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DETERMINATION OF THE TOTAL NUCLEAR SPIN IN A ROVIBRONIC STATE APPLICATION TO THE MOLECULES SF₆ AND PF₅

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Résumé. — Pour calculer la structure hyperfine magnétique des raies de vibration-rotation, il faut répondre d'abord à la question suivante : étant donné un état rovibronique, quelles sont les valeurs du spin nucléaire total qui peuvent lui être associées ? Nous donnons trois approches pour résoudre ce problème et nous présentons les résultats pour PF₅ et SF₆.

Abstract. — In calculating the hyperfine magnetic structure of vibration-rotation lines, one question arises first : which values of the total nuclear spin are allowed in a given rovibronic state ? We present three approaches to solve this problem and the application to SF₆ and PF₅ is worked out.

We consider a molecule having n identical nuclei each nucleus having a spin i . It has been established for a long time [1] in Molecular Spectroscopy how one should calculate the statistical weights : one determines the types of symmetry of the nuclear spin functions in the point group of the molecule. Recently, saturated absorption infrared spectra of CH₄ and SF₆ have been reported [2, 3], showing the hyperfine structure of vibration-rotation lines. This structure is due to the spin-spin and spin-rotation magnetic couplings, and in order to calculate these interactions, one must know, in addition to the symmetry types, the values of the total nuclear spin.

More precisely, given a rovibronic state Ψ_{evr} (which may belong to a degenerate level), the complete wave function must obey the Pauli principle and as a result only a subspace of the $(2i + 1)^n$ independent nuclear spin functions Φ_j may be used to construct the complete wave function. As a consequence, among all the functions which correspond to the possible values for the total nuclear spin I and its projection M_I , some are eliminated and cannot be associated with the space function Ψ_{evr} . We shall present methods which allow us to determine which values of I and M_I must be retained.

The result is only known for very simple molecules (the diatomics) or for some molecules for which the magnetic structure has already been studied in the fundamental vibronic state : NH₃ [4], CH₄ [5]. For these two molecules the result is simple : there is a one-to-one correspondance between the value of the total spin and the symmetry type (which is not the case for SF₆ nor PF₅) and no general method was needed. In reference [5], the particular *partitioning* method followed by the authors has also been applied to CD₄ for which a one-to-one correspondance is not valid and, in reference [12], the case of C₂H₄ is studied but with a method which is not easily extended to molecules such as SF₆.

We shall use G to designate the point group of the molecule and $D^{(\mu)}$ its irreducible representations (I.R.). $\Phi_{\beta}^{(\mu),\rho}$ will designate functions which are combinations of the Φ_j and which are basis for the I.R. $D^{(\mu)}$; β numbers the components in the basis of a I.R. $D^{(\mu)}$ ($\beta = 1, \dots, d_{\mu}$ if d_{μ} is the dimension of the I.R. $D^{(\mu)}$), ρ distinguishes different functions with the same (μ) and the same β ($\rho = 1, \dots, r_{(\mu)}$ if the I.R. $D^{(\mu)}$ can be constructed $r_{(\mu)}$ times with the Φ_j). We shall say that the $\Phi_{\beta}^{(\mu),\rho}$ are obtained by symmetry adapting the nuclear spin functions Φ_j in the group G . Similarly, we shall denote by S_n the group of permutation of n symbols, $D^{(\lambda)}$ its I.R. (λ represents a Young diagram $\lambda_1, \lambda_2, \dots, \lambda_n$), and $\Phi_{\alpha}^{(\lambda),\tau}$ are the nuclear spin functions symmetry adapted in S_n .

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In the rotation group $SO(3)$, the I.R. correspond to the values of the total spin I , the values of its projection, M_I , number the components of the I.R. basis and $\Phi_{M_I}^{(I),\sigma}$ are the symmetry adapted spin functions.

Let us recall first some essential results deduced from standard group theory [6, 7] : the $(2i+1)^n$ functions Φ_j form a basis for a reducible representation of the rotation group $SO(3)$; this representation, which will be noted $D^{(S)}$, is the n -th power of the I.R. $D^{(I)}$ ($I = i$) of $SO(3)$. Because of the commutation properties between the operations of the rotation group and the permutations of S_n , the matrices of the representation $D^{(S)}$, when expressed in the symmetrized basis $\Phi_{\alpha}^{(\lambda),\tau}$, have the following very simple structure :

$$D_{\{\lambda\},\tau,\alpha;\{\lambda'\},\tau',\alpha'}^{(S)} = \delta_{\{\lambda\}\{\lambda'\}} \delta_{\alpha\alpha'} M_{\tau\tau'}^{(\lambda)}. \quad (1)$$

