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### Publication Date

1980-10-01



# Lawrence Berkeley Laboratory

UNIVERSITY OF CALIFORNIA

## Materials & Molecular Research Division

Submitted to the Journal of Chemical Physics

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SPECTROSCOPY

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October 1980

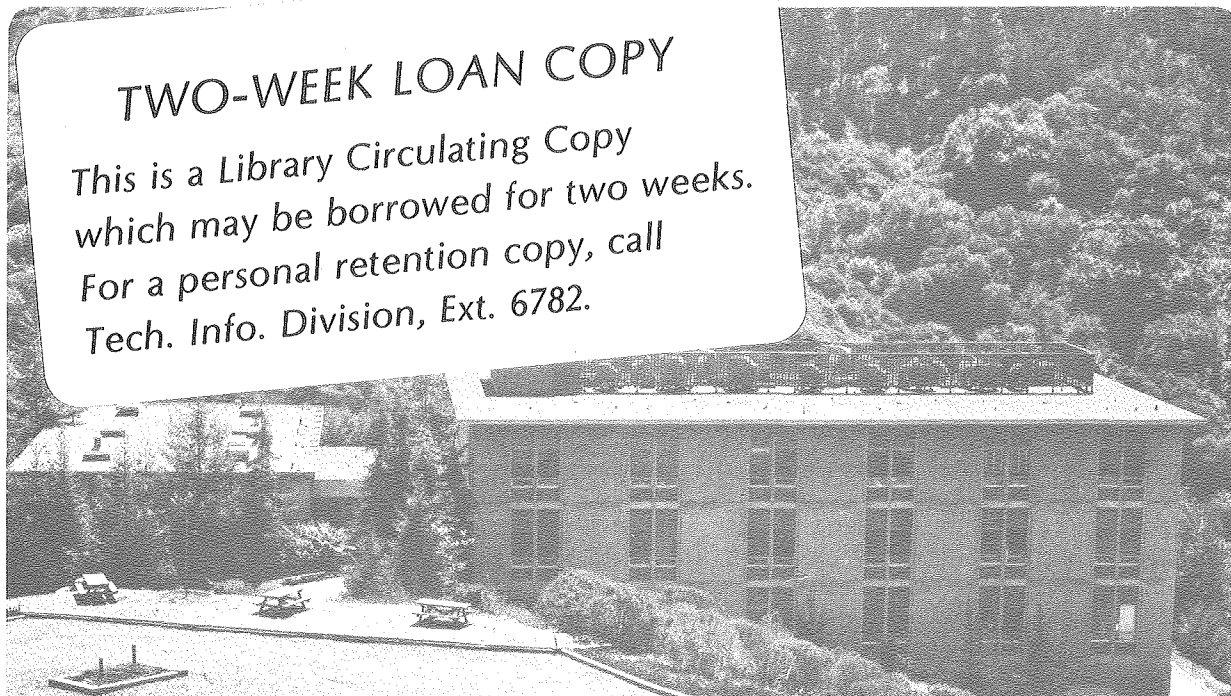
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# A Method for Nuclear Spin Statistics in Molecular Spectroscopy

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## Abstract

Using spin projection operator methods generating functions are developed for nuclear spin species. These operators also generate elegantly the irreducible representations spanned by  $a_1^{b_1} a_2^{b_2} \dots a_t^{b_t}$  nuclear spin functions where  $a_i$  is the number of possible spin states of the  $b_i$  nuclei of the same kind in the molecule. From these generating functions the statistical weights of the rovibronic levels of any polyatomic molecule can be obtained easily. The method is illustrated with  $SF_6$ ,  $C^{13}$ -Triphenylene and triphenylene with protons replaced by D. For  $C^{13}$ -Triphenylene there are 1073741824 nuclear spin functions from which we determine the statistical weights of the rovibronic levels  $A_1$ ,  $A_2$ , E,  $A_1'$ ,  $A_2'$  and E' to be 178940928, 178973696, 357913600, 178940928, 178973696, and 357913600, respectively.

