551. *Excited States of Acetylene. Part III.* Theoretical Methods for Analysis of Near-ultra-violet Band-systems of Acetylenes.*

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Rules of selection and intensity are developed in a sufficiently general form to permit discussion of coarse and fine structures, and also of intensity relations, in transitions of normal acetylene to non-linear but planar excited states.

(1) CONVENTIONS AND APPROXIMATIONS

(a) *Co-ordinate Axes.*—In order to specify the motion of, and within, a polyatomic molecule, apart from its translatory motion, with which we shall have no concern, we need two sets of Cartesian axes, an " external " set, X, Y, Z, which may be taken as having its origin at the centre of mass of the molecule, but must have its axial directions fixed in space, and an " internal " set, x, y, z, which also may be given an origin at the centre of mass but must have its axial directions fixed in the molecule. Three Eulerian angles will describe the instantaneous orientation of the internal set relatively to the external set, and, in the wave function of the molecule, will be independent variables of special significance for rotation, and for the directional behaviour in space of the total angular momentum. Co-ordinates taken relatively to the internal axes, or linear combinations of such co-ordinates, will specify instantaneous electron positions, and the nuclear displacements; and, in the wave function, such co-ordinates will enter as independent variables important for the description of the relative movements of the electrons and nuclei, and of the directional distribution of angular momentum, whether due to rotation of the molecule, or to relative movements of its constituent particles, or to the spins of the latter.

It is convenient to take the internal axes, x, y, z, as coincident with the principal axes of inertia, a, b, c, traditionally so labelled that the corresponding principal moments of inertia stand in the order $I_a \leqslant I_b \leqslant I_c$. By deciding to maintain the same one-to-one correlation between x, y, z and a, b, c, for the three models of acetylene that we shall be discussing, we can simplify notation by dropping the former labels, and employing the latter indiscriminately for internal co-ordinate axes and for the coincident axes of inertia. Indeed we shall use the same labels for axes of a third kind, *viz.*, axes of symmetry, since these, in so far as they are present at all, always coincide with axes of inertia, and therefore with our chosen internal co-ordinate axes. For the three acetylene models with which we shall be dealing, the internal axes are taken as indicated in Fig. 2.

The $D_{\infty h}$ model is a prolate symmetric top: two of its principal moments of inertia are equal, while the unique one is the smallest of the three, and, indeed, would be zero but for zero-point energy, and the finite mass of the electrons: $I_a \lll I_b = I_c$. The C_{2h} and C_{2v} models are asymmetric tops, but can be described as prolate near-symmetric tops: $I_a \ll I_b < I_c$. This arises from the considerably smaller mass of hydrogen than of carbon nuclei, taking into account also that, for such planar models, the relation $I_a + I_b = I_c$ will hold, apart from small deviations due to zero-point energy and electronic mass.

In the $D_{\infty h}$ model, a is an infinity-fold axis, and perpendicular axes are two-fold axes of symmetry. In the other models, a is not a symmetry axis, but in the C_{2h} model c, and in the C_{2v} model b, are two-fold axes. These symmetry properties are indicated in Fig. 2 by the symbols in brackets.

(b) *Approximate Factorisation of Wave Functions.*—It is a familiar idea that, in most circumstances, electronic orbital motion, nuclear vibration, and molecular rotation are nearly independent forms of motion, and that therefore, as an approximation, a wave-function ψ, which for energy E satisfies the wave equation of the molecule

$$H\psi = E\psi$$

can be represented as the product of electronic, vibrational, and rotational factors satisfying the separate wave equations,

$$H_e\psi_e = E_e\psi_e \quad H_v\psi_v = E_v\psi_v \quad H_r\psi_r = E_r\psi_r$$

* Part II, preceding paper.

in the construction of which the original energy-operator and energy are treated as sums, and split into their component terms:

$$\psi = \psi_e\psi_v\psi_r \quad H = H_e + H_v + H_r \quad E = E_e + E_v + E_r \quad . \quad . \quad . \quad (1)$$

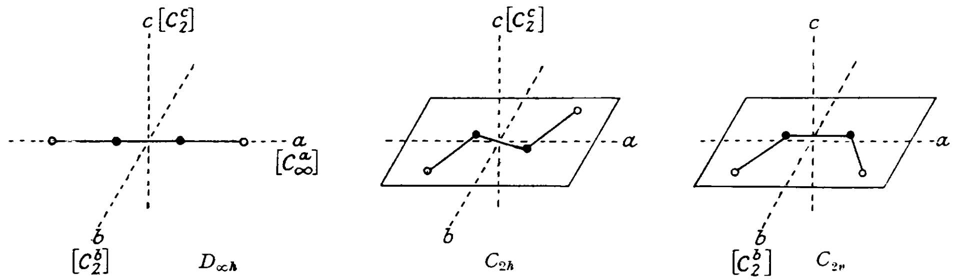
In discussing the symmetry properties of ψ and its factors, it is often convenient, following Mulliken, to group the first two factors together, calling their product the " vibronic " wave function ψ_{ev}, whose energy E_{ev} includes electronic and vibrational but not rotational energy

$$\psi_{ev} = \psi_e\psi_v \quad E_{ev} = E_e + E_v \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

$$\psi \;\; = \psi_{ev}\psi_r \quad E \;\; = E_{ev} + E_r \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

In this, as in any approximation, a complete representation of ψ should contain an electronic spin factor ψ_{es}, and a nuclear spin factor ψ_{ns}; but we shall not show either explicitly. As to ψ_{es}, we assume that Pauli's principle is satisfied, so that $\psi_e\psi_{es}$ is antisymmetric in the electrons; and we shall avoid discussing multiplicity by confining attention throughout to singlet electronic states, with the result that electron spin will not contribute to the total angular momentum represented in the quantum number J of rotational states and energy levels. Accordingly, we shall simplify rotation by omitting the spin-multiplicity symbol throughout. As to ψ_{ns}, we note that its effect on hyper-multiplicity and thus on the statistical weights of energy levels, and on the intensities of individual transitions, is standard and independent of the special features of the present problem, so that we can introduce it when necessary without having to carry its theory in our formulæ.

FIG. 2. *Internal co-ordinate axes, principal axes of inertia, and axes of symmetry of the three models of acetylene.*



(2) ELECTRONIC STATES AND TRANSITIONS

(a) *Classification of, and Selection Rules for, Electronic Wave Functions.*—Although we shall not have to discuss the explicit forms of ψ and its approximate factors, we shall have to make repeated use of their symmetry properties, most, though not all, of which differ according to the molecular model of acetylene taken. Discussion of the factors of ψ will lead to many selection rules, which are, however, approximate, because the factorisation is approximate. Discussion of ψ itself will yield a small number of exact selection rules. We deal now with the electronic factor ψ_e, using the internal system of axes, a, b, c, with respect to which the symmetry properties of the different models differ.

First, as to the linear, or $D_{\infty h}$ model, the possible types of behaviour of the electronic wave function, under the operations to which the electronic wave equation is invariant, are as shown in Table 1, a multiple-purpose table, of which we need now notice only the left and the middle section. The latter contains the factors (" characters ") which multiply the different species of wave function, as a result of the operations, $2C_\phi^a$, C_2^{bc}, and i, of rotation by any angle $\pm\phi$ around a, of rotation by π around b or c, and of inversion through the origin; and also in consequence of the operation, iC_2^{bc}, of reflexion across any plane through a. The first column of the Table shows the labels of the symmetry species, chosen to correspond to those of diatomic molecules. The four species Σ are non-degenerate, and devoid of electronic angular momentum about the molecular axis a ($\Lambda = 0$): the subscripts g and u mean symmetry and antisymmetry under operation i, while the superscripts $+$ and $-$ signify symmetry and antisymmetry for operation iC_2^{bc}. The infinitude of remaining species, Π, Δ, etc., are each doubly degenerate, and have 1, 2, etc., units $\boldsymbol{h}/2\pi$ of electronic angular momentum about the axis a ($\Lambda = 1, 2$, etc.): g and u mean the same as before.

TABLE 1. *Species of electronic and vibrational wave functions of model* $D_{\infty h}$.

Elec.	Λ	M	E	$2C_\phi^a$	C_2^{bc}	i	$2iC_\phi^a$	iC_2^{bc}	Vibs.	No.	l	T, R
Σ_g^+	0	—	1	1	1	1	1	1	Σ_g^+	2	0	—
Σ_u^-	0	—	1	1	1	−1	−1	−1	Σ_u^-	0	0	—
Σ^-	0	—	1	1	−1	1	1	−1	Σ_g^-	0	0	(R_a)
Σ_u^+	0	M_a	1	1	−1	−1	−1	1	Σ_u^+	1	0	T_a
Π_g	1	—	1	$2\cos\phi$	0	2	$2\cos\phi$	0	Π_g	1	1	R_{bc}
Π_u	1	M_{bc}	1	$2\cos\phi$	0	−2	$-2\cos\phi$	0	Π_u	1	1	T_{bc}
Δ_g	2	—	1	$2\cos 2\phi$	0	2	$2\cos 2\phi$	0	Δ_g	0	2	—
Δ_u	2	—	1	$2\cos 2\phi$	0	−2	$-2\cos 2\phi$	0	Δ_u	0	2	—
...	...	...	...	...	...	...	...	...	...	...	...	...

