Term Structure of the Non-Collinear Triatomic Molecule of Type X_2Y

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Group theory methods are applied to the molecule of type X_2Y (e.g., H_2O, SO_2) in which the equilibrium configuration of the nuclei is assumed to be that of an isosceles triangle. Electronic motion, vibration of the nuclei and rotation are successively taken into account, and symmetry with respect to interchange of the two equal nuclei, and with respect to inversion at the origin, is considered. Tables are given which allow one to determine, when the electronic, vibrational and rotational symmetries are known, the symmetry of a given term with respect to interchange of nuclei and inversion. Selection rules for all of the types of symmetry except rotational, are given; the selection rules of the asymmetrical rotator are then obtained from these, with the aid of the tables.

INTRODUCTION

THE fact that even the simplest types of polyatomic molecules are not amenable to exact quantum-mechanical treatment, while even approximate methods are not easily applicable, makes it of interest to consider what information about the term structure of polyatomic molecules may be obtained by the methods of group theory. The applicability of such methods to the problem has already been recognized by several investigators. Thus, Wigner[1] and Tisza[2] have given a thorough treatment of the vibrational motion of polyatomic molecules, while Mulliken[3] has discussed the electronic terms. It is now of interest to investigate also the effect of rotation, and here one will naturally attempt to follow as a program the corresponding treatment of the diatomic molecule by Wigner and Witmer.[4] In what follows, we shall attempt to obtain some information regarding the term structure of a simple triatomic molecule of the type X_2Y (e.g., H_2O) whose equilibrium configuration is that of an isosceles triangle, by the group theory method. We shall disregard the effect of spin for the present, reserving it for a later investigation, and shall consider, successively, electronic motion, vibrational motion of the nuclei, and rotation of the molecule as a whole.

THEORY

If, first, the nuclei are considered as fixed in the equilibrium configuration, the field of force admits the following symmetry operations (cf. Fig. 1):

(1) Identity, E
(2) Reflection on XZ plane, $iC_2(y)$
(3) Reflection on YZ (nuclear) plane, $iC_2(x)$
(4) Rotation with angle π about Z-axis, $C_2(z)$.

We have, obviously $iC_2(y)\cdot iC_2(x)=C_2(z)$.

These symmetry elements are isomorphic to the "vierergruppe" and hence possess the fol-

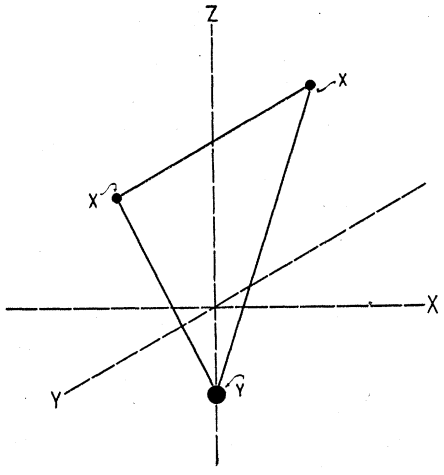

FIG. 1.

[1] E. Wigner, Goettinger Nachr., Math. Phys. Klasse, p. 133 (1930).
[2] L. Tisza, Zeits. f. Physik **82**, 48 (1933).
[3] R. S. Mulliken, Phys. Rev. **43**, 279 (1933).
[4] E. Wigner and E. E. Witmer, Zeits. f. Physik **51**, 859 (1928).

lowing four irreducible representations:

	E	$iC_2(x)$	$iC_2(y)$	$C_2(z)$
A_1	1	1	1	1
A_2	1	−1	−1	1
B_1	1	−1	1	−1
B_2	1	1	−1	−1

There will be, therefore, four types of electronic terms which we may designate as A_1, A_2, B_1, B_2 terms, in accordance with the notation adopted by Tisza and Mulliken.