## 1. Introduction

Almost any theory or experiment in molecular spectroscopy concerns with the selection rules for rovibronic levels and the statistical weights of these levels which in turn yield information on the possible spectral lines and their intensities.<sup>1-2</sup> The usual approach for finding the statistical weights of rovibronic levels is to find the character of the irreducible representations spanned by the nuclear spin species of the nuclei in the molecule and then take the inner product of the rovibronic species and nuclear spin species and see if this contains the species of the overall internal function which must obey the Pauli exclusion principle. For a molecule containing  $b_1$  nuclei of the type 1,  $b_2$  nuclei of the type 2, etc., with their possible number of spin states being  $a_1, a_2$  etc., there are  $a_1^{b_1} a_2^{b_2} \dots$  spin functions; thus the problem that we address is indeed a complicated one. Even for a simple molecule like triphenylene (in its simplest form i.e., nuclei present as  $C^{12}$  and  $^1H$ ) there are 4096 spin functions. Consequently, to find the irreducible representations that these spin functions span, if one has to enumerate all the 4096 functions, look at their transformation properties, then get their characters and break them into irreducible representations, then this problem will probably remain unsolved for complex polyatomics. However, fortunate we are, that there seems to be elegant methods to perform the above job instead of the brute force method outlined in the preceding line. It is to develop these methods that we undertake the present investigation.

The statistical weights of the rotational levels in the rotational subgroup have been discussed by Placzek and Teller,<sup>3</sup> Wilson,<sup>4-5</sup> Schäfer<sup>6</sup> and Mizushima.<sup>7</sup> Later Hougen<sup>8</sup> correlated these to the point groups of the molecules. Motivated by discussions with Hougen, Longuet-Higgins<sup>9</sup> developed the symmetry groups of nonrigid molecules and discussed the statistical weights of their rovibronic levels. Following this paper of Longuet-Higgins, several papers<sup>10-22</sup> have

appeared that describe the character tables and the properties of the symmetry groups of nonrigid molecules. The present author<sup>23</sup> showed that the symmetry groups of nonrigid molecules can be described by generalized wreath products. Further he<sup>24-25</sup> developed methods which essentially lead to generating functions for the character tables of the symmetry groups of nonrigid molecules. For nonrigid molecules, generating functions for spin species can be obtained using some theorems on generalized wreath products outlined in references 24-25 even without knowing the character table of the nonrigid molecules. Essentially these generating functions are generated combinatorially just using the character tables of the composing groups of the generalized wreath products. They will be studied in a future paper.

The present author<sup>23-31</sup> has been interested in developing group theoretical methods for problems in chemistry. Some of the preliminary ideas in this paper can be found in these papers. The preliminary concepts required for this paper can be found in the text books.<sup>32-35</sup> This paper uses formulations of Williamson<sup>36</sup> for characters of one dimensional representations which have been recently generalized to characters of higher dimensional representations by Merris.<sup>37</sup>

In sec 2 operator methods and preliminaries are outlined, in sec 3 methods are formulated for the generation of nuclear spin species with illustrative examples and in the last section we consider the statistical weights of rovibronic states.

## 2. Operator Theoretic Formulations

### A. Definitions and Preliminaries

Let  $G$  be a group acting on a discrete set  $D$ . Let  $F$  be the set of all maps from  $D$  to  $R$ . For the problem of nuclear spin statistics  $D$  is a set of nuclei and  $R$  is the set of possible spin states of the nuclei in  $D$ . For a set of spin  $1/2$  nuclei  $R$  would be a set consisting of 2 elements which can be denoted by  $\alpha$  (spin up)

and  $\beta$  (spin down).  $G$  is the rotational subgroup or the point group of the molecule. In this paper we will use  $G$  to denote the point group rather than the rotational subgroup. The image of  $F$  is the set of spin functions. For example, the map  $f_1$  from a set  $D$ , consisting of 4 nuclei, labeled 1, 2, 3 and 4, to  $R$  which consists of the spin states  $\alpha$  and  $\beta$  is shown below.

$$f_1(1) = \alpha$$

$$f_1(2) = \beta$$

$$f_1(3) = \beta$$

$$f_1(4) = \alpha$$

Then the spin function generated by  $f_1$  is  $\alpha \beta \beta \alpha$ .  $G$  acts on the elements of  $F$  by the procedure shown below.

$$g(f(i)) = f(g^{-1} i) \quad \text{for every } i \in D.$$

To illustrate if we take  $g$  to be the permutation (1234), then  $g^{-1} = (1432)$ . Thus for the map  $f_1$  shown above

$$gf_1(1) = f_1(g^{-1} 1) = f_1(4) = \alpha$$

$$gf_1(2) = f_1(g^{-1} 2) = f_1(1) = \alpha$$

$$gf_1(3) = f_1(g^{-1} 3) = f_1(2) = \beta$$

$$gf_1(4) = f_1(g^{-1} 4) = f_1(3) = \beta.$$

Thus by the action of the permutation (1234) on  $f$ , the spin function  $\alpha \beta \beta \alpha$  was permuted to  $\alpha \alpha \beta \beta$ . Any permutation can be assigned a cycle representation as given by its cycle decomposition. For example, the permutation considered above viz. (1234) has just one cycle of length 4 which can be denoted by the cycle representation  $x_4^1$ . Similarly, the permutation (12)(34) which has 2 cycles of

