ P^X_{D_3[C_3]}$
$(A_1\#A_1\#A_1) \otimes [3]' = A_1$	$x_1^9 + 6x_1^6x_3 + 12x_1^3x_3^2 + 26x_3^3 + 36x_9 + 9x_1^3x_2^3 + 18x_1^3x_6 + 18x_2^3x_3 + 36x_3x_6$
$(A_1\#A_1\#A_1) \otimes [1^3]' = A_2$	$x_1^9 + 6x_1^6x_3 + 12x_1^3x_3^2 + 26x_3^3 + 36x_9 - 9x_1^3x_2^3 - 18x_1^3x_6 - 18x_2^3x_3 - 36x_3x_6$
$(A_1\#A_1\#A_1) \times [2,1]' = E_1$	$2x_1^9 + 12x_1^6x_3 + 24x_1^3x_3^2 - 2x_3^3 - 36x_9$
$\begin{Bmatrix}(\gamma_1\#\gamma_1\#\gamma_1)\\(\gamma_2\#\gamma_2\#\gamma_2)\end{Bmatrix} \otimes [3]' = E_3$	$2x_1^9 - 6x_1^6x_3 + 6x_1^3x_3^2 + 34x_3^3 + 18x_1^3x_2^3 - 18x_1^3x_6 - 18x_3x_2^3 + 18x_3x_6 - 36x_9$
$\begin{Bmatrix}(\gamma_1\#\gamma_1\#\gamma_1)\\(\gamma_2\#\gamma_2\#\gamma_2)\end{Bmatrix} \otimes [1^3]' = E_4$	$2x_1^9 - 6x_1^6x_3 + 6x_1^3x_3^2 + 34x_3^3 - 18x_1^3x_2^3 + 18x_1^3x_6 + 18x_3x_2^3 - 18x_3x_6 - 36x_9$
$\begin{Bmatrix}(\gamma_1\#\gamma_1\#\gamma_1)\\(\gamma_2\#\gamma_2\#\gamma_2)\end{Bmatrix} \otimes [2,1]' = G$	$4x_1^9 - 12x_1^6x_3 + 12x_1^3x_3^2 - 40x_3^3 + 36x_9$
$\begin{Bmatrix}A_1\#\gamma_1\#\gamma_1\\A_1\#\gamma_2\#\gamma_2\end{Bmatrix} \otimes [2]' \uparrow D_3[C_3] = I_1$	$6x_1^9 - 18x_1^3x_3^2 + 18x_1^3x_2^3 - 18x_1^3x_6 + 12x_3^3 + 36x_2^3x_3 - 36x_3x_6$
$\begin{Bmatrix}A_1\#\gamma_1\#\gamma_1\\A_1\#\gamma_2\#\gamma_2\end{Bmatrix} \otimes [1^2]' \uparrow D_3[C_3] = I_2$	$6x_1^9 - 18x_1^3x_3^2 - 18x_1^3x_2^3 + 18x_1^3x_6 + 12x_3^3 - 36x_2^3x_3 + 36x_3x_6$

Table 3 (continued)

Irreducible Representation	$162\ P^{\chi}_{D_3[C_3]}$
$\begin{Bmatrix} A_1 \# A_1 \# \gamma_1 \\ A_1 \# A_1 \# \gamma_2 \end{Bmatrix} \otimes [2]'$ $\uparrow D_3[C_3] = I_3$	$6x_1^9 + 18x_1^6x_3 + 18x_1^3x_2^3 + 36x_1^3x_6 - 24x_3^3 - 18x_2^3x_3 - 36x_3x_6$
$\begin{Bmatrix} A_1 \# A_1 \# \gamma_1 \\ A_1 \# A_1 \# \gamma_2 \end{Bmatrix} \otimes [1^2]'$ $\uparrow D_3[C_3] = I_4$	$6x_1^9 + 18x_1^6x_3 - 18x_1^3x_2^3 - 36x_1^3x_6 - 24x_3^3 + 18x_2^3x_3 + 36x_3x_6$
$\begin{Bmatrix} \gamma_1 \# \gamma_1 \# \gamma_2 \\ \gamma_2 \# \gamma_2 \# \gamma_1 \end{Bmatrix} \otimes [2]'$ $\uparrow D_3[C_3] = I_5$	$6x_1^9 - 18x_1^6x_3 + 18x_1^3x_3^2 + 18x_1^3x_2^3 - 18x_1^3x_6 - 6x_3^3 - 18x_2^3x_3 + 18x_3x_6$
$\begin{Bmatrix} \gamma_1 \# \gamma_1 \# \gamma_2 \\ \gamma_2 \# \gamma_2 \# \gamma_1 \end{Bmatrix} \otimes [1^2]'$ $\uparrow D_3[C_3] = I_6$	$6x_1^9 - 18x_1^6x_3 + 18x_1^3x_3^2 - 18x_1^3x_2^3 + 18x_1^3x_6 - 6x_3^3 + 18x_2^3x_3 - 18x_3x_6$
$(A_1 \# \gamma_1 \# \gamma_2)$ $\uparrow D_3[C_3] = I_7$	$6x_1^9 - 18x_1^3x_3^2 + 12x_3^3$