The third column of Table 1 indicates the symmetry properties of the electric moment M. Their significance is that, when $\psi''\psi'$ contains a term with the symmetry properties of M, then, and then only, the intensity-controlling integral $\int\psi''M\psi'd\sigma$ will not vanish on account of the symmetry. Here the double prime marks the lower and the single the upper of the combining states. In order to determine the symmetry properties of $\psi''\psi'$ we have to multiply the characters of ψ'' and ψ', as given in Table 1, and then, using the products, re-read Table 1 to obtain the symmetry of the species of $\psi''\psi'$. This is one of several purposes requiring Table 2, which shows the results (" direct products ") of this procedure. From the occurrences there of Σ_u^+ (the species of M_a), and of Π_u (the species of M_{bc}), we can deduce the selection rules for transitions involving electronic oscillations parallel and perpendicular, respectively, to a.

TABLE 2. *Direct products of species of the model* $D_{\infty h}$.

	Σ_g^+	Σ_g^-	Σ_u^+	Σ_u^-	Π_g	Π_u	Δ_g	Δ_u
Σ_g^+	Σ_g^+	Σ_g^-	Σ_u^+	Σ_u^-	Π_g	Π_u	Δ_g	Δ_u
Σ_g^-		Σ_g^+	Σ_u^-	Σ_u^+	Π_g	Π_u	Δ_g	Δ_u
Σ_u^+			Σ_g^+	Σ_g^-	Π_u	Π_g	Δ_u	Δ_g
Σ_u^-				Σ_g^+	Π_u	Π_g	Δ_u	Δ_g
Π_g					$\Sigma_g^+\Sigma_g^-\Delta_g$	$\Sigma_u^+\Sigma_u^-\Delta_u$	$\Pi_g\Phi_g$	$\Pi_u\Phi_u$
Π_u						$\Sigma_g^+\Sigma_g^-\Delta_g$	$\Pi_u\Phi_u$	$\Pi_g\Phi_g$
Δ_g							$\Sigma_g^+\Sigma_g^-\Gamma_g$	$\Sigma_u^+\Sigma_u^-\Gamma_u$
Δ_u								$\Sigma_g^+\Sigma_g^-\Gamma_g$

These selection rules are as follows:

$$\left.\begin{array}{ll}\text{Parallel to } a: & \Delta\Lambda = 0,\ g \longleftrightarrow u,\ + \longleftrightarrow +,\ - \longleftrightarrow - \\ \text{Perpendicular to } a: & \Delta\Lambda = \pm 1,\ g \longleftrightarrow u\end{array}\right\} \quad . \quad . \quad . \quad (4)$$

The $\Delta\Lambda$ rule is general for symmetric tops, the gu rule for molecules with a centre of symmetry and the $\pm$ rule for linear molecules.

For the *trans*-bent or C_{2h} model there are four species of electronic wave function, as shown, with their symmetry properties, in the left and the middle section of Table 3. The operations which serve to classify the wave functions can be taken as any two out of the following three, namely, C_2^c, σ^{ab}, and i, that is, rotation by π around c, reflection across the plane ab, and inversion through the origin. The labels A and B mean symmetry and antisymmetry respectively, with respect to C_2^c, while g and u refer, as always, to i. The direct products are in Table 4, and from them, by comparison with the second column of Table 3, one may find the selection rules:

$$\left.\begin{array}{ll}\text{Parallel to } c: & A \longleftrightarrow A,\ B \longleftrightarrow B,\ g \longleftrightarrow u \\ \text{Perpendicular to } c: & A \longleftrightarrow B,\ g \longleftrightarrow u\end{array}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

TABLE 3. *Species of electronic and vibrational wave functions of model C_{2h}.*

Elec.	M	E	C_2^c	σ^{ab}	i	Vibs.	No.	T, R
A_g	—	1	1	1	1	A_g	3	R_c
A_u	M_c	1	1	−1	−1	A_u	1	T_c
B_g	—	1	−1	−1	1	B_g	0	R_{ab}
B_u	M_{ab}	1	−1	1	−1	B_u	2	T_{ab}

TABLE 4. *Direct products for model C_{2h}.*

	A_g	A_u	B_g	B_u
A_g	A_g	A_u	B_g	B_u
A_u		A_g	B_u	B_g
B_g			A_g	A_u
B_u				A_g

For the *cis*-bent model C_{2v} there are again four species of electronic wave function, distinguished, as Table 5 shows, by their behaviour under any two of the operations C_2^b, σ^{ab}, σ^{bc}, that is, rotation by π about b, and reflexion across the ab plane, or across the bc plane. Labels A and B mean respectively symmetry and antisymmetry under C_2^b, and subscripts 1 and 2 the same under σ^{ab}. The direct products in Table 6 lead to the following selection rules :

$$\left.\begin{array}{lll} \text{Parallel to } b: & A \longleftrightarrow A,\ B \longleftrightarrow B & 1 \longleftrightarrow 1,\ 2 \longleftrightarrow 2 \\ \text{Parallel to } a: & A \longleftrightarrow B & 1 \longleftrightarrow 1,\ 2 \longleftrightarrow 2 \\ \text{Parallel to } c: & A \longleftrightarrow B & 1 \longleftrightarrow 2 \end{array}\right\} \quad . \quad . \quad . \quad . \quad . \quad (6)$$

TABLE 5. *Species of electronic and vibrational wave functions of model C_{2v}.*

Elec.	M	E	C_2^b	σ^{ab}	σ^{bc}	Vibs.	No.	T	R
A_1	M_b	1	1	1	1	A_1	3	T_b	—
A_2	—	1	1	−1	−1	A_2	1	—	R_b
B_1	M_a	1	−1	1	−1	B_1	2	T_a	R_c
B_2	M_c	1	−1	−1	1	B_2	0	T_c	R_a

TABLE 6. *Direct products for model C_{2v}.*

	A_1	A_2	B_1	B_2
A_1	A_1	A_2	B_1	B_2
A_2		A_1	B_2	B_1
B_1			A_1	A_2
B_2				A_1

As we shall have to consider transitions between the linear ground state of acetylene and possible bent excited states, it is important to correlate the species of the linear model with those of the bent models. Only then can we follow what happens to states of a given species of the $D_{\infty h}$ model when the hybridisation changes, in particular, into what species of states of the C_{2h} or of the C_{2v} model they will go. For this purpose we determine, by comparison of Tables 1, 3, and 5, for each species of the $D_{\infty h}$ model, how it behaves under

TABLE 7. *Correlation of $D_{\infty h}$ species with C_{2h} species and with C_{2v} species (not of C_{2h} with C_{2v} species).*

C_{2h}	$D_{\infty h}$	C_{2v}	C_{2h}	$D_{\infty h}$	C_{2v}
A_g	Σ_g^+	A_1	$A_g + B_g$	Π_g, Φ_g, ...	$A_2 + B_1$
A_u	Σ_u^-	A_2	$A_g + B_g$	Δ_g, Γ_g, ...	$A_1 + B_2$
B_g	Σ_g^-	B_2	$A_u + B_u$	Π_u, Φ_u, ...	$A_1 + B_2$
B_u	Σ_u^+	B_1	$A_u + B_u$	Δ_u, Γ_u, ...	$A_2 + B_1$

the symmetry operations of the C_{2h} and of the C_{2v} model, and to what species of either model such behaviour corresponds. The resulting correlations of $D_{\infty h}$ species with C_{2h} species on the one hand, and with C_{2v} species on the other, are shown in Table 7. It must be emphasised that, because the correlations are not of one-to-one type throughout, the Table does not exhibit exclusive and complete correlations of C_{2h} species directly with C_{2v} species.

From the correlations in Table 7, and the selection rules already given for electronic transitions between states of the same model of acetylene (relations 4, 5, and 6), we are able to derive selection rules for transitions between any electronic state of the straight model $D_{\infty h}$ and electronic states of either bent model C_{2h} and C_{2v}. The procedure is to apply to the correlated species selection rules determined by the symmetry *common* to the models. As the symmetry of the C_{2h} model, and of the C_{2v} model, is totally included in that of the $D_{\infty h}$ model, the electronic selection rules here to be applied to correlated species are simply those of the C_{2h} and the C_{2v} model (relations 5 and 6). The results of these processes are given in Table 8.