length 2 can be denoted as  $x_2^2$ . In general, if the permutation  $g$  has  $b_1$  cycles of length 1,  $b_2$  cycles of length 2, etc., it has a cycle representation  $x_1^{b_1} x_2^{b_2} \dots$ . Define the cycle index of  $G$ , denoted as  $P_G$  to be the sum of all the cycle representations of  $G$  divided by  $|G|$ , the number of elements in  $G$ . In symbols,

$$P_G = \frac{1}{|G|} \sum_{g \in G} x_1^{b_1} x_2^{b_2} \dots$$

Two functions  $f_i$  and  $f_j$  in  $F$  are equivalent if there is a  $g$  in  $G$  such that

$$f_i(d) = f_j(gd), \text{ for every } d \in D$$

where we assume  $i \neq j$ . All equivalent maps can be grouped together and they form an equivalence class which is called a pattern. Then  $G$  divides  $F$  into patterns. For the sake of mathematical manipulation with  $P_G$  which will eventually yield generating functions for nuclear spin species we introduce the concept of weight of an element in  $R$ . With each  $r \in R$ , let us associate a weight  $w(r)$  which is just a symbol to differentiate the various spin states in the set  $R$ . For example, we may associate a weight  $\alpha$  to the spin state  $\alpha$  and a weight  $\beta$  to the spin state  $\beta$  for the spin 1/2 problem. We can now define the weight of any function  $f$  in  $F$  as the product of the weights of the weights of the corresponding images. Symbolically,

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

To illustrate consider the spin function map  $f_1$  which maps the 4 nuclei into the spin-function  $\alpha \beta \beta \alpha$ . The weight of this map would be  $\alpha^2 \beta^2$  since  $\alpha$  is the weight of  $\alpha$  and  $\beta$  is the weight of  $\beta$ .

Before we proceed further let us illustrate the cycle index  $P_G$  of a group with  $G$  as the point group  $O_h$ ,  $D$  as the set of 6  $^{19}\text{F}$  nuclei. A typical operation such as  $C_3$  (three fold rotation in  $O_h$ ) permutes the six vertices of the octahedron.



In fact, the result of this operation is the permutation (123)(456). This would be the representation of this operation in the Longuet-Higgins' permutation inversion group.<sup>9</sup> This has the cycle representation  $x_3^2$  (2 cycles of length 3). In this manner one finds the cycle representations of all the operations of  $O_h$ . Then one adds all these cycle representations and divides by the number of elements in  $O_h$  which is 48. Thus we get

$$P_G = \frac{1}{48} (x_1^6 + 8x_3^2 + 7x_2^3 + 6x_1^2x_4 + 9x_1^2x_2^2 + 6x_2x_4 + 8x_6 + 3x_1^4x_2).$$

### B. Spin Projection Operators

Let  $V$  be a vector space of dimension  $r$ , the number of elements in the set  $R$ . For example, for the spin 1/2 problem  $V$  would be a 2 dimensional vector space. Let  $V^d$  be the  $d$ -fold tensor product<sup>38</sup> of the vector space  $V$ . In symbols,

$$V^d = \bigotimes_d V$$

where  $d$  is the number of elements in  $D$ . Let  $e_1, e_2, \dots, e_r$  be a basis of  $V$ . With each  $f \in F$  there is an associated  $e_f$  defined below.

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

which is a tensor in the space  $V^d$ . The set of tensors  $S = \{e_f : f \in F\}$  forms a basis for  $V^d$ . For any  $g \in G$  let

$$P(g) e_f = e_{gf} = e_{f(g^{-1} 1)} \otimes e_{f(g^{-1} 2)} \otimes \dots \otimes e_{f(g^{-1} d)}$$

Thus  $P(g)$  is a permutation operation relative to the basis  $S$  since it permutes the tensors in  $S$  by way of the action of  $g$  on  $f$ . Let  $g \rightarrow \chi(g)$  be the character of an irreducible representation  $\Gamma$  in  $G$ . Williamson<sup>36</sup> considered  $\chi$  to the

character of an one dimensional representation. However, Merris<sup>37</sup> recently generalized this to characters of irreducible representations of higher dimension. Define an operator  $T_G^X$  as follows.

$$T_G^X = \frac{1}{|G|} \sum_{g \in G} \chi(g) P(g).$$

It can be shown that  $T_G^X$  is idempotent. That is,

$$(T_G^X)^2 = T_G^X.$$

It is thus a spin projection operator in the space  $V^d$ .

