The Statistical Weights of the Rotational Levels of Polyatomic Molecules, Including Methane, Ammonia, Benzene, Cyclopropane and Ethylene

E. Bright Wilson

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The Statistical Weights of the Rotational Levels of Polyatomic Molecules, Including Methane, Ammonia, Benzene, Cyclopropane and Ethylene

E. Bright Wilson, Jr.,* *Mallinckrodt Chemical Laboratory, Harvard University*

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A general method is described for calculating the statistical weights (degeneracies) of the energy levels of polyatomic molecules. Wave functions for a molecule are assumed to be expressible as linear combinations of products of the electronic, vibrational, rotational and nuclear spin functions. By using standard methods of group theory, the number of linear combinations of these products are found having the correct symmetry with respect to those permutations of identical atoms which are equivalent to rotations of the molecule. It is not necessary to find the combinations themselves. The molecules CH_4, CD_4, CH_3D, CHD_3, CH_2D_2, CH_3X, CD_3X, NH_3, ND_3, C_6H_6, C_3H_6 and C_2H_2 are treated. In addition noncombining species in polyatomic molecules and the splitting of energy levels due to the multiplicity of equilibrium configurations are discussed. Tables of statistical weights are given for the above molecules which could be used to interpret alternating intensities in rotation-vibration spectra or for more exact calculations of thermodynamic quantities than are usually made.

SEVERAL investigators[1] have calculated the quantum weights of the rotational states of a number of polyatomic molecules and the principles involved are well known. This paper indicates how such calculations can be considerably simplified (especially for complicated molecules) by the application of group theory. Methane is used as an illustration.

Construction of Approximate Wave Functions

The wave function for a molecule is usually approximately expressed as a product of functions of the various coordinates; i.e.,

$$\psi = \psi_E \psi_V \psi_R \psi_T \psi_S, \tag{1}$$

where the subscripts E, V, R, T and S indicate that the corresponding factor is a function of the electronic (including electron spin), vibrational, rotational, translational and nuclear spin coordinates. The electronic, vibrational and rotational wave functions depend on the choice of equilibrium configuration of the nuclei, regarded as distinguishable. Thus in defining the Eulerian angles θ, φ, and χ for $\psi_R(\theta, \varphi, \chi)$ it is necessary to define the moving Z' axis in terms of certain specified nuclei.

For this reason the wave function of Eq. (1) is not unique; there will exist a number of others, obtained from it by permuting identical nuclei. Some of these permutations may not, however, yield independent wave functions, since they may correspond to rotation of the molecule and therefore can be expressed in terms of other wave functions of the set in a manner which will be discussed later. Fig. 1 illustrates the two independent configurations for methane.

In addition to the degeneracy due to this cause, there may exist additional degeneracy due to the fact that ψ_R, ψ_S and sometimes ψ_V and ψ_E may themselves be degenerate. Thus for CH_4 ψ_S is 2^4 or 16-fold degenerate while ψ_S for CD_4 is 3^4 or 81-fold degenerate. Moreover, ψ_R for a spherical top (such as methane) has a degeneracy $(2J+1)^2$ for the energy level with quantum number J.

Although no one of the functions ψ of the type of Eq. (1) possesses such symmetry, the correct wave function for the molecule must be either completely symmetrical to interchange of members of a given set of identical particles or it must be completely antisymmetrical to such an interchange. Since protons obey Pauli's principle,

[1] F. Hund, Zeits. f. Physik **43**, 788 (1927); **43**, 805 (1927). These papers describe Hund's general method and treat NH_3; W. Elert, Zeits. f. Physik **51**, 6 (1928). This paper treats CH_4 by Hund's method which in this case is much more difficult than the group theory method; D. M. Dennison, Rev. Mod. Phys. **3**, 280 (1931).
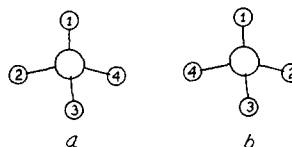
Fig. 1. The two different configurations or "frameworks" for methane.

CH$_4$ has antisymmetrical wave functions whereas CD$_4$ has symmetrical wave functions. In order to obtain a function with the proper symmetry character it is necessary to form linear combinations of the degenerate functions discussed above. The number of such combinations with the correct symmetry properties which can be formed is the quantum weight for that energy level.

In forming these combinations we first combine those functions for a given energy which correspond to the same configuration of the nuclei; i.e., the same "framework" of atoms, say a of Fig. 1. We form the combinations so that each one has the correct symmetry with respect to those permutations of identical particles which correspond to rotations of the molecule without change of framework. When we have done this for each framework, combinations involving functions based on different frameworks are made in such a manner that the resulting wave functions have the correct symmetry with respect to all possible permutations of identical nuclei.

In finding the number of combinations of functions based on one framework and possessing the correct symmetry properties, we use the methods of group theory.[2] The permutations of identical particles which are equivalent to rotations of the molecule form a group. The set of functions $\psi_E\psi_V\psi_R\psi_S$ based on one framework and belonging to one energy level constitute the basis of a reducible representation of this group which, by the construction of linear combinations, can be reduced so that the combinations divide into sets each of which forms an irreducible representation of the group. Only one certain irreducible representation will possess the required symmetry properties; we therefore seek the number of combinations of the functions $\psi_E\psi_V\psi_R\psi_S$ which correspond to this particular irreducible representation. (In methane this is the representation A of Table I, since all the rotations are equivalent to even permutations.) It is this number which is given by the formal methods of group theory without the need of

[2] See, for example, E. Wigner, *Gruppentheorie*, Vieweg and Sohn, 1931; B. L. van der Waerden, *Die gruppentheoretische Methode in der Quantenmechanik*, Springer, Berlin, 1932; A. Speiser, *Die Theorie der Gruppen von endlichen Ordnung*, Springer, Berlin, 1927; Also R. S. Mulliken, Phys. Rev. **43**, 279 (1933).

