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A method for nuclear spin statistics in molecular spectroscopy

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Using spin projection operator methods, generating functions are developed for nuclear spin species. These operators also generate elegantly the irreducible representations spanned by $a_1^{b_1} a_2^{b_2} \dots a_n^{b_n}$ 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 $^{33}\text{SF}_6$, ^{13}C -triphenylene, and triphenylene with protons replaced by D. For ^{13}C -triphenylene there are 1 073 741 824 nuclear spin functions from which we determined the statistical weights of the rovibronic levels A_1' , A_2' , E' , A_1'' , A_2'' , and E'' to be 178 940 928, 178 973 696, 357 913 600, 178 940 928, 178 973 696, and 357 913 600, respectively.

I. 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.^{1,2} 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 ^{12}C 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,³ Wilson,^{4,5} Schäfer,⁶ and Mizushima.⁷ Later, Hougen⁸ correlated these to the point groups of the molecules. Motivated by discussions with Hougen, Longuet-Higgins⁹ developed the symmetry groups of nonrigid molecules and discussed the statistical weights of their rovibronic levels. Following this paper of Longuet-Higgins, several papers¹⁰⁻²² have appeared that describe the character tables and the properties of the symmetry groups of nonrigid molecules. The present author^{23,26(a)} showed that the symmetry groups of nonrigid molecules can be described by generalized wreath products. Further he^{24,25} 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 Refs. 24-25 even without knowing the character tables 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. Wreath products were also used by Klemperer^{26(b)} for enumerating isomerization reactions.

Galbraith³⁹ obtained the nuclear spin statistical weights of molecules of the type XY_4 , XY_5 , and XY_6 of T_d , D_{3h} , and O_h symmetries, respectively, using the unitary group approach and Schur's theorem. More recently, Weber^{40,41} discussed the nuclear spin statistical weights of some molecules with point groups D_{nh} and D_{nd} ($n \leq 6$). The method developed in our paper is more general in that it is applicable to both rigid and nonrigid molecules of any symmetry. Further, with this method we can obtain not only the nuclear spin statistical weights but also the nuclear spin species.

The present author^{23-26(a), 27-31} has been interested in developing group theoretical methods for problems in chemistry. The preliminary concepts required for this paper can be found in the text books.³²⁻³⁵ This paper uses formulations of Williamson³⁶ for characters of one-dimensional representations which have been recently generalized to characters of higher dimensional representations by Merris.³⁷

In Sec. II operator methods and preliminaries are outlined, in Sec. III, 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.

II. 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 of the

same kind and R is the set of possible spin states of the nuclei in D . For a set of spin $\frac{1}{2}$ nuclei R would be a set consisting of two elements which can be denoted by α (spin up) and β (spin down). Even though, D is said to contain one kind of nuclei (for example, all the hydrogen nuclei in the molecule), the method developed here can be very easily used for molecules containing several kinds of nuclei such as H, ^{13}C , ^{19}F , etc. Either we can set D and R as the Cartesian product of the sets of nuclei of various kinds and the sets of respective spin states; or we can treat each kind of nuclei separately, obtain the nuclear spin species and eventually obtain the overall nuclear spin species as the direct product of different kinds of nuclear spin species. By either method one arrives at the same result. We shall, however, use the latter approach in this paper. G is the rotational subgroup of 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 α and β is shown below.

$$f_1(1)=\alpha, \quad f_1(2)=\beta, \quad f_1(3)=\beta, \quad f_1(4)=\alpha.$$

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_1 , the spin function $\alpha\beta\beta\alpha$ gets 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 $x_1^{b_1}x_2^{b_2}\dots$. Equivalently, if g has the cycle type (b_1, b_2, \dots) , it is said to have the 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

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

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 mathe-

matical 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 α to the spin state α and a weight β to the spin state β for the spin $\frac{1}{2}$ problem. We can now define the weight of any function f in F as the product 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 α is the weight of α and β is the weight of β .

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}F nuclei. A typical operation such as c_3 (threefold 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.⁹ 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 two-dimensional vector space. Let $V^{|D|}$ be the $|D|$ -fold tensor product³⁸ of the vector space V . In symbols $|D|$,

$$V^{|D|} = \otimes_{|D|} V,$$

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 operator 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 Γ in G . Williamson³⁶ considered χ to be the character of an one-dimensional representation. However, Merris³⁷ recently generalized this to characters of irreducible representations of higher dimensions. Define an operator T_G^χ as follows:

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

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. IIA. Let the restrictions of the operators T_G^x and $P(g)$ to the 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 α 's and β '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:

$$P_w(g) = \oplus_x x P_x(g),$$

$$T_G^{x,w} = \oplus_x x T_G^{x,x},$$

where \oplus denotes a finite direct sum. A definition of finite direct sum can be found in Hamermesh.³⁵ x 's vary over the weights of 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^{19}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:

$$\text{Theorem 1: } T_G^{x,w} = \frac{1}{|G|} \sum_{g \in G} \chi(g) P_w(g),$$

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

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^x which corresponds to the character $g \rightarrow \chi(g)$ of the irreducible representation Γ in the group G . P_G^x is defined below:

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

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

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

The coefficient of a typical term $w_1^{b_1} w_2^{b_2} \dots$ in $\text{tr} T_G^{x,w}$

gives the frequency of occurrence of the irreducible representation Γ whose character is χ in the set of spin functions with the weight $w_1^{b_1} w_2^{b_2} \dots$. For example, let $G = O_h$, $D = \{6 \text{ fluorine nuclei}\}$ and $R = \{\alpha, \beta\}$. Set χ 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 3α 's and 3β 's which transform as a reducible representation of the group O_h . An example will be 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 χ occurs in the reducible representation formed by all f in F is given by

$$P_G^x(x_k \rightarrow |R|),$$

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

III. GENERATING FUNCTIONS FOR NUCLEAR SPIN SPECIES

In this section we apply the methods outlined in Sec. II 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 ^{33}S then we consider S and 6F nuclei as separate D sets. The set R for F nuclei contains 2 elements since ^{19}F is a spin $1/2$ nucleus and hence can take two possible spin states. We may associate the weights α and β 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 $\alpha^3\beta^3$ in $\text{tr} T_G^{x,w}$ gives the number of times the irreducible representation whose character is χ occurs in the reducible representation formed by the spin functions containing $a_1\alpha$'s and $b_1\beta$'s. Since Theorem 1 relates $\text{tr} T_G^{x,w}$ to P_G^x , in order to obtain these generating functions for nuclear spin species all that we need to obtain is the set of P_G^x for all χ in O_h . They can be obtained very easily using the character table of the group O_h and are shown in Table I for O_h . From this table using Theorem 1, generating functions for the fluorine species can be obtained easily. To illustrate, consider the species E_g . The nuclear species which belong to this species can be obtained by replacing every x_k by $(\alpha^k + \beta^k)$ in the corresponding P_G^x . The result of this substitution is shown below:

$$P_{E_g}^x = \frac{1}{48} [2x_1^6 - 8x_3^2 + 6x_1^2x_2^2 + 2x_2^3 - 8x_6 + 6x_1^4x_2].$$

TABLE I. $48P_G^X$ for various irreducible representations in the group O_h .

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

Thus,

$$G.F. E_g = \frac{1}{48} [2(\alpha + \beta)^6 - 8(\alpha^3 + \beta^3)^2 + 6(\alpha + \beta)^2(\alpha^2 + \beta^2)^2 + 2(\alpha^2 + \beta^2)^3 - 8(\alpha^6 + \beta^6) + 6(\alpha + \beta)^4(\alpha^2 + \beta^2)] .$$

The above expression on simplification yields

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

Thus there is one E_g in the reducible representation spanned by spin functions containing 5α 's and 1β , $2E_g$ in the reducible representation spanned by spin functions containing 4α 's and 2β 's and so on. The generating functions thus obtained for the fluorine species are shown in Table II. Looking at these generating functions the spin species can be obtained immediately. The coefficient of a typical term $\alpha^a\beta^b$ in a generating function corresponding to the species Γ gives the number of functions belonging to the species Γ with the spin quantum number $m_x = (a - b)/2$. When we arrange these species according to their m_x values they separate into spin multiplets with m_x varying from $-S$ to S . For example, the generating function which corresponds to A_{1g} gives rise to species ${}^1A_{1g}$ and ${}^3A_{1g}$. In this manner when we group the spin species into multiplets as obtained from their generating functions we obtain the fluorine species as ${}^1A_{1g}$, ${}^3A_{1g}$, ${}^1A_{2g}$, 5E_g , 3E_g , ${}^3T_{2g}$, ${}^1A_{2u}$, ${}^5T_{1u}$, ${}^1T_{1u}$ and ${}^3T_{2u}$. The spin species of the ${}^{33}\text{S}$ nucleus is easily obtained as ${}^4A_{1g}$ since the spin of ${}^{33}\text{S}$ nucleus is $3/2$. The overall spin species is the direct product of sulfur and fluorine 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 series³⁵:

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

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

${}^4T_{1u}(2)$, ${}^2T_{1u}$, ${}^6T_{2u}$, ${}^4T_{2u}$ and ${}^2T_{2u}$. All these spin species span a reducible representation which is decomposed into the irreducible representation 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 Γ^{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 Γ^{spin} only rather than the whole spin multiplet pattern. This will be considered separately in the next section.

IV. STATISTICAL WEIGHTS OF ROVIBRONIC STATES

In order to obtain the statistical weights of the rovibronic states, we need the irreducible representations contained in Γ^{spin} , the reducible representation spanned by the spin functions. We will use Corollary 1 outlined in Sec. IIB to find Γ^{spin} . Let us start with the same SF_6 example. Let us find the representation spanned by the fluorine species. Since the set R has 2 elements (2 spin states of fluorine), the frequency of occurrence of an irreducible representation Γ in Γ_F^{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. Corollary 1.) For example, number of times A_{1g} occurs in the fluorine 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

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

TABLE II. Generating functions of fluorine species of SF_6 .