Now, consider the subspace  $V_x^d$  of  $V^d$  spanned by all tensors that have the same weight  $x$ . Equivalently  $V_x^d$  is spanned by the set  $S_x = \{e_f : W(f) = x\}$ , where  $W(f)$  was defined in sec 2A. Let the restrictions of the operators  $T_G^X$  and  $P(g)$  to be space  $V_x^d$  be  $T_G^{X,x}$  and  $P_x(g)$ , respectively.  $T_G^{X,x}$  is a spin projector of spin functions with the same weight  $x$ . For example, if we consider all functions of the type  $\alpha \alpha \beta \beta$ ,  $\alpha \beta \alpha \beta$ , etc which have the same weight  $\alpha^2 \beta^2 = x$ , then  $T_G^{X,x}$  projects only these functions that have the same number of  $\alpha$ 's and  $\beta$ 's in the spin subspace  $V_x^d$ . We can now define a weighted permutation operator  $P_W(g)$  and a weighted projector  $T_G^{X,W}$  as follows.

$$P_W(g) = \bigoplus_x x P_x(g)$$

$$T_G^{X,W} = \bigoplus_x x T_G^{X,x}$$

where  $\bigoplus$  denotes a finite direct sum. A definition of finite direct sum can be found in Hamermesh.<sup>35</sup>  $x$ 's vary over all the functions. In a matrix representation of  $P_W(g)$ , trace of  $P_W(g)$ ,  $\text{tr}P_W(g)$  is

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

where the sum is taken over all  $f$  such that  $gf = f$ . For example, for 2 F nuclei,  
 $R = \{\alpha, \beta, \}$  and  $g = (12)$

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

In this setup Williamson and later Merris proved the following theorem.

Theorem 1: 
$$T_G^{\chi, W} = \frac{1}{|G|} \sum_{g \in G} \chi(g) P_W(g)$$

Consequently, 
$$\begin{aligned} \text{tr}T_G^{\chi, W} &= \frac{1}{|G|} \sum_{g \in G} \chi(g) \text{tr}P_W(g) \\ &= \frac{1}{|G|} \sum_{g \in G} \chi(g) \sum_f^{(g)} W(f). \end{aligned}$$

For our problem this theorem implies that the weighted spin projector 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 irreducible representations contained in the set of spin functions and the spin species.

Let us now extend the concept of cycle index of a group  $G$  to a cycle index  $P_G^\chi$  which corresponds to the character  $g \rightarrow \chi(g)$  of the irreducible representation  $\Gamma$  in the group  $G$ .  $P_G^\chi$  is defined below.

$$P_G^\chi = \frac{1}{|G|} \sum_{g \in G} \chi(g) x_1^{b_1} x_2^{b_2} \dots$$

where  $x_1^{b_1} x_2^{b_2} \dots$  has the same meaning as in sec 2A. Then it can be shown that theorem 1 takes the form,

$$\text{tr} T_G^{\chi, W} = P_G^\chi (x_k \rightarrow \sum_{r \in R} w^k(r)).$$

The coefficient of a typical term  $w_1^{b_1} w_2^{b_2} \dots$  in  $\text{tr} T_G^{\chi, W}$  gives the frequency of

occurrence of the irreducible representation  $\Gamma$  whose character is  $\chi$  in the set of spin functions with the weight  $w_1^{b_1} w_2^{b_2} \dots$ . For example, let  $G = O_h$ , and  $D = \{6 \text{ fluorene nuclei}\} / R = \{\alpha, \beta\}$ . Set  $\chi$  to be the character of the representation,  $T_{2g}$ . Then the coefficient of  $\alpha^3 \beta^3$  would give the number of  $T_{2g}$  representations occurring in the set of spin functions containing  $3\alpha$ 's and  $3\beta$ 's which transform as a reducible representation of the group  $O_h$ . An example has been worked out in the next section.

If one is just interested in finding the irreducible representations occurring in the reducible representation spanned by all the functions in  $F$  (instead of the details of these enumerations) then we just set all the weights to unity in theorem 1. This gives the following corollary.

Corollary 1: The number of times the irreducible representation whose character is  $\chi$  occurs in the reducible representation formed by all  $f$  in  $F$  is given by

$$P_G^\chi (x_k \rightarrow |R|)$$

where  $|R|$  is the number of elements in the set  $R$ . Note that this corollary not require the character of the reducible representation to decompose it into irreducible representations. It generates these directly from just the cycle index corresponding to the character  $\chi$ . It is this aspect which makes this different and elegant in comparison to the conventional techniques.