Table 4. The GCCI's of the PI Group of $B(CH_3)_3$

Irreducible Representation	$324\ P_G^x$
A_1	$x_1^9 + 26\,x_3^3 + 6x_1^6x_3 + 12x_1^3x_3^2 + 36x_9 + 36x_1^3x_2^3 + 18x_1^3x_6 + 18x_2^3x_3 + 90x_3x_6 + 27x_1x_2^4 + 54x_1x_2x_6$
A_2	$x_1^9 + 26x_3^3 + 6x_1^6x_3 + 12x_1^3x_3^2 + 36x_9 - 36x_1^3x_2^3 - 18x_1^3x_6 - 18x_2^3x_3 - 90x_3x_6 + 27x_1x_2^4 + 54x_1x_2x_6$
A_3	$x_1^9 + 26x_3^3 + 6x_1^6x_3 + 12x_1^3x_3^2 + 36x_9 - 18x_1^3x_2^3 + 18x_1^3x_6 + 18x_2^3x_3 - 18x_3x_6 - 27x_1x_2^4 - 54x_1x_2x_6$
A_4	$x_1^9 + 26x_3^3 + 6x_1^6x_3 + 12x_1^3x_3^2 + 36x_9 + 18x_1^3x_2^3 - 18x_1^3x_6 - 18x_2^3x_3 + 18x_3x_6 - 27x_1x_2^4 - 54x_1x_2x_6$
E_1	$2x_1^9 - 2x_3^3 + 12x_1^6x_3 + 24x_1^3x_3^2 - 36x_9 + 54x_1^3x_2^3 - 54x_3x_6$
E_2	$2x_1^9 - 2x_3^3 + 12x_1^6x_3 + 24x_1^3x_3^2 - 36x_9 - 54x_1^3x_2^3 + 54x_3x_6$
E_3	$2x_1^9 + 34x_3^3 - 6x_1^6x_3 + 6x_1^3x_3^2 - 36x_9 + 18x_1^3x_2^3 - 18x_1^3x_6 - 18x_2^3x_3 + 18x_3x_6$
E_4	$2x_1^9 + 34x_3^3 - 6x_1^6x_3 + 6x_1^3x_3^2 - 36x_9 - 18x_1^3x_2^3 + 18x_1^3x_6 + 18x_2^3x_3 - 18x_3x_6$
G	$4x_1^9 - 40x_3^3 - 12x_1^6x_3 + 12x_1^3x_3^2 + 36x_9$

Table 4 (continued)

Irreducible Representation	$324\ P_G^x$
I_1	$6x_1^9 + 12x_3^3 - 18x_1^3x_3^2 + 18x_1^3x_2^3 - 18x_1^3x_6 + 36x_2^3x_3 - 36x_3x_6$
I_2	$6x_1^9 + 12x_3^3 - 18x_1^3x_3^2 - 18x_1^3x_2^3 + 18x_1^3x_6 - 36x_2^3x_3 + 36x_3x_6$
I_3	$6x_1^9 - 24x_3^3 + 18x_1^6x_3 + 18x_1^3x_2^3 + 36x_1^3x_6 - 18x_2^3x_3 - 36x_3x_6$
I_4	$6x_1^9 - 24x_3^3 + 18x_1^6x_3 - 18x_1^3x_2^3 - 36x_1^3x_6 + 18x_2^3x_3 + 36x_3x_6$
I_5	$6x_1^9 - 6x_3^3 - 18x_1^6x_3 + 18x_1^3x_3^2 + 18x_1^3x_2^3 - 18x_1^3x_6 - 18x_2^3x_3 + 18x_3x_6$
I_6	$6x_1^9 - 6x_3^3 - 18x_1^6x_3 + 18x_1^3x_3^2 - 18x_1^3x_2^3 + 18x_1^3x_6 + 18x_2^3x_3 - 18x_3x_6$
I_7	$6x_1^9 + 12x_3^3 - 18x_1^3x_3^2 + 54x_1x_2^4 - 54x_1x_2x_6$
I_8	$6x_1^9 + 12x_3^3 - 18x_1^3x_3^2 - 54x_1x_2^4 + 54x_1x_2x_6$