If vibration is now taken into account, each electronic wave function (the electronic terms are non-degenerate, since their representations are all one-dimensional) must be multiplied by a product of three Hermitean polynomials, functions, respectively, of the three normal coordinates of the problem. The admissible symmetry operations here are the identity and rotation about the axis of symmetry with angle π. Under this last operation the first two polynomials are invariant while the third becomes multiplied by $(-1)^{n_3}$ (since the third normal coordinate is an odd function of y).[5] Hence, the first two polynomials have the representation A_1 for all n_1 and n_2, while the third has the representation A_1 for even n_3 and the representation B_2 for odd n_3. The total vibrational factor, therefore, transforms according to A_1 if n_3 is even, and according to B_2 if n_3 is odd.

Considering now the effect of rotation, the Hamiltonian of our system becomes invariant under the wider group of rotations and inversions at the origin. This allows us to determine the dependence of the wave functions on Euler's angles of the nuclear skeleton (i.e., of the XYZ axes of Fig. 1 which now become moving axes fixed in the body). If q denote the coordinates of the electrons with respect to the XYZ axes fixed in the nuclear frame as in Fig. 1, and ξ the normal coordinates, we have[6]

$$\psi_m{}^{Nln_1n_2n_3}(\alpha, \beta, \gamma, q, \xi) = \sum_\lambda e^{-im\alpha} d_{m\lambda}{}^l(\beta) e^{-i\lambda\gamma} G_\lambda{}^{Nln_1n_2n_3}(q, \xi). \quad (1)$$

Here

$$G_\lambda{}^{Nln_1n_2n_3}(q, \xi) = H_{n_1}(\xi_1) H_{n_2}(\xi_2) H_{n_3}(\xi_3) \varphi^N(q) g_\lambda{}^l,$$

where the g's are constants, and N stands for one of the symbols A_1, A_2, B_1, B_2. $\varphi^N(q)$ is a function of the fixed center problem, $H_n(\xi)$ is a Hermitean polynomial of degree n, and l specifies the total angular momentum of the system. Eq. (1) may be regarded as an expansion of the wave functions of the asymmetrical rotator in terms of the wave functions of the symmetrical rotator. Such expansions are of fundamental importance in the theory of the asymmetrical rotator.[7] The validity of Eq. (1) depends only on the invariance of the system under the rotation-inversion group; it is, therefore, independent of the choice of axes. In the discussions of the asymmetrical rotator it is usual to take the axis of the greatest moment of inertia as the Z-axis. In our case, however, it is necessary to take the axis of symmetry as the Z-axis, and this will be the axis of either the least or middle moment of inertia, depending on the magnitude of the apex angle of the triangle XXY. While the choice of axes is, thus, immaterial for the discussion which follows, it will have to be taken into account when we make use of the results of the theory of the asymmetrical top which is ordinarily based on a different choice of axes.

Eq. (1) would enable us to compute the value of the wave function ψ for any configuration of the molecule obtainable by a rotation or rotation-inversion from some configuration for which ψ is known, were it not for the $2l+1$ constants which appear in the equation. The symmetry of the problem is insufficient to determine all these constants, as was possible in the case of the diatomic molecule; nevertheless, it is possible to obtain all the essential features of the term structure, as we now proceed to show.

It will be convenient to recall, at this point, the classification of the functions of the asymmetrical rotator. It is shown (for instance, in Casimir's monograph), that for any given wave function of the asymmetrical rotator we have in Eq. (1) either only terms with even values of λ or terms with odd values of λ. In the first case,

[5] D. M. Dennison, Revs. Mod. Phys. **3**, 280 (1931).

[6] E. Wigner, *Gruppentheorie*, p. 230, Eq. (10).

[7] S. C. Wang, Phys. Rev. **34**, 243 (1929); Kramers and Ittmann, Zeits. f. Physik **53**, 553 (1929); **58**, 217 (1929); **60**, 663 (1930); H. B. G. Casimir, *Rotation of a Rigid Body in Quantum Mechanics*, Groningen, 1931.