TABLE 8. *Selection rules for electronic transitions between the $D_{\infty h}$ model of acetylene and the C_{2h} and the C_{2v} model.*

C_{2h}					C_{2v}		
$\parallel c$	$\perp c$		$D_{\infty h}$		$\parallel a$	$\parallel b$	$\parallel c$
A_u	B_u	$\longleftrightarrow$	Σ_g^+	$\longleftrightarrow$	B_1	A_1	B_2
A_g	B_g	$\longleftrightarrow$	Σ_u^-	$\longleftrightarrow$	B_2	A_2	B_1
B_u	A_u	$\longleftrightarrow$	Σ_g^-	$\longleftrightarrow$	A_2	B_2	A_1
B_g	A_g	$\longleftrightarrow$	Σ_u^+	$\longleftrightarrow$	A_1	B_1	A_2
$A_u + B_u$		$\longleftrightarrow$	$\Pi_g, \Phi_g, \ldots.$	$\longleftrightarrow$	$A_1 + B_2$	$A_2 + B_1$	
$A_u + B_u$		$\longleftrightarrow$	$\Delta_g, \Gamma_g, \ldots.$	$\longleftrightarrow$	$A_2 + B_1$	$A_1 + B_2$	
$A_g + B_g$		$\longleftrightarrow$	$\Pi_u, \Phi_u, \ldots.$	$\longleftrightarrow$	$A_2 + B_1$	$A_1 + B_2$	
$A_g + B_g$		$\longleftrightarrow$	$\Delta_u, \Gamma_u, \ldots.$	$\longleftrightarrow$	$A_1 + B_2$	$A_2 + B_1$	

(b) *Species of Lower Electronic States of Acetylene as given by the Theory of Molecular Structure.*—The electronic ground state of acetylene is known to be a singlet state of the $D_{\infty h}$ model. Its electronic configuration is written below, by using, as is customary, lower-case letters for one-electron wave functions, that is, for orbitals. Each parenthesis contains the symmetry symbol of the molecular or bond orbital, which in some cases is followed by the quantum classification of the parent atomic orbital or orbitals. The symmetry of the total electronic wave function ψ_e will be the direct product of the symmetries of all those one-electron wave functions which enter ψ_e as factors. It follows from the absence of odd indices, or in detail by the use of Table 2, together with the Pauli principle, that ψ_e is totally symmetrical, having the species symbol (cf. Table 1) indicated on the right:

$$K^4(\sigma_g)^4_{\mathrm{CH}}(\sigma_g 2sp)^2_{\mathrm{CC}}(\pi_u 2p)^4_{\mathrm{CC}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \Sigma_g^+$$

As was noted in Part I, it would seem that the lowest orbital of the $D_{\infty h}$ model into which a π electron could be lifted would be one of two equivalent antibonding $\pi_g 2p$ orbitals one of them diagrammatically shown in Fig. 1 at (B). The resulting configuration is given below; and from Table 2 it can be found that electronic states ψ_e of three species thus arise, as indicated on the right:

$$K^4(\sigma_g)^4_{\mathrm{CH}}(\sigma_g 2sp)^2_{\mathrm{CC}}(\pi_u 2p)^3_{\mathrm{CC}}(\pi_g 2p)_{\mathrm{CC}} \quad . \quad . \quad . \quad \Sigma_u^+, \Sigma_u^-, \Delta_u$$

Another 2-quantum orbital which could conceivably be entered by an electron from the π_u shell is the antibonding counterpart, $\sigma_u 2sp$, of the σ_g bonding orbital. For a reason explained in Part I, this receiving orbital, and the resulting molecular states, are expected to lie considerably higher than those already considered. The configuration and symmetry species are as follows:

$$K^4(\sigma_g)^4_{\mathrm{CH}}(\sigma_g 2sp)^2_{\mathrm{CC}}(\pi_u 2p)^3_{\mathrm{CC}}(\sigma_u 2sp)_{\mathrm{CC}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \Pi_g$$

After this we come to 3-quantum and higher orbitals, $\sigma_g 3s$, etc., the states being classifiable as Rydberg states, which we need not now discuss.

Account must be taken, however, of the possibility that two or more of the π_u electrons might be promoted to any of the three originally unoccupied 2-quantum orbitals. The resulting group of states will lie higher in energy than the one-promotion group just discussed; but there could be overlap between the energy ranges, and hence we should consider at least the lowest set of states of the two-promotion group, namely, those given by double entry into the lowest of the initially unoccupied orbitals. The configuration and the species are as follows :

$$K^4(\sigma_g)^4{}_{\mathrm{CH}}(\sigma_g 2sp)^2{}_{\mathrm{CC}}(\pi_u 2p)^2{}_{\mathrm{CC}}(\pi_g 2p)^2{}_{\mathrm{CC}} \quad . \quad . \quad \Sigma_g^+,\ \Sigma_g^-,\ \Delta_g,\ \Gamma_g$$

Suppose now that the hybridisation changes, and that the hydrogen atoms go over into the *trans*-positions of the C_{2h} model. Then one π_u orbital must become uncoupled to give, in first approximation, two non-bonding atomic orbitals of type $2sp^2$, which, in second approximation, interact to form two molecular orbitals, one weakly bonding b_u, and the other weakly antibonding a_g. Omitting normalisation, these combinations are as written below, and their symmetries follow from Table 3 by comparison with Fig. 1 (C) (Part I), first as drawn, and then with the signs of one atomic orbital reversed :

$$(2sp^2)_{C_1} - (2sp^2)_{C_2} = b_u \quad (2sp^2)_{C_1} + (2sp^2)_{C_2} = a_g$$

Large excitations apart, the electrons of the decomposed π_u orbital must occupy two of the four places provided by these new orbitals, and the possibilities are that both go into either, and that one goes into each, to give any of three close-lying " unexcited " states, as they may roughly be called, although only one of them is the ground state, correlated with the normal state of linear acetylene. The configurations are written below, the symmetries of CC electrons with respect to the bent model being indicated by a prefixed symbol, so that, for the σ bond, for example, $a_g\sigma_g 2sp^2$ means a molecular orbital a_g, derived from a bond orbital σ_g, formed from atomic orbitals, $2sp^2$; the CC subscripts are dropped. The symmetries of ψ_e follow from Table 4 :

$$K^4(\sigma_g')^4{}_{\mathrm{CH}}(a_g\sigma_g 2sp^2)^2(a_u\pi_u 2p)^2(b_u 2sp^2)^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad A_g$$

$$\text{,, ,, ,, ,,} \quad (b_u 2sp^2)(a_g 2sp^2) \quad . \quad . \quad . \quad . \quad . \quad B_u$$

$$\text{,, ,, ,, ,,} \quad (a_g 2sp^2)^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad A_g$$

As compared with the linear normal state of acetylene, these " unexcited " bent states are energised; and the lowest of them would not even be metastable (unless it were made so by a spin change), but would revert immediately to the linear ground state. But the bent model offers nearly non-bonding, as well as anti-bonding, receiving orbitals for excitation; for in the orbitals b_u and a_g there are still two vacant places. Moreover, the excitation of one of the two electrons, which after the bending of the molecule first find themselves in the new, nearly non-bonding orbitals, up to an antibonding orbital, would require less energy than if the electron had to come from a bonding orbital. The former type of excitation, that is, one of an electron from the non-disrupted $a_u\pi_u$ bonding orbital to either new nearly non-bonding orbital, b_u or a_g, will give the lowest group of excited states, the two having the configurations and symmetries here written :

$$K^4(\sigma_g')^2{}_{\mathrm{CH}}(a_g\sigma_g 2sp^2)^2(a_u\pi_u 2p)(b_u 2sp^2)^2(a_g 2sp^2) \quad . \quad . \quad . \quad . \quad . \quad A_u$$

$$\text{,, ,, ,, ,,} \quad (b_u 2sp^2)(a_g 2sp^2)^2 \quad . \quad . \quad . \quad . \quad B_g$$

The other type of excitation, that from a nearly non-bonding orbital to an antibonding orbital, could employ the antibonding $\pi_g 2p$ orbital, which one can picture by supposing the orbital represented in Fig. 1 (*B*) to be turned by a right-angle about the C–C line, and then superposed on Fig. 1 (*C*). There will be two neighbouring states, depending on which nearly non-bonding orbital retains the unexcited electron :

$$K^4(\sigma_g')^2{}_{\mathrm{CH}}(a_g\sigma_g 2sp^2)^2(a_u\pi_u 2p)^2(b_u 2sp^2)(b_g\pi_g 2p) \quad . \quad . \quad . \quad . \quad . \quad A_u$$

$$\text{,, ,, ,, ,,} \quad (a_g 2sp^2) \quad \text{,,} \quad . \quad . \quad . \quad . \quad . \quad . \quad B_g$$

These excited orbitals are expected to lie higher than the other two of the same symmetries. These orbitals could be formed from those others by taking two electrons from nearly non-bonding orbitals, and putting one into the bonding $\pi_u 2p$ orbital, and the other into the antibonding $\pi_g 2p$ orbital. Two arguments may be given for supposing that this would require a nett input of energy. First, the energy curves for the hydrogen molecule ion, which can be exactly calculated, show that a $\sigma_u 1s$ antibonding electron is energetically more antibonding than a $\sigma_g 1s$ bonding electron is bonding. Secondly, from the viewpoint of the valency-bond method, resonance between structures $\dot{\text{C}}$–C and C–$\dot{\text{C}}$ should give more stable bonding than between structures $\dot{\text{C}}$–$\ddot{\text{C}}$ and $\ddot{\text{C}}$–$\dot{\text{C}}$ (if we neglect the effect on bonding of the nearly non-bonding electrons), because interaction between a single electron and an electron pair is repulsive: a three-electron bond is more stable than a five-electron bond.

