Theory of Color of Organic Compounds

Alfred L. Sklar

Theory of Color of Organic Compounds

ALFRED L. SKLAR

Departments of Physics and Chemistry, The Johns Hopkins University, Baltimore, Maryland

(Received July 9, 1937)

Several structural formulae can be written for a colored compound, since the molecule usually contains an alternation of single and double bonds. The color is attributed to absorption bands corresponding to transitions between the levels which arise from a resonance among these different possible structures. A calculation is made for the levels of benzene, cyclohexadiene, fulvene, and azulene; fulvene being a yellow compound, azulene a blue one; the others, although colorless, have absorption bands in the near ultraviolet. One parameter only enters the calculation and is evaluated by data on heats of hydrogenation. The absorption bands of the molecules are then calculated without using any optical data, the results agreeing well with experiment. The calculation is amplified in the case of benzene so as to include polar structures and also triplet states in the linear combination representing the molecule. The symmetry of the states is discussed in connection with selection rules, which are found to be in agreement with the relative intensity of the band groups in benzene. An interpretation of the structure of the 2600A band is proposed which is shown to account for many properties of this band system.

INTRODUCTION

EXPERIENCE has shown that absorption of visible or near ultraviolet light (>2000A) only occurs when certain groups are present in the molecule. Examples of such groups, called chromophores, are:

$$-N=N-; \quad \diagdown C=C \diagup \quad ; \quad \diagdown C=0;$$

$$\diagdown C=S; \quad \diagdown C=N-; \quad -N=0.$$
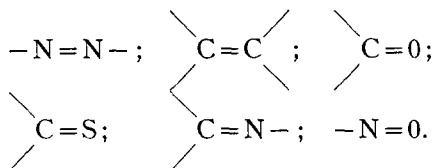
It will be noticed that each of these groups possesses an alternation of single and double bonds. In a colored compound these groups occur conjugated with other double bonds as is seen in the molecules of Fig. 1.

Although a colored molecule has many such conjugated double bonds, the color does not depend upon the number of these alternations alone. Fulvene, which is yellow, has three such alternations, whereas diphenyl, which does not absorb in the visible but only in the ultraviolet, has six. The color, then, is very strongly influenced by the way in which the chromophores are bound together; that is, it depends upon the structure of the entire molecule.

The role played by chromophores can be seen from the following qualitative discussion. The alternation of single and double bonds which is present in a chromophore always enables one to write several structural formulae for the molecule; benzene, for instance, may be written five ways (cf. Fig. 2).

When several structural formulae may be written the molecule is not truly represented by any one of them, but behaves somewhat like a mixture of all structures. The true states of a molecule of this kind are, then, not described by one structural formula but are obtained by taking
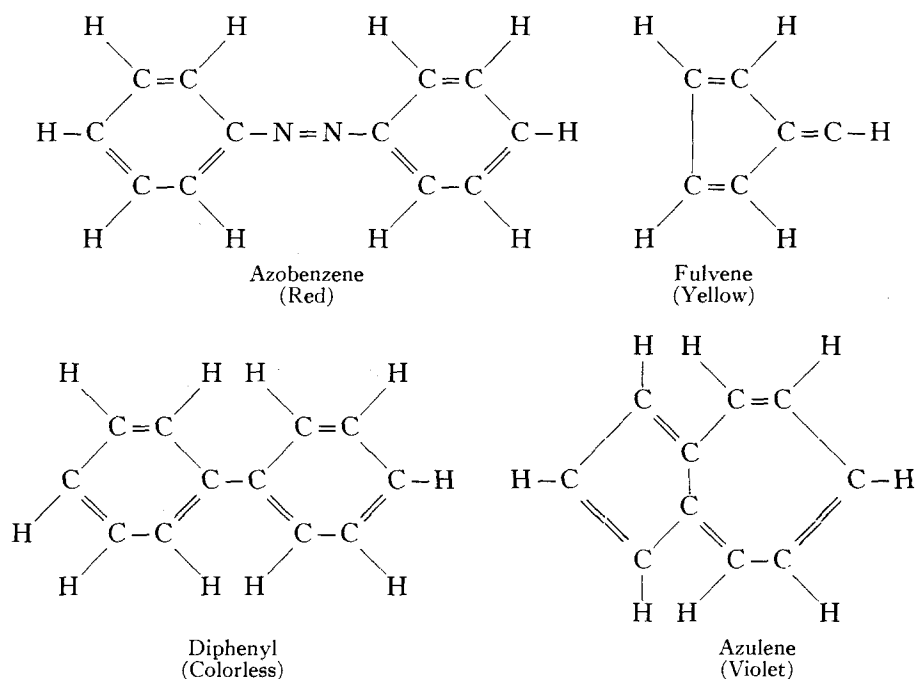
669

Azobenzene
(Red)

Fulvene
(Yellow)

Diphenyl
(Colorless)

Azulene
(Violet)

FIG. 1.

all the formulae into account.[1] Although the various structures may have identical or slightly different energies, the actual energy values of the molecule can be entirely different, due to a resonance phenomenon such as occurs in the simple case of two identical coupled pendula. In the case of benzene the two Kekule structures have identical energy, as do the three Dewar structures, the latter three having a higher energy than the former two since a *para* bond is weaker than an *ortho* bond. Now, when we calculate the true energy levels of the molecule (making a number of approximations) we find that the energy levels corresponding to the five structures
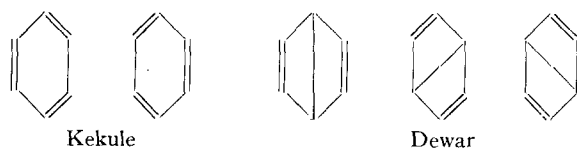
Kekule   Dewar

FIG. 2.

have split into five widely separated levels (cf. Fig. 3. The α which appears in the figure is a parameter which will be described and evaluated later[2]).

Now the transitions between these true levels of the molecule will give rise to absorption bands which, within the accuracy of this calculation, lie at the proper frequency. That is, the absorption bands are due to transitions between levels which arise from the resonance between the states corresponding to the different structures.[3]

The electronic transition of lowest energy has been calculated for several organic molecules. Benzene is treated in most detail, and an

---

[1] E. Hückel, Zeits. f. Physik **70**, 204 (31); L. Pauling and J. Sherman, J. Chem. Phys. **1**, 606, 679 (33).

[2] Two electrons present on neighboring atoms lower the energy of a structure (forbidding resonance between structures) by $-\alpha$ (α is negative) if the electrons are paired so as to form a bond, and raise the energy by $-\frac{1}{2}\alpha$ if they are not paired. The two Kekule structures hence have an energy lowering of $(3-3/2)\alpha=1.5\alpha$ whereas the three Dewar structures each have an energy lowering of $-(2-4/2)\alpha=0$.