TABLE I. *s = symmetrical; a = antisymmetrical.*

A_1 or A_2				B_1 or B_2			
n_3 even		n_3 odd		n_3 even		n_3 odd	
E	O	E	O	E	O	E	O
s	a	a	s	a	s	s	a

the function (in Casimir's notation) is said to belong to class E, otherwise to class O. Further, we always have either $g_\lambda{}^l = g_{-\lambda}{}^l$ or $g_\lambda{}^l = -g_{-\lambda}{}^l$; the function bears, in the first case, the subscript $+$, otherwise $-$. We thus obtain the four classes E_+, E_-, O_+, O_-. Selection rules hold for transitions between states belonging to the different classes, and we will consider them in greater detail later. It may be remarked here that the class to which a function belongs depends on the choice of axes; the manner in which the wave functions change class when axes are interchanged is given on page 64 of Casimir's book.

We proceed now to determine the connection between the several symmetries of the problem, i.e., of electronic and vibrational symmetry, rotational symmetry class (e.g., E_+, O_-), symmetry with respect to inversion at origin, and symmetry with respect to interchange of the two equal nuclei.

It is natural to require that, for the operations of the electronic symmetry subgroup, ψ^N should transform according to the representation whose index is N. In other words, replacing γ by $\gamma+\pi$ in the functions of Eq. (1), should be equivalent to applying the operation $C_2(z)$ to the function φ and the Hermitean polynomials, and then interchanging the coordinates of the two equal nuclei in ψ. This last operation yields $+1$ for functions symmetrical in the two equal nuclei (para-terms), and -1 for ortho-terms. These requirements will be satisfied if we have, for symmetrical functions:

$$\left.\begin{array}{ll} \text{(a) If } n_3 \text{ is even} & \\ \quad g_\lambda = 0 \quad \text{for } \lambda \text{ odd} & N = A_1 \text{ or } A_2 \\ \quad g_\lambda = 0 \quad \text{for } \lambda \text{ even} & N = B_1 \text{ or } B_2 \\ \text{(b) If } n_3 \text{ is odd} & \\ \quad g_\lambda = 0 \quad \text{for } \lambda \text{ odd} & N = B_1 \text{ or } B_2 \\ \quad g_\lambda = 0 \quad \text{for } \lambda \text{ even} & N = A_1 \text{ or } A_2 \end{array}\right\}. \tag{2}$$

Similar relations hold for functions antisymmetrical in the nuclei, with the difference that the words "even" and "odd" are interchanged. These results are summarized in Table I.

We now consider symmetry with respect to inversion at origin. Inversion at origin is equivalent to the following sequence of operations:[8]

(1) $\alpha \to \pi + \alpha$
(2) $\beta \to \pi - \beta$
(3) $\gamma \to \pi - \gamma$
(4) Reflection of the electronic and vibrational functions on YZ (nuclear) plane, $iC_2(x)$.

The last operation gives a factor $+1$ for A_1 and B_2 terms, and a factor -1 for A_2 and B_1 terms.

We also need the formula:[8]

$$d_{\mu\lambda}{}^l(\pi - \beta) = (-1)^{l+\mu} d^l{}_{\mu,\,-\lambda}(\beta). \tag{3}$$

We take first an A_1 term, symmetrical in the nuclei, and with n_3 even. Here λ must be even, and $iC_2(x)$ gives $+1$. Let a dash indicate inversion at origin.

Then

$$\psi_m{}^{A_1 l n} = \sum_\lambda e^{-im\alpha} e^{-im\pi} d_{m\lambda}{}^l(\pi - \beta) e^{i\lambda\gamma} e^{-i\lambda\pi} G_\lambda{}^{A_1 l n}(q, \xi);$$

now $e^{-i\lambda\pi} = 1$ since λ is even; hence

$$\bar{\psi}_m{}^{A_1 l n} = \sum_\lambda e^{-im\pi} e^{-im\alpha} (-1)^{l+m} d^l{}_{m,\,-\lambda}(\beta) e^{i\lambda\gamma} G_\lambda{}^{A_1 l n}(q, \xi)$$

$$= (-1)^{l+m}(-1)^m \sum_\lambda e^{-im\alpha} d^l{}_{m,\,-\lambda}(\beta) e^{i\lambda\gamma} G_\lambda{}^{A_1 l n}(q, \xi)$$

or

$$\bar{\psi}_m{}^{A_1 l n} = (-1)^l \sum_\lambda e^{-im\alpha} d^l{}_{m,\,-\lambda}(\beta) e^{i\lambda\gamma} G_\lambda{}^{A_1 l n}(q, \xi). \tag{4}$$

[8] Cf. Wigner and Witmer, reference 4, p. 865.

