

Classification of Spectra of CataCondensed Hydrocarbons

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same symmetry class. Each computed level properly refers to the center of gravity of a singlet and triplet of the same kind. The energies are expressed in units of β (Coulson's γ), where β , the resonance or bond integral *corrected for overlap*, must be determined empirically. For accurate comparison with experiment, we must know the triplet levels. In naphthalene, one of these, 3L_a , is known (Fig. 2), and the other, 3L_b , can be estimated from the estimated singlet-triplet separation in benzene¹⁶ and from the position of 1L_b . In azulene, it seems not unreasonable to assume the same singlet-triplet separations as for the corresponding levels in naphthalene.

The computed values for the two lowest states are compared with the observed values in Table III. With $\beta = 22,200 \text{ cm}^{-1}$ in naphthalene, both centers of gravity are predicted within 100 cm^{-1} . With the same value of β in azulene, errors of 4500 cm^{-1} are found, but a lower value of β , $18,500 \text{ cm}^{-1}$, will fit the data within 200 cm^{-1} .

The comparison of the computations on the upper states is quite crude since only the upper singlets are known in either molecule. The computed centers of gravity are on Fig. 2, using a β of about $23,000 \text{ cm}^{-1}$ for both molecules. (This figure is taken from reference 12, where this value of β was used in another comparison.) For each state, the deviations of computed levels from observed singlets are in the same direction and of about the same size in both molecules, if the assignments given are correct. The method of making these assignments

is discussed in detail elsewhere.¹² This qualitative agreement tends to support them. No intensity computations were made here.

It should be noted that the values for β for azulene and naphthalene obtained from these spectroscopic considerations are not in agreement with the corresponding β 's obtained from thermochemical (e.g., heats of combustion) measurements of resonance energies. For example, the β_{spect} 's for azulene, benzene, naphthalene, and anthracene are respectively $18,500 \text{ cm}^{-1}$, $20,600 \text{ cm}^{-1}$, $22,200 \text{ cm}^{-1}$, and $24,300 \text{ cm}^{-1}$. The corresponding β 's, calculated from heat-of-combustion resonance energies,¹⁵ are ($10,000 \text{ cm}^{-1}$?), $13,400 \text{ cm}^{-1}$, $14,000 \text{ cm}^{-1}$, and $14,000 \text{ cm}^{-1}$. No explanation of these discrepancies is offered, and their investigation is desirable.

Here we have not compared the observed energy levels in azulene with the HLSP computations of Sklar.^{5,13} Although his predicted frequencies for the lowest singlet-singlet transitions for a number of compounds agree well with the observed position of the first absorption bands, the spread in his excited electronic levels is much too large in azulene as well as in benzene and other molecules, and the sequence of his predicted levels is wrong, for example, in benzene. He attributes the unduly large spread to his neglect of ionic structures, which are known to be essential for describing excited states by the HLSP method.¹³ The LCAO description which Mayer and Sklar applied later to benzene¹⁷ is much more satisfactory in predicting excited states,¹⁶ and a modification of the latter approach has been used here for that reason.

¹⁶ C. C. J. Roothaan and R. S. Mulliken, J. Chem. Phys. 16, 118 (1948).

¹⁷ M. G. Mayer and A. L. Sklar, J. Chem. Phys. 6, 645 (1938).

Classification of Spectra of Cata-Condensed Hydrocarbons

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The classification of π -orbitals in a cata-condensed aromatic system is like that of the orbitals of a free electron traveling in a one-dimensional loop of constant potential around the perimeter. To take into account electron interaction, certain quantities corresponding to angular momenta may be added or subtracted. Introduction of the cross-links in the molecule removes the degeneracy. The first excited configuration in such systems gives two low frequency singlet weak absorption bands and two higher singlet strong dipole absorption bands. Selection and polarization rules are given. The levels are identified from the spectra and some of their properties are determined. An explanation is given of the regularities found by Kleven and Platt. A systematic nomenclature is given. The results agree qualitatively with LCAO theory, can be applied easily to unsymmetrical molecules, and can possibly be extended to other types of ring systems.

I. THE FREE-ELECTRON MODEL

THE aromatic spectra which were extended into the vacuum ultraviolet in the preceding paper¹ (hereafter called I) show many empirical

resemblances and regularities. In benzene, the LCAO (linear-combination-of-atomic-orbitals) mo-

¹ H. B. Kleven and J. R. Platt, J. Chem. Phys. 17, 470 (1949).

molecular orbital theory satisfactorily explains the excited levels.^{2,3} In the linear condensed-ring systems, or polyacenes, only the centers of gravity of singlet-triplet pairs have been calculated;⁴ and intensity predictions are too large, especially for the low-frequency bands,¹ probably because electron interactions have not been included. The LCAO theory has not yet been applied to account for the regularities in the spectra of the unsymmetrical condensed ring systems. (Complete and up-to-date bibliographies of other theoretical and experimental work on aromatics will be found in I and in references 2, 4, 7, 12, 13, 16, 19, 20, 25, and 27.)

Another molecular orbital approach—the free-electron orbital method—will give less accurate but more rapid results, if simplifying assumptions are made. It can describe electron interactions in a simple way. Without introducing parameters to be determined empirically, it will give the approximate height of the excited states. It gives correct polarizations, accounts for the general weakness of the low frequency bands, and can easily be extended to unsymmetrical molecules. It explains the regularities observed in I, and leads to a useful new classification for the electronic states. Empirically similar bands in different compounds are given the same symbol, instead of different symbols as they are in theories which emphasize symmetry considerations.

The method assumes that the π -electrons of a planar conjugated system are free to move along the bonds throughout the system under a potential field which is, in first approximation, constant. This description was used to explain the diamagnetism of aromatic molecules by Pauling⁵ and Lonsdale.⁶ Schmidt⁷ generalized it further by thinking of the conjugated system as simply a large flat box containing a Fermi gas of unsaturation electrons (π -electrons) in analogy to the two-dimensional metal model of graphite. He discussed excited states and spectra, but without any systematic correlation with the known levels. The idea of almost-free motion along the bonds has always lain in the background of molecular orbital discussion.⁸⁻¹¹ Lennard-Jones⁹ coined the term “mobile electrons” to indicate this motion of the π -electrons throughout the whole molecule. Hückel⁸ used complex molecular

orbital eigenfunctions in treating benzene and related problems. These represent electron waves traveling around the benzene ring. He also used “orbital ring quantum numbers” describing angular momentum, as we shall do here, and showed how they add and subtract to give a “total ring quantum number” which characterizes the state of the system. However, the LCAO method with real coefficients has usually been regarded as the best starting point in molecular orbital theory. Bayliss¹² has recently returned to the idea of the Fermi gas in one dimension to explain the spectra of polyene chains. Kuhn¹³ has announced that a modification will predict the strong allowed frequency in polyacenes; he makes no mention of the other transitions classified in the present paper.

In the present approach, it is assumed that the π -orbitals retain their main π -electron property, i.e., a node in the molecular plane. This quantization perpendicular to the plane of the molecule is assumed to be independent of the quantization in the plane. The closed-shell σ or single-bond electrons are assumed to be more tightly and locally bound than the π -electrons and cannot be treated by a free-electron approximation. They will not be further discussed here.

The cata-condensed ring systems, whose general formula is $C_{4n+2}H_{2n+4}$, include some of the most important aromatics and carcinogens. In them no carbon atom belongs to more than two rings and every carbon is on the periphery of the conjugated system. This makes possible a further simplification.