[3] The picture of the molecule resonating between different structures and a consequent splitting up of the energy levels is a description of the method of calculation rather than of the fundamental problem. To calculate the color of a molecule one must know the true energy levels of the molecule and the transition probabilities between them. The concept of resonance comes in when we attempt to calculate these levels by describing the molecule by structural formulae, since several formulae may be equally good; for example, the two Kekule forms for benzene. A resonance between these forms does not imply that the molecule changes quickly from one form to the other. The situation is rather that the molecule is in a stationary state in which it is simultaneously partially like each structure. We could avoid the discussion of resonance if as a first-order approximation we solved the problem of an electron moving in a potential field of the symmetry of the nuclei. This latter approach is the essence of the H-M-H method, whereas the resonance picture is the H-L-S-P. Both pictures should approach one another in higher order approximations.

interpretation of its spectrum is given. A calculation of azulene, a compound of physiological interest, points out a rather promising application of a calculation of spectra to physiological problems. The determination of the structure of a natural product, perhaps a hormone, is a matter of many years' work in which many guesses are

———— -4.6α

⊃———— -2α

——— ——— 0   ———— 0

——— ——— 1.5α

———— 2.6α

Levels of single structure   Levels of Benzene
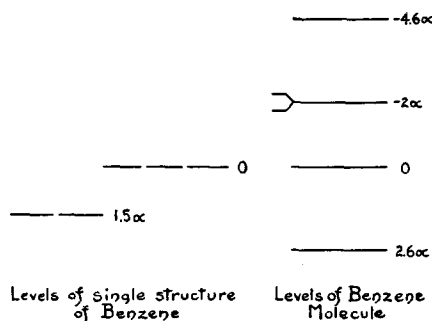of Benzene   Molecule

FIG. 3.

made and later rejected. One could calculate the spectrum of a proposed structure, check it against the experimental one, and so keep on the right track.

Since the problem of a complicated molecule is too difficult to solve exactly, we must resort to approximation methods. It is desirable to make a calculation of this sort with several methods based on quite different approximations. The two methods in use are the Hund-Mulliken-Hückel and the Heitler-London methods, the latter extended by Slater and Pauling. The former in its convenient but simplified application (without antisymmetrizing the molecular orbital) neglects the repulsion of the electrons. The latter method overemphasizes this repulsion and assumes that two electrons never pile up on the same atom; that is, writes the wave function for the molecule as a linear combination of the functions representing the structures in which all the atoms are neutral, neglecting ionic terms in the wave function.

In this calculation the H-L-S-P method has given much better quantitative results than the H-M-H. The H-M-H gives the relative spacing of the levels quite well, but not the absolute spacing. All of the quantitative calculations are, therefore, done by means of the H-L-S-P method.[4] It is possible to relieve the overemphasis on

electron repulsion of the H-L-S-P method very simply, since it is really not inherent in this method that one consider only those structures which have not more than one π electron on each atom. That is, one may write structures like
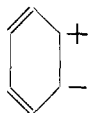
as well as those shown in Fig. 2, and include all the structures in the combination of functions which represents the molecule.

Since we are interested in resonance between double bonds in complicated molecules, we can simplify the problem greatly without much loss in accuracy by neglecting all electrons except those forming π bonds. Benzene is thus treated as a six-electron problem. The justification is that π wave functions have a node in the plane of the ring so that the overlap between them and the function for an electron forming a bond in the plane is very small.

We treat a molecule like benzene as follows: Each carbon has three bonds at 120° angles,[5] with the axes of the electron clouds in the plane of the ring (cf. Fig. 4). Now, each carbon has one
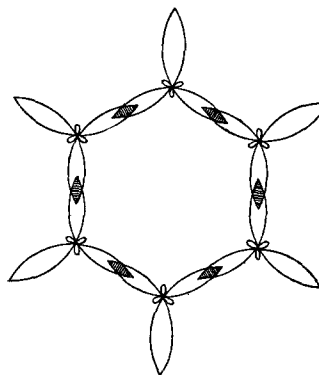

FIG. 4.

more electron whose density cloud is a dumbbell with its axis perpendicular to the plane of the ring (cf. Fig. 5). The clouds of these latter
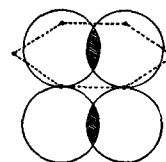

FIG. 5.

---

[4] In the following paper the calculation is made with the H-M-H method with good qualitative results.

[5] J. H. Van Vleck and A. Sherman, Rev. Mod. Phys. July 1935, p. 204.

electrons overlap the clouds of the electrons forming in-plane bonds only very slightly.

METHOD

We first write all possible structures for our molecules, a so-called canonical set. This set is found by using the following theorem of Rumer, Teller and Weyl[6] based on the theory of binary invariants: "Arrange the atoms in a circle which need have nothing to do with the actual arrangement in the molecule; any structure in which no bonds cross is one of the set." The wave function for a structure in which bonds cross can be written as a linear combination of functions involving no crossed bonds.

Now to each structure, k, of the canonical set attach a wave function[7]

$$\Psi^k = \frac{1}{2^{n/2}}\sum_R (-1)^R R \left\{ \frac{1}{(2n!)^{\frac{1}{2}}}\sum_P (-1)^P P \right.$$

$$\times \prod_{l=1}^{n} \psi_{2l-1}(2l-1)\alpha(2l-1)\psi_{2l}(2l)\beta(2l) \left. \right\}$$

$$= \frac{1}{2^{n/2}}\frac{1}{(2n!)^{\frac{1}{2}}}\sum_P (-1)^P P \psi_1(1)\psi_2(2)(\alpha_1\beta_2 - \beta_1\alpha_2)$$

$$\times \psi_3(3)\psi_4(4)(\alpha_3\beta_4 - \beta_3\alpha_4), \text{ etc.} \quad (1)$$

which expresses the fact that those π electrons which occur on atoms having a double bond between them are paired. Here ψ_{2l} is the wave function of the $2l$th isolated atom, R is the operation of interchanging spins of those electrons that are paired, P is a permutation of the electrons, α, β are the two spin functions, and n is the number of bonds. The structures differ from one another through the different pairings of the electrons.

We then write the wave function for the molecule Ψ as a linear combination of the Ψ^k for each structure, i.e.

$$\Psi = \sum C_k \Psi^k. \quad (2)$$

Ψ must satisfy the Schrodinger equation

$$(H - W)\Psi = 0, \quad (3)$$

where the operator

$$H = H^0 + \sum_{j=1}^{2n} H_{j,\,j+1} \qquad (2n+1) = 1, \quad (4)$$

H^0 is the Hamiltonian of the isolated atoms; $H_{i,\,i+1}$ is the interaction energy between the j and $(j+1)^{st}$ atoms. This means that we consider interaction only between neighboring atoms.

The energy levels are now given by the resulting secular equation

$$\det ||(\Psi^j | H - W | \Psi^k)|| = 0,$$

where

$$(\Psi^j | H - W | \Psi^k) = \int \Psi^j (H - W) \bar{\Psi}^k d\tau. \quad (5)$$

This determinant can easily be factored if one keeps in mind the group of symmetry operations on the molecule.

