

# THEORY OF ELECTRONIC SPECTRA OF ORGANIC MOLECULES

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**Abstract**—A theory of the electronic spectra of organic molecules is outlined. The wave-mechanical resonance characteristic for the excited states of polyelectronic systems involves a fluctuation of the transition energy and, in this sense, represents a physical phenomenon which is absent in ground states. An analysis of the electronic perturbations resulting from resonance offers a qualitative, but very detailed, understanding of the observations and conclusions summarised in the author's classification of electronic spectra, if molecular structures are considered to be built up of localised bonds only. The electronic transitions responsible for *R*-, *K*-, and Benzenoid-bands and the effect of terminal groups and of substituents of absorbing systems on the positions of these bands are interpreted.

## 1. INTRODUCTION

THE present paper outlines a general theory of the electronic spectra of organic molecules. Earlier investigations have established an empirical classification of the absorption bands (*R*-, *K*-, Benzenoid-bands) appearing above 2000 Å and the rules of their behaviour.<sup>1-6</sup>

The author realised that the interpretation of molecular structures with the help of the concept of non-localised bonds (resonance among several idealised valence-bond structures, many-centred molecular orbitals) and of mesomeric or electromeric electron displacements is unable to account for numerous observations and aspects of electronic spectra.<sup>5-7\*</sup> This dilemma led to a detailed analysis of other physical and chemical properties of organic compounds which resulted in a confirmation of the conclusions derived from the study of electronic spectra. It could be shown that a consideration of the electronic repulsions, which were previously neglected because they offer considerable difficulties to a mathematical analysis or to a qualitative formal representation, allows a consistent qualitative interpretation of the properties of organic molecules in terms of classical (not idealised) structures and inductive electron displacements only.<sup>8-12</sup> These repulsions also account for the absence of orbital delocalisations.

The foundation for a theoretical analysis of the electronic spectra of polyelectronic

<sup>1</sup> A. Burawoy *Ber. Dtsch. Chem. Ges.* **63**, 3155 (1930); **64**, 464, 1635 (1931); **65**, 941 (1932); *J. Chem. Soc.* 1865 (1937); 1177 (1939); 20 (1941).

<sup>2</sup> A. Gillam and E. S. Stern *Electronic Absorption Spectroscopy in Organic Chemistry* pp. 111. Edward Arnold, London (1954).

<sup>3</sup> A. Burawoy *Disc. Faraday Soc.* **9**, 70, 73 (1950).

<sup>4</sup> A. Burawoy *J. Soc. Dyers and Colourists* **15**, 616 (1949).

<sup>5</sup> A. Burawoy and E. Spinner *J. Chem. Soc.* 2085, 2557 (1955).

<sup>6</sup> A. Burawoy and A. R. Thompson *J. Chem. Soc.* 4314 (1956).

<sup>7</sup> A. Burawoy *Chem. and Ind.* **59**, 855 (1940).

<sup>8</sup> A. Burawoy *Trans. Faraday Soc.* **40**, 537 (1944); *Disc. Faraday Soc.* **10**, 104 (1951); *Chem. Ind. (Rev.)* **63**, 434 (1944).

<sup>9</sup> A. Burawoy *Contribution to the Study of Molecular Structure* p. 73. Desoer, Liège (1947-1948).

<sup>10</sup> A. Burawoy and J. T. Chamberlain *J. Chem. Soc.* 2310 (1952).

<sup>11</sup> A. Burawoy and E. Spinner *J. Chem. Soc.* 3752 (1954).

<sup>12</sup> J. E. Lennard-Jones and J. A. Pople *Disc. Faraday Soc.* **10**, 9 (1951); J. A. Pople, *Quart. Reviews* **XI**, 273 (1957).

\* Numerous additional examples will be given in subsequent publications.

systems has been laid by Heisenberg<sup>13</sup> who, in introducing the conception of wave-mechanical resonance, not only explained the fact that the simplest polyelectronic entity, the helium atom, forms two independent systems of energy levels, but also gave a wave-mechanical interpretation of electronic perturbation in an *excited* state. Moreover, this concept offered the explanation for the apparent paradox that in polyelectronic systems many electrons appear to participate in the transition, although (generally) only one electron can be excited.

As a result of the interaction (due to electronic repulsions) of its two valency electrons *a* and *b*, one of which is excited, the helium atom can exist in two types of excited states corresponding to the symmetrical and antisymmetrical wave-functions I and II respectively. The singlet, identified with I, is less stable, the triplet state, identified with II, which in absorption is already forbidden by spin requirements, is more stable than the interacting fictitious unperturbed excited states of the system corresponding to  $\psi_1(a) \cdot \psi_2(b)$  and  $\psi_1(b) \cdot \psi_2(a)$  respectively.

$$\text{I} \quad \Psi_S = \frac{1}{\sqrt{2}} [\psi_1(a) \cdot \psi_2(b) + \psi_1(b) \cdot \psi_2(a)]$$

$$\text{II} \quad \Psi_A = \frac{1}{\sqrt{2}} [\psi_1(a) \cdot \psi_2(b) - \psi_1(b) \cdot \psi_2(a)]$$