But, if w denote the symmetry character, we have

$$\bar{\psi}_m{}^{A_1 l n} = w \cdot \psi_m{}^{A_1 l n}. \tag{5}$$

Combining Eqs. (4) and (5)

$$(-1)^l \sum_\lambda e^{-im\alpha} d^l{}_{m,\,-\lambda}(\beta) e^{i\lambda\gamma} G_\lambda{}^{A_1 l n}(q,\,\xi) = w \sum_\lambda e^{-im\alpha} d^l{}_{m\lambda}(\beta) e^{-i\lambda\gamma} G_\lambda{}^{A_1 l n}(q,\,\xi)$$
$$= w \sum_\lambda e^{-im\alpha} d^l{}_{m,\,-\lambda}(\beta) e^{i\lambda\gamma} G_{-\lambda}{}^{A_1 l n}(q,\,\xi).$$

We thus obtain, in the case of symmetrical terms

$$\left.\begin{aligned} &\text{(a) For } A_1 \text{ and } B_2 \text{ terms} \\ &\qquad (-1)^{l+n_3} g_\lambda{}^{Nl} = w g_{-\lambda}{}^{Nl} \\ &\text{(b) For } A_2 \text{ and } B_1 \text{ terms} \\ &\qquad (-1)^{l+n_3} g_\lambda{}^{Nl} = -w g_{-\lambda}{}^{Nl} \end{aligned}\right\}. \tag{6}$$

For antisymmetrical terms, the minus sign occurs in Eq. (6a) instead of in Eq. (6b). These relations are summarized in Table II.

The Tables I and II may now be used in the following way: suppose we are given an electronic term of type B_2 with n_3 even, l odd, and with rotational symmetry E_+. Table I then shows that it is antisymmetrical, and Table II then gives $w=+1$.

To complete the analysis of the rotational structure, we must make use of the theorem of Kramers and Ittmann[9] that if the $2l+1$ eigenvalues with the same l are ordered according to their magnitude, i.e., $W_l < W_{l-1} < W_{l-2} < W_{l-3} < \cdots$, then, provided that $A_3 > A_2 > A_1$ (the A's are the principal moments of inertia), we have

$W_l,\ W_{l-4},\ W_{l-8},\ W_{l-12}\cdots$ are of class E_+
$W_{l-1},\ W_{l-5},\ W_{l-9},\ W_{l-13}\cdots$ " " " O_+
$W_{l-2},\ W_{l-6},\ W_{l-10},\ W_{l-14}\cdots$ " " " E_-
$W_{l-3},\ W_{l-7},\ W_{l-11},\ W_{l-15}\cdots$ " " " O_-.

We are using, however, a different set of axes, and allowance must be made for this. Two cases arise:

(A) The middle moment of inertia is associated with the symmetry axis. We must make the interchange $A_3 \longleftrightarrow A_2$.

(B) The least moment of inertia is associated with the symmetry axis. The proper transformation is here $A_3 \longleftrightarrow A_1$ and $A_2 \longleftrightarrow A_1$.

[9] Cf. Casimir, reference 7, p. 64.

When these interchanges are carried out in accordance with the rules given on page 64 of Casimir's monograph, the theorem of Kramers and Ittmann assumes the form:

	Class			
	Case A		Case B	
	l even	l odd	l even	l odd
$W_l,\ W_{l-4},\ W_{l-8}\cdots$	E_+	O_+	E_+	O_+
$W_{l-1},\ W_{l-5},\ W_{l-9}\cdots$	O_+	E_+	E_-	O_-
$W_{l-2},\ W_{l-6},\ W_{l-10}\cdots$	O_-	E_-	O_-	E_-
$W_{l-3},\ W_{l-7},\ W_{l-11}\cdots$	E_-	O_-	O_+	E_+.