To set up the determinant we must evaluate the matrix components $(\Psi^j | H - W | \Psi^k)$. This can be done by directly expanding or by expressing the results of this expansion into the following rules:[8]

$$(\Psi^j | H - W | \Psi^k) = U_{jk}(Q - W) + V_{jk}\alpha,$$

$$Q = \int \psi_1(1)\psi_2(2)\psi_3(3)\psi_4(4)\psi_5(5)\psi_6(6)H$$

$$\times \bar{\psi}_1(1)\bar{\psi}_2(2)\bar{\psi}_3(3)\bar{\psi}_4(4)\bar{\psi}_5(5)\bar{\psi}_6(6)d\tau,$$

$$\alpha = \int \psi_1(1)\psi_2(2)\psi_3(3)\psi_4(4)\psi_5(5)\psi_6(6)H$$

$$\times \bar{\psi}_1(2)\bar{\psi}_2(1)\bar{\psi}_3(3)\bar{\psi}_4(4)\bar{\psi}_5(5)\bar{\psi}_6(6)d\tau,$$

$$U_{jk} = 2^{-(n-i_{jk})},$$

$$V_{jk} = 2^{-(n-i_{jk})}\sum_\lambda f_\lambda^{jk}.$$

i^{jk} and f_λ^{jk} are obtained from the result of superimposing the bonds of the structure Ψ^j and of Ψ^k; i^{jk} is the number of islands, and the summation λ runs over all pairs of neighboring atoms in the superposition diagram. f_λ^{jk} turns out to be the following:

[6] A series of papers by Rumer, Teller and Weyl, Gott. Nach. N. P. Klasse 1930, 285; 1931–33; 1932, 337.

[7] J. C. Slater, Phys. Rev. 38, 1109 (1931).

[8] L. Pauling, J. Chem. Phys. 1, 280 (1933).

$$f_\lambda{}^{ik} = \begin{cases} 1 \text{ if the atoms have electrons paired.} \\ -\tfrac{1}{2} \text{ if the atoms do not have their electrons paired but are in different islands.} \\ 1 \text{ if the atoms have their electrons unpaired, and are in the same island and an odd number of bonds apart.} \\ -2 \text{ if the atoms have their electrons unpaired, and are in the same island an even number of bonds apart.} \end{cases}$$
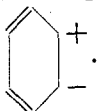
In this calculation, as is usually done, we neglect $T^2 = (\Psi^i \mid 1 \mid \Psi^j)$ $i \neq j$, compared to 1.

Disregarding T^2 and including only the interactions between neighboring atoms implies the omission of higher order permutations since:

$$(\psi_1(1)\psi_2(2)\psi_3(3)\psi_4(4)\psi_5(5)\psi_6(6) \mid H \mid$$
$$\times \psi_1(2)\psi_2(1)\psi_3(4)\psi_4(3)\psi_5(5)\psi_6(6))$$
$$\sim T^2(\psi_1(1)\psi_2(2) \mid H \mid \psi_1(2)\psi_2(1)).$$

CALCULATION OF WAVE-LENGTHS

In the first calculation only singlet nonpolar states of the molecule have been included in the linear combination in formula (2). A further calculation has been made including some ionic terms in the linear combination; that is, adding functions representing structures like ⬡$^+_-$.

This latter calculation clears up certain qualitative difficulties, but as yet has not been used for quantitative calculations.

The determinants evaluated for benzene and fulvene omitting the ionic structures are shown in Fig. 6. The canonical set of structures as well as the factored determinant are given.

In the case of azulene, the calculation has been simplified by including in the linear combination only the structures involving one long (i.e., weak) bond. It has been shown[9] that the structures having two long (i.e., of great internuclear distance) bonds do not affect the ground state by more than 1 percent; they would, however, affect the higher levels to a much greater extent. The calculation had to be simplified further since azulene has only two planes of symmetry. The wave functions having long bonds were all given the same coefficient. This approximation has been shown to give the ground state within 2 percent of that found by an amplified calculation.[9]
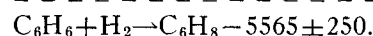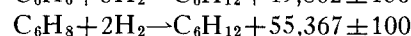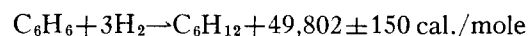
Giving all the structures with one long bond

[9] J. Sherman, J. Chem. Phys. **2**, 490 (1934).

the same coefficient means that we include in the linear combination (Eq. (2)) one additional function which is completely symmetrical; namely, the sum of all the functions having long bonds. This extra function only affects the energy value of those states which are completely symmetrical, among which is the ground state. To influence the energy value of a state which has a different symmetry, we must include in the linear combination of functions (Eq. (2)) a function which is itself a linear combination of the functions having long bonds and which has the symmetry of the level to be affected.

The lower roots of these determinants are given in Fig. 7.

In order to see whether the splitting up of the energy levels due to this resonance phenomenon is of the correct magnitude we must evaluate α. Instead of making a rough calculation for α, it can be evaluated from thermal data[10] as follows:

$$C_6H_6 + 3H_2 \rightarrow C_6H_{12} + 49,802 \pm 150 \text{ cal./mole}$$
$$C_6H_8 + 2H_2 \rightarrow C_6H_{12} + 55,367 \pm 100$$
$$- - - - - - - - - - - - - - - - - -$$
$$C_6H_6 + H_2 \rightarrow C_6H_8 - 5565 \pm 250.$$

Let B equal the hypothetical energy evolved on hydrogenation of a double bond in one structure for a molecule. Now the heat of hydrogenation of benzene to cyclohexadiene, C_6H_8, is smaller than B by an amount equal to the difference between the resonance energies of benzene and cyclohexadiene. Similarly the heat of hydrogenation of benzene to cyclohexane is smaller than $3B$ by the resonance energy of benzene, since cyclohexane has no resonance energy. The ground state of benzene has the energy 2.6α, whereas one Kekule structure which is the structure of lowest energy, has an energy of 1.5α. The difference between the energy of the ground state of the molecule and that of the lowest single structure, 1.1α for benzene, is attributed to resonance. By a similar calculation one finds the resonance energy of cyclohexadiene to be 0.232α. We may then evaluate the heats of hydrogenation of one and of three bonds in benzene, respectively.

$$1.1\alpha + 3B = 49,802, \quad \alpha = -1.92 \text{ volts,}$$
$$(1.1 - .232)\alpha + B = -5570,\text{[11]}$$
$$B = 32,872 \text{ cal./mole.}$$

[10] G. B. Kistiakowsky, Ruhoff, Smith, and Vaughan, J. A. C. S. **58**, 152 (1936).
[11] This reaction is used instead of $C_6H_{10} + H_2 \rightarrow C_6H_{12}$ since the $C=C$ has resonance energy.

Notation $4/6 = 4(Q-W)+6\alpha$

Benzene

A	B	C	D	E		I	II	III	IV	V	
4/6	1/6	2/6	2/6	2/6		5/12	2/6	0	0	0	$A=$
1/6	4/6	2/6	2/6	2/6		2/6	1/2	0	0	0	$B=$
2/6	2/6	4/0	1/6	1/6	=	0	0	1/0	0	0	$C=$
2/6	2/6	1/6	4/0	1/6		0	0	0	1/−2	0	$D=$
2/6	2/6	1/6	1/6	4/0		0	0	0	0	1/−2	$E=$

$$I = A+B$$
$$II = C+D+E$$

$$III = B-A$$
$$IV = (D-C)+(E-C)$$
$$V = (D-C)-(E-C)$$
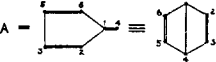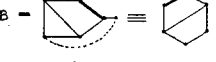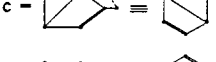
Fulvene

A	B	C	D	E		A	B+C	D+E	C−B	E−D
4/6	1/3	1/3	2/6	2/6		2/3	1/3	2/6	0	0
1/3	4/−6	1/3	2/3	2/−3		1/3	5/−3	4/0	0	0
1/3	1/3	4/−6	2/−3	2/3	=	2/6	4/0	5/3	0	0
2/6	2/3	2/−3	4/0	1/3		0	0	0	1/−3	0/2
2/6	2/−3	2/3	1/3	4/0		0	0	0	0/2	1/−1

2/3	1/3	0	0	0
1/3	1/1	0	0	0
0	0	1/−1	0	0
0	0	0	1/−3	0/2
0	0	0	0/2	1/−1

FIG. 6.