Postulate: *The classification of π -orbitals in cata-condensed systems is like that of the orbitals of a free electron traveling in a one-dimensional loop of constant potential around the perimeter.* The use of the perimeter is a convenience in visualization because of the importance of angular momentum in electron interactions and in selection rules. This postulate amounts to asserting that the wave equation for π -electrons is approximately separable in three coordinates, one along the perimeter, one perpendicular to the plane of the molecule, and one perpendicular to these two at the perimeter, and, further, that the main difference of the orbitals from each other is with respect to quantization in one of these coordinates only, i.e., along the perimeter.

To find the perimeter-free-electron orbitals and energies, the perimeter may first be distorted into a circle of the same length. The orbitals are those of a plane rotator. The energies are then

$$E = q^2 h^2 / 2ml^2 = 1,210,000 q^2 / l^2,$$

where q is an integer, 0, 1, 2, ...; h is Planck's constant; m is the mass of the electron, l is the

² C. C. J. Roothaan and R. S. Mulliken, J. Chem. Phys. 16, 118 (1948).

³ M. G. Mayer and A. L. Sklar, J. Chem. Phys. 6, 645 (1938).

⁴ C. A. Coulson, Proc. Phys. Soc. 60, 257 (1948).

⁵ L. Pauling, J. Chem. Phys. 4, 673 (1936).

⁶ K. Lonsdale, Proc. Roy. Soc. 159, 149 (1937).

⁷ O. Schmidt, Zeits. f. phys. Chem. 47B, 1 (1940), and previous papers.

⁸ E. Hückel, Zeits. f. physik. 70, 204 (1931).

⁹ J. E. Lennard-Jones, Proc. Roy. Soc. 158A, 280 (1937).

¹⁰ R. S. Mulliken, J. Chem. Phys. 7, 369 (1939).

¹¹ C. A. Coulson and G. S. Rushbrooke, Proc. Camb. Phil. Soc. 36, 193 (1940).

¹² N. S. Bayliss, J. Chem. Phys. 16, 287 (1948).

¹³ H. Kuhn, J. Chem. Phys. 16, 840 (1948).

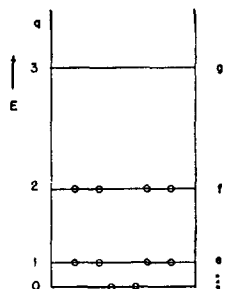


FIG. 1. One-electron states; and shells.

length of the perimeter (in angstroms), and E is the energy (in cm^{-1}) measured upward from the constant potential. The levels are quadratically spaced as shown in Fig. 1 and are all doubly degenerate except the lowest, since electrons that have a finite velocity may travel either clockwise or counterclockwise around the loop.

The orbital ring quantum number q , which measures angular momentum, determines the number of nodes of the wave function and the selection rules. It may be thought of as a vector perpendicular to the plane of the molecule. In the zig-zag perimeter, angular momentum is no longer a constant of the motion, because of the constraints, but linear momentum is. When the periodic potential due to the atoms is introduced, q no longer describes accurately any momentum. But it remains a good quantum number because it still determines the number of nodes around the perimeter.

In many-electron systems, the vector q 's of the different electrons may be added and subtracted—algebraically and not vectorially, since they are restricted to one dimension—to give a total ring quantum number Q for the system.¹⁴ This procedure gives a qualitative model for electron interactions similar to the vector model for representing these interactions in a diatomic molecule.

II. NAMES AND CHARACTERISTICS OF STATES

Shells, Configurations, and States

In cata-condensed systems of n rings, the $2(2n+1)$ carbons each bring one π -electron to the system. These will fill the successive shells as shown in Fig. 1. The highest filled shell will be for $q=n$, and we will designate the 4 electrons in this shell as f -electrons, those in the next lowest shell as e -electrons, and so on. The first empty shell will be the g -shell, with $q=n+1$, the next, the h -shell, and so on. Since the "optical" electrons are those in the last one or two filled shells, it will be convenient to have a notation which is the same for these top shells in molecules of the same general type even when the ring quantum numbers are different.

¹⁴ I am indebted to Prof. Mulliken for suggesting the names, "orbital ring" and "total ring quantum number" for q and Q . Hückel (see reference 8) used the symbols, k and K , for these quantities.

In the states of interest, the total momentum number, Q , may take on the values, 0, 1, 2, \dots . Such states we may designate by A, B, C, \dots . We will see that it may also take on the values $\dots, 2n, 2n+1, 2n+2, \dots$. These states we may designate \dots, K, L, M, \dots , the letters being kept the same regardless of the value of n .

In the perimeter-constant-potential approximation, all of the states are doubly degenerate except the A state since the total momentum may be in either direction. Introduction of the crosslinks and of the periodic potential due to the atoms along the perimeter removes the degeneracy except in some states of highly symmetric molecules such as benzene and triphenylene. Because of its removal, the states will be split. The two components may be given subscripts a and b , whose significance we will examine later.

The most important spectra will be electron-hole spectra, produced like those of the rare-gas atoms by the excitation of one electron from a filled shell to an empty one. Spectra produced by the excitation of two electrons will be weak, as in atoms, and will require higher excitation energies. The excited electron interacts with the remaining tenants of its former shell, or, more simply, with the hole it leaves behind.

Thus, when an electron goes from an f to a g orbital, the new system has states with the f and g ring quantum numbers added or subtracted, i.e., with $Q = (n+1) \pm n = 1$ or $(2n+1)$. These are B and L states. Removing the degeneracy, they become B_a, B_b, L_a, L_b . The electron and hole spins may be antiparallel or parallel, giving two sets of excited states, singlets and triplets. This makes 8 types of states for this f^3g configuration. All singly excited configurations will have 8 states.* The Pauli principle makes the ground state singlet and single.

The lower configurations, and the states to which they give rise, are given in Table I.

The configurations have been grouped according to their arithmetic sum of momentum numbers, Σq .

TABLE I.

$\Delta \Sigma q$ (from ground state)	Configuration	States
3	$\left\{ \begin{array}{l} \dots f^3i \\ \dots e^3f^4h \\ \dots d^3e^4f^4g \end{array} \right.$	$1, 3D_{a,b} \quad 1, 3N_{a,b}$ $1, 3D_{a,b} \quad 1, 3L_{a,b}$ $1, 3D_{a,b} \quad 1, 3J_{a,b}$
2	$\left\{ \begin{array}{l} \dots f^3h \\ \dots e^3f^4g \end{array} \right.$	$1, 3C_{a,b} \quad 1, 3M_{a,b}$ $1, 3C_{a,b} \quad 1, 3K_{a,b}$
1	$\dots f^3g$	$1, 3B_{a,b} \quad 1, 3L_{a,b}$
0	$\dots f^4$	$1A$

* Note added in proof: This assumes that degenerate states are counted twice. There is also the obvious exception of excitation from $q=0$ states as in the e^3f^4g configuration of benzene.