Table 5. Generating functions for deuterium species of $B(CD_3)_3$

Γ	λ^9	$\lambda^8\mu$	$\lambda^7\mu^2$	$\lambda^6\mu^3$	$\lambda^5\mu^4$	$\lambda^4\mu^5$	$\lambda^3\mu^6$	$\lambda^2\mu^7$	$\lambda\mu^8$	μ^9	$\lambda^8\nu$	$\lambda^7\mu\nu$	$\lambda^6\mu^2\nu$	$\lambda^5\mu^3\nu$	$\lambda^4\mu^4\nu$	$\lambda^3\mu^5\nu$	$\lambda^2\mu^6\nu$	$\lambda\mu^7\nu$	$\mu^8\nu$	$\lambda^7\nu^2$	$\lambda^6\mu\nu^2$	$\lambda^5\mu^2\nu^2$	$\lambda^4\mu^3\nu^2$	$\lambda^3\mu^4\nu^2$	$\lambda^2\mu^5\nu^2$	$\lambda\mu^6\nu^2$	$\mu^7\nu^2$	$\lambda^6\nu^3$
A_1	1	1	2	3	3	3	3	2	1	1	1	2	4	5	6	5	4	2	1	2	4	8	10	10	8	4	2	3
A_2	0	0	0	0	0	0	0	0	0	0	0	0	1	1	2	1	1	0	0	0	1	2	3	3	2	1	0	0
A_3	0	0	0	0	0	0	0	0	0	0	0	1	1	2	2	2	1	1	0	0	1	2	3	3	2	1	0	0
A_4	0	0	0	1	1	1	1	0	0	0	0	1	2	4	4	4	2	1	0	0	2	4	6	6	4	2	0	1
E_1	0	1	2	3	4	4	3	2	1	0	1	3	6	9	10	9	6	3	1	2	6	12	16	16	12	6	2	3
E_2	0	0	0	0	0	0	0	0	0	0	0	1	2	3	4	3	2	1	0	0	2	4	6	6	4	2	0	0
E_3	0	0	0	1	1	1	1	0	0	0	0	0	1	3	4	3	1	0	0	0	1	4	8	8	4	1	0	1
E_4	0	0	0	0	0	0	0	0	0	0	0	0	0	1	2	1	0	0	0	0	0	2	5	5	2	0	0	0
G	0	0	0	0	1	1	0	0	0	0	0	0	1	4	6	4	1	0	0	0	1	6	13	13	6	1	0	0
I_1	0	0	1	2	3	3	2	1	0	0	0	1	5	10	12	10	5	1	0	1	5	16	25	25	16	5	1	2
I_2	0	0	0	1	1	1	1	0	0	0	0	1	4	8	10	8	4	1	0	0	4	12	21	21	12	4	0	1
I_3	0	1	2	3	4	4	3	2	1	0	1	4	9	14	16	14	9	4	1	2	9	20	29	29	20	9	2	3
I_4	0	0	1	2	3	3	2	1	0	0	0	2	7	12	14	12	7	2	0	1	7	18	26	26	18	7	1	2
I_5	0	0	0	1	2	2	1	0	0	0	0	0	2	7	10	7	2	0	0	0	2	10	21	21	10	2	0	1
I_6	0	0	0	0	1	1	0	0	0	0	0	0	1	5	8	5	1	0	0	0	1	8	18	18	8	1	0	0
I_7	0	0	1	2	3	3	2	1	0	0	0	1	5	9	12	9	5	1	0	1	5	16	25	25	16	5	1	2
I_8	0	0	0	1	1	1	1	0	0	0	0	1	4	9	10	9	4	1	0	0	4	12	21	21	12	4	0	1

Table 5 (continued)