The other 2-quantum antibonding orbital which could receive the excited electron, $\sigma_u 2sp^2$, provides the following excited electronic states:

$$K^4(\sigma_g')^4{}_{\text{CH}}(a_g\sigma_g 2sp^2)^2(a_u\pi_u 2p)^2(b_u 2sp^2)(b_u\sigma_u 2sp^2) \quad . \quad . \quad . \quad . \quad A_g$$
$$,, \quad ,, \quad ,, \quad ,, \quad (a_g 2sp^2) \quad ,, \quad . \quad . \quad . \quad . \quad B_u$$

Taking account as before of the lowest set of two-promotion states, we find that it has only one member, and arises when the two bonding $a_u\pi_u$ electrons are elevated to the two vacant places in the nearly non-bonding orbitals:

$$K^4(\sigma_g')^4{}_{\text{CH}}(a_g\sigma_g 2sp^2)^2(b_u 2sp^2)^2(a_u 2sp^2)^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad A_g$$

The other bent model C_{2v} furnishes a similar pattern of 2-quantum states. By putting the evicted tenants of the converted orbital into the lowest of the conversion-product orbitals, we obtain three "unexcited" states:

$$K^4(\sigma_g')^4{}_{\text{CH}}(a_1\sigma_g 2sp^2)^2(b_2\pi_u 2p)^2(a_1 2sp^2)^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad A_1$$
$$,, \quad ,, \quad ,, \quad ,, \quad (a_1 2sp^2)(b_1 2sp^2) \quad . \quad . \quad . \quad . \quad . \quad B_1$$
$$,, \quad ,, \quad ,, \quad ,, \quad (b_1 2sp^2)^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad A_1$$

Promotion of an electron from the bonding π orbital to a nearly non-bonding orbital produces two excited states:

$$K^4(\sigma_g')^4{}_{\text{CH}}(a_1\sigma_g 2sp^2)^2(b_2\pi_u 2p)(a_1 2sp^2)^2(b_1 2\text{sp}^2) \quad . \quad . \quad . \quad . \quad . \quad A_2$$
$$,, \quad ,, \quad ,, \quad ,, \quad (a_1 2sp^2)(b_1 2sp^2)^2 \quad . \quad . \quad . \quad . \quad . \quad B_2$$

Two more result from the promotion, alternatively, of a nearly non-bonding electron to the antibonding π orbital,

$$K^4(\sigma'_g)^4{}_{\text{CH}}(a_1\sigma_g 2sp^2)^2(b_2\pi_u 2p)^2(a_1 2sp^2)(a_2\pi_g 2p) \quad . \quad . \quad . \quad . \quad . \quad A_2$$
$$,, \quad ,, \quad ,, \quad ,, \quad (b_1 2sp^2) \quad ,, \quad . \quad . \quad . \quad . \quad . \quad B_2$$

and still two more, if the anti-bonding σ orbital receives the electron:

$$K^4(\sigma_g')^4{}_{\text{CH}}(a_1\sigma_g 2sp^2)^2(b_2\pi_u 2p)^2(a_1 2sp^2)(b_1\sigma_u 2sp^2) \quad . \quad . \quad . \quad . \quad B_1$$
$$,, \quad ,, \quad ,, \quad ,, \quad (b_1 2sp^2) \quad ,, \quad . \quad . \quad . \quad . \quad . \quad A_1$$

Another state results, if we put both the $b_u\pi_u$ electrons into the two vacant places in the nearly non-bonding orbitals:

$$K^4(\sigma_g')^4{}_{\text{CH}}(a_1\sigma_g 2sp^2)^2(a_1 2sp^2)^2(b_1 2sp^2)^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad A_1$$

Using Table 7, we may correlate the linear with the bent states of acetylene, as in Fig. 3, in which the energy spacings, although largely arbitrary, reproduce the qualitative considerations already mentioned. As to the $D_{\infty h}$ states, we have the guidance of Ross's recent calculations (*Trans. Faraday Soc.*, 1952, **48**, 973), without which we would not know, for example, how to place the lower two-promotion states relatively to the higher one-promotion states. The "unexcited" C_{2v} states are raised relatively to the corresponding set of C_{2h} states, mainly because we know from vibration frequencies (next Section) that about twice as much force is needed to bend the normal acetylene molecule in the direction of the *cis*-model as to bend it towards the *trans*-model.

With the aid of Table 8 one can indicate which bent upper states are allowed to combine with the linear ground state of acetylene, and, using relations (4), which upper states become allowed only in consequence of the bending. This is done in Fig. 3 by the notes in parentheses, giving the direction of the electronic oscillation accompanying transition from the ground states to the various excited states.

(3) Vibronic states and transitions

(a) *Classification of Vibrational Wave Functions and Vibrations; Ground-state Vibrational Energies.*—Total-vibrational wave functions ψ_v will contain parameters of ψ_e, and thus will be different in different electronic states. However, the factorisation which led to the isolation of ψ_v implies that its symmetry classification is the same for all ψ_e. Furthermore, the system of classification of ψ_v will be the same as that of ψ_e: for, although the first is a function of nuclear *displacements* and the second a function of electron *positions*, both can retain or lose the various symmetry elements of the models, that is, behave in the same way under transformations of the internal axes *a*, *b*, *c*. So it comes about that we have already given the symmetry classification of ψ_v for the three acetylene models, in the centre and right-hand portions of Tables 1, 3, and 5.

A total-vibrational wave function ψ_v is taken as the product of all the n harmonic-oscillator wave functions $\psi_m(v_m)$, one for each vibrational degree of freedom, each being that

Fig. 3. *Correlation of lower electronic states of the* $D_{\infty h}$ *model with those of the* C_{2h} *and* C_{2v} *models of acetylene. The upper states of transitions which are allowed with the ground state are marked to indicate the directions of electronic oscillations.*

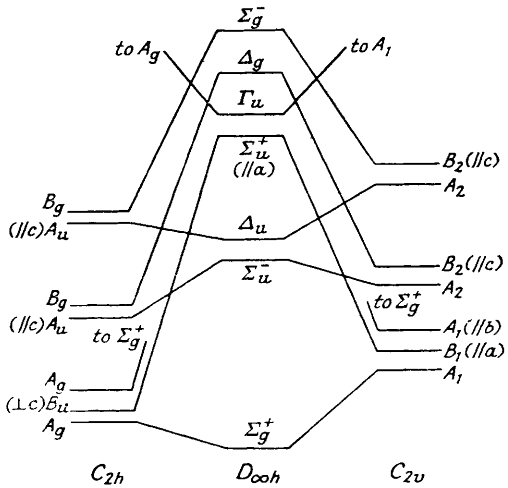
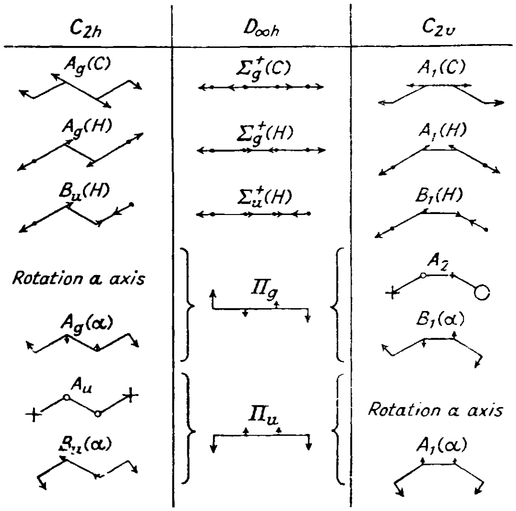


Fig. 4. *Correlation of vibrations of the three acetylene models.*



function of the vibrational co-ordinate σ_m which corresponds to the quantum number v_m of the vibration:

$$\psi_v = \psi_1(v_1) \cdot \psi_2(v_2) \; . \; . \; . \; . \; \psi_m(v_m) \; . \; . \; . \; . \; \psi_n(v_n)$$

The species of ψ_v is thus the direct product of the species of all the ψ_m, and, if the latter are known, can be obtained from Tables 2, 4, and 6. The species of ψ_m depends on the quantum number v_m: if the latter is zero, ψ_m is totally symmetrical; if unity, then ψ_m has the species of the vibrational co-ordinate; and if m, then the species of ψ_m is the direct product of m factor-species, each one that of the vibrational co-ordinate. The symmetry species of the vibrational co-ordinates of the three acetylene models are indicated by the positions of the non-zero entries in the second columns of the right-hand parts of Tables 1, 3, and 5. The figures there inserted show how many different vibrations have co-ordinates belonging to the various species; though in reading Table 1, it has to be remembered that each Π vibration has two orthogonal co-ordinates. How such numbers of vibrations may be calculated has been illustrated before (cf. *J.*, 1936, 971). When the linear molecule becomes bent, one co-ordinate of a Π vibration becomes the co-ordinate of a rotation: the symmetry species of rotations, and of translations, are indicated in the last columns of Tables 1, 3, and 5. Some symmetry species contain no individual vibrations, but all will contain total vibrational wave functions ψ_v involving the simultaneous excitation of several vibrations. Total-vibrational wave functions of the degenerate species, Π, Δ, Φ, etc., are associated with 1, 2, 3, etc., units $h/2\pi$ of vibrational angular momentum about the axis a ($l =$ 1, 2, 3, etc.).

Knowing the numbers of vibrations in the various symmetry species, and also the correlation of species, given in Table 7, among the acetylene models, we can correlate the individual vibrations of these models, as is done in the approximate graphical representation of Fig. 4.