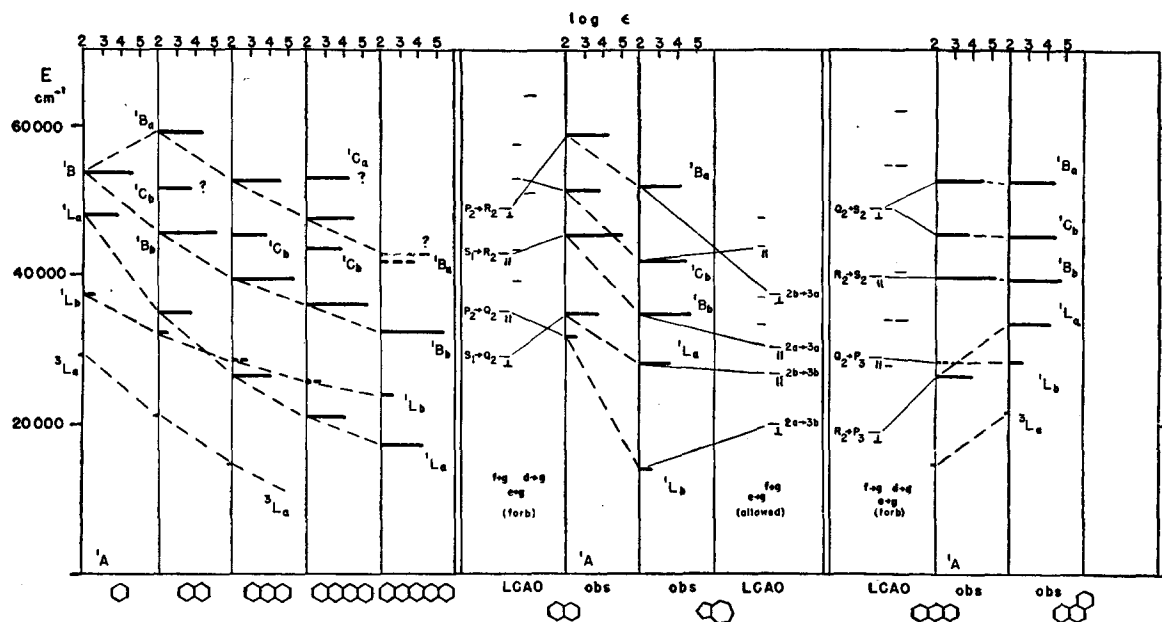


FIG. 2. Electronic energy levels of polyacenes and isomers. Comparison of LCAO center-of-gravity predictions with observed singlets in naphthalene, azulene, anthracene.

Note: Lowest vibrational level shown. Remaining structure of each electronic band omitted for clearness. Length of horizontal lines indicates $\log \epsilon_{\max}$ of transition from ground state on scale at top of the figure. Lines for triplets drawn to left to indicate $\log \epsilon_{\max}$ is less than 2.

In a large system with almost equally spaced one-electron states, the configuration energies will be grouped the same way. In smaller molecules with increasing spacing near the f -shell, the $e \rightarrow g$ absorption bands will lie at lower frequencies than the $f \rightarrow h$ bands. The first ultraviolet bands will therefore be of $f \rightarrow g$ type and the next of $e \rightarrow g$ type. Such groupings may be seen in the energy levels of Fig. 2. Higher bands become weak, and only the Rydberg series bands, which fall outside this π -electron classification, can be seen at very short wavelengths.

Empirically, the order of states of a given configuration is determined by the Hund rule, which holds for molecules as well as atoms.^{15a} Triplets lie below singlets; and within the singlet group, or the triplet group, states of high Q lie below low Q states. Thus in the states in Fig. 2, which have been identified by this scheme as described below, one 3L always lies below any 1L ; and the 1L 's always below the 1B 's.

Selection and Intensity Rules

The selection rules are as follows.

1. *Singlet-triplet strongly forbidden.* This is the familiar rule in light atoms and in molecules containing light atoms. Triplet states in aromatics are known only from phosphorescence and from absorption with very long paths.

^{15a}G. Herzberg, *Molecular Spectra and Molecular Structure. I. Diatomic Molecules* (Prentice-Hall, New York, 1939), (a) p. 360, (b) pp. 136, 264.

2. ΔQ must be odd in centrally symmetric systems. This will be justified under Rule 3. $\Delta Q = 1$ is always allowed and strong—the dipole transition when the perimeter is a circle. The higher values of ΔQ would be forbidden multipole transitions if the perimeter were a circle. They would be allowed but weak, as in polyenes,^{10,12} if it were a double straight line. They will therefore be generally weak, but their exact strength will depend on the molecular shape. Very high ΔQ values, near $2n$, will be practically forbidden, but may become stronger through vibrational interaction, like the forbidden bands in benzene.

Thus, in the observed spectra (see I), the $^1A - ^1B$ transitions have oscillator strengths from 0.5 to 3.0. The $^1A - ^1L_b$ transitions in benzene as well as in the other molecules have oscillator strengths near 0.002; and the $^1A - ^1L_a$, near 0.1.

3. $\Delta \Sigma q$ must be odd in centrally symmetric systems. This is equivalent to Rule 2 in the molecules we are discussing. In centrally symmetric systems, the states may be divided into "even" and "odd," or "g" and "u," depending on whether the electronic wave function is symmetric or antisymmetric with respect to reflection in the center of symmetry. Even states have Σq even; odd states have Σq odd.

The proof of Rule 3 is therefore the same as the proof of the selection rule even \leftrightarrow odd, even \leftrightarrow even, odd \leftrightarrow odd; the procedure for this proof is like that indicated for diatomic molecules by Herzberg.^{15b}

Vibrations destroy the symmetry, and in several

symmetric polyacenes, what seem to be even-even transitions ($^1A \rightarrow ^1C_b$) have been found (see Fig. 2) with intensities $1/5$ to $1/2$ as strong as in the unsymmetric isomers. Large values of $\Delta\Sigma q$ become more and more improbable by the Franck-Condon principle, because they begin to involve large changes in electron velocity.

By correspondence-principle, $\Delta\Sigma q$ gives the order of the harmonic in the analogous classical flat metal oscillator. $\Delta\Sigma q = 1$ corresponds to the fundamentals, $\Delta\Sigma q = 2$ to the first harmonics, and so on.

The Polarization Diagram

At this point we examine the meaning of the subscripts *a* and *b*, which are related to the polarization of absorption bands.

If the perimeter were a circle, the states *A*, *B*, *C*, ... would correspond to Σ , Δ , Π , ... of a plane rotator configuration. A transition $A \rightarrow B$ corresponds to $\Sigma \rightarrow \Pi$, and so on. The possible polarizations of such a transition are the same as those of the corresponding one-electron transition, $\sigma \rightarrow \pi$. They are determined by the location of the nodes of a π -orbital.

This leads to a convenient diagram for determining polarization of absorption from the ground state. Draw the perimeter line. Indicate the atom positions, and mark where the line is cut by planes of symmetry. Expand the line to a circle. For the transition between the ground state and a state of momentum number *Q*, draw the nodes for a free-electron standing-wave orbital of momentum number $q = Q$. Since the orbitals are doubly degenerate, there will be two independent sets of these nodes. Each set will have $2Q$ nodal cuts across the perimeter. The nodes of one set will lie at antinodes of the other set. Where there is a symmetry axis, they are easy to construct. In one set the nodes will lie on the axis, in the other set the antinodes. We will call that set, *a*, which proves to have a nodal line cutting crosslinks (see Fig. 3) when the perimeter is returned to its normal shape; *b*, that set in which the crosslinks are uncut.

The polarizations of transitions from the ground state will be the same as if we located + and - point charges at alternate antinodes, shrank the perimeter back to its normal shape, and determined the direction of the resulting electric moment.

If we normalize the sum of all + charges to $+\frac{1}{4}$, and the sum of all - charges to $-\frac{1}{4}$, the size of the electric moment in this diagram will give a rough qualitative idea of the transition moment integral, or effective dipole length *Z* (*Q* in the usual notation). From this we can estimate the oscillator strength,¹⁶

$$f = 1.08 \times 10^{-5} \nu G Z^2 \text{ cm/A}^2$$

¹⁶ R. S. Mulliken and C. A. Rieke, Rep. Prog. Phys. **VIII**, 231 (1941).