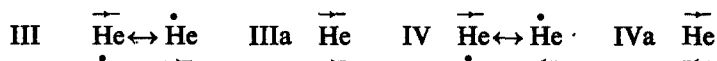
The theoretical developments of the past 25 years have been governed by the aim to systematise qualitatively or to account quantitatively for molecular states in terms of atomic orbitals. The complexity of polyatomic molecules and mathematical limitations necessitated the introduction of numerous simplifying conceptions (e.g. (i) the distinction between the two bonds ( $\sigma$ ,  $\pi$ ) in the ethylene double bond, (ii) the concept of non-localised bonds, (iii) the attempt to build up electronic structures of molecules with the help of many-centred (as distinct from two-centred) molecular orbitals by analogy to the building-up principle in atomic structures, (iv) the consideration of  $\pi$  electrons only). Unfortunately, these concepts became widely accepted as representing a true physical picture of molecular states. It is the author's contention that these simplifying assumptions are unsuitable or unable to offer a basis for a detailed understanding of the experimental observations related to the electronic spectra of the more complicated organic molecules.

In contrast, the present analysis will be based on the bond orbitals present in covalent linkages, no reduction to atomic orbitals being attempted. It aims at an interpretation of the electronic transitions responsible for the *R*-, *K*- and Benzenoid-bands and of the changes in the transition energies resulting from structural modifications (constitutive changes or replacements of covalent linkages). This analysis, being in the first instance only a qualitative one and, thus, independent of mathematical limitations, does not require any structural simplifications and will be strictly based on and governed by classified experimental data. It will be shown that, on this basis, a consistent consideration of the electronic perturbations in the excited states due to Heisenberg resonance offers a qualitative, but very detailed understanding of the electronic spectra of organic molecules, if the latter are accepted as being built up of localised bonds only.

In view of the increasing complexity of the systems to be discussed, no further use of wave-mechanical formulation will be made, which problem should be left to more

<sup>13</sup> W. Heisenberg *Z. Physik* 38, 411; 39, 499 (1926); 41, 239 (1927).

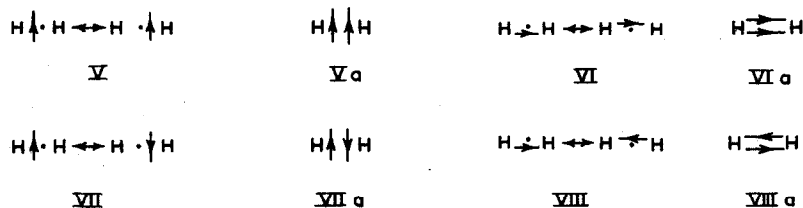
competent theoretical physicists. However, it will be convenient to express an excited electron (orbital) by an arrow such as  $\rightarrow^*$ , at the same time indicating its symmetry type, i.e. the direction of the electron (charge) migration† (on one side of the nodal plane formed). Thus, the excited  $P^1$  and  $P^3$  states of the helium atom, in which the excited orbital has a nodal plane through the nucleus, may be expressed by III and IV respectively. Moreover, the representation of a normal excited state by a symbol, in which each unperturbed state is expressed by a separate formula, would, obviously, become much too involved in more complicated polyelectronic systems. It may, therefore, be suggested that they be replaced by one simplifying formula only, in which each unperturbed state is expressed by an arrow (indicating the excited electron involved). Thus, III and IV may be replaced by IIIa and IVa respectively. Such formulations have the additional advantage that they give a qualitative picture of the time-averaged electron migrations in the excited electronic system.



To be more precise, each unperturbed state will be assumed to include already the effect of perturbation arising from the different Coulomb repulsions of the electrons in the ground and excited state as distinct from the effect of that part of the perturbation attributed to "resonance" (for simple non-mathematical descriptive discussions of this matter, cf. also Heitler<sup>14</sup> and Pauling and Wilson<sup>15</sup>).

## 2. SINGLE BONDS ( $H_2$ ) AND DOUBLE BONDS

The excited states of the hydrogen molecule are well understood.<sup>16</sup> Those of interest to the following discussion may be expressed in the terms of our qualitative analysis by V ( $^1\Pi_u$ ), VI ( $^1\Sigma_u$ ), VII ( $^3\Pi_u$ ) and VIII ( $^3\Sigma_u$ ) which, again, may be replaced by the simplifying symbols Va-VIIIa. Va and VIa appear in absorption (at approximately 1000 and 1100 Å respectively), whereas transitions from the ground state ( $^1\Sigma_g$ ) to the more stable "triplet" states VIIa and VIIIa are forbidden by spin requirements as well as by the absence of a transition moment.



\* This arrow has been chosen to distinguish it from the normal one widely used to indicate an inductive effect or spin. The direction of the arrow is not intended to indicate the change of the total charge distribution within an excited state, which would require also the consideration of the (out-of-phase) migration in the opposite direction, i.e. on the other side of the nodal plane (cf. also below).

† Spherically symmetrical excited orbitals, e.g. those corresponding to the  $S^1$  and  $S^3$  states of the helium atom, are forbidden in absorption and, being unimportant for the absorption spectra of organic molecules, may be ignored. The expression "migration" is used in place of "displacement," the latter being reserved for the movement of the maxima of absorption bands.