TABLE I. *Irreducible representations of the group* **T**. $N = 12$.

T	E	$3C_2$	$4C_3$	$4C_3'$
A	1	1	1	1
E_1	1	1	ω	ω^2
E_2	1	1	ω^2	ω
T	3	-1	0	0
		$\omega = e^{2\pi i/3}$		

actually constructing the combinations themselves.

The work is further simplified by the fact that the symmetry of the set $\psi_E\psi_V\psi_R\psi_S$ can be obtained by finding the symmetry of ψ_E, ψ_V, ψ_R and ψ_S separately and then taking the "direct product" of their irreducible components. We shall therefore study each of these functions separately.

The electronic wave function ψ_E is ordinarily completely symmetrical for the normal state and the modifications in the method which are necessary in case this is not true will be obvious. The translational function ψ_T does not involve internal coordinates and is therefore symmetrical.

SYMMETRY OF THE ROTATIONAL FUNCTIONS FOR METHANE

The functions $\psi_R = \psi_{JKM}(\theta, \varphi, \chi)$ for methane are the solutions of the spherical top wave equation. The angles θ, φ and χ are the Eulerian angles, θ and φ being the ordinary polar coordinates of an arbitrarily chosen axis in the molecule. The group of permutations which correspond to rotations is in methane isomorphous with the symmetry point group **T**, which consists of those pure rotations which carry methane into itself. The irreducible representations of **T** have the characters[3] shown in Table I.

The symbols E, C_2, C_3 refer to the operations identity, twofold rotation, and threefold rotation, respectively. C_3' differs from C_3 in the sense of rotation. The symbols A, E_1, E_2 and T represent the irreducible representations. Applied to Fig. 1a, one C_2 is equivalent to the permutation $(12)(34)$ while one C_3 is equivalent to (234), both of which are even permutations.

[3] This table is taken from R. S. Mulliken, Phys. Rev. **43**, 279 (1933) which contains similar tables for all the crystallographic point groups; See also E. Wigner, Gött. Nachr., p. 133 (1930) and L. Tisza, Zeits. f. Physik **82**, 48 (1933).

TABLE II. *Characters for the representation of T formed by ψ_R.*

$(p, k = 0, 1, 2, \cdots.$ Multiply all characters by $2J+1$.$)$

	χ'_E	χ'_{C_2}	χ'_{C_3}	$\chi'_{C_{3'}}$
$J = 6p+k$	$12p+2k+1$	$(-1)^k$	$(2/\sqrt{3}) \sin \frac{2}{3}\pi(1-k)$	$(2/\sqrt{3}) \sin \frac{2}{3}\pi(1-k)$

In order to reduce[3a] the representation formed by the functions $\psi_{JKM}(\theta, \varphi, \chi)$ for a given value of J it is necessary to know how these functions transform under the operations C_2 and C_3. If we choose the Z' axis in the molecule so that it coincides with one of the threefold axes, the operation C_3 will affect only the angle χ, changing it to $\chi \pm \frac{2}{3}\pi$. Since χ enters $\psi_{JKM}(\theta, \varphi, \chi)$ only by way of the factor[4] $e^{iK\chi}$, the transformation C_3 has the effect

$$\psi_{JKM}(\theta, \varphi, \chi) \xrightarrow{C_3} \psi_{JKM}(\theta, \varphi, \chi \pm \tfrac{2}{3}\pi)$$
$$= e^{\pm(2\pi i/3)K}\psi_{JKM}(\theta, \varphi, \chi). \quad (2)$$

The character[5] χ'_{C_3} (which is the sum of the diagonal elements in the transformation matrix for C_3) is therefore[6]

$$(2J+1) \sum_{K=-J}^{J} e^{(2\pi i/3)K},$$

which has the values given in Table II.

With the choice of axis used above it is awkward to obtain χ'_{C_2}. However, we may make use of the fact that the choice of axis in a spherical top molecule is entirely arbitrary. Changing the axis is equivalent to a linear transformation of the functions $\psi_{JKM}(\theta, \varphi, \chi)$, with J and M fixed. Furthermore the diagonal sum of a matrix is invariant under such transformations. It is therefore convenient to calculate χ'_{C_2} with the axis coinciding with C_2, so that

$$\psi_{JKM}(\theta, \varphi, \chi) \xrightarrow{C_2} \psi_{JKM}(\theta, \varphi, \chi + \pi)$$
$$= e^{K\pi i}\psi_{JKM}(\theta, \varphi, \chi), \quad (3)$$

which yields

$$\chi'_{C_2} = (2J+1) \sum_{K=-J}^{J} (-1)^K,$$

whose values are also given in Table II.