Γ	$\lambda^5\mu\nu^3$	$\lambda^4\mu^2\nu^3$	$\lambda^3\mu^3\nu^3$	$\lambda^2\mu^4\nu^3$	$\lambda\mu^5\nu^3$	$\mu^6\nu^3$	$\lambda^5\nu^4$	$\lambda^4\mu\nu^4$	$\lambda^3\mu^2\nu^4$	$\lambda^2\mu^3\nu^4$	$\lambda\mu^4\nu^4$	$\mu^5\nu^4$	$\lambda^4\nu^5$	$\lambda^3\mu\nu^5$	$\lambda^2\mu^2\nu^5$	$\lambda\mu^3\nu^5$	$\mu^4\nu^5$	$\lambda^3\nu^6$	$\lambda^2\mu\nu^6$	$\lambda\mu^2\nu^6$	$\mu^3\nu^6$	$\lambda^2\nu^7$	$\lambda\mu\nu^7$	$\mu^2\nu^7$	$\lambda\nu^8$	$\mu\nu^8$	ν^9
A_1	5	10	11	10	5	3	3	6	10	10	6	3	3	5	8	5	3	3	4	4	3	2	2	2	1	1	1
A_2	1	3	3	3	1	0	0	2	3	3	2	0	0	1	2	1	0	0	1	1	0	0	0	0	0	0	0
A_3	2	3	5	3	2	0	0	2	3	3	2	0	0	2	2	2	0	0	1	1	0	0	1	0	0	0	0
A_4	4	6	9	6	4	1	1	4	6	6	4	1	1	4	4	4	1	1	2	2	1	0	1	0	0	0	0
E_1	9	16	19	16	9	3	4	10	16	16	10	4	4	9	12	9	4	3	6	6	3	2	3	2	1	1	0
E_2	3	6	7	6	3	0	0	4	6	6	4	0	0	3	4	3	0	0	2	2	0	0	1	0	0	0	0
E_3	3	8	12	8	3	1	1	4	8	8	4	1	1	3	4	3	1	1	1	1	1	0	0	0	0	0	0
E_4	1	5	8	5	1	0	0	2	5	5	2	0	0	1	2	1	0	0	0	0	0	0	0	0	0	0	0
G	4	13	18	13	4	0	1	6	13	13	6	1	1	4	6	4	1	0	1	1	0	0	0	0	0	0	0
I_1	10	25	33	25	10	2	3	12	25	25	12	3	3	10	16	10	3	2	5	5	2	1	1	1	0	0	0
I_2	8	21	29	21	8	1	1	10	21	21	10	1	1	8	12	8	1	1	4	4	1	0	1	0	0	0	0
I_3	14	29	36	29	14	3	4	16	29	29	16	4	4	14	20	14	4	3	9	9	3	2	4	2	1	1	0
I_4	12	26	32	26	12	2	3	14	26	26	14	3	3	12	18	12	3	2	7	7	2	1	2	1	0	0	0
I_5	7	21	30	21	7	1	2	10	21	21	10	2	2	7	10	7	2	1	2	2	1	0	0	0	0	0	0
I_6	5	18	26	18	5	0	1	8	18	18	8	1	1	5	8	5	1	0	1	1	0	0	0	0	0	0	0
I_7	9	25	31	25	9	2	3	12	25	25	12	3	3	9	16	9	3	2	5	5	2	1	1	1	0	0	0
I_8	9	21	31	21	9	1	1	10	21	21	10	1	1	9	12	9	1	1	4	4	1	0	1	0	0	0	0