<sup>14</sup> W. Heitler *Elementary Wave Mechanics* Oxford University Press (1945).

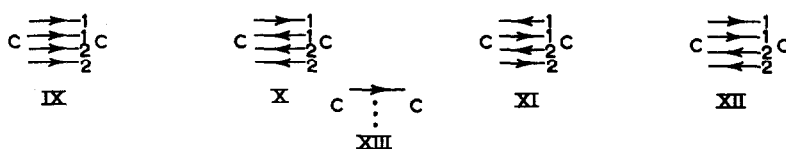
<sup>15</sup> L. Pauling and E. B. Wilson *Introduction to Quantum Mechanics* p. 354. McGraw-Hill, New York (1935); R. S. Mulliken *J. Chem. Phys.* 7, 20 (1939).

<sup>16</sup> G. H. Dieke and J. J. Hopfield *Phys. Rev.* 30, 400 (1927); O. W. Richardson *Molecular Hydrogen and its Spectrum* University Press Yale (1934); G. Herzberg *Spectra of Diatomic Molecules* Van Nostrand, New York (1930); E. J. Bowen *Chemical Aspects of Light* pp. 89, 101. Clarendon Press, Oxford (1946); also *Ann. Rep. Chem. Soc. London* 40, 16 (1943).

State V (Va) corresponds to the absorption system at shorter wavelengths and, since the bond axis lies in the nodal plane of the excited orbital, i.e. the charge migrates from both nuclei as in excited atoms, it is generally referred to as a Rydberg transition. We are, particularly, interested in state VI (VIa), which has a nodal plane perpendicular to the bond axis corresponding to an electron migration along this axis ( $N-V$  transition in Mulliken's terminology<sup>17</sup>), since this same type of transition is characteristic of the  $R$ -,  $B$ -, and  $K$ -bands of the more complicated organic molecules. Using valence bond terminology, this state has been qualitatively described as an ionic state  $H^+H^- \leftrightarrow H^-H^+$ .<sup>15</sup>

The spectra of ethylene and its homologues possess three band systems, at  $\sim 1650$  Å (high intensity), at  $\sim 1750$  Å (shoulder of moderate intensity) and above  $2000$  Å (observed in ethylene homologues and of very low intensity ( $\epsilon < 1$ ))<sup>18, 19</sup>. The two bands of higher intensity are generally recognised to be of the same type as the two band systems of the hydrogen molecule. Experimental evidence based on an analysis of the effect of substituents on these two bands supports the view that the band system at  $1750$  Å corresponds to a transition involving an electron migration along the bond-axis ( $K$ -band;  $N-V$  transition) and the superposed band system of higher intensity at  $1650$  Å to the Rydberg transition (perpendicular to the bond-axis).<sup>20</sup>

It is at this stage that our analysis, which (in agreement with views also expressed by Lewis and Calvin and by Lennard-Jones and Pople<sup>18</sup>) is based on the equivalency of the two electron pairs of a double bond, separates, in principle, from the widely held views which consider the interpretation of the spectrum only or mainly as a  $\pi$  electron problem. Whereas in the helium atom or the hydrogen molecule the two interacting electrons belong (in the ground state) to the same orbital, in ethylene the interaction now extends to the electrons of a second neighbouring orbital. Ignoring Rydberg transitions (perpendicular to the bond axis), this allows for four different normal excited states (IX–XII), each arising from resonance of the four unperturbed states of type XIII.



State IX corresponds to an allowed transition (of the  $N-V$  type) and, since it involves a migration of all electrons towards the same carbon nucleus, should be the least stable state (cf. below) responsible for the band system at  $1750$  Å ( $K$ -band). States X–XII will be more stable, but forbidden in absorption by change of spin (X, XI) and/or a negligible transition moment. One of these should be identified with the absorption band of very low intensity. The problem of ethylene reappears in all double bonds such as  $C:N$ ,  $C:O$ ,  $C:S$ ,  $N:N$ ,  $N:O$ , and  $NO:O$  which bonds, in addition

<sup>17</sup> R. S. Mulliken *J. Chem. Phys.* 3, 375, 506, 514, 517, 564 (1935); 7, 14, 20, 121, 339, 353, 356, 364 (1939).

<sup>18</sup> E. P. Carr, M. Walker and G. F. Walter *J. Chem. Phys.* 4, 751, 756 (1936); E. P. Carr and H. Stücklen *J. Chem. Phys.* 4, 760 (1936); 6, 55 (1938); 7, 631 (1939); *Z. phys. Chem.* B 25, 57 (1934).

<sup>19</sup> W. Lüthy *Z. Phys. Chem.* A 107, 285 (1923); C. P. Snow and C. B. Allsopp *Trans. Faraday Soc.* 30, 93 (1934); G. Scheibe and H. Grieneisen *Z. Phys. Chem.* B 25, 52 (1934). W. J. Potts, *J. Chem. Phys.* 23, 65 (1955).