These characters and those in Table I are used in the standard group theory formula[7] to obtain the symmetries of the rotational functions ψ_R. These are given in Table III. (Since E and T

TABLE III. *Symmetry of the rotational functions for methane.*

		$(p=0, 1, 2, 3, \cdots; E=E_1+E_2)$
$J=6p$	$(2J+1)$	$\{(p+1)A + \quad p \quad E+ \quad 3p \quad T\}$
$J=6p+1$	$(2J+1)$	$\{ \quad p \quad A + \quad p \quad E+(3p+1)T\}$
$J=6p+2$	$(2J+1)$	$\{ \quad p \quad A +(p+1)E+(3p+1)T\}$
$J=6p+3$	$(2J+1)$	$\{(p+1)A + \quad p \quad E+(3p+2)T\}$
$J=6p+4$	$(2J+1)$	$\{(p+1)A +(p+1)E+(3p+2)T\}$
$J=6p+5$	$(2J+1)$	$\{ \quad p \quad A +(p+1)E+(3p+3)T\}$

are degenerate representations their coefficients in Table III need to be multiplied by 2 and 3, respectively, to give the number of linear combinations with these symmetries.)

SYMMETRY OF VIBRATIONAL FUNCTIONS

A permutation of identical particles equivalent to a rotation of the molecule may affect ψ_V also. A simple illustration is shown in Fig. 2. Before interchange the distance (2–3) is greater than (1–3); after interchange these distances have exchanged magnitudes. But the normal coordinate for this motion is

$$Q = (2\text{–}3) - (1\text{–}3), \quad (4)$$

so that interchanging the magnitudes of these distances changes the sign of Q.

Since the wave function ψ_V is a function of the normal vibrations Q_k, the functions ψ_V may be transformed when the Q_k's are. In particular, the wave functions for a state with one quantum of one normal vibration excited transform in the same manner as the corresponding normal coordinates Q for that vibration.[7a] It is known[8]

[3a] The results of this paragraph may also be obtained from C. Eckart, Rev. Mod. Phys. **2**, 344 (1930) Eq. (111).

[4] Reiche and Rademaker, Zeits. f. Physik **39**, 444 (1926).

[5] See reference 2.

[6] The factor $(2J+1)$ comes from the $2J+1$ values of M associated with a given J.

[7] See reference 2.

[7a] The wave functions corresponding to overtone and combination levels usually have transformation properties different from those possessed by the normal coordinates, but obtainable from them. See Tisza, reference 3.

[8] For the application of group theory to molecular vibrations see E. Wigner, Gött. Nachr., p. 133 (1930); L.
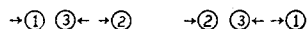
FIG. 2. The effect of the permutation (12) on one of the normal coordinates of a linear triatomic molecule.

that the normal coordinates Q_k and the vibrational wave functions ψ_V have symmetry properties corresponding to the various irreducible representations of the symmetry point group for the molecule. This point group may contain reflections, inversions, etc., besides pure rotations. We are only interested in the pure rotations, but the effect of these on ψ_V may be easily obtained from a knowledge of the irreducible representation of the complete symmetry group to which ψ_V belongs.

Methane belongs to the point group[9] $\mathbf{T}_d$ (of which $\mathbf{T}$ is the rotational subgroup). Using the notation of Mulliken,[10] we can find[11] that there is one non-degenerate normal vibration (irreducible representation A_1 of $\mathbf{T}_d$), one doubly-degenerate vibration (E), and two triply-degenerate vibrations (T_2). The fundamental levels of ψ_V therefore have these symmetries. In this case it is very simple to find to what representations of $\mathbf{T}$ these various representations of $\mathbf{T}_d$ belong. One finds[10] that A_1 and A_2 of $\mathbf{T}_d$ belong to A of $\mathbf{T}$, E belongs to $E=E_1+E_2$, and T_1 and T_2 belong to T. Therefore, knowing[8] the symmetry of ψ_V with respect to $\mathbf{T}_d$, we can find its symmetry with respect to $\mathbf{T}$.

SYMMETRY OF THE NUCLEAR SPIN FUNCTIONS

The nuclear spin functions ψ_S form a basis of a representation of the group of permutations of identical atoms which are equivalent to rotations. For CH_4 there are 16 functions ψ_S, typical members of which are listed in Table IV, which gives the quantum number m_s for each atom. To obtain the characters for the representation formed by these functions, use is made of the fact that if a given permutation transforms one spin function into a different function that row of the transformation matrix has a zero diagonal

Tisza, Zeits. f. Physik **82**, 48 (1933); E. B. Wilson, Jr., J. Chem. Phys. **2**, 432 (1934).
[9] $\mathbf{T}_d$ contains planes of symmetry, etc., in addition to the pure rotations of $\mathbf{T}$.
[10] R. S. Mulliken, reference 2.
[11] See, for example, E. B. Wilson, Jr., reference 8, Table III, 4.4a.

TABLE IV. *Nuclear spin functions for CH_4.*

	1	2	3	4	No.
I	$+\frac{1}{2}$	$+\frac{1}{2}$	$+\frac{1}{2}$	$+\frac{1}{2}$	1
II–V	$-\frac{1}{2}$	$+\frac{1}{2}$	$+\frac{1}{2}$	$+\frac{1}{2}$ etc.	4
VI–XI	$-\frac{1}{2}$	$-\frac{1}{2}$	$+\frac{1}{2}$	$+\frac{1}{2}$ etc.	6
XII–XV	$-\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$	$+\frac{1}{2}$ etc.	4
XVI	$-\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$	1

element; if it transforms a function into itself, the diagonal element is unity. The character χ' for a given permutation is therefore equal to the number of spin functions unchanged by the given permutation. Thus the permutation $(14)(23)$ (which is equivalent to a twofold rotation) leaves I and XVI invariant and also two functions from VI–XI; the character χ'_{c_2} is therefore 4. Similarly χ'_{c_3} is found to be 4 and evidently χ'_E is 16. Using these data and Table I we find that for CH_4

$$\psi_S = 5A + E + 3T. \tag{5}$$

For CD_4, $m_s = 1$, 0, or -1 so that there are 81 functions ψ_S, of which typical members are given in Table V. From these the characters are