In this basis, the representation $D^{(S)}$ of $SO(3)$ is thus decomposed in blocks, $M_{\tau\tau'}^{(\lambda)}$; each block is of dimension $r_{\{\lambda\}}$, $r_{\{\lambda\}}$ being the number of times the I.R. $D^{(\lambda)}$ occurs. Each of these blocks may be decomposed as a sum of I.R. of $SO(3)$; these decompositions lead to a new basis of spin functions $\Phi_{\alpha,M_I}^{(\lambda),(I),\xi}$. Each of these functions has a definite type of symmetry in the group S_n and corresponds to a definite value for the total nuclear spin and its projection. This allows us to make a correspondance between some of the possible values for the total nuclear spin I and each I.R. $D^{(\lambda)}$ of S_n . We must emphasize that if a value of I is associated with an I.R. $D^{(\lambda)}$, it means that the I.R. $D^{(I)}$ of $SO(3)$ is contained in the representation $M^{(\lambda)}$ and so all the values of M_I , $M_I = -I, \dots, +I$, will be associated with $D^{(\lambda)}$.

In the preceding paragraph, we have considered first the group S_n and secondly the group $SO(3)$ in the construction of the functions $\Phi_{\alpha,M_I}^{(\lambda),(I),\xi}$ which are symmetry adapted in both groups. There is obviously a second way to construct them, by considering the two groups in the inverse order, first $SO(3)$ secondly S_n : the $(2i+1)^n$ functions $\Phi_{M_I}^{(I),\sigma}$ form a basis for a reducible representation of S_n ; the matrices of this representation have non-zero off-diagonal elements only if the two basis functions have identical I and M_I . These blocks, of dimension $r_{(I)}$, will then be decomposed as sums of I.R. of S_n , $D^{(\lambda)}$ (or as sums of I.R. of any subgroup of S_n). We shall present three methods to obtain the results we look for ; the first two methods are deduced from the first way of constructing the $\Phi_{\alpha,M_I}^{(\lambda),(I),\xi}$ (S_n then $SO(3)$), the third method is based on the second way ($SO(3)$ then S_n).

In the case where $i = \frac{1}{2}$, a great simplification occurs : only one value of I is associated with each $D^{(\lambda)}$: it can be shown that, first, the only I.R. of S_n appearing in the reduction of $D^{(S)}$ are characterized by the Young diagrams such that : $\{\lambda\} = \{\lambda_1, \lambda_2, 0, 0, \dots, 0\}$ and, second, that the blocks $M_{\tau\tau'}^{(\lambda)}$ form the

I.R. of $SO(3)$ corresponding to $I = \frac{\lambda_1 - \lambda_2}{2}$. When $i > \frac{1}{2}$, one must decompose the matrices $M_{\tau\tau'}^{(\lambda)}$ as sums of I.R. of $SO(3)$. In order to do this, it is possible either to calculate the characters of these matrices [6], or to follow an iteration method [7].

To apply all this to a molecule, one must introduce the fact that the point group G is in general isomorphic not to S_n but to a subgroup of $S_n^* = S_n \times C_i$, where C_i is the two-elements group constituted by identity and inversion ⁽¹⁾. Each I.R. of S_n^* , $D^{(\lambda)p}$ ($p = g$ or u), supplies a reducible representation of G which can be decomposed on the I.R. $D^{(u)}$ of G . Conversely, each I.R. $D^{(u)}$ of G induces, by extending if needed its space of representation, a representation of S_n^* which can be decomposed on the I.R. $D^{(\lambda)p}$. According to Frobenius' theorem, if the I.R. $D^{(u)}$ induces the representation $\sum_{\{\lambda\}p} a_{\{\lambda\}p} D^{(\lambda)p}$, it implies that the representation of G supplied by the matrices $D^{(\lambda)p}$ contains $a_{\{\lambda\}}$ times the I.R. $D^{(u)}$ of G . In particular, the representation of S_n^* which satisfies the Pauli principle, being of dimension 1, supplies only one I.R. of G (the I.R. which satisfies the Pauli principle in G) and, according to Frobenius, can be induced only by this I.R. of G . This gives a proof that the statistical weights obtained from any subgroup of S_n^* are identical to those one would obtain from S_n^* .