For the characterisation of any upper electronic state of acetylene from ultra-violet spectra, we require a complete knowledge of the frequencies of the vibrations of the ground state. This information is available for acetylene and dideuteroacetylene, and the figures we have used are in Table 9: they were obtained from infra-red spectra, some as fundamentals and some as difference frequencies, by Bell and Nielsen (*J. Chem Phys.*, 1950, **18**, 1382) and Talley and Nielsen (*Phys. Review*, 1951, **82**, 338).

TABLE 9. *Fundamental vibration frequencies (cm.$^{-1}$) of the linear ground state of acetylene and of dideuteroacetylene.*

Vibrations	Σ_g^+(C)	Σ_g^+(H)	Σ_u^+(H)	Π_g	Π_u
C_2H_2	1974·0	3373·2	3282·5	613·3	730·74
C_2D_2	1764·9	2701·84	2439·1	511·38	538·66

If from the Π_g frequencies we compute a bending force constant, and then try to calculate the Π_u frequencies from it, we obtain 500 cm.$^{-1}$ for C_2H_2 and 360 cm.$^{-1}$ for C_2D_2 (Herzberg, " Infra-red and Raman Spectra," van Nostrand, New York, 1945, p. 180). The real values, more than $\sqrt{2}$ times larger, show that the energy curve from the linear ground state to the *cis*-bent ground state must *start* more than twice as steeply as the curve to the *trans*-bent ground state. How the curves continue we do not know, though it is unlikely that a difference of anharmonicity could reverse the order of the gradients.

(b) *Classification of Vibronic Wave Functions.*—In preparation for the study of the symmetry and combining properties of rotational levels, which may belong to any vibrational state associated with any electronic state, it is convenient to be able to assign a collective symmetry to the " vibronic " state, described by $\psi_{ev} = \psi_e\psi_v$ (eqn. 2). This relation shows that, for any one molecular model, the vibronic wave function ψ_{ev} must be subject to the same classification of species (Tables 1, 3, and 5) as that which is common to ψ_e and ψ_v. It follows, furthermore, that the species of any particular ψ_{ev} is simply the direct product (Tables 2, 4, and 6) of the species of its factors ψ_e and ψ_v.

When taking direct products of species of ψ_e and ψ_v of the linear model, one necessarily combines the quantum numbers Λ and l, which measure the components, respectively, of electronic and degenerate-vibrational angular momentum around the ∞-fold axis a. Each quantum number, when not zero, is the magnitude of numbers that can have either sign, their common magnitude covering a doubly degenerate state. Hence their combined value K, to which the same convention applies, is given by

$$K = |\Lambda \pm l| \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

(c) *Selection Rules and Intensities of Vibronic Transitions.*—It follows from the correspondence between the systems of classifications of ψ_{ev} and ψ_e that the selection rules for transitions between particular vibronic states, that is, those governing the appearances of individual bands, are the same in general form as those for transitions between electronic states, that is, those which determine the occurrence of band-systems.

For transitions between vibronic states of the linear model of acetylene, allowance must be made for vibrational contributions to the angular momentum about a, and thus relations (4) must be rewritten, as at (8), with K, defined by equation (7), replacing Λ:

$$\left.\begin{array}{ll} \| \ a: & \Delta K = 0, g \longleftrightarrow u, + \longleftrightarrow +, - \longleftrightarrow - \\ \perp \ a: & \Delta K = \pm 1, g \longleftrightarrow u \end{array}\right\} \quad . \quad . \quad . \quad . \quad (8)$$

To transitions between vibronic states of the *trans*-bent model, relations (5) apply without modification, except with respect to the interpretation of the species labels. To transitions between vibronic states of the *cis*-bent model, relations (6) similarly apply.

The correlation of vibronic species between the straight and the bent models of acetylene, is exactly the same as the correlation of electronic species, given in Table 7. This, together with the principle that selection rules for vibronic, as for electronic, transitions, between states of different molecular models, are to be deduced by treating as total symmetry what is common to the combining models, determine that the selection rules for vibronic transitions between states of the straight model and those of either bent model will be as given in Table 8.

The above discussion is an application of the symmetry aspect of the Franck–Condon principle, as generalised for application to polyatomic molecules by Herzberg and Teller (*Z. physikal. Chem.*, 1933, **21**, *B*, 410). The extended principle tells us what vibrations may change their quantum numbers, and by how much, and with what transition probability, during an electronic transition, thus contributing bands of varying intensity to the band system.

In an allowed band system, $\psi_e''\psi_e'$ belongs to a certain symmetry species. A band is allowed in this system, if $\psi_{ev}''\psi_{ev}'$ belongs to the same species, that, is, if $\psi_v''\psi_v'$ has total symmetry. In absorption at temperatures not too high, nearly all the transitions start from the vibrationless ground state, $\psi_e''\psi_v''(0)$, in which $\psi_v''(0)$ has total symmetry; and therefore in this case the condition for the appearance of a band is that the upper vibrational state ψ_v' has total symmetry. Thus, only totally symmetrical vibrations can suffer unrestricted quantum changes, and so give rise to progressions, $0 \longleftarrow 0$, $1 \longleftarrow 0$, $2 \longleftarrow 0$, . . ., in the upper-state frequency. Non-totally symmetrical vibrations may be excited as even harmonics in the upper electronic state, $2 \longleftarrow 0$, etc., but only with low intensity.

If the temperature is high enough for collisions to excite vibrations in the lower electronic state, other band-series may appear. Totally symmetrical vibrations may yield progressions such as $0 \longleftarrow 0$, $0 \longleftarrow 1$, $0 \longleftarrow 2$, . . ., in their lower-state frequencies; and any vibration may produce a sequence without quantum change, $0 \longleftarrow 0$, $1 \longleftarrow 1$, $2 \longleftarrow 2$, . . ., in the difference between its frequencies in the two electronic states. All these combinations give total symmetry to $\psi_v''\psi_v'$.

When the allowed electronic transition takes place between states belonging to molecular models of different symmetry, then total symmetry, as used in the two preceding paragraphs, must be taken as the common symmetry of the combining models. In our problem, this is the symmetry of either bent model, which is fully included in that of the straight model.

Quantitatively, band intensities are given by the product of the molecular population of the initial vibrational state, the transition probability, and the magnitude of the involved energy quantum. As to the first factor, the proportion of molecules in the vibrationless state is $1/Q$, where Q is the partition function. Relatively to the population of the vibrationless state, the populations of the vibrationally excited initial states are given by Boltzmann factors $ge^{-E/\boldsymbol{k}T} = ge^{-\nu/0\cdot695T}$, where g is the degeneracy of the vibrational state, and ν is in cm.$^{-1}$. The intensities of vibronic transitions starting from the vibrationless state depend little on temperature, relatively to transitions from vibrating states: the latter are strengthened by heating, the more so the higher the initial vibrational energy.

The calculation of vibronic transition probabilities, and thus of the intensities of the bands of a band-system, was first carried through for a diatomic molecule by Hutchisson in the example of hydrogen (*Phys. Review*, 1930, **36**, 410). More recently, the corresponding calculation for the polyatomic molecule, benzene, has been accomplished by Craig (*J.*, 1950, 2146). In the present study of acetylene, we shall be concerned with the distribution of intensity within a progression of bands due to transitions which, as shown by temperature effects, start from the vibrationless ground state, and end on a series of states of quantum number v of a totally symmetrical vibration $\boldsymbol{m}$ of the upper electronic state. For any band $v \longleftarrow 0$ of this progression, the Einstein absorption coefficient is

$$(8\pi^3/3\boldsymbol{h}^2)[\textstyle\int\psi_e''M\psi_e'\mathrm{d}\sigma_{\text{elec.}} \,.\, \int\psi_v''(0)\psi_v'(\boldsymbol{m}, v)\mathrm{d}\sigma_{\text{nucl.}}]^2$$

and thus the intensity distribution among the bands is given by

$$K(\nu_{0v}/\nu_{00})[\textstyle\int\psi_m''(0)\psi_m'(v)\mathrm{d}\sigma_m]^2 = K(\nu_{0v}/\nu_{00})(S^q{}_{0v})^2 \quad . \quad . \quad . \quad . \quad (9)$$

where the ν's are frequencies of the vibronic transitions * $v \longleftarrow 0$ and $0 \longleftarrow 0$, and the constant K includes the electronic transition probability, the integrals in the co-ordinates of vibrations whose quantum numbers do not change, the molecular population factor, and universal constants. Apart from the only slightly varying ratio of vibronic energy quanta, ν_{0v}/ν_{00}, intensity distribution in the progression is governed by the overlap integral, $S^q{}_{0v}$, which in turn depends on the separation q of the origins of the co-ordinates of the lower- and upper-state vibrations $\boldsymbol{m}$. For the purpose of expressing $S^q{}_{0v}$ as a function of q, we have made the simplifying assumption of treating the CH groups as "compound atoms," thus neglecting the motion of hydrogen relatively to carbon. This was one of the several sets of assumptions used by Craig, who, on this basis, gives $S^q{}_{0v}$ in the following form :

$$\left.\begin{aligned} S^q{}_{0v} &= e^{-\beta_1[q^2/2(1+\rho)]}\sum_r\left(\frac{\sqrt{\beta_2}q\rho}{1+\rho'}\right)^{v-r}\left\{\frac{v!}{r!\,(v-r)!}\right\}^{\frac{1}{2}}\left\{\frac{2^{v-r}}{(v-r)!}\right\}^{\frac{1}{2}}S^0{}_{0r} \\ S^0{}_{0r}\ (\text{even } r) &= \frac{1}{(r/2)!}\sqrt{\frac{r!}{2^r}}\left(\frac{2\sqrt{\rho}}{1+\rho}\right)^{\frac{1}{2}}\left(\frac{1-\rho}{1+\rho}\right)^{r/2};\quad S^0{}_{0r}\ (\text{odd } r) = 0 \end{aligned}\right\} \quad . \quad . \quad (10)$$