### 3. Generating Functions for Nuclear Spin Species

In this section we apply the methods outlined in sec 2 for obtaining generating functions for nuclear spin species. For this purpose we choose  $D$  to be the set of nuclei present in the molecule,  $R$  as the set of possible spin states. For example, if we consider the molecule  $SF_6$ , with  $^{19}F$  and  $^{32}S$  then we consider  $S$  and  $6F$  nuclei as separate  $D$  sets. The set  $R$  for  $F$  nuclei contains 2 elements

since  $^{19}\text{F}$  is a spin 1/2 nucleus and hence can take 2 possible spin states. We may associate the weights  $\alpha$  and  $\beta$  to these states. Then any spin function formed by F nuclei is an image of a map from D to R. For example,  $\alpha \alpha \beta \alpha \beta \beta$  is such an image of a map from D to R. The weight of this particular map is  $\alpha^3 \beta^3$ . In this example  $G = O_h$ . The coefficient of  $\alpha^{a_1} \beta^{b_1}$  in  $\text{tr} T_G^{\chi, W}$  gives the number of times the irreducible representation whose character is  $\chi$  occurs in the reducible representation formed by the spin functions containing  $a_1 \alpha$ 's and  $b_1 \beta$ 's. Since theorem 1 relates  $\text{tr} T_G^{\chi, W}$  to  $P_G^\chi$ , in order to obtain these generating functions for nuclear spin species all that we need to obtain is the set of  $P_G^\chi$  for all  $\chi$  in  $O_h$ . They can be obtained very easily using the character table of the group  $O_h$  and are shown in table 1 for  $O_h$ . From this table using theorem 1, generating functions for the fluorene species can be obtained easily. To illustrate, consider the species  $E_g$ . The nuclear spin species which belong to this species can be obtained by replacing every  $x_k$  by  $(\alpha + \beta)^k$  in the corresponding  $P_G^\chi$ . The result of this substitution is shown below.

$$P_G^{Eg} = \frac{1}{48} [2x_1^6 - 8x_3^2 + 6x_1^2 x_2^2 + 2x_2^3 - 8x_6 + 6x_1^4 x_2]$$

Thus,

$$\begin{aligned} \text{G.F.}^{Eg} = \frac{1}{48} [ & 2(\alpha + \beta)^6 - 8(\alpha^3 + \beta^3)^2 + 6(\alpha + \beta)^2(\alpha^2 + \beta^2)^2 \\ & + 2(\alpha^2 + \beta^2)^3 - 8(\alpha^6 + \beta^6) + 6(\alpha + \beta)^4(\alpha^2 + \beta^2) ]. \end{aligned}$$

The above expression on simplification yields

$$5\alpha^5\beta + 2\alpha^4\beta^2 + 2\alpha^3\beta^3 + 2\alpha^2\beta^4 + \alpha\beta^5.$$

Thus there is one  $E_g$  in the reducible representation spanned by spin functions containing 5 $\alpha$ 's and 1 $\beta$ , 2 $E_g$  in the reducible representation spanned by spin functions containing 4 $\alpha$ 's and 2 $\beta$ 's and so on. The generating functions thus obtained for the fluorene species are shown in Table 2. Looking at these generating

functions the spin species can be immediately obtained. The coefficient of a typical term  $\alpha^{a_1} \beta^{b_1}$  in a generating function corresponding to the species  $\Gamma$  gives the number of functions belonging to the species with the spin quantum number  $m_z = (a_1 - b_1)/2$ . When we arrange these species according to their  $m_z$  values they separate into spin multiplets with  $m_z$  varying from  $-S$  to  $S$ . For example, the generating functions which corresponds to  $A_{1g}$  give rise to species  ${}^7A_{1g}$  and  ${}^3A_{1g}$ . In this manner when we group the spin species into multiplets as obtained from their generating functions we obtain the fluorene species as  ${}^7A_{1g}$ ,  ${}^3A_{1g}$ ,  ${}^1A_{2g}$ ,  ${}^5E_g$ ,  ${}^3E_g$ ,  ${}^3T_{2g}$ ,  ${}^1A_{2u}$ ,  ${}^5T_{1u}$ ,  ${}^1T_{1u}$  and  ${}^3T_{2u}$ . The spin species of the  ${}^{32}\text{S}$  nucleus is easily obtained as  ${}^4A_{1g}$  since the spin of  ${}^{32}\text{S}$  nucleus is  $3/2$ . The overall spin species is the direct product of Sulfur and Fluorene 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-Gordon series.<sup>35</sup>

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

where

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

the direct sum of irreducible representations  $D_k$ 's contained in  $D_i \otimes D_j$ . This way we obtain the overall spin species as

$${}^{10}A_{1g}, {}^8A_{1g}, {}^6A_{1g}(2), {}^4A_{1g}(2), {}^2A_{1g}, {}^4A_{2g}, {}^8E_g, {}^6E_g(2), {}^4E_g(2), {}^2E_g(2), {}^6T_{2g},$$

$${}^4T_{2g}, {}^2T_{2g}, {}^4A_{2u}, {}^8T_{1u}, {}^6T_{1u}, {}^4T_{1u}(2), {}^2T_{1u}, {}^6T_{2u}, {}^4T_{2u} \text{ and } {}^2T_{2u}.$$