TABLE V. *Nuclear spin functions for CD_4.*

1	2	3	4	No.	1	2	3	4	No.
1	1	1	1		1	-1	-1	-1	-1		1
0	1	1	1	etc.	4	-1	0	0	0	etc.	4
0	0	1	1	"	6	-1	-1	0	0	"	6
0	0	0	1	"	4	-1	-1	-1	0	"	4
0	0	0	0		1	1	1	-1	0	"	12
-1	1	1	1	"	4	0	0	1	-1	"	12
-1	-1	1	1	"	6	-1	-1	1	0	"	12
-1	-1	-1	1	"	4						

found to be $\chi'_E = 81$, $\chi'_{c_2} = 9$, $\chi'_{c_3} = 9$ so that for CD_4

$$\psi_S = 15A + 6E + 18T. \tag{6}$$

SYMMETRY OF $\psi_T \psi_E \psi_V \psi_R \psi_S$

The symmetry of the product of two functions is obtained by the use of the rule that the character χ' for the product of two independent functions is equal to the product of the characters for the two functions. In this way a multiplication table for the irreducible representations A, E, T can be built up. For $\mathbf{T}$ it is given in Table VI.

If a function x has the symmetry E_1, for example, while y has the symmetry T, the

TABLE VI. *Multiplication table for irreducible representations of* T.

A	E_1	E_2	T
E_1	E_2	A	T
E_2	A	E_1	T
T	T	T	$A+E_1+E_2+2T$

product xy has the symmetry given under E_1 and opposite T in Table VI; namely, T.

By using the results of Table III, and Eqs. (5) or (6) in conjunction with Table VI, the symmetry of the functions $\psi_T\psi_E\psi_V\psi_R\psi_S$ can be obtained. It will be later shown that states involving nuclear spin functions of different permutation symmetries do not readily combine. It is therefore convenient to tabulate separately the states with different spin symmetry. The products $\psi_T\psi_E\psi_V\psi_R\psi_S$ must have the symmetry A in order to occur in nature.. The number of linear combinations of these products (based on one framework) with the symmetry A and with the spin symmetry and vibration symmetry shown are listed in Table VII for CH_4 and in Table VIII for CD_4. It will be shown that these numbers are the statistical or quantum weights of the corresponding energy levels of the molecule.

CONSTRUCTION OF THE COMPLETE WAVE FUNCTIONS

The linear combinations enumerated in Tables VII and VIII are functions of all the coordinates, including spin, and have the correct symmetry

properties with respect to those permutations of identical nuclei which correspond to rotations of the framework of nuclei upon which these functions are based. They do not have the correct symmetry with respect to other permutations of the identical atoms, since such permutations alter the framework. However, by adding (with the proper sign) the correct linear combination (call it ψ_A) for the framework A and the corresponding linear combination ψ_B for the framework B, a function can be constructed which has the correct symmetry properties with respect to any permutation of identical atoms. Thus the function

$$\Psi = \psi_A - \psi_B \tag{7}$$

will be completely antisymmetric for any interchange of protons; for example

$$(12)\Psi = \psi_B - \psi_A = -\Psi, \tag{8}$$

while

$$(123)\Psi = (123)\psi_A - (123)\psi_B$$
$$= \psi_A - \psi_B = \Psi, \text{ etc.} \tag{9}$$

Furthermore no new degeneracy is introduced by this step, because even when there are many independent frameworks for a molecule there will be only one combination of the functions based on the different frameworks with the correct symmetry.

To prove this, let us consider the representation of the entire permutation group (not the subgroup we have previously used) by the set of functions ψ_A, ψ_B, etc., one for each framework, the rotational properties of each being the

TABLE VII. *Weights of rotation-vibration levels for* CH_4.
($p=0, 1, 2, \cdots$. Multiply each weight by $2J+1$.)

$\psi_E\psi_V$	ψ_S	$J=6p$	$6p+1$	$6p+2$	$6p+3$	$6p+4$	$6p+5$
A	$5A$	$5(p+1)$	$5p$	$5p$	$5(p+1)$	$5(p+1)$	$5p$
	E	$2p$	$2p$	$2(p+1)$	$2p$	$2(p+1)$	$2(p+1)$
	$3T$	$9p$	$3(3p+1)$	$3(3p+1)$	$3(3p+2)$	$3(3p+2)$	$3(3p+3)$
	Total	$16p+5$	$16p+3$	$16p+5$	$16p+11$	$16p+13$	$16p+11$
E	$5A$	$10p$	$10p$	$10(p+1)$	$10p$	$10(p+1)$	$10(p+1)$
	E	$4p+2$	$4p$	$4p+2$	$4p+2$	$4p+4$	$4p+2$
	$3T$	$18p$	$18p+6$	$18p+6$	$18p+12$	$18p+12$	$18p+18$
	Total	$32p+2$	$32p+6$	$32p+18$	$32p+14$	$32p+26$	$32p+30$
T	$5A$	$15p$	$15p+5$	$15p+5$	$15p+10$	$15p+10$	$15p+15$
	E	$6p$	$6p+2$	$6p+2$	$6p+4$	$6p+4$	$6p+6$
	$3T$	$27p+3$	$27p+6$	$27p+12$	$27p+15$	$27p+21$	$27p+24$
	Total	$48p+3$	$48p+13$	$48p+19$	$48p+29$	$48p+35$	$48p+45$

TABLE VIII. *Weights of rotation-vibration levels for CD_4.*
($p=0, 1, 2, \cdots$. Multiply each weight by $2J+1$.)