<sup>20</sup> A. Burawoy *Disc. Faraday Soc.* 9, 78 (1950).

to bands of higher intensity below approximately  $2000 \text{ \AA}^*$ , are again responsible for bands of very low intensity generally at considerably longer wavelengths ( $\epsilon < 20$  in simple derivatives).<sup>1</sup> In the absence of any evidence to the contrary, these *R*-bands may be considered to correspond to a transition of the same type since, as far as accessible to experimental test, they have been shown to obey the same very characteristic optical rules† (effect of substituents, of solvents and of proton addition).<sup>1-3, also 21-24</sup>

These bands have been assigned to transitions involving an excited triplet (radical) state,<sup>1,3,4,25-27</sup> i.e. originating in the bonding electrons, or to  $n-\pi$  transitions involving the non-bonding (unshared) electrons.<sup>21,22,28</sup> A critical analysis of the available experimental data (which has also taken into account numerous, as yet unpublished, observations) has already led to the conclusion that they all originate in the bonding electrons, which is certain for the *R*-bands of the ethylene derivatives.<sup>3</sup> On the other hand, the molecular extinction coefficients ( $\epsilon$ ) of these bands on suitable substitution of the double bonds reach values as high as 2000, which may make their interpretation as singlet-triplet transitions, forbidden both by spin requirements and by small transition moments, uncertain.

In contrast, state XII which symmetrically and probably energetically is similar to the (least probable) triplet state XI and which corresponds to an electron migration around a two-membered ring does not involve a change of spin and is "forbidden" only by the comparatively small transition moment. It is considered as an alternative and, indeed, the most likely interpretation for the low intensity *R*-bands (cf. below). It should be noted that the present analysis does not allow for a transition of the  $n-\pi$  type which matter will be more fully discussed elsewhere.

### 3. EFFECT OF TERMINAL GROUPS OF ABSORBING SYSTEMS ON *K*-BANDS

#### *Empirical Conclusions*

Recently,<sup>5,6</sup> experimental evidence has been given that the electron migration in one direction along an absorbing system such as XIV (the "effective" electron migration) determines the stability of the excited state corresponding to the *K*-band. It has also been shown<sup>1,5,6</sup> that the displacement of a *K*-band to longer wavelengths by structural modifications of the terminal groups (XIV, A—C or C—B) can be due to two factors:

(a) An electron-shift (in the ground state) of the substituted system which will increase its polarisability and facilitate the electron migration in this direction.

\* This refers only to simple compounds such as formaldehyde, azomethane, nitrosobutane or nitromethane.

† Unfortunately, none of these tests can be applied to the ethylene *R*-bands.

<sup>21</sup> J. R. Platt *J. Chem. Phys.* **19**, 101 (1951); F. Halverson and R. C. Hirt *J. Chem. Phys.* **19**, 711 (1951).

<sup>22</sup> M. Kasha *Disc. Faraday Soc.* **9**, 14 (1950); G. J. Brealey and M. Kasha *J. Amer. Chem. Soc.* **77**, 4462 (1955).

<sup>23</sup> H. McConnell *J. Chem. Phys.* **20**, 700 (1952).

<sup>24</sup> A. Burawoy, M. Cais, J. T. Chamberlain, F. Liversedge and A. R. Thompson *J. Chem. Soc.* 3721 (1955).

<sup>25</sup> M. Kasha *Chem. Rev.* **41**, 401 (1947).

<sup>26</sup> E. P. Carr *Chem. Rev.* **41**, 293 (1947).

<sup>27</sup> G. N. Lewis and M. Kasha *J. Amer. Chem. Soc.* **67**, 934 (1945).

<sup>28</sup> R. S. Mulliken *J. Chem. Phys.* **3**, 564 (1935); H. L. McMurry and R. S. Mulliken *Proc. Nat. Acad. Sci.* **26**, 312 (1940); H. L. McMurry *J. Chem. Phys.* **9**, 231, 241 (1941).

(b) An increase of the polarisability of the terminal group itself.



This is illustrated by a few simple examples in Tables 1 and 2. The *K*-bands of the *p*-nitrotoluene derivatives (XV), in which the effective electron migration of the transition is towards the nitro group, are displaced to shorter wavelengths, whereas those of the *p*-toluidine or 4-methoxy-4'-methyl diphenyl derivatives (XVI, XVII), in which the effective electron migration is towards the  $\text{CH}_2\text{X}$  group, are displaced to longer wavelengths as the electron attracting power (inductive effect) of the substituent X increases ( $\text{H} < \text{NH}_2 < \text{OH} < \text{Cl} < \text{CN} < \text{NH}_3^+ < \text{NO}_2$ ). However, the electronic polarisability of the substituent  $\text{CH}_2\text{X}$  makes an additional contribution which, in the case of substituents of high polarisability, may become the dominating factor. Thus, in both the *p*-nitrotoluene and the 4-methoxy-4'-methyl diphenyl series, the *K*-bands are displaced to longer wavelengths in the order of substituents  $\text{CH}_2\text{Cl} < \text{CH}_2\text{Br} < \text{CH}_2\text{I}$ . It is noteworthy that in the latter series the red-shifts due to the  $\text{CH}_2\text{Br}$  and  $\text{CH}_2\text{I}$  groups (+172; +315 Å) are of the same order and greater respectively than that due to a  $\text{CH}=\text{CH}_2$  group (+272 Å).