All these spin species span a reducible representation which is decomposed into the irreducible representations of  $O_h$  by adding all the multiplicities times the frequency of occurrence of the same species. The result is shown below.

$$\Gamma^{\text{spin}}(\text{SF}_6) = 40A_{1g} + 4A_{2g} + 32E_g + 12T_{2g} + 4A_{2u} + 24T_{1u} + 12T_{2u}.$$

If one is interested in obtaining  $\Gamma^{\text{spin}}$  instead of the actual spin multiplets then this can be generated directly by another method without generating the nuclear spin multiplets. For the purpose of statistical weights of rovibronic levels we need  $\Gamma^{\text{spin}}$  only rather than the whole spin multiplet pattern. This will be considered separately in the next section.

#### 4. Statistical Weights of Rovibronic States

In order to obtain the statistical weights of the rovibronic states we need the irreducible representations contained in  $\Gamma^{\text{spin}}$ , the reducible representation spanned by the spin functions. We will use Corolary 1 outlined in sec 2B to find  $\Gamma^{\text{spin}}$ . Let us start with the same  $\text{SF}_6$  example. Let us find the representation spanned by the fluorene species. Since the set R has 2 elements (2 spin states of fluorene), the frequency of occurrence of an irreducible representation  $\Gamma$  in  $\Gamma_F^{\text{spin}}$  is obtained by replacing every  $x_k$  in the corresponding  $P_G^X$  by the number of elements in R, which is 2 in this example. (cf. Cor.1). For example, number of times  $A_{1g}$  occurs in the fluorene species is given by

$$\frac{1}{48} [2^6 + 8 \cdot 2^2 + 7 \cdot 2^3 + 6 \cdot 2^2 \cdot 2 + 9 \cdot 2^2 \cdot 2^2 + 6 \cdot 2 \cdot 2 + 8 \cdot 2 + 3 \cdot 2^4 \cdot 2] = 10.$$

Similarly, the frequency of occurrence of the species  $T_{2g}$  is given by

$$\frac{1}{48} [3 \cdot 2^6 + 9 \cdot 2^3 - 6 \cdot 2^2 \cdot 2 + 3 \cdot 2^2 \cdot 2^2 - 6 \cdot 2 \cdot 2 - 3 \cdot 2^4 \cdot 2] = 3.$$

In this way when we apply this to all the irreducible representations of  $O_h$ , we obtain

$$\Gamma_F^{\text{spin}} = 10A_{1g} + A_{2g} + 8E_g + 3T_{2g} + A_{2u} + 6T_{1u} + 3T_{2u}.$$

Since the  $^{32}\text{S}$  nucleus spans the representation

$$\Gamma_S^{\text{spin}} = 4A_{1g},$$

The total spin representation  $\Gamma^{\text{spin}} = \Gamma_S^{\text{spin}} \otimes \Gamma_F^{\text{spin}}$ , is given by

$$\Gamma^{\text{spin}} = 40A_{1g} + 4A_{2g} + 32E_g + 12T_{2g} + 4A_{2u} + 24T_{1u} + 12T_{2u}.$$

This agrees with our result in sec 3. The beauty of this method is that it did not require the character of  $\Gamma^{\text{spin}}$ , a reducible representation of dimension 256, to decompose/into its irreducible components. For  $C^{12}$  Triphenylene  $\Gamma^{\text{spin}}$  is a reducible representation of dimension 4096.

This method can be applied easily to complex polyatomic molecules. We give triphenylene in 3 forms as examples of such molecules. The point group of triphenylene can be easily seen to be  $D_{3h}$  whose character table can be readily obtained. We now consider  $^{12}C$  triphenylene. In this molecule only the 12 protons possess nuclear spin and hence we consider D as just these protons. The various cycle indices for these protons are shown below.

$$P^A_1 = \frac{1}{12} (2x_1^{12} + 4x_3^4 + 6x_2^6)$$

$$P^A_2 = \frac{1}{12} (2x_1^{12} + 4x_3^4 - 6x_2^6)$$

$$P^E = \frac{1}{12} (4x_1^{12} - 4x_3^4).$$

All the other cycle indices are zero. The number of  $A_1$ 's,  $A_2$ 's and E's in  $\Gamma_H^{\text{spin}}$  are shown below.