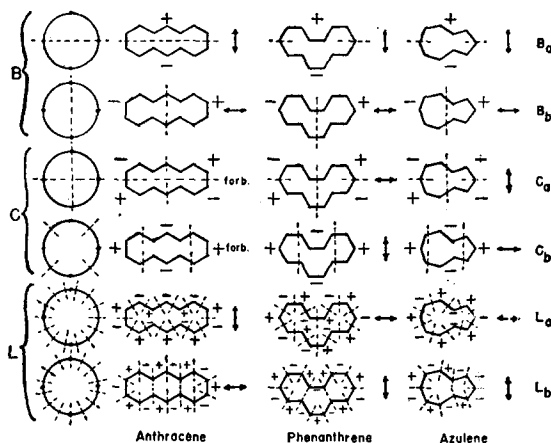


FIG. 3. Polarization diagrams for low absorption bands of representative molecules.

where ν is the frequency of the absorption band (in wave numbers); where *G* is 1 for a non-degenerate state, 2 for a doubly-degenerate state; and where *Z* is the dipole length (in Å).

This method of estimating *Z* and *f* amounts to replacing $(\Psi_{gd}\Psi_{exc})$ in the transition moment integral

$$Z = \int \Psi_{gd}(\sum \mathbf{r}_i) \Psi_{exc} d\tau$$

by a real charge density, ρ , which has the same symmetry properties and which represents the corresponding transition in a one-electron system. A normalization of ρ to $+\frac{1}{2}$ and $-\frac{1}{2}$ would correspond to approximating the ψ 's by two normalized, orthogonal point functions which each take the absolute value $1/(n)^{1/2}$ at *n* points in the molecule. However, since the effective charges are not so localized, but are distributed, the effective dipole lengths are shorter by about a factor of 2, and this can be taken into account by normalizing the ρ 's to $+\frac{1}{4}$ and $-\frac{1}{4}$ as indicated above. Thus, for a long polyene chain transition with one node, we would have effective charges of $+\frac{1}{4}$ and $-\frac{1}{4}$ at each end of the chain, effective dipole length $\frac{1}{4}$ the chain length. Bayliss gives this dipole length from the transition moment integral as 0.21 times the chain length.¹² Similarly in benzene, the one-electron transition moment integral for an $f \rightarrow g$ transition in a circular ring is $\frac{1}{4}$ the diameter, and the polarization diagram using the rules above would give about the same value for the effective dipole length.

Perhaps it should be emphasized that such a polarization diagram is a device for visualization and not a classical model. It is not suited for accurate intensity predictions, since they require proper introduction of the total wave functions in the transition moment integral; but it will give polarizations correctly. Several of these diagrams are

shown in Fig. 3 for some important transitions in anthracene, phenanthrene, and azulene.

The two highly allowed ${}^1A-{}^1B$ transitions are always polarized along mutually perpendicular axes in the molecule. It is these two transitions which go over by the correspondence principle into the classical fundamental electrical oscillations of a flat metal plate, which were used as analogies by Lewis and Calvin.^{17,18} Classically, ν would vary inversely with Z in the above formulas, and the intensity of each of these transitions would be proportional to the molecular diameter, suitably averaged, parallel to the transition axis.¹⁰ Empirically, according to the assignment of Fig. 2, the longitudinal transition, ${}^1A-{}^1B_b$, lies at the longer wave-length, as does its classical counterpart.

The ${}^1A-{}^1C$ bands, as shown by Rule 2 and as confirmed in Fig. 3, will be forbidden in centrally symmetric systems. The polarization diagram for the ${}^1A-{}^1C_b$ band in long, non-centrally-symmetric systems will presumably be cut by roughly parallel nodal lines transverse to the length, as ${}^1A-{}^1B_b$ was, and as shown in Fig. 3. If the system has no center of symmetry, but has an axis of symmetry, as phenanthrene and azulene do, the transition, ${}^1A-{}^1C_b$, will then be allowed and will have a moment parallel to the symmetry axis. In all long bent systems, this moment will probably be roughly transverse to the long dimension, as in phenanthrene. The moment of ${}^1A-{}^1C_a$ will be perpendicular to the symmetry axis, if any, or roughly longitudinal in long bent systems.

The ${}^1A-{}^1L$ bands will have the following special property. In their polarization diagram, the number of nodes on the perimeter is $2Q=2(2n+1)$, which is just the number of carbons on the perimeter, so the nodal separation is just the mean carbon-carbon distance. In the diagram for ${}^1A-{}^1L_a$, every peripheral bond will be cut by a node and we must put the effective charges on the atoms. For ${}^1A-{}^1L_b$, the atoms are at nodes and the effective charges go on the bonds. It is seen from Fig. 3 that in these transitions the elementary dipoles are nearly canceled within each ring, regardless of gross molecular shape, so the total intensity will be very small. Other transitions of high ΔQ are weak for the same reason.

For hexagonal ring systems, when some bonds are just parallel or perpendicular to a symmetry axis, the ${}^1A-{}^1L_a$ moment will be parallel to these bonds, the ${}^1A-{}^1L_b$ moment perpendicular. In azulene, which has an odd number of carbons in each ring, the a and b naming is ambiguous by the rule given above, but we can continue to draw the effective charges at the atoms in ${}^1A-{}^1L_a$. As may

be seen in Fig. 3, this interchanges the polarizations in the two L bands from their directions in the isomer, naphthalene (whose polarization diagrams are like those of anthracene).

In the classical macroscopic flat plate analogy, the intensity of these very high multipole ${}^1A-{}^1L$ transitions must approach zero, as they would correspond to the oscillations of a line of microscopic dipole charges around the edge of the plate. They should therefore not correspond to the Lewis and Calvin fundamental vibrations; Coulson⁴ emphasized that this correspondence did not hold for the lowest frequency bands, which are the ones identified here with ${}^1A-{}^1L$.

Height of Levels

The average height of a configuration should be given by the energy of the one-electron jump from the ground configuration. It is easily shown that this would predict an average frequency of absorption almost inversely proportional to the perimeter length. Actually, the frequency of the strongest band varies about inversely as the 0.3–0.5 power of the length (see I). The same difficulty, that the predicted frequency varies too rapidly with length, is found in the free-electron theory of polyenes¹² and in the LCAO theory of polyenes¹⁰ and of polyacenes.⁴ Addition of the periodic potential in the free-electron model may improve the predictions.¹³

The arrangement of levels of a given configuration is given by the Hund rule, as noted above.

The particular advantage of the free-electron model is that it may be extended easily to unsymmetrical cata-condensed systems. For all systems of a given number of rings, the perimeter is the same, the number of crosslinks is the same and the area is the same. Therefore the location of the levels should be approximately the same in isomers. This is seen in the spectra of I for isomers having the usual 6-carbon rings. The levels of azulene, with a 5-carbon and a 7-carbon ring are systematically lower than those of its 6-carbon isomer, naphthalene.

Electron Density

The possible importance of high local charge density in determining reactivity and potency in carcinogenic hydrocarbons such as benzanthracene, dibenzanthracene, and their derivatives, has been emphasized by Schmidt,⁶ and quantitative predictions of density variations have been made by Daudel and Pullman and others.¹⁹ The free-electron model with suitable boundary conditions will give alternating charge densities in successive bonds near the end of a polyene chain, though Bayliss

¹⁷ G. N. Lewis and M. Calvin, *Chem. Rev.* **25**, 273 (1939).