The older value[12] of $\alpha = -1.55$ is not used, since in obtaining this value it was assumed that the $\underset{/}{\overset{\backslash}{C}} = \underset{\backslash}{\overset{/}{C}}$ bond has the same energy regardless of the nature of the four groups attached to it, and also the effect of the geometry of the structure upon the strength of binding was neglected. That the former assumption is not justified is seen from the data on heat of hydrogenation of ethylene, heptene[1], pentene[2], etc.[13]

[12] Pauling and Wheland, J. Chem. Phys. **1**, 365 (1933).

[13] Kistiakowsky, Ruhoff, Smith and Vaughn, J. A. C. S. **58**, 144 and 153 (1936).

Benzene Butadiene Fulvene Azulene

FIG. 7.

More serious is the neglect of the resonance energy of an isolated $C=C$ bond since there may be ionic structures. Furthermore, the -1.55 value is obtained as a small difference between large numbers.

The resonance energy of an isolated carbon-carbon double bond may be evaluated from the following data[13] on cyclohexene, which may resonate between the three structures:

$$H_2+C_6H_{10}\rightarrow C_6H_{12}+28,592\pm100 \text{ cal.}$$
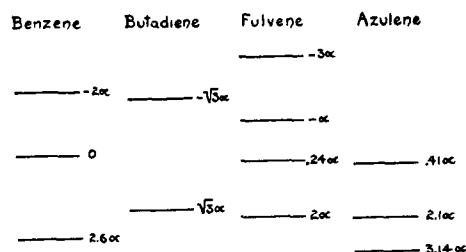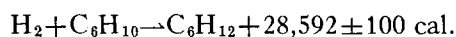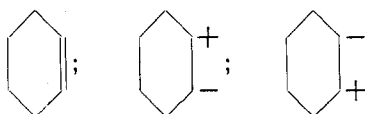
The resonance energy of the double bond is the difference between B and the heat of hydrogenation of cyclohexene.

$$=B-28,592=4280 \text{ cal.}=0.19 \text{ volt.}$$

Using $\alpha=-1.92$ we can evaluate the longest wave-lengths from the data of Fig. 7. These are given in Table I together with the experimental values.

The calculation on azulene, the parent substance of a group of naturally occurring substances of physiological interest, is especially illuminating since it is the only hydrocarbon of known structure which is blue. It should be recalled that the values for the wave-lengths given in Table I were calculated without using any spectroscopic values at all. The only experimental data used were heats of hydrogenation.

SELECTION RULES

The symmetry of the wave functions will be discussed with reference to benzene only since its spectrum has been perhaps most thoroughly investigated. The symmetry of the levels may be found from the group theoretical formula[14]

$$a_j=\frac{1}{h}\sum_R\chi(R)\bar{x}^{(j)}(R)=\frac{1}{h}\sum_C h_c\chi(C)\bar{x}^j(C). \quad (6)$$

Here a_j is the number of levels belonging to states which transform like the jth irreducible representation of the group of h symmetry operations, R. The label R runs over operators of the group whereas C runs over the classes of operators; h_c being the number of operators in the class C. $\chi^j(C)$ is the character of the cth class in the jth irreducible representation and $\chi(c)$ is the class character in the reducible representation whose basis is the canonical set of structures. The reducible representation Γ may then be broken into its irreducible parts: $\Gamma=\sum_j a_j\Gamma_j$. The characters of the symmetry operations in the reducible representation, Γ, for benzene are[15]

	E	C_2	C_3	C_6	C_2'	C_2''	i	σ_h	S_6	S_3	σ_v''	σ_v'
Γ	5	3	2	0	1	3	3	5	0	2	3	1

It follows from a comparison with the character table that $\Gamma=2\Gamma_1+\Gamma_{10}+\Gamma_5$. The Γ_5 representation is doubly degenerate as is seen from the character of the identity operation.

The wave functions for the two lowest states are $\Psi_0=\Psi_B+\Psi_A$ and $\Psi_1=\Psi_B-\Psi_A$ respectively (refer Fig. 6). From the table of characters for the group of symmetry operations we can see that Ψ_0 transforms like the first irreducible representation, Γ_1, under the symmetry operations of the group, while Ψ_1 transforms like Γ_{10}. Let us attach a coordinate system to the equilibrium position of each carbon nucleus, placing the z axis perpendicular to the plane of the ring. Now a displace-

TABLE I.

	CALCULATED	OBSERVED
Benzene[a]	2470	2590
Fulvene[b]	3645	3650
Butadiene[c]	1900	2100
Azulene[d]	6914	7000

[a] Cuthbertson and Kistiakowsky, J. Chem. Phys. 4, 9 (1936).
[b] Handbuch der Physik, Vol. 21, p. 105.
[c] Stark and Lipp, Zeits. f. physik. Chemie 86, 36 (1914).
[d] Plattner and St. Pfau, Helv. Chem. Acta 20, 225 (1937).

[14] E. Wigner, Gruppentheorie (Leipzig, 1931), p. 95.
[15] The notation is the same as that used by E. B. Wilson, Phys. Rev. 45, 706 (1934). This paper contains the whole character table.

ment in the z direction transforms like Γ_8. The X and Y displacements transform into one another and belong to the degenerate Γ_{12}. The selection rule in its general form may be stated in the following way. "A transition between states transforming like Γ_k and Γ_l respectively is forbidden unless the Kronecker (direct) product $\Gamma_k\Gamma_j\Gamma_l$, where Γ_j is the representation of the electric moment, p, contains the identity representation. Now for benzene

$$p_z{}^{01} \text{ transforms like } \Gamma_1\Gamma_8\Gamma_{10} = \Gamma_3,$$
$$p_{x,y}{}^{01} \text{ transforms like } \Gamma_1\Gamma_{12}\Gamma_{10} = \Gamma_5.$$

Since the reduced form does not contain Γ_1 the transition from the ground state of benzene to the first excited state is forbidden. The implications of this result will be discussed later in the paper.