$$N(A_1) = \frac{1}{6} (2^{12} + 2 \cdot 2^4 + 3 \cdot 2^6) = 720$$

$$N(A_2) = \frac{1}{6} (2^{12} + 2 \cdot 2^4 - 3 \cdot 2^6) = 656$$

$$N(E) = \frac{1}{6} (2 \cdot 2^{12} - 2 \cdot 2^4) = 1360.$$

Thus

$$\Gamma_H^{\text{spin}} = 720A_1 + 656A_2 + 1360 E.$$



When all the  $^{12}\text{C}$  carbon nuclei are replaced by  $^{13}\text{C}$  carbon nuclei then we have to consider the set of 18 carbon atoms to obtain  $\Gamma^{\text{spin}}$ . We now let D be the set of  $^{13}\text{C}$  carbon nuclei and R as their spin states. Then the various cycle indices are as follows.

$$P^{A_1} = \frac{1}{6} [x_1^{18} + 2x_3^6 + 3x_2^9]$$

$$P^{A_2} = \frac{1}{6} [x_1^{18} + 2x_3^6 - 3x_2^9]$$

$$P^E = \frac{1}{6} [2x_1^{18} - 2x_3^6] .$$

Again, the other cycle indices are zeros. Thus  $N(A_1)$ ,  $N(A_2)$ ,  $N(E)$  for carbon species are shown below.

$$N(A_1) = \frac{1}{6} (2^{18} + 2 \cdot 2^6 + 3 \cdot 2^9) = 43968$$

$$N(A_2) = \frac{1}{6} (2^{18} + 2 \cdot 2^6 - 3 \cdot 2^9) = 43456$$

$$N(E) = \frac{1}{6} (2 \cdot 2^{18} - 2 \cdot 2^6) = 87360.$$

Hence

$$\Gamma_C^{\text{spin}} = 43968 A_1 + 43456 A_2 + 87360 E$$

The overall spin species,  $\Gamma^{\text{spin}} = \Gamma_C^{\text{spin}} \otimes \Gamma_H^{\text{spin}}$  is as follows

$$\Gamma^{\text{spin}} = 178973696 A_1 + 178940928 A_2 + 357913600 E.$$

As a last example we consider triphenylene with all protons replaced by deuterium and all carbons being  $^{12}\text{C}$ . (The case of  $^{13}\text{C}$  and D combination will be left to the reader!). Then we look at the transformation of D nuclei which is identical to those of H nuclei. However, we have to replace every  $x_k$  by 3 instead of 2 since the number of spin states of D is 3. Thus  $N(A_1)$ ,  $N(A_2)$  and  $N(E)$  are the ones shown below.

$$N(A_1) = \frac{1}{6} (3^{12} + 2 \cdot 3^4 + 3 \cdot 3^6) = 88965$$

$$N(A_2) = \frac{1}{6} (3^{12} + 2 \cdot 3^4 - 3 \cdot 3^6) = 88236$$

$$N(E) = \frac{1}{6} (2 \cdot 3^{12} - 2 \cdot 3^4) = 177120.$$

Hence the deuterium spin species,  $\Gamma_D^{\text{spin}}$  is as follows.

$$\Gamma_D^{\text{spin}} = 88965 A_1 + 88236 A_2 + 177120E.$$

Once  $\Gamma^{\text{spin}}$  is known obtaining the statistical weights is not difficult. This is done by stipulating that  $\Gamma^{\text{spin}} \otimes \Gamma^{\text{rve}}$  should contain  $\Gamma^{\text{int}}$ , where  $\Gamma^{\text{rve}}$  is the rovibronic species and  $\Gamma^{\text{int}}$  is the species of the overall internal wavefunction. By the Pauli exclusion principle  $\Gamma^{\text{int}}$  must be antisymmetric and hence the character of  $\Gamma^{\text{int}}$  must be antisymmetric with respect to permutations alone.

Let us now find the statistical weights of the rovibronic species of the molecules we have been considering as examples. We start with  $\text{SF}_6$ . The overall internal wavefunction of this molecule can belong to species  $A_{2u}$  or  $A_{2g}$  by the Pauli principle. Thus  $\Gamma^{\text{int}} = A_{2u}$  or  $A_{2g}$ .  $\Gamma^{\text{spin}}$  for  $\text{SF}_6$  was already obtained. Using the condition that  $\Gamma^{\text{spin}} \otimes \Gamma^{\text{rve}}$  should contain  $A_{2u}$  or  $A_{2g}$  we obtain the statistical weights of all the rovibronic levels which are shown below with statistical weights in parenthesis.

$$A_{1g}(8), A_{2g}(40), E_g(32), T_{1g}(24), T_{2g}(24), A_{1u}(8), A_{2u}(40), E_u(32), T_{1u}(24), \\ T_{2u}(24).$$