¹⁸ G. N. Lewis and J. Bigeleisen, *J. Am. Chem. Soc.* **65**, 520, 2102, 2107 (1943).

¹⁹ For bibliography, see P. Daudel and R. Daudel, *J. Chem. Phys.* **16**, 639 (1948).

did not point this out. However, the perimeter model gives uniform charge density for condensed systems, if they are unsubstituted. Introduction of crosslinks will produce local density variations of Schmidt's type. Substitution on the perimeter will introduce a perturbing potential, and cause mixing of the wave functions and further variation of charge density. In this way, the free-electron model could probably be extended to account for directing effects in benzene rings and for similar effects in the carcinogens.

It is unfortunate that the terminology proposed here uses two letters, *A* and *B*, in different senses from their use in group theory. But spectroscopy has taken its toll throughout the alphabet and there seems to be no other series of consecutive letters with fewer conflicts. Especially, it seemed wise to avoid the established angular momentum letters in either English or Greek, since the case here is so different. It is hoped that the different subscripts will help to avoid confusion with the group theory designations.

III. CORRELATION WITH SPECTRA

In I the levels of 17 cata-condensed systems were identified according to the scheme just outlined. Levels of a few important molecules are given again in Fig. 2. Justification of this system of naming must be in two parts: (a) justification of giving the same names at all to levels of different compounds; and (b) justification of the particular names chosen, since they now imply definite properties. Subsequently some general support from LCAO theory, and some ambiguous identifications, will be discussed.

(a) Empirical Identity of Levels in Different Compounds

The following general results are derived from I; details may be found there.

1. *Levels of a given type have unambiguous identifying characteristics, which do not change from compound to compound. The most useful characteristics are intensity and vibrational sharpness of the transition from the ground state to the level in question. There is almost no mixing or confusion of properties.*

2. *Levels of a given type move in a systematic way from compound to compound. All lie on smooth and almost parallel curves as a function of length. They generally lie near the same energy in isomers.*

3a. *Each empirical type occurs once and only once in each compound.*

3b. *The number of lower levels remains constant from compound to compound up to any particular*

upper level as far as the spectra have been carried. There are a few reasonable exceptions where degeneracies occur or where a weak band is expected to be overlapped by a stronger band and its upper state cannot be located accurately.

Levels that resemble each other so much in different compounds must have some important properties in common. The same name should be given to all of them to indicate these properties. Actually, according to any present theories, including the free-electron method used for the interpretation here, we should expect more change than there is in the band characteristics, such as the "forbiddenness" of the ${}^1A-{}^1L_b$ bands, in going from benzene to the unsymmetrical 4-ring systems, and we should expect more mixing and loss of identity of band types than there is in the spectrum of any of these larger systems. Nevertheless, the empirical evidence for distinctness and preservation of identity of band types seems fairly convincing. We can proceed only by taking that evidence at face value in justifying the names and predicting the properties of the different types of states.

(b) Justification of Names

1L_b

There is a band in benzene at $39,000\text{ cm}^{-1}$. LCAO theory shows the upper state is a singlet, probably of symmetry B_{2u} ,³ though B_{1u} is not ruled out.² Assuming B_{2u} is correct, the polarization diagram must have nodal lines through the atoms. This kind of state we have named 1L_b . If anything like it exists in the larger molecules, it will also be 1L_b . There is just one similar band found in every aromatic molecule, except where it is expected to be hidden by a stronger one. It always has nearly the same intensity, $\log \epsilon \sim 2.5$, and the same kind of sharp vibrational structure running to about 6 bands, as in benzene. The upper states of these bands, when plotted against the number *n* of rings, lie on a smooth curve starting with the $39,000\text{ cm}^{-1}$ state of benzene. We therefore call them 1L_b , and hope that we have guessed correctly the common property.

1L_a

Similarly, by LCAO theory, the benzene $48,000\text{ cm}^{-1}$ state is ${}^1B_{1u}$,³ though ${}^1B_{2u}$ is not ruled out.² Assuming the former, our diagram must have nodes between atoms. This state lies on a smooth curve with similar levels in the longer molecules. All transitions to these levels have 5 or 6 diffuse bands with $\log \epsilon \sim 3.8$. They are therefore 1L_a , according to this scheme. The scheme predicts transverse

polarization for ${}^1A-{}^1L_a$ in polyacenes (Fig. 3). This has been found in naphthalene and anthracene.^{4,20} This correct prediction is an argument for the correctness of our assumption that 1L_b has symmetry ${}^1B_{2u}$ in benzene and that 1L_a has symmetry ${}^1B_{1u}$.

${}^1B_b, {}^1B_a$

These should be together in benzene and split in the other molecules studied in I. The benzene 55,000 cm^{-1} transition is the strongest in benzene. By LCAO it is allowed and of type ${}^1A_g-{}^1E_{1u}$, which corresponds to our definition of ${}^1A-{}^1B$. It lies on a smooth curve with the strongest transitions in the longer compounds, when plotted against length. With increasing length, these bands have an increasingly sharp first peak followed by two or three weaker diffuse bands. The intensity of transitions on this curve increases with molecular length as expected. In naphthalene and anthracene these transitions are longitudinally polarized.^{4,20} They are at the same wave-length as the strong bands of polyenes of the same molecular length (see I). Therefore they have all the properties expected of the longitudinal ${}^1A-{}^1B_b$ bands.

In each of the compounds except benzene another strong band lies higher. Its intensity does not increase much with molecular length. It can therefore be the transverse ${}^1A-{}^1B_a$, which should have this property.

${}^1C_b, {}^1C_a$

A band appears between the two 1B bands in every compound but benzene. (A band which may be similar appears above the B band in unsymmetrical alkylbenzenes.) It is doubtful in naphthalene, but clear in anthracene, about as strong as ${}^1A-{}^1L_a$. Its intensity increases in the non-centrally symmetric isomers azulene and phenanthrene, becoming about as strong as ${}^1A-{}^1B_a$. Therefore it is possibly forbidden in centrally symmetric molecules. Among the low transitions, this behavior is expected of ${}^1A-{}^1C$ and ${}^1A-{}^1K$ bands. The intensity when it is strong is more like the dipole ${}^1A-{}^1B$ than the multipole ${}^1A-{}^1L$ so it is probably ${}^1A-{}^1C$. Since no similar band appears lower, but one appears higher in the 4-ring systems, the band between the two 1B bands can be assigned to ${}^1A-{}^1C_b$ and the higher one to ${}^1A-{}^1C_a$. Presumably the ${}^1A-{}^1K$ bands lie lower but are weaker than ${}^1A-{}^1C$ (and also forbidden in centrally symmetric molecules), and are concealed by the strong ${}^1A-{}^1B_b$ bands or by ${}^1A-{}^1L_a$.