Inclusion of Polar Terms

Great accuracy cannot be expected when the preceding calculation is applied to band groups other than the one at the longest wave-length, since no attempt was made to consider the effect of many highly excited states. Since the high energy states will, no doubt, lower the excited levels more than the ground state, the calculated wave-lengths will be too short. This is indeed found to be so. Fulvene has a second band at 2700A which is calculated to be 2100; the band at 3500 of azulene comes out to be 2400; benzene has a second band at 2000 which is calculated to be 1400. More serious than the inaccuracy in the wave-length is the difficulty that appears in
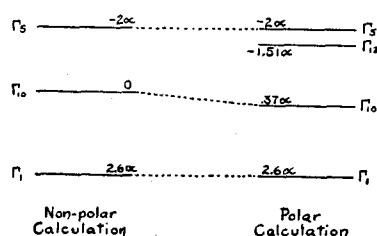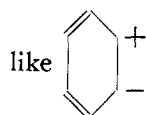

Non-polar Calculation   Polar Calculation

FIG. 8.

intensity considerations. The intensity of the 2000A band in benzene is 1000 times as great as the 2600 band.[18] On the basis of the nonpolar calculation the transition to both the first and second excited states is forbidden. We have seen that the transition from the ground state, Γ_1, to the first excited state, Γ_{10}, is forbidden. The transition to the excited second state, Γ_5, is like-

wise forbidden, since the third level in benzene has the symmetry Γ_5 and $\Gamma_1\Gamma_8\Gamma_5 = \Gamma_{11}$ and $\Gamma_1\Gamma_{12}\Gamma_5 = \Gamma_9 + \Gamma_{10} + \Gamma_{12}$, neither containing Γ_1.
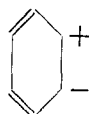
A calculation was next made including polar structures in the canonical set, that is structures like ⬡ . In this calculation two additional constants appear; namely, the coulomb integral for polar states and the resonance integral that occurs in polar nonpolar matrix components.

Twelve polar structures were included in the linear combination for benzene making seventeen structures in all. This is not the total canonical set, as some structures were omitted on energetic grounds in order to keep the determinants small. The twelve structures included are those obtained by rotating and reflecting the structure ⬡ . The symmetry of the twelve new states can be found by formula (6) from the characters of the reducible representation on the basis of the twelve structures. The reducible representation Γ is reduced yielding the twelve new states:

$$\Gamma = \Gamma_1 + \Gamma_2 + 2\Gamma_5 + \Gamma_9 + \Gamma_{10} + 2\Gamma_{12}.$$

The new Γ_1 and Γ_{10} levels interact with the nonpolar levels of benzene of the same respective symmetry; it is found, however, that the polar and nonpolar Γ_5 levels do not affect one another. The two new parameters are evaluated from the resonance energy of cyclohexene and from its lowest absorption frequency.[16] A solution of the secular determinant after substituting the values of the parameters yields the following energy levels (Fig. 8). That is, a new polar level of symmetry Γ_{12} appears below the Γ_5 level.

This new level, which is now the third level, has the symmetry Γ_{12} and the transition to it is allowed since $\Gamma_1 \times \Gamma_{12} \times \Gamma_{12} = \Gamma_1 + \Gamma_2 + \Gamma_5$.

The 1000-fold relative intensity is then due to the fact that the 2000A band is not forbidden.

Triplet States

The preceding calculations have included in the linear combination of functions representing the

16 E. Carr and M. K. Walker, J. Chem. Phys. 4, 755 (1936). Since the spectrum of cyclohexene was not reported the frequency of pentene-2 was used.

$$\left|\begin{array}{ccccccccc} 4/-2, & 1/2, & 0/2, & 1/2, & 0/2, & 1/2, & 2/2,2/2,0/2 \\ 1/2, & 4/-2, & 1/2, & 0/2, & 1/2, & 0/2, & 0/2,2/2,2/2 \\ 0/2, & 1/2, & 4/-2, & 1/2, & 0/2, & 1/2, & 2/2,0/2,2/2 \\ 1/2, & 0/2, & 1/2, & 4/-2, & 1/2, & 0/2, & 2/2,2/2,0/2 \\ 0/2, & 1/2, & 0/2, & 1/2, & 4/-2, & 1/2, & 0/2,2/2,2/2 \\ 1/2, & 0/2, & 1/2, & 0/2,, & 1/2, & 4/-2, & 2/2,2/2,2/2 \\ 2/2, & 0/2, & 2/2, & 2/2, & 0/2, & 2/2, & 4/0,1/2,1/2 \\ 2/2, & 2/2, & 0/2, & 2/2, & 2/2, & 0/2, & 1/2,4/0,1/2 \\ 0/2, & 2/2, & 2/2, & 0/2, & 2/2, & 2/2, & 1/2,1/2,4/0 \end{array}\right| = \left|\begin{array}{ccccccccc} 7/8, 4/6, & 0, & 0, & 0, & 0, & 0, & 0, & 0 \\ 4/6, 3/2, & 0, & 0, & 0, & 0, & 0, & 0, & 0 \\ 0, & 0, & 1/-4, & 0, & 0, & 0, & 0, & 0, & 0 \\ 0, & 0, & 0, & 1/-1, & 0, & 0, & 0, & 0, & 0 \\ 0, & 0, & 0, & \cdot0, & 1/-1, & 0, & 0, & 0, & 0 \\ 0, & 0, & 0, & 0, & 0, & 2/-2, & 2/0, & 0, & 0 \\ 0, & 0, & 0, & 0, & 0, & 2/0, & 3/-2, & 0, & 0 \\ 0, & 0, & 0, & 0, & 0, & 0, & 0, & 2/-2, & 2/0 \\ 0, & 0, & 0, & 0, & 0, & 0, & 0, & 2/0, & 3/-2 \end{array}\right|$$

$$\underbrace{\quad}_{2\Gamma_9}\;\underbrace{\quad}_{\Gamma_2}\;\underbrace{\quad}_{\Gamma_5}\;\underbrace{\qquad\qquad}_{2\Gamma_{12}}$$

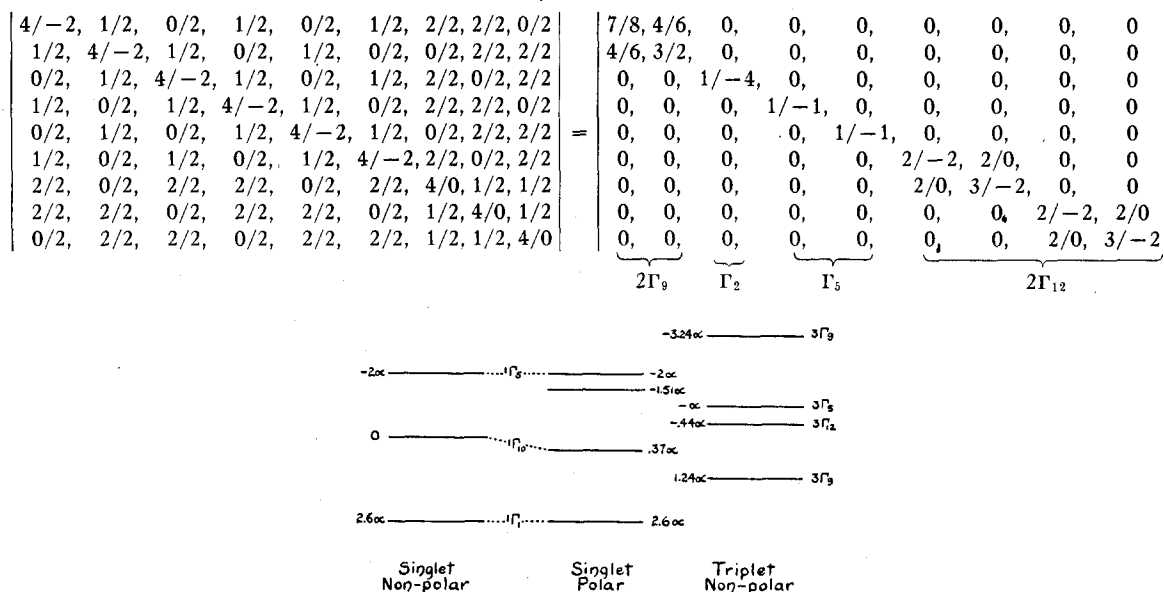| Singlet | Singlet | Triplet |
| Non-polar | Polar | Non-polar |