$\psi_E\psi_V$	ψ_S	$J=6p$	$6p+1$	$6p+2$	$6p+3$	$6p+4$	$6p+5$
A	15A	$15p+15$	$15p$	$15p$	$15p+15$	$15p+15$	$15p$
	6E	$12p$	$12p$	$12p+12$	$12p$	$12p+12$	$12p+12$
	18T	$54p$	$54p+18$	$54p+18$	$54p+36$	$54p+36$	$54p+54$
	Total	$81p+15$	$81p+18$	$81p+30$	$81p+51$	$81p+63$	$81p+66$
E	15A	$30p$	$30p$	$30p+30$	$30p$	$30p+30$	$30p+30$
	6E	$24p+12$	$24p$	$24p+12$	$24p+12$	$24p+24$	$24p+12$
	18T	$108p$	$108p+36$	$108p+36$	$108p+72$	$108p+72$	$108p+108$
	Total	$162p+12$	$162p+36$	$162p+78$	$162p+84$	$162p+126$	$162p+150$
T	15A	$45p$	$45p+15$	$45p+15$	$45p+30$	$45p+30$	$45p+45$
	6E	$36p$	$36p+12$	$36p+12$	$36p+24$	$36p+24$	$36p+36$
	18T	$162p+18$	$162p+36$	$162p+72$	$162p+90$	$162p+126$	$162p+144$
	Total	$243p+18$	$243p+63$	$243p+99$	$243p+144$	$243p+180$	$243p+225$

same. There will be N/σ of these functions if N is the number of permutations in the group and σ the number of permutations equivalent to rotations (the symmetry number). Assume first that we seek symmetric Ψ's. For each ψ_A, etc., there will be σ permutations transforming ψ_A into itself. Each function will therefore contribute the quantity σ to $\Sigma(j)\chi'_j$ and since there are N/σ functions, $\Sigma(j)\chi'_j = N$. The number of linear combinations in the symmetrical irreducible representation is $n_1 = (1/N)\Sigma(j)\chi'_j$ since every permutation has the character unity in this irreducible representation. We thus have $n_1 = 1$ as stated. For the antisymmetrical case, the same result is true, because whereas odd permutations have the character minus one in the antisymmetric irreducible representation, these same permutations will either change one function into another, contributing zero to the character, or they will transform ψ_A, etc., into $-\psi_A$ contributing -1 for each function so transformed. The minus signs cancel and we have the result as before that there is only one completely antisymmetric combination.

The numbers in Tables VII and VIII, which are the degeneracies of ψ_A or ψ_B are therefore the correct degeneracies or weights of Ψ.

As has been pointed out by other writers,[12] statistical mechanical calculations for high temperatures, at which many rotational levels are occupied, can be made with sufficient accuracy by disregarding the alternation in the weights of the various rotational states, assigning to each state the average weight obtained by dividing the total nuclear spin multiplicity (16 for CH_4, 81 for CD_4) by the classical symmetry number (here 12). That this is the correct average weight can be checked by the use of the numbers in Tables VII and VIII.

[12] Ludloff, Zeits. f. Physik **57**, 227 (1929); Mayer, Brunauer and Mayer, J. Am. Chem. Soc. **55**, 37 (1933); Kassel, J. Am. Chem. Soc. **55**, 1351 (1933).

NONCOMBINING SPECIES

Most types of perturbation which cause transitions do not involve the nuclear spin coordinates. Consequently, two states of a molecule with mutually orthogonal spin functions will be noncombining if only such perturbations occur. A well-known example is the case of the hydrogen molecule which may have either singlet or triplet spin functions and therefore exists in two noncombining forms (in the absence of catalysts). The deuterium molecule D_2, on the other hand, can have singlet, triplet, and quintet nuclear spin states, which presumably have long lifetimes. However, the singlet and quintet states have the same permutation symmetry and therefore are associated with the same set of rotational levels. Their equilibrium proportions will thus be the same at all attainable temperatures and there will be no way of changing their relative proportions.

A similar situation exists for polyatomic molecules. The spin functions can be divided according to their permutation symmetry and according to their multiplicity. States with spin functions differing either in symmetry or multiplicity will rarely combine unless a catalyst is present. However, as in D_2, the equilibrium proportions of certain sets of noncombining states will be unaffected by temperature so that for all practical purposes these sets of states constitute the noncombining states of interest. If two spin functions belong to the same irreducible representation of the group of permutations equivalent to rotations of the molecule (a subgroup of the

complete permutation group) the corresponding species will always exist in the same proportions and may be considered for practical purposes as one species. If they belong to different irreducible representations, they may have equilibrium proportions varying with the temperature. This is the justification for the statement previously made that there are three noncombining species in CH_4 and CD_4, having nuclear spin functions with symmetries A, E and T, respectively.