Here $\rho = \beta_1/\beta_2 = \nu_1/\nu_2$, the subscripts 1 and 2 referring respectively to the lower and upper electronic states, and the oscillator constant $\beta = (2\pi/\boldsymbol{h})\sqrt{\mu k}$, where μ is the "reduced mass," and k the force constant of the oscillator, whose frequency is ν, so that $k = 4\pi^2\nu^2\mu$. Equations (9) and (10) together give the distribution of intensity among the bands as a function of q; and, having measured the intensities of a number of the bands, one can choose q to fit the distribution, thereby obtaining, not only a geometrical parameter of the upper electronic state, but also a means of computing, as described below, the intensity of the whole electronic transition (even if partly obscured by overlapping) from observations on a few of its bands.

With respect to the vth band, what is measured is the optical density D_L, at a series of frequencies ν within the band, and hence the optical density integral $\int D_L d\nu$ taken over the band, for an absorption-path L defined as in Part II (p. 2707). The intensity is then calculated as the absorption-coefficient integral $\int \alpha d\nu$, which, Beer's law being obeyed, is independent of L. Finally, it is re-expressed, conventionally, as an oscillator strength :

$$f_v = (\boldsymbol{mc}^2/\pi\boldsymbol{Ne}^2)(\int\alpha d\nu)_v \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

Here $\boldsymbol{m}$ and $\boldsymbol{e}$ are the mass and charge of an electron, $\boldsymbol{c}$ is the velocity of light, and $\boldsymbol{N}$ is the number of molecules per cm.^{3} in the vibrationless ground state, at the temperature of the measurement, but at the density the gas would have at 0° and 1 atm. For acetylene at 0°, the partition function Q is 1·14, so that $\boldsymbol{N} = 2{\cdot}36 \times 10^{19}$, and therefore the first factor in parentheses in eqn. (11), for temperatures near 0°, has the value $4{\cdot}78 \times 10^{-8}$ cm.^{2}.

In order to obtain the intensity of the whole electronic transition from the measured intensity of the vth band, we can use the sum rule :

$$\sum_{v=0}^{\infty} (S^q{}_{0v})^2 = 1$$

If we disregard the weaker combinations of the vibrationless ground state, that is, its combinations with vibrations other than the $\boldsymbol{m}$th of the upper electronic state, and if we also neglect the effect on intensity distribution of the proportionately small change in ν_{0v} between the vth band and the most intense part of the progression, it follows from this rule that the oscillator-strength of the whole electronic transition is given by the relation

$$f = f_v/(S^q{}_{0v})^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

The numerator on the right-hand side having been measured, and the denominator calculated, following the estimation of q, each measured band should give the same value of f, for the whole electronic transitions. It should be emphasised that intensity measurements, like the calculations based on them, are only approximate, but are nevertheless of value because spectroscopic intensities vary so widely.

* Prof. Craig asks us to mention that, although $(\nu_n/\nu_0)^4$ is inadvertently written in his formula (4), his calculations were made with the correct formula containing only the first power of (ν_n/ν_0).

(4) Gyrovibronic states and transitions

(a) *Classification of Rotational Wave Functions: Rotational Energies.*—Rotational wave functions contain parameters of the vibronic states with which they are associated, but this does not affect the principles of their classification. They are classed, first, with respect to their behaviour under rotations of the external axes, X, Y, Z, and, secondly, for any given molecular model, under those transformations of the internal axes, a, b, c, to which the rotational wave equation is invariant.

Rotations of the external axes lead to the familiar classification of ψ_r according to the values $J = 0, 1, 2, \ldots$, each J with $(2J + 1)$-fold degeneracy, where J is the number of units $\boldsymbol{h}/2\pi$ of total angular momentum, including any supplied by electronic orbital motion and by degenerate vibrations. This is one way in which ψ_r may depend on ψ_{ev}. Apart from one exception, the selection rule

$$\Delta J = -1, 0, +1 \qquad (13)$$

holds, and accounts for the usual division of bands into P, Q, and R branches, respectively. The exception relates to linear molecules, and it is that, in transitions between two vibronic states both having $K = 0$ (two Σ states), the allowed J combinations are reduced to

$$\Delta J = -1, +1 \quad (\text{for } \Sigma - \Sigma) \qquad (14)$$

so that the bands, which by equations (8) are of " parallel " type, have no Q branches.

The rotational wave equation of the $D_{\infty h}$ model is invariant to the transformations of a, b, c, summarised in the symbol D_∞; and thus ψ_r may be, in this case, classified according to its behaviour under rotations C^a_ϕ by $\pm\,\phi$ round a, and C_2^{bc} by π round b or c, as shown in Table 10. The species are labelled Σ, Π, Δ, . . ., according as K, the number of units of vibronic angular momentum about a, is 0, 1, 2, . . . In this respect also ψ_r is dependent on ψ_{ev}. The two non-degenerate Σ species together cover, and each degenerate species, Π, Δ, etc., separately covers, all possible values of J, which, as a measure of total angular momentum, cannot be less than K, the measure of its figure-axial component. The direct products of Table 11, in combination with the species of the electric moment M in Table 10, give the selection rules:

$$\text{Parallel to } a: \ \Delta K = 0. \quad \text{Perpendicular to } a: \ \Delta K = \pm 1 \qquad (15)$$

Table 10. *Species of rotational wave functions of $D_{\infty h}$ model.*

Rotn.	K	M	E	$2C_\phi^a$	C_2^{bc}
Σ_1 (even J)	0	—	1	1	1
Σ_2 (odd J)	0	M_a	1	1	-1
Π (all J)	1	M_{bc}	2	$2\cos\phi$	0
Δ (all J)	2	—	2	$2\cos 2\phi$	0
. . . (all J)	. . .	. . .	. . .	. . .	. . .

Table 11. *Direct products of rotation species D_∞ of $D_{\infty h}$ model.*

	Σ_1	Σ_2	Π	Δ
Σ_1	Σ_1	Σ_2	Π	Δ
Σ_2		Σ_1	Π	Δ
Π			$\Sigma_1\Sigma_2\Delta$	$\Pi\Phi$
Δ				$\Sigma_1\Sigma_2\Gamma$

The rotational wave equation for *both* the bent models C_{2h} and C_{2v} is invariant to those transformations of the internal axes which are denoted by V; and thus the species of ψ_r depend on its behaviour under rotations by π round any two of the axes a, b, and c, as shown in Table 12. Symmetry under all three rotations is denoted by A, and under one only by B with the appropriate subscript. The direct products in Table 13, together with the electric-moment species in Table 12, give the selection rules:

$$\|\, a: \ A \longleftrightarrow B_a,\ B_b \longleftrightarrow B_c \quad \|\, b: \ A \longleftrightarrow B_b,\ B_c \longleftrightarrow B_a \quad \|\, c: \ A \longleftrightarrow B_c,\ B_a \longleftrightarrow B_b\} \qquad (16)$$

Table 12. *Species of rotational wave functions of the C_{2h} and C_{2v} models.*

Rotn.	M	E	C_2^a	C_2^b	C_2^c
A	—	1	1	1	1
B_a	M_a	1	1	-1	-1
B_b	M_b	1	-1	1	-1
B_c	M_c	1	-1	-1	1

Table 13. *Direct products of rotation species V of the C_{2h} and C_{2v} models.*

	A	B	B_b	B_c
A	A	B_a	B_b	B_c
B_a		A	B_c	B_b
B_b			A	B_a
B_c				A

By examining the behaviour of the rotational species of the $D_{\infty h}$ model (Table 10) with respect to the symmetry operations determining the rotational species of the C_{2h} and the C_{2v} models (Table 12), we can correlate the two sets of species, as is done in Table 14. If now, in the light of this correlation, we compare the selection rules (15) and (16), in order to discover what is common between them, or, in other words, derive selection rules for the combination of rotational states of the straight model with those of either bent model, we find the results summarised in Table 15.