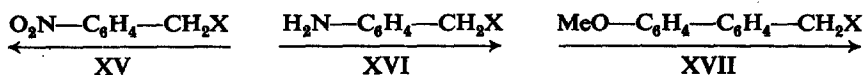


TABLE 1.—MAXIMA OF *K*-BANDS IN Å

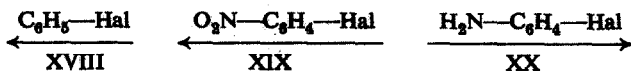
| A  | <i>p</i> -O <sub>2</sub> N—C <sub>6</sub> H <sub>4</sub> —A<br>in hexane | <i>p</i> -H <sub>2</sub> N—C <sub>6</sub> H <sub>4</sub> —A<br>in ethanol | <i>p</i> -MeO—C <sub>6</sub> H <sub>4</sub> —C <sub>6</sub> H <sub>4</sub> —A<br>in hexane |
|--|--|---|--|
| H  | 2513 (2595*)   | 2344  | 2595   |
| CH <sub>2</sub> NO <sub>2</sub>              | 2513   | —   | —  |
| CH <sub>2</sub> NH <sub>2</sub> <sup>+</sup> | — (2620*)  | 2455  | —  |
| CH <sub>2</sub> CN                           | 2547   | 2424  | 2657   |
| CH <sub>2</sub> Cl                           | 2581   | —   | 2712   |
| CH <sub>2</sub> OH                           | 2610   | 2410  | 2638   |
| CH <sub>2</sub> Br                           | 2641   | —   | 2767   |
| CH <sub>2</sub> NH <sub>2</sub>              | 2651   | 2410  | —  |
| CH <sub>2</sub>                              | 2645   | 2355  | 2602   |
| CH <sub>2</sub> I                            | 2649   | —   | 2910   |
| CH=CH <sub>2</sub>                           | —  | —   | 2867   |

\* In ethanol.

Similarly, the *K*-bands are displaced to longer wavelengths in the order of substituents  $\text{F} < \text{Cl} < \text{Br} < \text{I}$ , not only in the case of the halogenobenzenes (XVIII) and *p*-nitrohalogenobenzenes (XIX), in which the halogens are at the "donating" end of the effective electron migration, but also in the case of the *p*-halogenoanilines (XX), in which they are at the "receiving" end. However, in the latter series the displacements are much smaller and the fluorine atom is responsible for a blue-shift. The polarisability of the C—Hal electrons is the dominating factor and is smaller towards the halogen atom than in the opposite direction.

Again, the contribution of the polarity factor is clearly shown (i) by the fact that the displacements of the *K*-bands on introduction of the halogen atoms are greater

in the *p*-nitrohalogenobenzenes (hexane: +56, 139, 184, 352 Å) than in the halogenobenzenes (+48, 132, 140, 280 Å), since the electron attracting nitro group is responsible in the ground state for electron shifts in the C-Hal systems towards the carbon atom, and (ii) by the fact that on replacing hexane by the more polar ethanol, the red-shifts due to the halogen atoms (cf. Table 2, D) are reduced in the two former and enhanced in the latter series.

TABLE 2.—MAXIMA OF *K*-BANDS IN Å

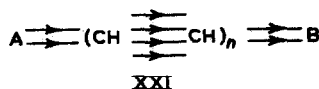
| X  | C <sub>6</sub> H <sub>5</sub> —X |         |     | <i>p</i> -O <sub>2</sub> N—C <sub>6</sub> H <sub>4</sub> —X |         |     | <i>p</i> -H <sub>2</sub> N—C <sub>6</sub> H <sub>4</sub> —X |         |     |
|----|----------------------------------|---------|-----|---|---------|-----|---|---------|-----|
|    | hexane                           | ethanol | D   | hexane  | ethanol | D   | hexane  | ethanol | D   |
| H  | ~2020                            | ~2030   | —   | 2513  | 2595    | —   | 2340  | 2344    | —   |
| F  | 2068                             | 2068    | -10 | 2569  | 2622    | -29 | 2305  | 2334    | +25 |
| Cl | 2152                             | 2130    | -32 | 2652  | 2699    | -35 | 2414  | 2445    | +27 |
| Br | 2160                             | 2135    | -35 | 2697  | 2755    | -24 | 2418  | 2452    | +30 |
| I  | 2300                             | 2275    | -35 | 2865  | 2940    | -7  | 2463  | 2502    | +35 |

It may be noted that the electrons of the halogen atoms in the CH<sub>2</sub>X groups of the systems XVI and XVII and in the *p*-halogenoanilines (XX) (and related series), in which the halogen atoms are at the "receiving" end of the effective electron migration, participate in the transition. This cannot be accounted for by a consideration of  $\pi$  electrons only and of mesomeric (electromeric) electron displacements. The hypsochromic effect of the fluorine atom in *p*-fluoroaniline (and related series) can only be explained by a smaller polarisability of the C—F electrons towards the fluorine atom as compared with that of the C—H electrons. This clearly demonstrates that even the latter participate in the electron migration of the *K*-band transition.