From all the previous considerations, we can state that three methods are possible to determine which values of I may be associated with a rovibronic state $\Psi_{\text{evr}}^{(u)}$ belonging to the symmetry type $D^{(u)}$:

1st METHOD. — a) One determines which I.R. $D^{(\lambda)p}$ of S_n^* are induced by the I.R. $D^{(u)}$ of G ;

b) from a) one deduces which symmetry types $D^{(\lambda')p'}$ the nuclear spin functions must belong to, so that the complete wavefunction obeys the Pauli principle ;

c) from the correspondance between the values of I and each $D^{(\lambda')p'}$, one finds the values of I for the state $\Psi_{\text{evr}}^{(u)}$.

2nd METHOD. — We can restrict the use of S_n^* to the spin functions :

a) one determines the I.R. $D^{(u')}$ of G to which the spin functions must belong so that the Pauli principle is satisfied ;

b) one determines the I.R. $D^{(\lambda')p'}$ induced by $D^{(u')}$;

c) as in 1c).

3rd METHOD. — We can avoid introducing the group S_n^* and work only in the point group G . The principle of this method is also to construct doubly

⁽¹⁾ In the inversion of the space fixed axes, the spin functions are gerade and the previous results of group theory can immediately be extended from the two groups S_n and $SO(3)$ to the two groups S_n^* and $O(3)$.

(*) The cycles structure of the permutation operating on the indices of the spins is given under the geometrical notation.

As a sample application of our tables, let us take two examples for SF₆ :

a) given a rovibronic level of type A_{2g} ; the spin function must be of type A_{1g} or A_{1u}. It is only possible to construct 10 spin functions of type A_{1g} and which correspond respectively to the spin quantum numbers :

$$\begin{aligned} I = 3, M_I = -3 ; \quad I = 3, M_I = -2 ; \\ I = 3, M_I = -1 ; \quad I = 3, M_I = 0 ; \\ I = 3, M_I = 1 ; \quad I = 3, M_I = 2 ; \\ I = 3, M_I = 3 ; \quad I = 1, M_I = -1 ; \\ I = 1, M_I = 0 ; \quad I = 1, M_I = 1 ; \end{aligned}$$

b) given a rovibronic level of type F_{2g} ; the spin functions must be of type F_{1u} or F_{1g}. It is only possible to construct six basis of type F_{1u}. Each basis is composed of three functions, each of these three functions may be taken as an eigenfunction of I² and I_z with the same value of I and M_I for all three. The six basis correspond respectively to the following values of I and M_I :

$$\begin{aligned} I = 2, M_I = -2 ; \quad I = 2, M_I = -1 \\ I = 2, M_I = 0 ; \quad I = 2, M_I = -1 \\ I = 2, M_I = 2 ; \quad I = 0, M_I = 0 . \end{aligned}$$

Finally, we shall give an example of application of method 1 for a level A₁' of PF₅ so that the reader be convinced that different methods give the same result.

In S₅^{*}, symmetry adapted nuclear spin functions are of type D^{(5)g}, D^{(4,1)g} and D^{(3,2)g} and symmetry adapted vibration-rotation functions induced by a A₁' function are D^{(5)g}, D^{(4,1)g}, D^{(3,2)g}, D^{(13)u}, D^{(2,13)u}, D^{(22,1)u}. According to Pauli, these space functions may be associated with the spin functions D^{(5)g} (associated with D^{(13)u}), D^{(4,1)g} (associated with D^{(2,13)u}) and D^{(5,2)g} (associated with D^{(22,1)u}).

To these symmetry adapted spin functions correspond respectively the values of I, 5/2, 3/2 and 1/2 and so these three values of the total nuclear spin exist for a A₁' vibration-rotation level. The same conclusion may be read in table II since, according to Pauli, the spin functions must be A₁' or A₁' in D_{3h} for a A₁' vibration-rotation level.

TABLE II
Correspondance between the values of the total nuclear spin I and the symmetry types of the spin functions for PF₅

		Classes of the operations (*) of the point group D _{3h}						
		E 1 ⁵	2C ₃ 1 ² 3 ¹	3C ₂ 1 ¹ 2 ²	σ _h 1 ³ 2 ¹	2S ₃ 2 ¹ 3 ¹	3σ _v 1 ³ 2 ¹	
χ _R ^(I)	I = 5/2	1	1	1	1	1	1	A ₁ '
	I = 3/2	4	1	0	2	- 1	2	A ₁ ' + A ₂ ' + E'
	I = 1/2	5	- 1	1	1	1	1	A ₁ ' + E' + E''

(*) The cycles structure of the permutation operating on the indices of the spins is given under the geometrical notation.

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