Irreducible representation	
A_{1g}	$\alpha^6 + \alpha^5\beta + 2\alpha^4\beta^2 + 2\alpha^3\beta^3 + 2\alpha^2\beta^4 + \alpha\beta^5 + \beta^6$
A_{2g}	$\alpha^3\beta^3$
E_g	$\alpha^5\beta + 2\alpha^4\beta^2 + 2\alpha^3\beta^3 + 2\alpha^2\beta^4 + \alpha\beta^5$
T_{1g}	0
T_{2g}	$\alpha^4\beta^2 + \alpha^3\beta^3 + \alpha^2\beta^4$
A_{1u}	0
A_{2u}	$\alpha^3\beta^3$
E_u	0
T_{1u}	$\alpha^5\beta + \alpha^4\beta^2 + 2\alpha^3\beta^3 + \alpha^2\beta^4 + \alpha\beta^5$
T_{2u}	$\alpha^4\beta^2 + \alpha^3\beta^3 + \alpha^2\beta^4$

Since the ^{33}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. III. The beauty of this method is that it did not require the character of Γ^{spin} , a reducible representation of dimension 256, to decompose it into its irreducible components. For C^{12} -triphenylene Γ^{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 the set of 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 Γ_H^{spin} are shown below:

$$N(A_1') = \frac{1}{8} (2^{12} + 2 \cdot 2^4 + 3 \cdot 2^6) = 720,$$

$$N(A_2') = \frac{1}{8} (2^{12} + 2 \cdot 2^4 - 3 \cdot 2^6) = 656,$$

$$N(E') = \frac{1}{8} (2 \cdot 2^{12} - 2 \cdot 2^4) = 1360.$$

Thus

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

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

$$P^{A_1'} = \frac{1}{8} [x_1^{18} + 2x_3^6 + 3x_2^9],$$

$$P^{A_2'} = \frac{1}{8} [x_1^{18} + 2x_3^6 - 3x_2^9],$$

$$P^{E'} = \frac{1}{8} [2x_1^{18} - 2x_3^6].$$

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

$$N(A_1') = \frac{1}{8} (2^{18} + 2 \cdot 2^6 + 3 \cdot 2^9) = 43\,968,$$

$$N(A_2') = \frac{1}{8} (2^{18} + 2 \cdot 2^6 - 3 \cdot 2^9) = 43\,456,$$

$$N(E') = \frac{1}{8} (2 \cdot 2^{18} - 2 \cdot 2^6) = 87\,360.$$

Hence

$$\Gamma_C^{\text{spin}} = 43\,968A_1' + 43\,456A_2' + 87\,360E'$$

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

$$\Gamma^{\text{spin}} = 178\,973\,696A_1' + 178\,940\,928A_2' + 357\,913\,600E'.$$

As a last example we consider triphenylene with all pro-

tons replaced by deuterium and all carbons being ^{12}C . (The case of ^{13}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 nuclei is 3. Thus $N(A_1')$, $N(A_2')$, and $N(E')$ are the ones shown below.

$$N(A_1') = \frac{1}{8} (3^{12} + 2 \cdot 3^4 + 3 \cdot 3^6) = 88\,965,$$

$$N(A_2') = \frac{1}{8} (3^{12} + 2 \cdot 3^4 - 3 \cdot 3^6) = 88\,236,$$

$$N(E') = \frac{1}{8} (2 \cdot 3^{12} - 2 \cdot 3^4) = 177\,120.$$

Hence the deuterium spin species Γ_D^{spin} is as follows:

$$\Gamma_D^{\text{spin}} = 88\,965A_1' + 88\,236A_2' + 177\,120E'.$$

Once Γ^{spin} is known obtaining the statistical weights is not difficult. This is done by stipulating that $\Gamma^{\text{spin}} \otimes \Gamma^{\text{rv}}$ should contain Γ^{int} , where Γ^{rv} is the rovibronic species and Γ^{int} is the species of the overall internal wave function. By the Pauli exclusion principle Γ^{int} must be antisymmetric and hence the character of Γ^{int} must be antisymmetric with respect to *permutations alone* for fermions. For bosons it must be symmetric.

Let us now find the statistical weights of the rovibronic species of the molecules we have been considering as examples. We start with SF_6 . The overall internal wave function 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} . Γ^{spin} for SF_6 was already obtained. Using the condition that $\Gamma^{\text{spin}} \otimes \Gamma^{\text{rv}}$ 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 parentheses:

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

For the molecule triphenylene (^{12}C -H) Γ^{int} can be A_1' or A_1'' . For the normal triphenylene (^{12}C -H), the statistical weights of the rovibronic levels are indicated below:

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

Since 18 ^{13}C nuclei of ^{13}C -triphenylene transform as x_2^9 under the operation c_2 and since they are fermions Γ^{int} is A_2' or A_2'' . Here the statistical weights are as follows:

$$A_1'(178\,940\,928), A_2'(178\,973\,696), E'(357\,913\,600), A_1''(178\,940\,928), A_2''(178\,973\,696), E''(357\,913\,600).$$

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

$$A_1'(88\,965), A_2'(88\,236), E'(177\,120), A_1''(88\,965), A_2''(88\,236), E''(177\,120).$$

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.

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