TABLE 14. *Correlation of rotational species among the $D_{\infty h}$, C_{2h} and C_{2v} models.*

Symmetric top (model $D_{\infty h}$)	Σ_1	Σ_2	Π, Φ, etc.	Δ, Φ, etc.
Asymmetric top (models C_{2h} and C_{2v})	A	B_a	$B_b + B_c$	$A + B_a$

TABLE 15. *Rotational selection rules for transitions between the $D_{\infty h}$ model of acetylene and either the C_{2h} or C_{2v} models.*

	C_{2h} or C_{2v}		
$D_{\infty h}$	$\parallel a$	$\parallel b$	$\parallel c$
Σ_1	B_a	B_b	B_c
Σ_2	A	B_c	B_b
Π	B_b, B_c	A, B_a	A, B_a
Δ	A, B_a	B_b, B_c	B_b, B_c

The energy levels of the linear model, considered as a rigid symmetric top, are given by the formula

$$E = BJ(J + 1) + (A - B)K^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

If E is to be expressed in cm.$^{-1}$, then $A = \boldsymbol{h}/8\pi^2\boldsymbol{c}I_a$ and $B = \boldsymbol{h}/8\pi^2\boldsymbol{c}I_b$, the constant $\boldsymbol{h}/8\pi^2\boldsymbol{c}$ having the value $27{\cdot}983 \times 10^{-40}$ g.-cm.

Because of the relative lightness of hydrogen, both the bent acetylene models, although they are asymmetric tops, will be nearly symmetric tops, so that an analogous energy formula, containing the average of B and C in place of either, will apply approximately :

$$E = \tfrac{1}{2}(B + C)J(J + 1) + \{A - \tfrac{1}{2}(B + C)\}K^2 \quad . \quad . \quad . \quad . \quad (18)$$

when $C = \boldsymbol{h}/8\pi^2\boldsymbol{c}I_c$. However, the precise formula for the asymmetric top, supposed rigid, is

$$E = \tfrac{1}{2}(A + C)J(J + 1) + \tfrac{1}{2}(A - C)E(\kappa) \quad . \quad . \quad . \quad . \quad . \quad (19)$$

where κ is a parameter measuring the degree of asymmetry,

$$\kappa = (2B - A - C)/(A - C)$$

and $E(\kappa)$ is the energy quantity (Ray's modification of the Wang function) which has been evaluated by King, Hainar, and Cross (*J. Phys. Chem.*, 1943, **11**, 27; 1949, **17**, 826) for all J, K values up to $J = 12$ ($K = 0, 1, \ldots J$, and $J = K, K + 1, \ldots\ldots 12$).

For analysis of the rotational structure of bands due to transitions from the normal electronic state of acetylene, we need information concerning the moments of inertia B of the latter, which depend on I_b, and thus on the internuclear distances. These quantities are evaluated by the rotational analysis of infra-red bands of C_2H_2 and C_2D_2, and we have used the data in Table 16, furnished by Saksena's recent studies of bands in the photographic infra-red (*J. Chem. Phys.*, 1952, **20**, 95).

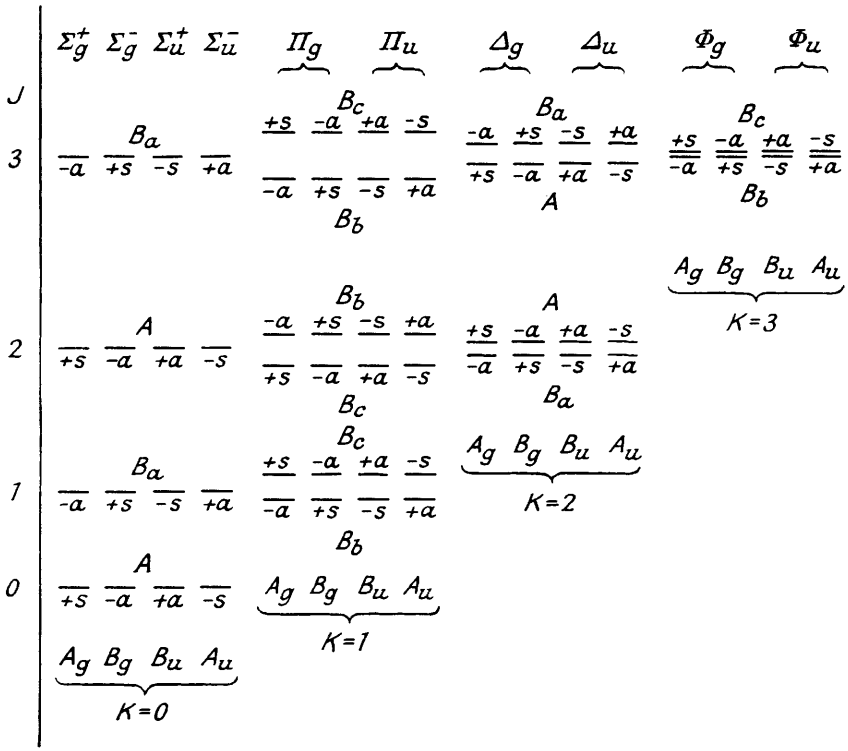
TABLE 16. *Dimensions of acetylene at zero-point energy in its normal electronic state.*

	B (cm.$^{-1}$)	I_b (10^{-40} g.-cm.^{2})	r_{CC} (Å)	r_{CH} (Å)
C_2H_2	1·1769	23·776	1·208	1·058
C_2D_2	0·8479	33·004		

(b) *Classification and Correlation of Gyrovibronic States of the Three Models of Acetylene.*—In his papers on the theory of transitions between straight and bent states of a triatomic molecule (*locc. cit.*), Mulliken showed that, even when the atomic masses are of the same order of magnitude, a fairly large bending angle will still allow the resulting asymmetric top to obey approximately the K-containing energy formulæ of the symmetric top, thus justifying description as a prolate near-symmetric top. This must be still more true of a molecule, such as acetylene, in which bending only moves light atoms off the line of considerably heavier ones: indeed, acetylene must be a prolate near-symmetric top independently of the bending angle. Thus for either bent model of acetylene, a quantity K exists with approximate significance as a quantum number measuring the angular momentum about a, though it can be defined exactly only by the limit to which it goes as the bent molecule is straightened. In the last stages of this imaginary process, the angular momentum will pass over from being carried by rotation and described in ψ_r, to being carried by the electronic motion, or by degenerate vibrations, and described in ψ_{ev}. However, the component of angular momentum itself will experience no discontinuity, but will merely become more definite, as the straightening process goes to completion.

As can be seen from Table 7 (p. 2711) in its application to vibronic states, any vibronic state of either bent model is correlated with an infinite series of vibronic states of the straight model: they differ with respect to angular momentum about a, that is, with respect to K. For example, a vibronic A_g state of the *trans*-bent model is correlated with

FIG. 5. *Rotational, gyrovibronic, and overall classification of energy levels of the* C_{h2} *model of acetylene : correlation with the* $D_{\infty h}$ *model.*



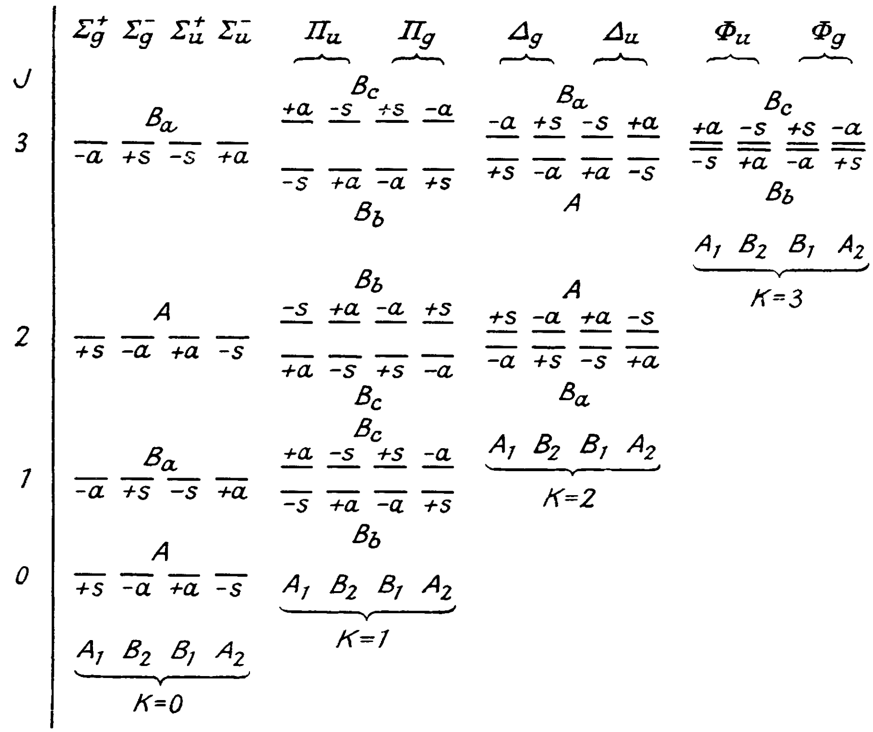
linear Σ_g^+ Π_g, Δ_g, . . ., states for which $K = 0, 1, 2, \ldots$ The detailed meaning of this must be that to a vibronic bent state belong rotational states supplying infinitely various amounts and directions of angular momentum, which, as the molecule is straightened, converge, with respect to the component of angular momentum about a, on the infinitude of discrete limits, corresponding to $K = 0, 1, 2, \ldots$ Mulliken has given the name gyrovibronic state to a set of energy levels, such as those of any single column in Figs. 5 and 6, which belong to a particular vibronic state and to a particular value of K, whether precisely actual or defined by its limiting value. In either bent model of acetylene, one vibronic state contains infinitely many gyrovibronic states, but in the straight model, the vibronic is the same as the gyrovibronic state (because here rotation does not contribute to K). One bent gyrovibronic state is correlated with one linear gyrovibronic, non-degenerate state.