FIG. 9.

state of the molecule only functions in which the molecule has no total spin. There is an entire set of new states, which have a resultant spin of unity, the triplet states. The transition from a singlet to a triplet state is forbidden since the spin functions are orthogonal.

It was supposed that an intercombination band would be very weak in comparison to the other bands. This will be valid for molecules of not too high a symmetry, but may not be valid for benzene since the transition of lowest energy between singlet states is also forbidden, on symmetry grounds. The triplet states of benzene were therefore calculated by the H-L-S-P method. The canonical set is composed of nine structures, as can be seen if one notices that a linear relationship exists between certain structures, namely,
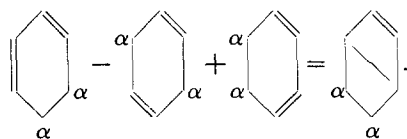
The nine structures forming the canonical set were taken to be the nine orientations of
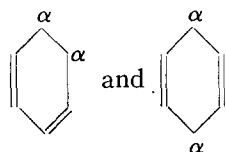
and . That there are nine struc-

tures can also be seen from formula (7) which gives the number of structures $N(\sigma)$, for each value of σ, the projection of the spin upon an axis; n being the number of nuclei.

$$N(\sigma) = \frac{n!}{((n/2)-\sigma)!\,((n/2)+\sigma)!}. \tag{7}$$

The number having a total spin of 1 is $N(1) - N(2) = 9$.

The symmetry can be found from formula (6). The characters of the reducible representation on the basis of the nine structures are

	E	C_2	C_3	C_6	C_2'	C_2''	i	σ_h	S_6	S_3	σ_v''	σ_v'
Γ	9	−3	0	0	1	−3	−3	9	0	0	−3	1

so that $\Gamma = \Gamma_2 + \Gamma_5 + 2\Gamma_9 + 2\Gamma_{12}$.

The secular determinant is given in Fig. 9. Its solution yields the energy levels of the triplet states[17] which are also shown in the figure, the same parameter, α, appearing as it did in the energy of the singlet states.

INTERPRETATION OF BENZENE SPECTRUM

The transitions from the ground state $^1\Gamma_1$ to the $^1\Gamma_{10}$, $^3\Gamma_9$ and $^3\Gamma_{12}$ are all forbidden. The only

[17] The triplet levels obtained by this calculation are in complete agreement with those obtained by Hückel with a more cumbersome method.

allowed transition is to the $^1\Gamma_{12}$ so that we must identify this transition, $^1\Gamma_1 \to {}^1\Gamma_{12}$ with the 2000A band which is 1000 times as intense as that of 2600. We now have three excited levels remaining and only one observed band, that at 2600A of electron number 10^{-4}. The transition $^1\Gamma_1 \to {}^3\Gamma_{12}$ has an energy between that of $^1\Gamma_1 \to {}^1\Gamma_{10}$ and of $^1\Gamma_1 \to {}^1\Gamma_{12}$ and hence should fall between these
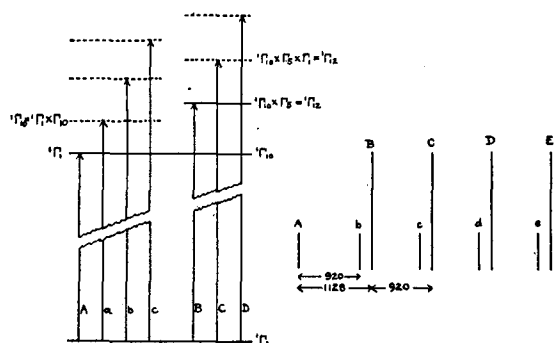

FIG. 10.

bands in the spectrum. Now if the transition $^3\Gamma_2$ is very weak compared to the $^1\Gamma_1 \to {}^1\Gamma_{10}$ transition, as will be shown to be the case, the former will be marked since it is certainly very weak compared to the allowed transition $^1\Gamma_1 \to {}^1\Gamma_{12}$ which overlaps the band of the $^1\Gamma_1 \to {}^1\Gamma_{10}$ transition; the minimum between these two bands (about 150A) is still 20 times as intense as the transition to $^3\Gamma_{12}$ should be. This still leaves the $^1\Gamma_1 \to {}^3\Gamma_9$ to explain; since this band occurs near the visible, it should be detected. A new band system has now been found by the author at 3400A and will be reported in a later paper. It must be mentioned that in order to observe this 3400 band one needs at least a 20 cm path of liquid benzene, whereas the 2600A band when observed in a 50 cm tube at a pressure of 2 mm shows two progressions clearly, one much weaker than the other. That is, the new band is weaker than the weak progression of the 2600 band by a factor 2×10^{-5}.

We, therefore, identify the 2000A band system as the transition from the ground electronic level to the $^1\Gamma_{12}$ level; the 3400A band is identified with a transition to $^3\Gamma_9$, and the 2600A band is to be correlated with the transition to $^1\Gamma_{10}$. This identification of the band as arising from a transition forbidden on symmetry grounds will be seen to account for the following points in connection with the 2600A band of benzene.

1. The oscillator strength of the band group at 2600A is very weak,[18] being about 10^{-4} electrons.

2. The electric susceptibility of benzene increases with temperature,[19] which contradicts the Langevin-Debye formula.

3. V. Henri[20] has found that the total intensity of absorption of the 2600 band decreases with decreasing temperature.

4. Cuthbertson and Kistiakowsky[21] found two progressions in fluorescence at high pressures, one starting at 38,609 cm^{-1} = 4.77 volts, and the other starting at 37,481 cm^{-1} = 4.62 volts. Henri had previously found these two progressions in the absorption of benzene vapor.[22]

5. W. V. Mayneard and E. M. F. Roe[23] find that as one lowers the temperature the extinction coefficient of some band maxima in the 2600A band system increases, whereas that of other band maxima, especially the one at the longest wave-length, decreases as one decreases the temperature.

The transition from the $^1\Gamma_1$ to the $^1\Gamma_{10}$ electronic level may occur in two ways, in spite of the selection rule discussed above. If the molecule is perturbed by other molecules or has its symmetry destroyed by some internal vibration, we can expect a very weak transition in violation of the selection rule.