3L_a

The phosphorescent level has been assigned to ${}^3B_{1u}$ (our 3L_a) in benzene³ but ${}^3B_{2u}$ (3L_b) has not

been ruled out.² In the whole group of molecules, its separation from 1L_a varies smoothly with length, from 19,000 cm^{-1} in benzene to 12,000 cm^{-1} in three- and four-ring systems, and is constant among isomers even when both levels move far. On the other hand, its separation from 1L_b varies widely, especially among isomers (cf. anthracene-phenanthrene in Fig. 2). Since the singlet-triplet separation should be roughly constant, this phosphorescent level then must be of the same type as 1L_a , and so is called 3L_a . In turn, this is an argument for the assignment of ${}^3B_{1u}$ to the phosphorescent level in benzene, if we accept the reasoning above as establishing the 1L_a level as ${}^1B_{1u}$ in benzene.²¹

(c) Identifications and LCAO Predictions

Coulson⁴ calculated, by the LCAO method without neglect of overlap integrals, the center of gravity positions and the polarizations of singlet-triplet pairs in polyacenes. If the center of gravity of the lowest transverse pair of bands, as given by the present assignments, is close to his lowest predicted transverse center; and if the observed lowest longitudinal center is close to his predicted lowest longitudinal, then his calculations give a general support to these assignments. This is found to be the case, as was shown in I. Coulson's ignorance of the triplet states and of 1L_b caused confusion in his original comparison with the data.

The upper triplets are unknown, so Coulson's calculations must there be compared with the singlets, and they show as good agreement as they do with the lower singlets. (See Fig. 2.) Thus his predicted total spread of the states corresponding to our $f \rightarrow g$ system is about 20,000 cm^{-1} in naphthalene, 30,000 cm^{-1} in anthracene where the total spread of the singlets, according to our identifications, is about 27,000 cm^{-1} in both cases. In his upper two singlet transitions, the longitudinal one should be at lower frequencies. This agrees with the present identifications of 1B_b and 1B_a .

His predictions for the third forbidden transition of $e \rightarrow g$ type in naphthalene and anthracene also lie within about 5000 cm^{-1} of the level we have

²¹ H. Shull at the University of California has also shown from analysis of the phosphorescent band in benzene that it is made allowed by the same types of vibrations as those which would make the ${}^1A_g-{}^1B_{1u}$ band allowed. (Private communication.) The two other independent pieces of evidence in the present paper which show its empirical relation to this singlet band are: (a) the almost constant separation of the phosphorescent band in benzene and the larger molecules from ${}^1A-{}^1L_a$, which we have concluded is probably ${}^1A_g-{}^1B_{1u}$ in benzene; and (b) the good agreement between the center of gravity of this pair of bands in the different molecules and the LCAO calculations—any other pairing would destroy the agreement. Nevertheless, R. S. Mulliken points out that we cannot conclude with certainty that the phosphorescent state in benzene should be labelled ${}^3B_{1u}$ until the theoretical spectroscopic combining properties of corresponding singlet and triplet states have been established.

²⁰ R. N. Jones, Chem. Rev. 41, 353 (1947).

named correspondingly, 1C_b . (See Table I.) The two lower forbidden transitions, our ${}^1A-{}^1K$ bands, should also be weaker according to the present arguments, and have not been found.

Mann's LCAO calculations on the azulene levels²² also support the identifications, as shown in Fig. 2. The predicted centers of gravity deviate from the singlets in the same direction and about the same amount as the corresponding LCAO predictions deviate in naphthalene. A mistake in identification would have been revealed by large changes in these deviations.

Because of the reversal of polarizations from naphthalene to azulene, Mann's results also confirm the correctness of the nodal properties assumed here in the polarization diagrams for the L bands. In azulene, ${}^1A-{}^1L_b$ should be transverse, ${}^1A-{}^1L_a$ longitudinal, as indicated by the diagram in Fig. 3. These bands are identified at 14,000 cm^{-1} and 28,000 cm^{-1} , respectively, by the usual empirical resemblances. Now the LCAO calculation also gives the low singlet-triplet pair as transverse, the next pair as longitudinal. The separation of the pairs is great enough that the sequence of the singlet levels could not reasonably be interchanged from the LCAO-predicted sequence of the pairs, if we remember how accurate the LCAO energy predictions are in the polyacenes (I). Therefore, if the LCAO has predicted these polarizations correctly, then the properties assumed here for the L states also predict them correctly.

The failure of the LCAO predictions of intensities does not much weaken the importance of the good agreement on energies, because intensities are known to be generally much more sensitive to the accuracy of the wave functions than the energies are.

(d) Possible Misidentifications

There are three bands described in I in which there is some question about the identifications according to the present scheme.

The weak band called 1C_b in naphthalene, and presumed to be forbidden, seems to be still weaker or has moved in acenaphthene, which is essentially an alkyl-substituted naphthalene. One would expect it to be somewhat stronger. On the other hand, the difference in strength is not much larger than the experimental error.

The band called ${}^1A-{}^1C_b$ in naphthacene, and presumed to be forbidden, becomes stronger in bent 4-ring systems, as it should. However, the band we have called ${}^1A-{}^1C_b$ is also stronger in chrysene. This molecule again has a center of symmetry, so that this band should again be forbidden. If there is not a mistake in identification, perhaps some

interaction with allowed transitions nearby will account for the larger intensity.

On almost any theory, the 1B state in triphenylene, which has D_{3h} symmetry, should be single and doubly degenerate. However, two strong bands have been found with about the usual ${}^1B_b-{}^1B_a$ separation, about 10,000 cm^{-1} . The higher band must be of some type other than 1B_a , but it is not certain what.

These points deserve further study. It does not seem likely that they will invalidate the classification, since the latter is supported by nearly a hundred other identifications in which the band properties and their variations among isomers are correctly predicted.

IV. COMPARISON WITH THE LCAO METHOD: BENZENE

The free-electron method will also be justified by its close basic correspondence with LCAO method in the construction of orbitals and states, in cases where the latter method has been worked out. The comparison will be made for two such cases: benzene and anthracene.

In benzene, one free electron in the loop of perimeter $l=8.4\text{\AA}$ would have energies

$$E=17,000q^2\text{ cm}^{-1}.$$

No arbitrary constants are involved in this formula. These one-electron states are plotted in the left half of Fig. 4.

The quadratic spacing with interval ratios 1:3:5 agrees qualitatively with LCAO calculations which include overlap integrals. The latter give the interval ratios 1:4:5, as shown on the right in Fig. 4.²³ If the LCAO bond integral, $-\beta$, is set at 28,000 cm^{-1} , the energies agree within about 10 percent with the free-electron energies. However, a smaller value of β , about 20,000 cm^{-1} , fits the observed states better.²

The LCAO theory predicts only four one-electron states, with the top one single, where free-electron model predicts an infinity of higher states, all doubly degenerate. The difference is due to the restriction of LCAO to combinations of atomic p -orbitals. The additional free-electron states correspond to combinations of d - and f -orbitals and so on. The difference is unimportant in practice since the observed spectra involve only the lowest excited states.

On the free-electron model, the classification of the lower states in the six- π -electron benzene problem is as given in Table II.

Excitation of an electron from the f -shell to the g -shell leads to states with $Q=2-1$ and $Q=2+1$, according as the electron and hole q -vectors are

²² D. Mann, J. R. Platt, and H. B. Klevens, *J. Chem. Phys.* **17**, 481 (1949).

²³ C. C. J. Roothaan, private communication.

added or subtracted. These have angular momentum 1 (*B*-state) and 3 (*L*-state) and would correspond to Π - and Φ -states, in diatomic notation, with respect to the 6-fold axis. Because of the high symmetry the *B*-state is not split, but the *L*-state is so this configuration gives three singlet and three triplet states.

Four of these six excited states are known as shown in Fig. 2. The group-theory classification is fairly well established^{2,3} except for the triplet whose identity seemed to be established by the arguments of the last section. The position of the other levels has been estimated.² The forbidden $^1A \rightarrow ^1L$ bands are supposed to become somewhat allowed through vibrational interactions of the proper symmetry.