Table 6. Non-rigid Deuterium Spin Species of $B(CD_3)_3$

Γ'	Spin Species
A_1	$^3A_1(6)$, $^5A_1(2)$, $^7A_1(8)$, $^9A_1(3)$, $^{11}A_1(4)$, $^{13}A_1(2)$, $^{15}A_1(2)$, $^{19}A_1(1)$
A_2	$^3A_2(2)$, $^5A_2(1)$, $^7A_2(2)$, $^9A_2(1)$, $^{11}A_2(1)$
A_3	$^1A_3(3)$, $^5A_3(3)$, $^7A_3(1)$, $^9A_3(2)$, $^{13}A_3(1)$
A_4	$^1A_4(3)$, $^3A_4(1)$, $^5A_4(4)$, $^7A_4(3)$, $^9A_4(4)$, $^{11}A_4(1)$, $^{13}A_4(2)$
E_1	$^1E_1(1)$, $^3E_1(7)$, $^5E_1(8)$, $^7E_1(9)$, $^9E_1(7)$, $^{11}E_1(6)$, $^{13}E_1(3)$, $^{15}E_1(2)$, $^{17}E_1(1)$
E_2	$^1E_2(2)$, $^3E_2(2)$, $^5E_2(4)$, $^7E_2(3)$, $^9E_2(3)$, $^{11}E_2(1)$, $^{13}E_2(1)$
E_3	$^1E_3(2)$, $^3E_3(4)$, $^5E_3(4)$, $^7E_3(5)$, $^9E_3(3)$, $^{11}E_3(1)$, $^{13}E_3(1)$
E_4	$^1E_4(2)$, $^3E_4(3)$, $^5E_4(3)$, $^7E_4(3)$, $^9E_4(1)$
G	$^1G(2)$, $^3G(7)$, $^5G(9)$, $^7G(6)$, $^9G(4)$, $^{11}G(2)$
I_1	$^1I_1(4)$, $^3I_1(12)$, $^5I_1(14)$, $^7I_1(14)$, $^9I_1(9)$, $^{11}I_1(6)$, $^{13}I_1(2)$, $^{15}I_1(1)$
I_2	$^1I_2(5)$, $^3I_2(10)$, $^5I_2(13)$, $^7I_2(11)$, $^9I_2(8)$, $^{11}I_2(3)$, $^{13}I_2(2)$
I_3	$^1I_3(4)$, $^3I_3(13)$, $^5I_3(17)$, $^7I_3(15)$, $^9I_3(12)$, $^{11}I_3(8)$, $^{13}I_3(4)$, $^{15}I_3(2)$, $^{17}I_3(1)$
I_4	$^1I_4(4)$, $^3I_4(11)$, $^5I_4(15)$, $^7I_4(14)$, $^9I_4(11)$, $^{11}I_4(7)$, $^{13}I_4(3)$, $^{15}I_4(1)$
I_5	$^1I_5(4)$, $^3I_5(11)$, $^5I_5(13)$, $^7I_5(11)$, $^9I_5(7)$, $^{11}I_5(3)$, $^{13}I_5(1)$
I_6	$^1I_6(4)$, $^3I_6(10)$, $^5I_6(12)$, $^7I_6(9)$, $^9I_6(5)$, $^{11}I_6(2)$

Table 6 (continued)

Γ'	Spin Species
I_7	$^1I_7(2)$, $^3I_7(14)$, $^5I_7(12)$, $^7I_7(15)$, $^9I_7(8)$, $^{11}I_7(6)$, $^{13}I_7(2)$, $^{15}I_7(1)$
I_8	$^1I_8(7)$, $^3I_8(8)$, $^5I_8(15)$, $^7I_8(10)$, $^9I_8(9)$, $^{11}I_8(3)$, $^{13}I_8(2)$