Two bent gyrovibronic states are correlated with one linear gyrovibronic doubly degenerate state. The correlations, which follow from Table 7, are shown by the top and the bottom sets of symbols in Figs. 5 and 6. Each gyrovibronic state of any model contains infinitely many energy levels which are distinguished with respect to J. The way in which the levels of pairs of bent gyrovibronic states mix and converge to give the levels of linear degenerate gyrovibronic states will be noted in the next Section.

(5) Energy levels and their transitions

(a) *Classification of Unfactorised Wave Functions.*—As Mulliken has pointed out (*locc. cit.*), this is a useful classification, because the few " overall " selection rules to which it leads

FIG. 6. *Rotational, gyrovibronic, and overall classification of energy levels of the* C_{2v} *model of acetylene : correlation with the* $D_{\infty h}$ *model.*



are strictly obeyed, even when the factorisation of ψ is far from strict, as may happen in the presence of perturbations. Three groups of operations are involved.

The first consists of the infinitude of rotations of the external axes, X, Y, Z. This leads to the J classification, already described on p. 2719. If ψ is factorised, and ψ_r is a factor, then care is taken of the J classification in ψ_r. If ψ is not factorised, then the J classification applies without modification to ψ itself.

The second " group " of operations amounts only to the inversion I of external axes, X, Y, Z, through their origin. This process multiples the wave function either by $+1$ or by -1, and so gives rise to the " parity " classification of ψ as $+$ or $-$. The condition under which the intensity-controlling integral $\int\psi''M\psi'd\sigma$ does not vanish, is that the integrand shall not change sign under I, and, since the electric moment M does change sign, the product $\psi''\psi'$ must change sign also. The selection rule follows :

$$+ \longleftrightarrow - \qquad (20)$$

The remaining group of operations consists in the possible permutations of labels between sets of nuclei whose positions can be interchanged by rotation without making any physical difference. In the case of acetylene, on any of our models, there is just one such permutation, P_2, and this exchanges the labels of the two carbon atoms and of the two hydrogen atoms. According as P_2 does not or does change the sign of ψ, the latter is classed as symmetric s or antisymmetric a. Since M does not change sign under P_2, the selection rule is as follows:

$$s \longleftrightarrow s \qquad a \longleftrightarrow a \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (21)$$

(b) *Classification and Correlation of Energy Levels of the Three Models of Acetylene.*—It is necessary first to factorise I and P_2, each into two operators, the first of which acts on ψ_r only, while the second acts on ψ_{ev} only. The factors differ according to the molecular model. For the C_{2h} model the operational equations are as follows:

$$I(\psi) = C_2^c(\psi_r) \cdot \sigma^{ab}(\psi_{ev}) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (22)$$

$$P_2(\psi) = C_2^c(\psi_r) \cdot C_2^c(\psi_{ev}) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (23)$$

The first factor in (22) turns the molecule by π around c. In a general case everything thus turned would have to be reflected across the plane ab, in order to complete the operation I. The second factor in (22) thus reflects the electron positions, and the nuclear *displacements*. The nuclear *positions* remain unreflected, but as they lie in the plane ab, no reflexion of them is needed for the completion of I. In equation (23), the first factor rotates the electron positions, the nuclear equilibrium positions, and the nuclear displacements, while the second restores the electron positions, and nuclear displacements, but not the nuclear positions. Thus the two operations together amount to the nuclear permutation P_2.

For the C_{2v} model the corresponding operational equations are as follows:

$$I(\psi) = C_2^c(\psi_r) \cdot \sigma^{ab}(\psi_{ev}) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (24)$$

$$P_2(\psi) = C_2^b(\psi_r) \cdot C_2^b(\psi_{ev}) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (25)$$

The justifying arguments are similar to those in the preceding paragraph. For the $D_{\infty h}$ model either pair of equations can be used, since the axes b and c have in this model become equivalent symmetry axes.

For any of the rotational species of the $D_{\infty h}$ model, as listed in Table 10, and for some particular J and K, we note the correlated rotational species of the C_{2h} and C_{2v} models in Table 14 (p. 2720), and then find the effects of C_2^c and of C_2^b on such species of ψ_r in Table 12 (p. 2719). These are to multiply ψ_r by either $+1$ or -1. The effects of σ^{ab} and of C_2^c on ψ_{ev} for each of the four vibronic species of the C_{2h} model are then found from Table 3 (p. 2711); and likewise the effects of σ^{ab} and of C_2^b on ψ_{ev} for each of the four vibronic species of the C_{2v} model are found from Table 5 (p. 2711). These effects are always to multiply ψ_{ev} by either $+1$ or -1. By multiplying the results obtained in these ways, we can find what the operators I and P_2 will do to ψ, thus determining the overall species of the energy levels, as recorded in Figs. 5 and 6.

Correlation of the gyrovibronic states of either bent model, as shown below the energy levels of Figs. 5 and 6, with those of the linear model, as indicated above the columns of levels, has been discussed; but it remains to be considered how, when $K > 0$, groups of individual levels of a bent model coalesce to give degenerate levels as the molecule is straightened. It will suffice to take, as an example, the *trans*-bent model (Fig. 5), and, in particular, its gyrovibronic states A_g and B_g, and their energy levels which have the quantum numbers $J = 1$ and $K = 1$. There are four such levels, each gyrovibronic state containing a doublet, whose separation depends on the degree of asymmetry. As the molecule straightens, so that the distinction between b and c, I_b and I_c, B and C, and therefore between B_b and B_c, becomes lost, the wave functions of the two $+s$ levels mix, either with the other, to eventual equality, as also do those of the two $-a$ levels, while at the same time the energy separation of the equally mixed $+s$ level and the equally mixed $-a$ level becomes zero, so that we now have a doubly degenerate level of the gyrovibronic state Π_g. Such mixings and convergencies occur in sets of four "bent" levels, each set to give one degenerate " straight " level, over the whole manifold of levels for which $K > 0$.

In practice the convergencies may not be completed to coincidence, if the factors ψ_{ev} and ψ_r cannot accurately be separated, so that angular momentum is not sharply partitioned between rotations and degenerate vibrations (l-type doubling), or between rotations and electronic orbital motion (Λ-type doubling). This being taken into account, each set of four " bent " levels will yield two " straight " levels, one s and one a, which will not be degenerate but will form a definite doublet. We may summarise such phenomena under the collective term " K-type doubling." It is expected to be a small effect, except where perturbations spoil the factorisation of ψ.

(c) *Intensities of Rotational Lines: Effects of Nuclear Spin in Acetylene and Dideutero-acetylene.*—The way in which, in any P, Q, or R branch of a band, the intensities of successive rotational lines in general rise at first with the J-degeneracy as J increases, later to fall with the eventually dominating Boltzmann factor, presents no special features in our problem. However, the effect of nuclear spin in giving different statistical weights to the s and a levels, and thus leading to a superposed alternation, or other periodicity, of intensity, is deserving of comment.

In $^1H \cdot ^{12}C \vdots ^{12}C \cdot ^1H$, the carbon nuclei have no spin, while each proton has the spin quantum number $\frac{1}{2}$ with 2-fold space-degeneracy, so that there are 4 nuclear-spin functions, of which 3 are symmetric and 1 antisymmetric to P_2 (Fowler and Guggenheim, " Statistical Thermodynamics," Cambridge Univ. Press, 1939, p. 84). The former spin functions must multiply the ψ of a levels, and the latter the ψ of s levels, in order to make the complete molecular wave function antisymmetric in (odd mass-numbered) protons. Thus the a levels of C_2H_2 have three times the statistical weight of s levels. In $^2D \cdot ^{12}C \vdots ^{12}C \cdot ^2D$, each deuteron has spin quantum number 1 with 3-fold space-degeneracy, and hence there are 9 nuclear-spin functions, 6 symmetric and 3 antisymmetric, with which to make the complete wave function symmetric in (even mass-numbered) deuterons. Thus the s levels of C_2D_2 have twice the statistical weight of the a levels.

In transitions between two gyrovibronic states of the linear acetylene model, provided that at least one of the states has $K = 0$, the rotational lines of a branch of a band will alternate in intensity, in opposite ways for C_2H_2 and C_2D_2, as can be followed in detail from Fig. 5 or 6. If neither gyrovibronic state has $K = 0$, then, in the absence of l-type doubling, no such alternation will occur, since both combining levels will be degenerate, each having an s and an a component. When l-type doubling can be observed, there will be alternation over all lines, each doublet having a weak and a strong component.

In transitions between a gyrovibronic state of the linear model and one of either bent model, provided that in one of the states $K = 0$, similar alternations will appear; for the overall selection rules (20, 21, pp. 2722, 2723) will always exclude from combination one member of each doublet for which in the other state $K = 1$. If neither gyrovibronic state has $K = 0$, a slightly more complicated periodicity of intensities should be found. The successive J values along a branch of a band will each be represented by a doublet with a stronger and a weaker component; and these components will change sides on passing from any doublet to the next. These expected relationships can easily be followed from Figs. 5 and 6; and they have diagnostic value in our analytical problem.

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