It now remains to consider selection rules. To begin with, the following may be expected to hold rigorously:

(1) Symmetry with respect to inversion must change in any transition.
(2) $\Delta l = \pm 1$ but not $0 \to 0$.
(3) Ortho-terms combine with ortho-terms only; para-terms with para-terms.

The rules governing transitions in which change of electronic type or vibrational quantum numbers takes place, on the other hand, may be expected to be strictly fulfilled only as long as interactions between the several types of motion do not become great.

We consider first the selection rules of the fixed center problem (electronic selection rules). The procedure for obtaining these rules is given in the paper of Mulliken[3] and we merely state the results which one obtains in our particular case:

X	Y	Z
$A_1 \longleftrightarrow B_1$	$A_1 \longleftrightarrow B_2$	$A_1 \longleftrightarrow A_1$
$A_2 \longleftrightarrow B_2$	$A_2 \longleftrightarrow B_1$	$A_2 \longleftrightarrow A_2$
		$B_1 \longleftrightarrow B_1$
		$B_2 \longleftrightarrow B_2$

(7)

But not $A_1 \longleftrightarrow A_2$ or $B_1 \longleftrightarrow B_2$ for any component.

If now vibrational transitions also take place,

TABLE II.

Symmetrical terms								*Antisymmetrical terms*							
A_1 or B_2				A_2 or B_1				A_1 or B_2				A_2 or B_1			
$(l+n_3)$ even		$(l+n_3)$ odd		$(l+n_3)$ even		$(l+n_3)$ odd		$(l+n_3)$ even		$(l+n_3)$ odd		$(l+n_3)$ even		$(l+n_3)$ odd	
+	−	+	−	+	−	+	−	+	−	+	−	+	−	+	−
$w=1$	$w=-1$	$w=-1$	$w=1$	$w=-1$	$w=1$	$w=1$	$w=-1$	$w=-1$	$w=1$	$w=1$	$w=-1$	$w=1$	$w=-1$	$w=-1$	$w=1$

we must distinguish two cases: Δn_3 even and Δn_3 odd. In the first case, the same set of rules is obtained as is given above; in the second case, we obtain a different set, namely:

Δn_3 *odd.*

X	Y	Z
$A_1 \longleftrightarrow A_2$	$A_1 \longleftrightarrow A_1$	$A_1 \longleftrightarrow B_2$
$B_2 \longleftrightarrow B_1$	$A_2 \longleftrightarrow A_2$	$A_2 \longleftrightarrow B_1$
	$B_1 \longleftrightarrow B_1$	
	$B_2 \longleftrightarrow B_2$	

(8)

But not $A_1 \longleftrightarrow B_1$ or $A_2 \longleftrightarrow B_2$ for any component.

Since the rules (7) may be expected to hold fairly rigorously, because of greater energy involved, transitions of the type (8) which involve electronic transitions forbidden by (7) will not occur, or, at most, will give rise to very weak lines.

Since we have now obtained selection rules affecting all possible symmetry changes except rotational, we may, with the aid of Tables I and II, find now the selection rules between the functions of the four classes. They are given in Table III, and may easily be seen to be equivalent to the known selection rules of the asymmetrical top.

TABLE III.

$l \to l$	E_+	E_-	O_+	O_-
K_{iz}	←	←	→	→
K_{iy}	←	←	→	→
K_{iz}	←	→	←	→

$l \to l-1$	E_+	E_-	O_+	O_-
K_{iz}	←	←	→	→
K_{iy}	←	←	→	→
K_{iz}	⟷	⟷	⟷	⟷

In conclusion, the author wishes to express his thanks to Professor E. E. Witmer for many stimulating discussions and criticisms.