In the strong allowed transition, the polarization diagram method gives an effective dipole length, *Z*, about 1/4 of the greatest diameter, or 0.7Å. This gives $f=0.59$. This is in fair agreement with the experimental value, 0.79 for the integrated $f \rightarrow g$ transition intensity.²⁴ Because of the crudeness of the method, only the relative intensity estimate as compared to anthracene (below) is of significance. The relative agreement is fairly good. The LCAO method predicts $f=2.35$.¹⁶ When this is corrected by a standard empirical factor of 0.3, it is in fair agreement with the observed value.

The center of gravity of the levels of the f^3g system in benzene is estimated² from the spectrum to lie at about 44,000 cm^{-1} which may be compared with the free-electron prediction of 51,000 cm^{-1} .

V. COMPARISON WITH THE LCAO METHOD: ANTHRACENE

For anthracene, with one free electron on an ideal perimeter loop of length $l=19.6\text{\AA}$, the energies will be

$$E = 3150q^2 \text{ cm}^{-1}.$$

Again this quadratic spacing agrees well qualitatively with the increasing spacing found in Coulson's LCAO calculations⁴ (Fig. 5).

TABLE II.

Configuration	Free-electron states	Group theory notation
...
... f^3g	$\begin{Bmatrix} ^1B & ^3B \\ ^1L_a & ^3L_a \\ ^1L_b & ^3L_b \end{Bmatrix}$	$\begin{Bmatrix} ^1E_{1u} & ^3E_{1u} \\ ^1B_{1u} & ^3B_{1u} \\ ^1B_{2u} & ^3B_{2u} \end{Bmatrix}$
... f^4	1A	$^1A_{1g}$

Coulson's orbitals are divided into two groups: without (*P*, *Q*) and with (*R*, *S*) a longitudinal nodal line; and each of these into two sub-groups: without (*P*, *R*) and with (*Q*, *S*) a transverse nodal

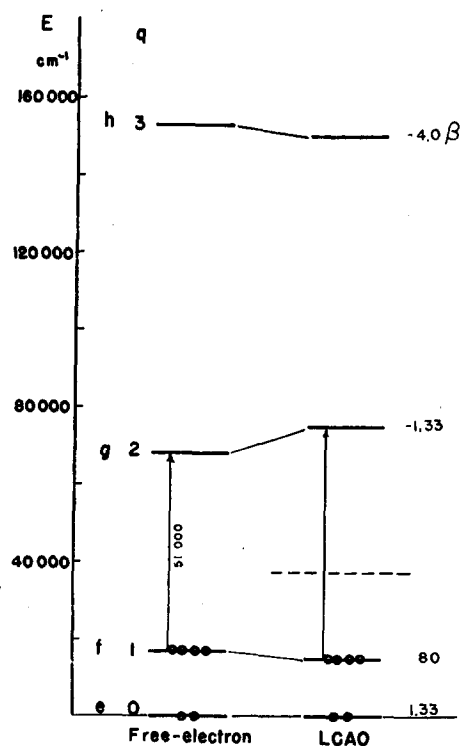


FIG. 4. Comparison of free-electron and LCAO states and shells: benzene.

line across the center of the molecule. The free-electron $q=0$ orbital with no nodes corresponds to his P_1 . The free-electron degenerate $q=1$ with two nodes on the perimeter corresponds to his two non-degenerate orbitals, Q_1 with nodes at the sides, and R_1 with nodes at the ends of the perimeter. Similarly $q=2$ with 4 nodes on the perimeter corresponds to his P_2 and S_1 ; and so on. The number of nodes for corresponding levels is the same in the two systems, and the only difference is in the removal of the free-electron degeneracy. The surprising thing is not that the degeneracy is removed, but that the splits are not wider. Thus in naphthalene and anthracene, the LCAO levels are arranged in order of increasing free-electron q ; and crossovers occur first in naphthalene. (Coulson's levels for anthracene are accidentally degenerate, as shown in Fig. 5.) By choosing Coulson's LCAO factor $\gamma=23,000 \text{ cm}^{-1}$, the energy predictions of the two schemes agree as shown in Fig. 5. All but two of the 7 excited free-electron states lie between their split LCAO counterparts. The maximum separation of any free-electron state from the center of gravity of its split counterparts is 7000 cm^{-1} .

The lower states of anthracene would then have the correspondence in the two systems shown in Table III.

The identification of the observed states by this system in Fig. 2 differs from Coulson's identifica-

²⁴ J. R. Platt and H. B. Klevens, Chem. Rev. 41, 301 (1948).

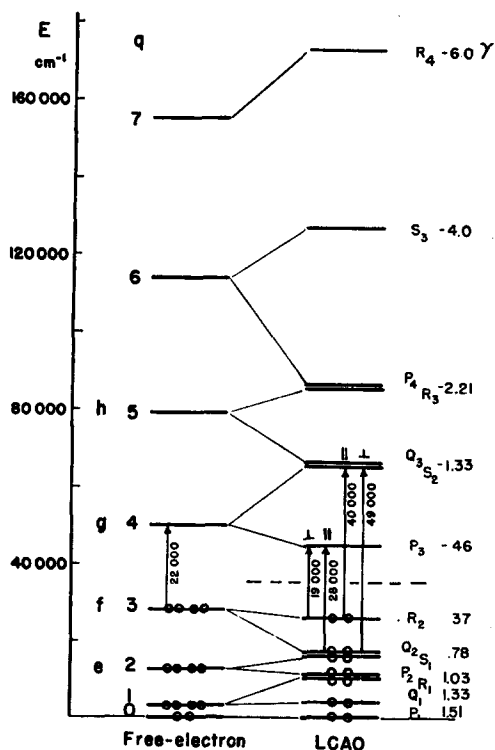


FIG. 5. Comparison of free-electron and LCAO states and shells: anthracene.

tion. Coulson knew only the two singlet bands 26,000 cm^{-1} (experimentally transverse) and 39,000 cm^{-1} (experimentally longitudinal), and naturally identified the latter with his longitudinal $N-V_2$. The identifications of Fig. 2, setting 39,000 cm^{-1} as his R_2-S_2 state and the hidden 28,000 cm^{-1} as V_2 , are in much better agreement with his energy predictions, as was shown in I.

If this is correct, his intensity calculations on $N-V_1$ are about ten times too high, and those on $N-V_2$ are several hundred times too high.^{1,4} Configurations involving his P_3 state actually make only weak transitions to ground. The qualitative success of the present model would imply that electron interactions, and the mixing of transverse R_2-P_3 with transverse Q_2-S_3 , and of longitudinal Q_2-P_3 with longitudinal R_2-S_3 , may have to be considered in order to get the correct intensities by LCAO theory.

The free-electron prediction of about 22,000 cm^{-1} for the center of gravity of the f^3g states (Fig. 5) is to be compared with its experimental location near 30,000 cm^{-1} . The frequencies predicted by either method become too low in long chains, as remarked above.

For intensities, the effective dipole lengths may be estimated from the polarization diagram, giving the values shown in Table IV. The ${}^1A-{}^1B_a$ transition is across the molecule and its dipole length is

correspondingly near that of benzene, about $1/4$ the width, or 0.7A. The ${}^1A-{}^1B_b$ transition is along the molecule and its dipole length is taken as $1/4$ the chain length. The ${}^1A-{}^1L_a$ band has a polarization diagram with nodes between the atoms, as seen in Fig. 3. If we think of the end rings as having balanced charges, the remaining center dipole with $1/7$ of the charge will give an effective transverse dipole length of about $\frac{1}{7}(\frac{1}{4} \cdot 2.8\text{A})$ or about 0.1A. The ${}^1A-{}^1L_b$ has a polarization diagram with nodes at the atoms, as seen in Fig. 3. This would give a zero moment if all the effective charges were equal and the rings were perfectly hexagonal, but will give a small longitudinal moment otherwise.