SYMMETRY OF ROTATIONAL FUNCTIONS FOR SYMMETRICAL TOP MOLECULES

In discussing other molecules it is necessary to know the transformation properties of symmetrical top functions. There are two types of rotations of interest. One is a rotation by an angle $2\pi j/n$ about the symmetry axis, where j and n are integers. Such a rotation changes the Eulerian angle χ into $\chi+2\pi j/n$ and therefore has the effect

$$\psi_R = \psi_{JKM}(\theta, \varphi, \chi) \xrightarrow{C_n{}^i} \psi_{JKM}(\theta, \varphi, \chi+2\pi j/n)$$
$$= e^{2\pi ijK/n}\psi_{JKM}(\theta, \varphi, \chi), \quad (10)$$

since the angle χ enters ψ_R only through the factor[4] $e^{iK\chi}$. Since there are only two functions for a given value of J and M and for a given energy; namely, ψ_{JKM} and ψ_{J-KM}, the character for such a rotation C is

$$\chi'_C = e^{2\pi ijK/n}+e^{-2\pi ijK/n} = 2\cos(2\pi jK/n), \quad (11)$$

if $K\neq 0$, and unity if $K=0$. The other type of rotation is a twofold rotation about an axis perpendicular to the symmetry axis and making an angle α with the axis X' which is the origin of the angle χ measuring the rotation of the molecule about its symmetry axis. This rotation corresponds to changing θ into $\pi-\theta$, φ into $\pi+\varphi$ and as can be seen from Fig. 3, χ into $\pi-\chi+2\alpha$. Using the properties[4] of the symmetrical top functions we can find that

$$\psi_{JKM}(\pi-\theta, \pi+\varphi, \pi-\chi+2\alpha)$$
$$= (-1)^{J+\zeta+M}e^{iK(\pi+2\alpha)}\psi_{J-KM}(\theta, \varphi, \chi), \quad (12)$$

where ζ is the larger of $|K|$ and $|M|$. Therefore if $K\neq 0$, the character for this rotation is zero; if $K=0$, the character is $(-1)^J$.
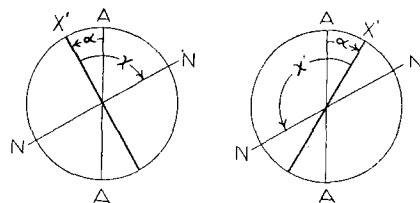

FIG. 3. The $X'Y'$ plane of a symmetrical top, showing the effect on the angle χ of a twofold rotation about an axis AA in the $X'Y'$ plane. NN is the nodal line. χ', the angle after the rotation, equals $\pi-\chi+2\alpha$.

RESULTS FOR CH_3X, CD_3X, NH_3 AND ND_3

These molecules belong to the rotational point group C_3, which has the elements E, C_3 and $C_3{}^2$. Symmetrical top functions have the characters given in Table IX for these symmetry elements, obtained by using Eq. (11). Using these and the characters[13] $\chi_j{}^{(i)}$ for C_3 we find that the rotational functions have the symmetries shown in Table X.

The spin functions for CH_3X (if X has no spin) are given in Table XI. From this it is seen that $\chi'_E=8$, $\chi'_{C_3}=2$, $\chi'_{C_3{}^2}=2$, so that ψ_S has the symmetry $4A+2E$. Combination of this result with the data of Table X yields Table XII

TABLE IX. *Characters for the representation of C_3 formed by ψ_R.*
($p=0, 1, 2, \cdots$. Multiply all characters by $2J+1$.)

	χ'_E	χ'_{C_3}	$\chi'_{C_3{}^2}$
$K=0$	1	1	1
$|K|=3p$	2	2	2
$|K|=3p\pm 1$	2	-1	-1

TABLE X. *Symmetry of the rotational functions for a molecule with rotational symmetry C_3.*
($p=0, 1, 2, \cdots$.)

$K=0$	$(2J+1)A$
$|K|=3p$	$2(2J+1)A$
$|K|=3p\pm 1$	$(2J+1)E$

TABLE XI. *Nuclear spin functions for CH_3X.*

1	2	3	No.
$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	1
$-\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	3
$-\frac{1}{2}$	$-\frac{1}{2}$	$\frac{1}{2}$	3
$-\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$	1

[13] See Mulliken, reference 2, for values of $\chi_j{}^{(i)}$ for C_3.

TABLE XII. *Weights of the vibration-rotation levels of CH_3X.*
($p=0$, 1, 2, $\cdots$. Multiply all weights by $2J+1$.
No spin on X.)

| $\psi_E\psi_V$: ψ_S: | ———A——— | | | ———E——— | | |
	4A	2E	Total	4A	2E	Total
$K=0$	4	0	4	0	4	4
$\lvert K\rvert=3p$	8	0	8	0	8	8
$\lvert K\rvert=3p\pm1$	0	4	4	8	4	12

when the multiplication properties of C_3 are used, which are: $A\times A=A$, $A\times E=E$, $E\times E=2A+E$. The complete wave function must have the symmetry A.

If X has a spin s, these weights must be multiplied by $2s+1$. Thus if X is D, a deuterium nucleus, $2s+1$ has the value 3. Table XII also can be used for NH_3, if all weights are multiplied by three, since nitrogen has a unit nuclear spin.

A similar treatment for CD_3X shows that if X has no spin ψ_S has the symmetry $11A+8E$, from which the weights in Table XIII may be deduced. If X has a spin s, these weights must be multiplied by $2s+1$, so that the factor for CD_3H is 2. By multiplying all weights by 3, Table XIII can also be used for ND_3.