The molecule may also be excited from the $^1\Gamma_1$ state to certain vibrational levels of the $^1\Gamma_{10}$ electronic state. A transition from $^1\Gamma_1$ to a state of vibrational symmetry Γ_v in the $^1\Gamma_{10}$ electronic state is not forbidden if $\Gamma_1\Gamma_{12}\Gamma_v\Gamma_{10}$ contains Γ_1.

Any transition that is allowed is also allowed in combination with a vibration of symmetry Γ_1. The frequency of the totally symmetrical frequency in benzene is 990 cm^{-1} in the ground state and 920 cm^{-1} in the excited state. Progressions of 920 cm^{-1} spacing should therefore be found in absorption and of 990 cm^{-1} spacing in fluorescence. Now there is in benzene a vibration of symmetry Γ_5 which does make the transition allowed since $\Gamma_1\Gamma_{12}\Gamma_5\Gamma_{10} = \Gamma_1 + \Gamma_2 + \Gamma_5$.

[18] N. Chako, J. Chem. Phys. 2, 644 (1934).
[19] Sanger, Physik. Zeits. 27, 165 (1926).
[20] V. Henri, Comptes rendus 200, 1532 (1935).
[21] Cuthbertson and Kistiakowsky, J. Chem. Phys. 4, 14 (1936).
[22] V. Henri, Structure des Molecules (1925), p. 709.
[23] W. V. Mayneard and E. M. F. Roe, Proc. Roy. Soc. A895, 647 (1937).

This Γ_5, Raman active, vibrational frequency of 1175 cm^{-1} has been observed in the ground state of benzene. The value of this frequency in the first excited state is not known but will probably be slightly less than 1175 cm^{-1}. It is assumed here that this vibrational frequency in the upper state is 1128 cm^{-1} in order to obtain quantitative agreement with experiments.

The band system in absorption will then appear as two progressions A, b, c, d and B, C, D, E each having its bands spaced 920 cm^{-1}; the two progressions having a relative displacement of 1128 cm^{-1} (Fig. 10). The A, a, b, c band will be weak since it violates the selection rule and can occur only due to perturbations. The perturbations depend upon the temperature since as one cools a crystal down to absolute zero the motions within and between molecules die down. That is, one expects that the extinction coefficient of this progression should decrease with decreasing temperature.

The B, C, D, E progression is also weak since we may write the wave function for electronic and vibrational degrees of freedom.

$$\Psi(e, v) = \psi(e)\psi(v) + \epsilon\psi(e, v).$$

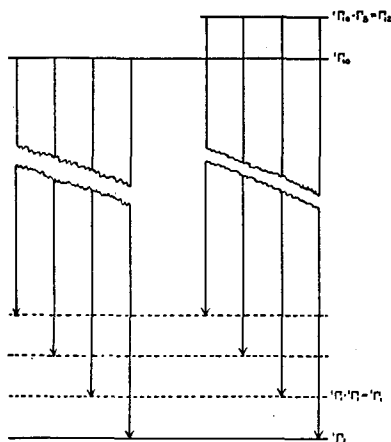The product $\psi(e)\psi(v)$ gives a zero electric

FIG. 11.

moment. The value of ϵ is small, its magnitude depending upon the interaction between vibration and electronic energy. This interaction is affected by temperature only to a second order.

These views are in good agreement with the experiments of Henri and of Mayneard and Roe. Henri finds two progressions in absorption with a relative displacement of 1129 and having a 920

cm^{-1} spacing within each progression. From Fig. 13[23] it is seen that as the temperature is decreased the shoulders of the bands B, C, D, E split into a separate series of peaks, A, a, b, c. Now if the transition probability is independent of the temperature, the peaks should increase in height as
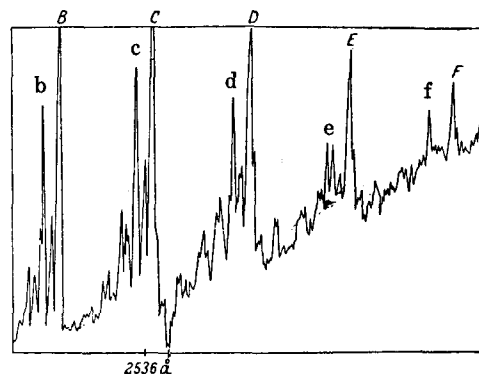
FIG. 12.

the temperature is lowered, first, since a drop in temperature causes a sharpening up of the band; and second, due to the contraction of the absorbing layer which amounts to 15 percent[24] in a fall of 130°. The peaks of the series B, C, D, E do increase greatly as the temperature falls whereas the peaks A, b, c, d, however, decrease, the band A dying out completely at -120°C. The anomalous position of the band A is, of course, evident.

In fluorescence[21] two progressions (excited by the 2536 line of Hg) are also observed, each one being spaced 990 cm^{-1}, the two progressions having a relative displacement of 1128 cm. The 37,481 band is more intense than the 38,609 in fluorescence although it is much weaker in absorption. This relative intensity is independent of the wave-length of the exciting line, as reported by Pringsheim.[25] This can be understood if the vibrational energy in the excited state is lost very quickly so that the fluorescence takes place only from the two levels shown in Fig. 11. That one gets transitions from a molecule vibrating in the upper state at all, is due to the fact that the transition from the Γ_5 vibration in the upper state down to the ground state is not forbidden as are the other vibrations. Its lifetime is therefore much shorter and it may fluoresce before an inelastic collision. Molecules having other vibra-

[24] C. P. Smyth and Stoop, J. C. S. 51, 3315 (1929).
[25] Pringsheim and Reimann, Zeits. f. Physik 29, 115 (1924).

tions have a long lifetime and suffer inelastic collisions before radiation and hence can only radiate from the vibrationless excited state.[26] That the 38,609 band system is the weaker of the two in fluorescence, although it is stronger in
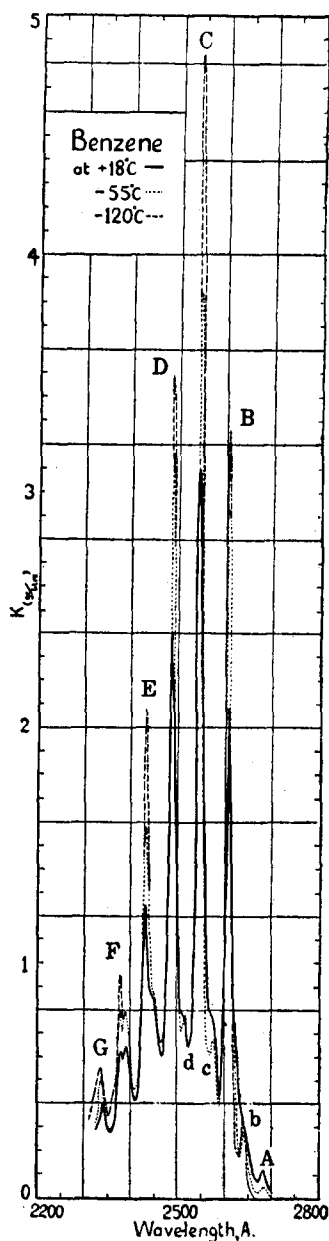

FIG. 13.