#### Theoretical analysis

The theoretical analysis may now be extended to the effect of the electrons of the terminal groups (A—C or C—B) of ethylene or, indeed, of any other absorbing (conjugated) system (XIV) on the corresponding *K*-bands. The qualitative consideration of the mathematically well-established effects resulting from perturbations attributable to Heisenberg resonance affords a consistent theoretical interpretation of the empirical conclusions summarised above.

Most organic molecules (even conjugated hydrocarbons) contain covalent linkages of a varying degree of polarity, which fact is known to offer considerable difficulties to the mathematical treatment of molecular states and limits its scope. In contrast, the present qualitative analysis is able to take full account of this important property of covalent linkages.



The normal excited state corresponding to a *K*-band can be represented as a "hybrid" of unperturbed states each involving one excited electron. The contribution of each of the  $(2 + 6n)$  unperturbed states (again, indicated for convenience by one formula XXI) to the "hybrid" will be proportional to their stability. States involving neighbouring excited electrons will interact.

The excited orbital of each unperturbed state is divided by an (additional) nodal plane into two parts corresponding to wave-functions of opposite sign. In an unsymmetrical bond, it will extend more to one side of the nodal plane, i.e. the probability of finding the electron in this more stable part-orbital will be greater. In valence bond terminology, this would be equivalent to the statement that in the excited state of a molecule AB described as a hybrid  $A^+B^- \leftrightarrow A^-B^+$  the stability and contribution to the hybrid of  $A^+B^-$  is different from that of  $A^-B^+$ . The present qualitative analysis is independent of the valence bond or molecular orbital description of localised bonds and of unperturbed excited states. These descriptions are known to represent only different mathematical methods of approximation (in terms of atomic orbitals), i.e. their distinction has only a mathematical and no real physical significance.

The degree of interaction will increase, the lower and the energetically nearer each pair of interacting (unperturbed) energy levels are, but, in the first instance, only their part-orbitals in phase with the effective electron migration of the transition, the direction of which is indicated by the arrows, will be important. Thus, if A and B in XXI are identical, e.g. halogen or hydrogen atoms, the unperturbed energy levels involving the excited electrons of the unsymmetrical bonds A—C and C—B will be equal. However, the degree of interaction (determining the degree of stabilisation of the normal excited state), will be different since it depends on the different extension (stability) of the excited orbital in the two directions of these bonds, i.e. on both sides of the dividing nodal plane.

It is realised that the degree of interaction (in the excited state) will also depend on the distance (degree of repulsion) between the interacting electrons, e.g. on the size of the common atom or on the angle formed by the orbitals, but in the qualitative comparison of the varying effects of terminal atoms or groups within the same series (XXI, A or B), this effect may be neglected.

The factors determining the stability of the normal excited state are (i) the most stable (the "basic") unperturbed excited state and (ii) the degree of its interaction with the unperturbed states involving excited neighbouring electrons. Again, the stability of the latter will be modified by interaction with other neighbouring states, the effect of which is transmitted (in a diminishing degree) along the whole absorbing system. (In this connection, cf. the interesting mathematical treatment of the excited states (corresponding to the *K*-bands) of *p*-polyphenyls by Murrell and Longuet-Higgins,<sup>29</sup> who have shown that even in absence of delocalisation between the electron systems of the phenyl groups, their interactions would account semiquantitatively for the observed band displacements.)

According to this view, in a system such as  $C=C-C=C$ , the direct interaction of the unperturbed energy levels involving the excited electrons of one double bond with those involving the excited electrons of the other is considered to be of secondary importance. Moreover, the transmitted effect in a system such as  $C=C-C-C=C$ ,

<sup>29</sup> J. N. Murrell and H. C. Longuet-Higgins *J. Chem. Soc.* 2552 (1955).



in agreement with experience, is much smaller because the interaction of the transmitting states, which involve excited electrons of the single C—C bonds, and which are of low stability compared with the basic unperturbed state, is only small.<sup>5</sup> It should be noted, however, that the contribution to the hybrid of the unperturbed states involving the excited electrons of each double bond will be of the same magnitude.

A more precise definition of the conclusion arrived at empirically that the electron migration in one direction of the absorbing system determines the stability of the normal excited state can now be given. It indicates that the additional stabilisation arising from the interactions of the part-orbitals corresponding to the complementary electron migration of the system is only negligible, although it has to be taken into account even in qualitative comparative discussions, if only very small differences are involved.<sup>6</sup> A fuller experimentally supported discussion of this matter will be given elsewhere.

Our investigations have also shown that any electron shift in the ground state of an absorbing system or individual bond (as, for example, caused by a change of the terminal group or by a solvent) increases the electron polarisability in this direction (and reduces it in the opposite direction) and, thus, dependent on the direction of the effective electron migration of the transition, stabilises or otherwise the normal excited state. This indicates that in each bond the increased stability of the (unperturbed) part orbital in phase with the effective electron migration (which results from both the reduction of the ionisation potential of the "donating" atom and/or the increase of the electron affinity of the "receiving" atom\*) is the determining factor. It is also more important than the increased destabilisation to be expected from the accompanying increased interaction of the two part orbitals corresponding to the electron pair forming the bond.