Table 7. The Overall Nuclear Spin Species of $^{11}B(^{12}CD_3)_3$

Γ	Spin Species
A_1	$^{22}A_1(1)$, $^{20}A_1(1)$, $^{18}A_1(3)$, $^{16}A_1(5)$, $^{14}A_1(8)$, $^{12}A_1(11)$, $^{10}A_1(17)$, $^{8}A_1(17)$, $^{6}A_1(19)$, $^{4}A_1(16)$, $^{2}A_1(8)$
A_2	$^{14}A_2(1)$, $^{12}A_2(2)$, $^{10}A_2(4)$, $^{8}A_2(5)$, $^{6}A_2(6)$, $^{4}A_2(5)$, $^{2}A_2(3)$
A_3	$^{16}A_3(1)$, $^{14}A_3(1)$, $^{12}A_3(3)$, $^{10}A_3(4)$, $^{8}A_3(6)$, $^{6}A_3(6)$, $^{4}A_3(7)$, $^{2}A_3(3)$
A_4	$^{16}A_4(2)$, $^{14}A_4(3)$, $^{12}A_4(7)$, $^{10}A_4(10)$, $^{8}A_4(12)$, $^{6}A_4(12)$, $^{4}A_4(11)$, $^{2}A_4(5)$
E_1	$^{20}E_1(1)$, $^{18}E_1(3)$, $^{16}E_1(6)$, $^{14}E_1(12)$, $^{12}E_1(18)$, $^{10}E_1(25)$, $^{8}E_1(30)$, $^{6}E_1(31)$, $^{4}E_1(25)$, $^{2}E_1(15)$
E_2	$^{16}E_2(1)$, $^{14}E_2(2)$, $^{12}E_2(5)$, $^{10}E_2(8)$, $^{8}E_2(11)$, $^{6}E_2(12)$, $^{4}E_2(11)$, $^{2}E_2(6)$
E_3	$^{16}E_3(1)$, $^{14}E_3(2)$, $^{12}E_3(5)$, $^{10}E_3(10)$, $^{8}E_3(13)$, $^{6}E_3(16)$, $^{4}E_3(15)$, $^{2}E_3(8)$
E_4	$^{12}E_4(1)$, $^{10}E_4(4)$, $^{8}E_4(7)$, $^{6}E_4(10)$, $^{4}E_4(11)$, $^{2}E_4(6)$
G	$^{14}G(2)$, $^{12}G(6)$, $^{10}G(12)$, $^{8}G(21)$, $^{6}G(26)$, $^{4}G(24)$, $^{2}G(16)$
I_1	$^{18}I_1(1)$, $^{16}I_1(3)$, $^{14}I_1(9)$, $^{12}I_1(18)$, $^{10}I_1(31)$, $^{8}I_1(43)$, $^{6}I_1(49)$, $^{4}I_1(44)$, $^{2}I_1(26)$
I_2	$^{16}I_2(2)$, $^{14}I_2(5)$, $^{12}I_2(13)$, $^{10}I_2(24)$, $^{8}I_2(35)$, $^{6}I_2(42)$, $^{4}I_2(39)$, $^{2}I_2(23)$
I_3	$^{20}I_3(1)$, $^{18}I_3(3)$, $^{16}I_3(7)$, $^{14}I_3(15)$, $^{12}I_3(26)$, $^{10}I_3(39)$, $^{8}I_3(52)$, $^{6}I_3(57)$, $^{4}I_3(49)$, $^{2}I_3(30)$

Table 7 (continued)

Γ	Spin Species
I_4	$^{18}I_4(1)$, $^{16}I_4(4)$, $^{14}I_4(11)$, $^{12}I_4(22)$, $^{10}I_4(35)$, $^{8}I_4(47)$, $^{6}I_4(51)$, $^{4}I_4(44)$, $^{2}I_4(26)$
I_5	$^{16}I_5(1)$, $^{14}I_5(4)$, $^{12}I_5(11)$, $^{10}I_5(22)$, $^{8}I_5(34)$, $^{6}I_5(42)$, $^{4}I_5(39)$, $^{2}I_5(24)$
I_6	$^{14}I_6(2)$, $^{12}I_6(7)$, $^{10}I_6(16)$, $^{8}I_6(28)$, $^{6}I_6(36)$, $^{4}I_6(35)$, $^{2}I_6(22)$
I_7	$^{18}I_7(1)$, $^{16}I_7(3)$, $^{14}I_7(9)$, $^{12}I_7(17)$, $^{10}I_7(31)$, $^{8}I_7(41)$, $^{6}I_7(49)$, $^{4}I_7(43)$, $^{2}I_7(26)$
I_8	$^{16}I_8(2)$, $^{14}I_8(5)$, $^{12}I_8(14)$, $^{10}I_8(24)$, $^{8}I_8(37)$, $^{6}I_8(42)$, $^{4}I_8(40)$, $^{2}I_8(23)$

Table 8. The Non-rigid Proton Spin Species of $B(CH_3)_3$

Γ	Spin Species
A_1	$^4A_1(1)$, $^6A_1(1)$, $^{10}A_1(1)$
A_2	None
A_3	None
A_4	$^4A_4(1)$
E_1	$^2E_1(1)$, $^4E_1(1)$, $^6E_1(1)$, $^8E_1(1)$
E_2	None
E_3	$^4E_3(1)$
E_4	None
G	$^2G(1)$
I_1	$^2I_1(1)$, $^4I_1(1)$, $^6I_1(1)$
I_2	$^4I_2(1)$
I_3	$^2I_3(1)$, $^4I_3(1)$, $^6I_3(1)$, $^8I_3(1)$
I_4	$^2I_4(1)$, $^4I_4(1)$, $^6I_4(1)$
I_5	$^2I_5(1)$, $^4I_5(1)$
I_6	$^2I_6(1)$
I_7	$^2I_7(1)$, $^4I_7(1)$, $^6I_7(1)$
I_8	$^4I_8(1)$

Table 9. The Non-zero GCCI's of the Hydrogen Nuclei Corresponding to the P Group of a Non-rigid Triphenyl