FIG. 14.

absorption, is to be attributed to the fact that only few molecules vibrating with a Γ_5 vibration in the excited state will fluoresce before an inelastic collision. Therefore the 38,609 band can be the weaker of the two in spite of the fact that far more molecules are excited to a Γ_5 vibration, as one must conclude from the relative intensity in absorption coupled with the independence of the relative intensity in fluorescence of the exciting line.

The existence of the two progressions is seen in the absorption spectrum of gaseous benzene (Fig. 12).[27] One progression being lettered A, b, c, d, e, (the band A appears outside of this figure but can be seen in Fig. 13), the other B, C, D; each progression having a 920 cm^{-1} spacing. The progressions are also seen in the photometer trace of the liquid (Fig. 13), but in the trace at $(-180°)$ one sees that band A has died out.

The electric susceptibility of benzene (Fig. 14)[19] is seen to increase very slightly with T instead of to decrease as required by the Langevin-Debye formula:

$$\chi = \frac{\epsilon-1}{\epsilon+2}\frac{3}{4\pi} = N\left(\alpha + \frac{\mu^2}{3kT}\right),$$

where

$$\alpha = \frac{2}{3}\sum_{n=1}^{\infty}\frac{|P_{n0}|^2}{h\nu_{0n}},$$

the sum running over all excited states.

The anomaly may be interpreted as due to the fact that α is not a constant but increases with

---

[26] That the 38,609 cm^{-1} band is due to transitions from a vibrating excited level was suggested as a possibility by Cuthbertson and Kistiakowsky. They state that for this view to be correct it would be necessary to assume that the energy of the vibration was much less readily lost than that of the other vibrations.
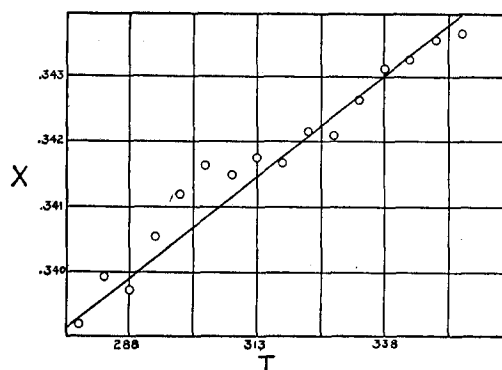
[27] A. Kronenberger and P. Pringsheim, Zeits. f. Physik **40**, 83 (1927).

temperature as a result of the increased transition probability of the low frequency transitions at the higher-temperatures.

Returning to the levels of benzene shown in Fig. 9 we recall that the entire preceding discussion rests upon and lends weight to the identification of the 2600A bands as a $^1\Gamma_1 \to {}^1\Gamma_{10}$ transition instead of a transition to $^3\Gamma_{12}$. If this view is correct the transition to $^3\Gamma_{12}$ must be masked by the $^1\Gamma_{10}$ transition and $^1\Gamma_{12}$ transitions as previously discussed. We can estimate the strength of the transition to $^3\Gamma_{12}$ in the following way. The oscillator strength of the $^1\Gamma_1 \to {}^1\Gamma_{12}$ band is 10^{-1}. The 2600 band, which has a total oscillator strength of 10^{-4}, consists of two progressions, one due to a $^1\Gamma_1 \to {}^1\Gamma_{10}$ transition, the other arising from a $^1\Gamma_1 \to {}^1\Gamma_{10} \cdot \Gamma_5$ transition. The former of these bands is 400 times[28] weaker than the latter in the vapor but only 20 times weaker in solution[29] at room temperature. Hence we can say that in solution the $^1\Gamma_1 \to {}^1\Gamma_{10}$ transition has a strength of 5×10^{-6}. Now the band group at 3400 is 5×10^4 times weaker than the $^1\Gamma_1 \to {}^1\Gamma_{10}$ transition.[30] Hence the strength of the 3400A band can be estimated to be $\sim 10^{-10}$. Now the 3400 band, although it has not been resolved, should also consist of two progressions, one due to a $^1\Gamma_1 \to {}^3\Gamma_9$ and the other due to $^1\Gamma_1 \to {}^3\Gamma_9 \cdot \Gamma_5$. The $^1\Gamma_1 \to {}^3\Gamma_9$ transition would then have an intensity of 5×10^{-12}. Hence we can say an intercombination causes a decrease in intensity of 5×10^5 whereas a violation of symmetry decreases the intensity by 10^6. The $^1\Gamma_1 \to {}^3\Gamma_{12}$ should therefore have an intensity of 10^{-7} which would make it 10^3 times weaker than the strong progression of $^1\Gamma_1 \to {}^1\Gamma_{10}$ and fifty times weaker than the very weak progression. It would therefore be masked, being

much weaker than transitions to both the $^1\Gamma_{10} \to {}^1\Gamma_{12}$ levels. The intensities are summarized in Fig. 15.

It is *a priori* possible that the 2600A band is in reality a $^1\Gamma_1 \to {}^3\Gamma_{12}$ transition instead of the $^1\Gamma_1 \to {}^1\Gamma_{10}$ upon which the preceding discussion was based. The great difference in intensity between the two progressions forming this band system speaks against the possibility of a transi-
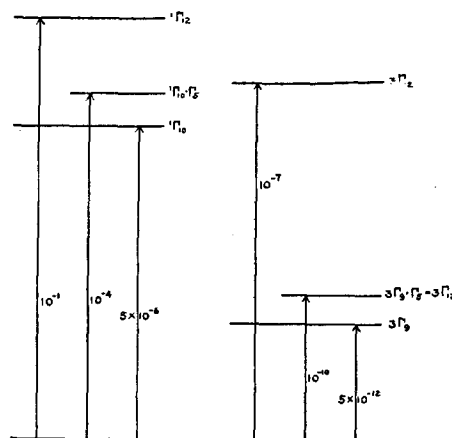

FIG. 15.

tion to $^3\Gamma_{12}$ since the transition to a Γ_5 vibrational level in the excited state, although allowed, should not be particularly stronger than the $0 \to 0$ transition which in this case would also be allowed on symmetry grounds. That is, the $^1\Gamma_1 \to {}^3\Gamma_{12}$ and a $^1\Gamma_1 \to {}^3\Gamma_{12} \cdot \Gamma_5$ are both forbidden as intercombinations but neither violates symmetry rules. The change in relative intensity from 400 : 1 to 20 : 1 as one goes from the gaseous to the liquid state also favors the $^1\Gamma_{10}$ interpretation, as do also the experiments of W. V. Mayneard and E. M. F. Roe, which show that the relative intensity of the weaker progression compared to the stronger decreases with temperature.

I wish to express my sincere thanks to Professor K. F. Herzfeld for suggesting, and together with Dr. M. Goeppert-Mayer, for directing this research.

[28] V. Henri, J. de phys. 3, 181 (22) Fig. 2. Compare spectra at 0.01 and 3, 4.5, and 5.5 mm pressure.

[29] W. V. Mayneard and E. M. F. Roe, reference .24 Compare bands *A* and *B* at room temperatures.

[30] The weak progression in the 2600 band, i.e., the $^1\Gamma_1 \to {}^1\Gamma_{10}$ can be observed in a 50 cm tube at 2 mm pressure of benzene whereas one needs at least 20 cm of liquid benzene to see the 3400 band.