TABLE XIII. *Weights for the vibration-rotation levels of CD_3X.*
($p=0$, 1, 2, $\cdots$. Multiply all weights by $2J+1$.
X has no spin.)

| $\psi_E\psi_V$: ψ_S: | ———A——— | | | ———E——— | | |
	11A	8E	Total	11A	8E	Total
$K=0$	11	0	11	0	16	16
$\lvert K\rvert=3p$	22	0	22	0	32	32
$\lvert K\rvert=3p\pm1$	0	16	16	22	16	38

THE SPLITTING OF ENERGY LEVELS

In certain cases the energy levels which we have previously considered as degenerate are really split into two or more experimentally separable components. A well-known example is NH_3 in which the energy levels are nearly all doublets.[14] This splitting is due to the fact that the nitrogen atom can pass through the plane of the three hydrogen atoms without great difficulty so that it has two equivalent positions of minimum potential energy. Such an inversion corresponds to an interchange of identical hydrogen atoms (which changes the sign of Ψ),

[14] Dennison and Hardy, Phys. Rev. **39**, 938 (1932).

followed by a rotation of the molecule, which may or may not again change the sign of Ψ, depending on the nature of the functions ψ_R. The rotation required is equivalent to the transformation $\theta\to\pi-\theta$, $\varphi\to\pi+\varphi$, $\chi\to\pi-\chi$, which has the following effect on the symmetric top function ψ_{JKM}:

$$\psi_{JKM}(\theta,\varphi,\chi)\to\psi_{JKM}(\pi-\theta,\pi+\varphi,\pi-\chi)$$
$$=(-1)^{J+\zeta+K+M}\psi_{J-KM}(\theta,\varphi,\chi),$$

where ζ is the larger of $\lvert K\rvert$ and $\lvert M\rvert$. From this one finds that the levels with $K=0$ are not split but have total wave functions Ψ which are antisymmetric with respect to inversion when J is even and symmetric when J is odd. When $K\neq0$, the energy level is split into two components to each of which corresponds an equal number of wave functions, one component having functions which are symmetric towards inversion, the other component having antisymmetric functions.

The criterion as to whether or not the splitting is appreciable is the magnitude of the potential hill separating the two forms. Methane also possesses two forms but to pass from one to the other would require passing through too great a potential barrier so that no doubling is observed.

Since the electric moment changes sign on inversion, transitions in absorption occur only between states of opposite symmetry character with respect to inversion, whereas Raman transitions occur between states of like symmetry.

WEIGHTS FOR BENZENE

If benzene is a regular plane hexagon it has the point group symmetry D_{6h}, the rotational subgroup for which is D_6, with the elements E, C_2, $2C_3$, $2C_6$, $3C_2'$, $3C_2''$. Benzene is a symmetrical top, and so by using Eqs. (11) and (12) we can obtain the characters χ' shown in Table XIV for the representation of D_6 formed by ψ_R. Using the character table for D_6 given by Mulliken[2] and the values in Table XIV, we obtain the symmetries of the linear combinations of ψ_R given in Table XV.

The 2^6 nuclear spin functions for C_6H_6 are easily shown by the methods employed for the other molecules to combine to functions with the

TABLE XIV. *Characters for the representation of* D_6 *formed by* ψ_R.
(p, $k = 0, 1, 2, 3, \cdots$. Multiply all characters by $2J+1$.)

	χ'_E	χ'_{C_2}	χ'_{C_3}	χ'_{C_6}	$\chi'_{C_2'}$	$\chi'_{C_2''}$
$K=0$	1	1	1	1	$(-1)^J$	$(-1)^J$
$K=6p+k$	2	$2(-1)^k$	$2\cos 2\pi k/3$	$(-1)^k 2\cos 2\pi k/3$	0	0

symmetries $13A_1 + A_2 + 7B_1 + 3B_2 + 11E^* + 9E_*{}^*$. The total wave function for the molecule must fall in class B_1 since this represents complete antisymmetry.

TABLE XV. *Symmetry of the rotational functions for a molecule with rotational symmetry* D_6.

($p = 0, 1, 2, 3, \cdots$.)

$K=0$, J even:	$(2J+1)A_1$
$K=0$, J odd:	$(2J+1)A_2$
$K=6p$:	$(2J+1)(A_1+A_2)$
$K=6p\pm1$:	$(2J+1)E_*{}^*$
$K=6p\pm2$:	$(2J+1)E^*$
$K=6p\pm3$:	$(2J+1)(B_1+B_2)$

The multiplication properties of the representations of D_6 are

$A_2 \times A_2 = A_1$, $A_2 \times B_i = B_j$, $A_2 \times E^* = E^*$, $A_2 \times E_*{}^* = E_*{}^*$,
$B_i \times B_i = A_1$, $B_1 \times B_2 = A_2$, $B_i \times E^* = E_*{}^*$, $B_i \times E_*{}^* = E^*$,
$E^* \times E^* = E_*{}^* \times E_*{}^* = A_1 + A_2 + E^*$, $E^* \times E_*{}^* = B_1 + B_2 + E_*{}^*$; where $i = 1, 2$, $j = 2, 1$.

With the use of these we can find the symmetry of $\psi_E \psi_V \psi_R \psi_S$ and from that the number of combinations with the total symmetry B_1; i.e., the quantum weights. These are given in Table XVI. Only the total weights are given.

TABLE XVI. *Weights of the vibration-rotation levels of* C_6H_6.
($p = 0, 1, 2, 3, \cdots$. Multiply all weights by $2J+1$.)