#### 4. EFFECT OF SIDE-CHAIN SUBSTITUENTS ON K-BANDS

An analysis of the electronic transitions corresponding to *K*-bands is not complete without consideration of the most characteristic and very different effects of substituents in a branch (side-chain) of the main absorbing system. These effects represented an important part of the evidence advanced by the author for his original classification of electronic spectra, but, in more recent years, they have been almost completely neglected and their significance generally not realised.

As illustrated by the examples of a few carbonyl and thiocarbonyl derivatives in Table 3, replacement of a branching hydrogen atom by a methyl group may now cause a blue-shift (acetophenone,  $-40 \text{ \AA}$ ; diphenyl methyl ketone,  $-70 \text{ \AA}$ ), by a phenyl group only a small red-shift (benzophenone,  $+72 \text{ \AA}$ ; diphenylphenyl ketone,  $+32 \text{ \AA}$ ) which is only very slightly enhanced by a diphenyl group (bis-diphenyl ketone,  $+65 \text{ \AA}$ ). Replacement by an amino or hydroxyl group or a charged oxygen atom (in anions) may cause appreciable blue-shifts on direct substitution (benzamide,  $-200 \text{ \AA}$ ; benzoic acid,  $-159 \text{ \AA}$ ; benzoate anion,  $-213 \text{ \AA}$ ) and smaller displacements in aromatic (side-chain) substituents. This is in contrast to the always bathochromic and generally much greater effects of these atoms or groups in

\* In the case of unshared (non-bonding) electrons, only one of these factors is relevant.

terminal positions of an absorbing (conjugated) system.<sup>1,2,5,6,30-32</sup> Thus, the *K*-band of thiobenzophenone (XXII, A = A' = H) is displaced very strongly to longer wavelengths (375, 395 and 1205 Å respectively) on introduction of one phenyl, hydroxyl or dimethylamino group into the first and terminal para position (XXII, A = Ph, OH, NMe<sub>2</sub>; A' = H), whereas the effect of these groups on introduction into the para position of the second (branching) phenyl group (XXII, A' = A) is very small and often in the opposite direction (+10, -85, -70 Å respectively).

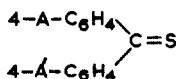
TABLE 3.—COMPARISON OF THE EFFECT OF SUBSTITUENTS ON *K*- AND *R*-BANDS

| Substance  | Solvent     | X   | <i>K</i> -band       |            | <i>R</i> -band       |            |
|--|-------------|---|----------------------|------------|----------------------|------------|
|  |             |   | $\lambda_{\max}$ , Å | $\epsilon$ | $\lambda_{\max}$ , Å | $\epsilon$ |
| C <sub>6</sub> H <sub>5</sub> .C(X):O                                | hexane      | H   | 2408                 | 14,000     | 3280                 | 28†        |
|  | hexane      | Me  | 2368                 | 14,000     | 3210                 | 44         |
|  | hexane      | Ph  | 2480                 | 20,000     | 3440                 | 100        |
|  | ethanol     | H   | 2445                 | 13,000     | —                    | —          |
|  | ethanol     | OH  | 2286                 | 14,500     | —                    | —          |
|  | ethanol     | NH <sub>2</sub>                                 | 2245                 | 13,500     | —                    | —          |
|  | +0.1% NaOEt | O <sup>-</sup>                                  | 2232                 | 11,000     | —                    | —          |
| Me.C(X):O <sup>30</sup>  | water       | Me  | —                    | —          | 2645                 | 17         |
|  | water       | OH  | —                    | —          | 2035                 | 40         |
|  | water       | NH <sub>2</sub>                                 | —                    | —          | 2040*                | 200        |
|  | water       | O <sup>-</sup>                                  | —                    | —          | 2000*                | —          |
| C <sub>6</sub> H <sub>5</sub> :C <sub>6</sub> H <sub>4</sub> .C(X):O | ethanol     | H   | 2895                 | 23,000     | —                    | —          |
|  | ethanol     | Me  | 2820                 | 28,000     | —                    | —          |
|  | ethanol     | Ph  | 2912                 | 26,000     | —                    | —          |
|  | ethanol     | C <sub>6</sub> H <sub>4</sub> .Ph               | 2977                 | 42,000     | —                    | —          |
| C <sub>6</sub> H <sub>5</sub> .C(X):S                                | benzene     | Ph  | 3195                 | 17,000     | 6065                 | 210        |
| (4-Ph).C <sub>6</sub> H <sub>4</sub> .C(X):S                         | benzene     | Ph  | 3570                 | 18,100     | 6087                 | 260        |
|  | benzene     | C <sub>6</sub> H <sub>4</sub> .Ph               | 3365                 | 16,000     | 6110                 | 300        |
| (4-HO).C <sub>6</sub> H <sub>4</sub> .C(X):S                         | benzene     | Ph  | 3590                 | 13,800     | 5930                 | 240        |
|  | benzene     |   | 3270                 | 11,400     | —                    | —          |
|  | benzene     | C <sub>6</sub> H <sub>4</sub> .OH               | 3505                 | 23,000     | 5885                 | 340        |
| (4-Me <sub>2</sub> N).C <sub>6</sub> H <sub>4</sub> .C(X):S          | benzene     | Ph  | 4400                 | 23,400     | 5837                 | 380        |
|  | benzene     |   | 3350                 | 11,000     | —                    | —          |
|  | benzene     | C <sub>6</sub> H <sub>4</sub> .NMe <sub>2</sub> | 4330                 | 40,000     | 5750                 | 900        |

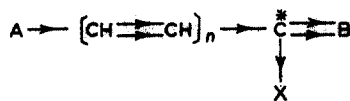
\* Inflection.