Γ	x_1^{14}	$x_1^{10}x_2^2$	$x_1^6x_2^4$	x_2^7	$x_2^3x_4^2$	$x_1^2x_2^6$
$A_1'^+$	1	3	3	4	4	1
$B_1'^+$	1	3	3	-4	-4	1
$A_2'^+$	1	-1	-1	-4	4	1
$B_2'^+$	1	-1	-1	4	-4	1
$A_1''^+$	1	1	-1	0	0	-1
$B_1''^+$	1	1	-1	0	0	-1
$A_2''^+$	1	-3	3	0	0	-1
$B_2''^+$	1	-3	3	0	0	-1
E'^+	2	2	-2	0	0	-2
E''^+	2	-2	-2	0	0	2

Table 10. The Deuterium Species of the Non-rigid Triphenyl Molecule $C_{18}D_{14}$

Γ	Spin Species
$A_1'^+$	$^1A_1'^+(2472)$, $^3A_1'^+(6336)$, $^5A_1'^+(9036)$, $^7A_1'^+(9384)$, $^9A_1'^+(8456)$, $^{11}A_1'^+(6338)$, $^{13}A_1'^+(4306)$, $^{15}A_1'^+(2462)$, $^{17}A_1'^+(1298)$, $^{19}A_1'^+(557)$, $^{21}A_1'^+(227)$, $^{23}A_1'^+(67)$, $^{25}A_1'^+(21)$, $^{27}A_1'^+(3)$, $^{29}A_1'^+(1)$
$B_1'^+$	$^1B_1'^+(2259)$, $^3B_1'^+(6531)$, $^5B_1'^+(8841)$, $^7B_1'^+(9530)$, $^9B_1'^+(8310)$, $^{11}B_1'^+(6429)$, $^{13}B_1'^+(4215)$, $^{15}B_1'^+(2507)$, $^{17}B_1'^+(1253)$, $^{19}B_1'^+(575)$, $^{21}B_1'^+(209)$, $^{23}B_1'^+(72)$, $^{25}B_1'^+(16)$, $^{27}B_1'^+(4)$
$A_2'^+$	$^1A_2'^+(1678)$, $^3A'_2{}^+(4855)$, $^5A_2'^+(6441)$, $^7A_2'^+(6780)$, $^9A_2'^+(5668)$, $^{11}A_2'^+(4165)$, $^{13}A_2'^+(2523)$, $^{15}A_2'^+(1364)$, $^{17}A_2'^+(588)$, $^{19}A_2'^+(227)$, $^{21}A_2'^+(61)$, $^{23}A_2'^+(15)$, $^{25}A_2'^+(1)$
$B_2'^+$	$^1B_2'^+(1858)$, $^3B_2'^+(4693)$, $^5B_2'^+(6603)$, $^7B_2'^+(6660)$, $^9B_2'^+(5788)$, $^{11}B_2'^+(4095)$, $^{13}B_2'^+(2593)$, $^{15}B_2'^+(1332)$, $^{17}B_2'^+(620)$, $^{19}B_2'^+(217)$, $^{21}B_2'^+(71)$, $^{23}B_2'^+(13)$, $^{25}B_2'^+(3)$
$A_1''^+$	$^1A_1''^+(2025)$, $^3A_1''^+(5551)$, $^5A_1''^+(7612)$, $^7A_1''^+(7980)$, $^9A_1''^+(6920)$, $^{11}A_1''^+(5152)$, $^{13}A_1''^+(3309)$, $^{15}A_1''^+(1851)$, $^{17}A_1''^+(889)$, $^{19}A_1''^+(367)$, $^{21}A_1''^+(125)$, $^{23}A_1''^+(35)$, $^{25}A_1''^+(7)$, $^{27}A_1''^+(1)$
$B_1''^+$	$^1B_1''^+(2025)$, $^3B_1''^+(5551)$, $^5B_1''^+(7612)$, $^7B_1''^+(7980)$, $^9B_1''^+(6920)$, $^{11}B_1''^+(5152)$, $^{13}B_1''^+(3309)$, $^{15}B_1''^+(1851)$, $^{17}B_1''^+(889)$, $^{19}B_1''^+(367)$, $^{21}B''_1{}^+(125)$, $^{23}B_1''^+(35)$, $^{25}B_1''^+(7)$, $^{27}B_1''^+(1)$

Table 10 (continued)