The known polarizations agree with these assignments, and the sequence of intensities is correctly predicted. More accurate calculations do not seem justified without introducing the periodic potential and connecting links, and the vibrations, especially in computing the multipole bands.

It is strange that the benzene ${}^1A-{}^1L$ transitions should have the same intensities as their counterparts in larger, and even in unsymmetrical, molecules. In the latter there are many mechanisms—variations in bond distance and electron density, the crosslinks, and so on—by which even multipole transitions should gain intensity and “become allowed,” just as Coulson expected for the L bands. It is similarly strange that these benzene bands have much the same diffuseness or sharpness as in the larger molecules. It is usually supposed that ${}^1A-{}^1L_a$ is moderately strong and diffuse in benzene, and ${}^1A-{}^1L_b$ is weak and sharp, because the former is nearer the allowed transition and more perturbed, or possibly because of predissociation in the former. But ${}^1A-{}^1L_a$ gets far away from strong allowed transitions in the other molecules and remains moderately strong and diffuse, while ${}^1A-{}^1L_b$ comes between it and the strong allowed transitions in pentacene, yet remains weak and sharp. It seems improbable that predissociation would occur just

TABLE III. Anthracene: names of states and polarizations of absorption bands abbreviated.

Configuration	Free-electron states (Singlets and triplets)	Coulson notation	Symmetry species	Polarization of transition to ground
..... $d^3e^1f^2g$	D_a	Q_1-S_2	B_{2u}	trans
	D_b	R_1-S_2	B_{1u}	long
	J_b	Q_1-P_3	B_{1u}	long
	J_a	R_1-P_3 or V_4	B_{2u}	trans
..... e^3f^2g	C_a	P_2-S_2	B_{3g}	forb
	C_b	S_1-S_2	A_{1g}	forb
	K_b	P_2-P_3 or V_5	A_{1g}	forb
	K_a	S_1-P_3 or V_3	B_{3g}	forb
..... f^3g	B_a	Q_2-S_2	B_{2u}	trans
	B_b	R_2-S_2	B_{1u}	long
	L_b	Q_2-P_3 or V_2	B_{1u}	long
	L_a	R_2-P_3 or V_1	B_{2u}	trans
..... f^4	1A	N	A_{1g}	—

at the 1L_a level in all these molecules, especially since this level moves more widely than any other. Evidently there is more in common in corresponding bands than current theory will allow. This is useful for identification but puzzling.

Possibly all these sources of extra intensity in the larger molecules are negligible, like the ones used in the rough calculations of Table IV, which predicted too low L -band intensities. If this were so, the only important contribution to intensity in these bands would always be the result of vibrations, just as in benzene. Then, since vibration amplitudes and charge densities must be much the same in compounds with similar force constants and masses and π -electron densities, we would have an explanation of the constancy of the L -band properties.

In benzene and anthracene, we see that the free-electron model does not contradict the LCAO method in principle at any point. The only practical divergence is on predicted L -band intensities, but this may disappear when electron interaction is included in the LCAO treatment. No doubt by introducing the periodic potential and making vector-model-type estimates of the size of the electron interactions in the free-electron scheme, we could improve the quantitative predictions and determine the sequence and location of the excited states. This might mean a considerable increase in the ease and accuracy with which we can describe the spectra of unsymmetrical systems.

VI. SPECTRA OF OTHER TYPES OF MOLECULES

The free-electron model can be adapted to classifying other conjugated ring and ring-chain spectra. The kind of classifications required may vary with the type of topological connectedness of the conjugated system. In simple polyene chains, for example, the levels of the first excited configuration reduce to our 1B_b and 3B_b , with selection rules and intensities depending only on the bending of the chain and its dimensions.

For ring-chain systems and peri-condensed systems (in which some carbon atoms belong to three rings), study of the spectra^{25,26} shows that in many cases the lowest bands still seem to be of B and L types. However, there is more mixing of characters, both vibrational and intensity, just as is expected in the larger cata-systems (Fig. 8 of I). Identification of types is correspondingly less certain in many of the spectra.

We can account for the existence in these molecules of L states and other states giving weak multipole absorption bands, by means of a theorem of Coulson and Rushbrooke.¹⁰ This applies to sys-

TABLE IV. Estimated oscillator strengths in anthracene.

Transition	Polarization	Z	ν	f_{est} (free-elect)	f_{obs} (from I)
${}^1A-{}^1B_a$	trans	.7A	54,000	0.30	0.65
${}^1A-{}^1B_b$	long	1.8A	39,000	1.4	2.28
${}^1A-{}^1L_a$	trans	.1A	26,000	.003	.10
${}^1A-{}^1L_b$	long	.00A	(28,000)	.0000	(.002)

(phenanthrene)

tems containing rings with only an even number of carbon atoms. By LCAO theory with neglect of overlap, the theorem says that the occupied and unoccupied one-electron states may be classed in pairs with equal and opposite binding energy. Call the members of any pair, a and a' . If we translate this into the language of classical interacting oscillators, state a corresponds to a particular phase difference between adjacent oscillators. Call this difference $(\pi/2) - \alpha$. Then state a' corresponds to phase difference $(\pi/2) + \alpha$. Similarly, translating into free-electron terms, the phase difference in the Schrödinger wave between the two ends of a bond will be $(\pi/2) - \alpha$ in state a , and $(\pi/2) + \alpha$ in state a' .

When an electron jumps from state a to a' , the electron and hole momenta in the two-dimensional network may be added or subtracted. This gives two kinds of states, with total momenta corresponding to a phase difference between adjacent carbons of either 2α or π . On the polarization diagram, an absorption band to the state with 2α has only a few nodal lines across the molecule, i.e., it is a dipole or a low "multipole." An absorption band diagram to the state π will have nodal lines either in the middle of every bond, in which case it is like ${}^1A-{}^1L_a$; or at the ends of bonds, in which case it is like ${}^1A-{}^1L_b$.

Thus it seems reasonable that the first few singlet bands of the more complicated systems can again be called ${}^1A-{}^1L_b$, 1L_a , 1B_b , 1B_a . If mixing of characters is strong, a more exact treatment, or perhaps a different kind of approximation, will be required. Probably the first four distinctive bands in the spectrum of pyrene²⁵ are of these four types. In aniline and styrene there are also four prominent bands.²⁶ In diphenyl,²⁶ only three are seen, but the fourth weak one reappears in fluorene, which is a bent alkyl-substituted diphenyl so this weak band may simply be hidden in diphenyl itself.

I must express my especial debt to Herzfeld²⁷ for his emphasis on the importance of the nodes, and to Mulliken, Longuet-Higgins, and many other colleagues for helpful criticisms and discussion.

Note added in proof: Several very recent applications of the free-electron method are described in a footnote at the end of I.

²⁵ E. Clar, *Aromatische Kohlenwasserstoffe* (Springer-Verlag, Berlin, 1941).

²⁶ H. B. Klevens and J. R. Platt, unpublished results.

²⁷ K. F. Herzfeld, Chem. Rev. **41**, 233 (1947).