$\psi_E \psi_V$:	A_1	A_2	B_1	B_2	E^*	$E_*{}^*$
$K=0$, J even	7	3	13	1	9	11
$K=0$, J odd	3	7	1	13	9	11
$K=6p$	10	10	14	14	18	22
$K=6p\pm1$	11	11	9	9	25	19
$K=6p\pm2$	9	9	11	11	19	25
$K=6p\pm3$	14	14	10	10	22	18

CYCLOPROPANE

The most reasonable model for C_3H_6, cyclopropane, has the point group symmetry D_{3h}, for which the rotational subgroup is D_3. Since the work of finding the weights for this molecule follows exactly the method previously used, only

the results will be listed. These are given in Table XVII.

TABLE XVII. *Weights of the vibration-rotation levels of* C_3H_6.
($p = 0, 1, 2, 3, \cdots$. Multiply all weights by $2J+1$.)

$\psi_E \psi_V$:	A_1	A_2	E
$K=0$, J even	8	16	20
$K=0$, J odd	16	8	20
$K=3p$	24	24	40
$K=3p\pm1$	20	20	44

ETHYLENE—AN ASYMMETRIC TOP

Ethylene[15] will serve as an illustration of how this method is to be used for asymmetric top molecules. The rotational functions for the asymmetrical top are of four kinds, differing in their symmetry with respect to the twofold rotations about the three principal axes of the molecule. Table XVIII gives the symmetries of

TABLE XVIII. *Characters for the representation of* V *formed by the four kinds of asymmetric top functions.*

	χ'_E	$\chi'_{C_2(z')}$	$\chi'_{C_2(y')}$	$\chi'_{C_2(x')}$	Irred. Rep.
$++$	1	1	1	1	A_1
$+-$	1	1	-1	-1	B_1
$--$	1	-1	1	-1	B_2
$-+$	1	-1	-1	1	B_3

these four kinds, which are labeled by the notation $++$, $+-$, etc., introduced by Dennison.[16]

The spin functions for C_2H_4 are 16 in number and have the symmetry $7A_1 + 3B_1 + 3B_2 + 3B_3$, as can be verified by using the methods previously described. The multiplication table for V is: $A_1 \times A_1 = A_1$, $A_1 \times B_i = B_i$, $B_i \times B_i = A_1$, $B_1 \times B_2 = B_3$, $B_1 \times B_3 = B_2$, $B_2 \times B_3 = B_1$. The symmetry of $\psi_E \psi_V \psi_R \psi_S$ can be found by the use of this information and the number of combinations with the symmetry A_1 (which corresponds to antisymmetric or symmetric wave functions)

[15] These weights have been previously calculated by Professor R. M. Badger but have not been published.
[16] D. M. Dennison, Rev. Mod. Phys. **3**, 280 (1931).

TABLE XIX. *Weights for the vibration-rotation levels of C_2H_4.*
(Multiply all weights by $2J+1$.)

$\psi_E\psi_V$:	A_1	B_1	B_2	B_3
$++$	7	3	3	3
$+-$	3	7	3	3
$--$	3	3	7	3
$-+$	3	3	3	7

TABLE XX. *Weights for the vibration-rotation levels of CH_2D_2.*
(Multiply all weights by $2J+1$.)

$\psi_E\psi_V$:	A	B
sym. (K even)	15	21
antisym. (K odd)	21	15

obtained. These are the weights given in Table XIX.

The molecule CH_2D_2 (methane) is also an asymmetric top with the rotational symmetry C_2. There will be only two symmetry classes of rotational levels (with respect to C_2), those symmetrical to the twofold axis and those antisymmetrical. The vibrational and spin functions can likewise be divided into these two classes. The weights obtained are given in Table XX.

In conclusion I should like to express my appreciation to Professor J. H. Van Vleck for suggesting this problem and for valuable criticism in connection with it.

Dielectric Constant Studies

V. Anomalous Dispersion of Lecithin in Viscous Mineral Oils

A. L. FERGUSON, L. O. CASE AND G. HARLOWE EVANS,[*] *Chemical Laboratory, University of Michigan*
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A unique receiver and accompanying cell for determining dielectric constants by the resonance method were constructed. Their design is such as to reduce to a minimum several types of error inherent in the resonance method. Dielectric constant measurements were made on five solutions of lecithin in very viscous mineral oils at three temperatures and at six wavelengths. Three distinct methods were employed: (1) refractometer method—frequency of D line of sodium, (2) resonance method—32.8 m, 94 m, 320 m, 1308 m, (3) bridge method—precision Wheatstone bridge, 1036 cycles. Analyses of the experimental curves and comparisons with theoretical Debye curves definitely indicate dispersion though not of a simple type. Another series of measurements made on one solution at 16 different wavelengths covering the range from 40 m to 5,000,000 m still failed to show any individual simple dispersion regions. A qualitative explanation based on varying viscosities of the components of the solvent, the presence of polar radicals in the solute molecules, and the extensive association of the solute is offered.

E VIDENCE is becoming more convincing that the viscosity affecting the rotation of dipole molecules in an alternating field, referred to as microscopic viscosity, is not the same as that measured by the ordinary method, known as macroscopic viscosity.

The determination of microscopic viscosity by means of dielectric constant measurements is based upon the theoretical work of Debye on anomalous dispersion, the decrease in dielectric constant with increasing frequency. A large absorption of energy occurs simultaneously with anomalous dispersion.

In an alternating electric field four things increasingly oppose the turning of molecular dipoles. These are: Increasing viscosity, increasing particle size, increasing frequency, and decreasing temperature, the last due largely to its effect on the viscosity.

The effect of these factors is to throw the orientation of the molecules out of phase with the applied field. It is this lagging of the molecules behind the field that causes the great absorption of energy in the region of anomalous dispersion.