For the molecule triphenylene  $\Gamma^{\text{int}}$  can be  $A_2$  or  $A_2'$ . For the normal triphenylene ( $^{12}\text{C-H}$ ), the statistical weights of the rovibronic levels are indicated below.

$$A_1(656), A_2(720), E(1360), A_1'(656), A_2'(720), E'(1360).$$

For  $^{13}\text{C}$ -triphenylene the statistical weights are as follows.

$$A_1(178940928), A_2(178973696), E(357913600),$$

$$A'_1(178940928), A'_2(178973696), E'(357913600).$$

In the end we consider D-triphenylene for which the statistical weights of the rovibronic levels are shown below.

$$A_1(88236), A_2(88965), E(177120),$$

$$A'_1(88236), A'_2(88965), E'(177120).$$

Generating functions for the statistical weights of rovibronic levels of nonrigid molecules can be obtained by composing elegantly the cycle indices of the composing groups. This subject will be treated separately in a future publication.

#### Acknowledgment

The author is indebted to Professor Kenneth S. Pitzer for his encouragement. This work was supported in part by the division of Chemical Sciences, Office of Basic Energy Sciences, U. S. Department of Energy under Contract No. W-7405-ENG-48.

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Table 1

 $48P_G^X$  for Various Irreducible Representations in the Group  $O_h$ 

Irreducible Representation	$48 P_G^X$
$A_{1g}$	$x_1^6 + 8x_3^2 + 7x_2^3 + 6x_1^2x_4 + 9x_1^2x_2^2 + 6x_2x_4 + 8x_6 + 3x_1^4x_2$
$A_{2g}$	$x_1^6 + 8x_3^2 - 5x_2^3 - 6x_1^2x_4 - 3x_1^2x_2^2 - 6x_2x_4 + 8x_6 + 3x_1^4x_2$
$E_g$	$2x_1^6 - 8x_3^2 + 6x_1^2x_2^2 + 2x_2^3 - 8x_6 + 6x_1^4x_2$
$T_{1g}$	$3x_1^6 - 3x_2^3 + 6x_1^2x_4 - 9x_1^2x_2^2 + 6x_2x_4 - 3x_1^4x_2$
$T_{2g}$	$3x_1^6 + 9x_2^3 - 6x_1^2x_4 + 3x_1^2x_2^2 - 6x_2x_4 - 3x_1^4x_2$
$A_{1u}$	$x_1^6 + 8x_3^2 + 5x_2^3 + 6x_1^2x_4 - 3x_1^2x_2^2 - 6x_2x_4 - 8x_6 - 3x_1^4x_2$
$A_{2u}$	$x_1^6 + 8x_3^2 - 7x_2^3 - 6x_1^2x_4 + 9x_1^2x_2^2 + 6x_2x_4 - 8x_6 - 3x_1^4x_2$
$E_u$	$2x_1^6 - 8x_3^2 + 6x_1^2x_2^2 - 2x_2^3 + 8x_6 - 6x_1^4x_2$
$T_{1u}$	$3x_1^6 - 9x_2^3 + 3x_1^2x_2^2 + 6x_1^2x_4 - 6x_2x_4 + 3x_1^4x_2$
$T_{2u}$	$3x_1^6 + 3x_2^3 - 9x_1^2x_2^2 - 6x_1^2x_4 + 6x_2x_4 + 3x_1^4x_2$

Table 2  
 Generating Functions of Fluorene Species of SF<sub>6</sub>

Irreducible Representation	G. F.
A <sub>1g</sub>	$\alpha^6 + \alpha^5\beta + 2\alpha^4\beta^2 + 2\alpha^3\beta^3 + 2\alpha^2\beta^4 + \alpha\beta^5 + \beta^6$
A <sub>2g</sub>	$\alpha^3\beta^3$
E <sub>g</sub>	$\alpha^5\beta + 2\alpha^4\beta^2 + 2\alpha^3\beta^3 + 2\alpha^2\beta^4 + \alpha\beta^5$
T <sub>1g</sub>	0
T <sub>2g</sub>	$\alpha^4\beta^2 + \alpha^3\beta^3 + \alpha^2\beta^4$
A <sub>1u</sub>	0
A <sub>2u</sub>	$\alpha^3\beta^3$
E <sub>u</sub>	0
T <sub>1u</sub>	$\alpha^5\beta + \alpha^4\beta^2 + 2\alpha^3\beta^3 + \alpha^2\beta^4 + \alpha\beta^5$
T <sub>2u</sub>	$\alpha^4\beta^2 + \alpha^3\beta^3 + \alpha^2\beta^4$