Γ	Spin Species
$A_2''^+$	$^1A_2''^+(1524)$, $^3A_2''^+(4140)$, $^5A_2''^+(5580)$, $^7A_2''^+(5684)$, $^9A_2''^+(4724)$, $^{11}A_2''^+(3308)$, $^{13}A_2''^+(1948)$, $^{15}A_2''^+(964)$, $^{17}A_2''^+(388)$, $^{19}A_2''^+(124)$, $^{21}A_2''^+(28)$, $^{23}A_2''^+(4)$
$B_2''^+$	$^1B_2''^+(1524)$, $^3B_2''^+(4140)$, $^5B_2''^+(5580)$, $^7B_2''^+(5684)$, $^9B_2''^+(4724)$, $^{11}B_2''^+(3308)$, $^{13}B_2''^+(1948)$, $^{15}B_2''^+(964)$, $^{17}B_2''^+(388)$, $^{19}B_2''^+(124)$, $^{21}B_2''^+(28)$, $^{23}B_2''^+(4)$
E'^+	$^1E'^+(4050)$, $^3E'^+(11102)$, $^5E'^+(15224)$, $^7E'^+(15960)$, $^9E'^+(13840)$, $^{11}E'^+(10304)$, $^{13}E'^+(6618)$, $^{15}E'^+(3702)$, $^{17}E'^+(1778)$, $^{19}E'^+(734)$, $^{21}E'^+(250)$, $^{23}E'^+(70)$, $^{25}E'^+(14)$, $^{27}E'^+(2)$
E''^+	$^1E''^+(3536)$, $^3E''^+(9548)$, $^5E''^+(13044)$, $^7E''^+(13440)$, $^9E''^+(11456)$, $^{11}E''^+(8260)$, $^{13}E''^+(5116)$, $^{15}E''^+(2696)$, $^{17}E''^+(1208)$, $^{19}E''^+(444)$, $^{21}E''^+(132)$, $^{23}E''^+(28)$, $^{25}E''^+(4)$

Table 11. The GCCI's of the Protons of Ammonia Dimer

Γ	x_1^6	$x_1^4x_2$	$x_1^3x_3$	$x_1^2x_2^2$	x_3^2	$x_1x_2x_3$	x_2^3	x_6	x_2x_4
A_1	1	6	4	9	4	12	6	12	18
A_2	1	6	4	9	4	12	-6	-12	-18
A_3	1	-6	4	9	4	-12	-6	-12	18
A_4	1	-6	4	9	4	-12	6	12	-18
G_1	4	0	-8	0	4	0	12	-12	0
G_2	4	0	-8	0	4	0	-12	12	0
G_3	4	12	4	0	-8	-12	0	0	0
G_4	4	-12	4	0	-8	12	0	0	0
E	2	0	8	-18	8	0	0	0	0

Table 12. The Proton Species of the Ammonia Dimer

Γ	Spin Species
A_1^+	$^3A_1^+(1)$, $^7A_1^+(1)$
A_2^+	$^1A_2^+(1)$, $^5A_2^+(1)$
A_3^+	None
A_4^+	None
E^+	None
G_1^+	$^3G_1^+(1)$
G_2^+	$^1G_2^+(1)$
G_3^+	$^3G_3^+(1)$, $^5G_3^+(1)$
G_4^+	None

Table 13. The Deuterium Species of the Ammonia Dimer $(ND_3)_2$

Γ	Spin Species
A_1^+	$^1A_1^+(2)$, $^5A_1^+(3)$, $^7A_1^+(1)$, $^9A_1^+(2)$, $^{13}A_1^+(1)$
A_2^+	$^3A_2^+(2)$, $^5A_2^+(1)$, $^7A_2^+(2)$, $^9A_2^+(1)$, $^{11}A_2^+(1)$
A_3^+	None
A_4^+	$^1A_4^+(1)$
E^+	$^3E^+(1)$, $^7E^+(1)$
G_1^+	$^1G_1^+(2)$, $^3G_1^+(1)$, $^5G_1^+(3)$, $^7G_1^+(1)$, $^9G_1^+(1)$
G_2^+	$^3G_2^+(3)$, $^5G_2^+(1)$, $^7G_2^+(2)$
G_3^+	$^1G_3^+(1)$, $^3G_3^+(3)$, $^5G_3^+(4)$, $^7G_3^+(3)$, $^9G_3^+(2)$, $^{11}G_3^+(1)$
G_4^+	$^3G_4^+(1)$, $^5G_4^+(1)$

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