† Fine structure.

<sup>30</sup> K. Bowden, E. A. Braude and E. R. H. Jones *J. Chem. Soc.* 948 (1946).<sup>31</sup> E. A. Braude *Ann. Rep. Chem. Soc. London* 42, 105 (1945).<sup>32</sup> L. Doub and J. M. Vandenberg *J. Amer. Chem. Soc.* 69, 2714 (1947).<sup>33</sup> H. Ley and B. Arends *Z. Phys. Chem. B* 17, 177 (1932); G. Scheibe *Ber. Dtsch. Chem. Ges.* 58, 586 (1925).



XXII

XXIII<sup>†</sup>

The effect of these substituents is due to the same two factors shown to be responsible for the effect of terminal groups, i.e. (i) a change of polarisability (stability of the unperturbed excited states) of the substituted system due to electron shifts in the ground state, and (ii) the degree of the electronic polarisability of the substituent, but both factors are now of much greater complexity.

Thus, in the most common system of the general type XXIII, an electron repelling group such as methyl ( $X = Me$ ) will cause electron shifts in the ground state towards both A and B. This will inhibit the effective electron migration (from A to B) in the former and facilitate it in the latter branch of the (main) absorbing system. The separation of the electrons at the substituted (starred) carbon atom in the ground state will also reduce the degree of their interaction in the excited state, which effect will be similar to that which might result from any inhibition of "conjugation" by intramolecular steric hindrance (for a tentative interpretation of the latter effect based on molecular structures containing localised bonds only, see Burawoy and Chamberlain<sup>10</sup>).

The blue-shifts observed on introduction of the branching electron repelling methyl, hydroxyl, and amino groups and charged oxygen atom in anions (XXIII,  $X = Me, HO, NH_2, O^-$ ) should be accounted for by these factors.

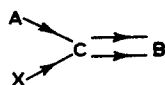
The participation of the electrons of the side-chain substituent (see XXIII, X) in the electron migration of the transition will have an additional, again rather complex effect (consisting of the stabilisation of one branch and destabilisation of the other) on the stability of the excited state. Detailed systematic investigations aiming at the difficult separation of the various effects, which depend to a high degree upon the individual substituted systems, will be reported elsewhere.

However, an unambiguous experimental solution of the more fundamental problem of the direction of the effective electron migration within the side-chain is possible. This direction is governed by the principle that by far the most stable excited state is obtained, if the effective electron migration towards a nucleus is accompanied by a recession of all the other electrons away from it (as shown in XXIII). Elsewhere, this conclusion will be confirmed by an analysis of the effect of such substituents, but it is already strongly supported by the following absolute observations.

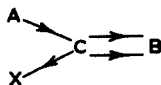
In a system such as  $A-CX=B$ , in which the main effective charge migration (towards B) is certain, a charge migration in the branch  $C-X$  towards the carbon atom would allow for only one electronic transition (XXIV), whereas in the alternative case two similar electronic transitions could be expected (XXV and XXVI). They would be responsible for two *K*-bands which, in favourable conditions, i.e. if sufficiently separated, would be capable of observation. The latter is in agreement with

<sup>†</sup> Subsequently, for convenience, the symbols will be further simplified. The arrow  $\rightarrow$  will be used to indicate the combined "unperturbed" state involving the electron pair of each single bond.

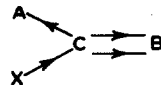
experience. (This does not exclude a possible existence of *K*-bands corresponding to an excited state XXIV, to be expected at considerably shorter wavelengths.)



XXIV

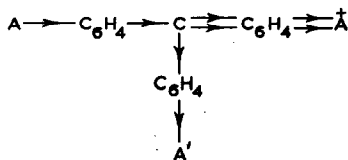


XXV

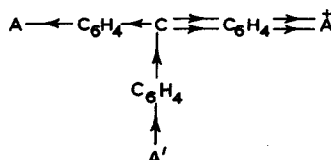


XXVI

The author,<sup>34</sup> in discussing the competition between the various absorbing systems of an organic molecule, has shown that the spectra of di-substituted *pp'*-triphenylmethyl ions possess two *K*-bands. They could be assigned to the two absorbing conjugated systems present and, in the light of the present discussion, correspond to the excited states XXVII and XXVIII ( $A = \text{NMe}_2, \text{OMe}, \text{SMe}, \text{Ph}$ ;  $A' = \text{H}$ ). In contrast, all *pp'*-trisubstituted derivatives ( $A' = A$ ), in which both excited states become equivalent, are responsible for the appearance of only one band of increased intensity. The different direction of the electronic vectors of the transitions corresponding to the two *K*-bands of Malachite Green (XXVII and XXVIII,  $A = \text{NMe}_2$ ;  $A' = \text{H}$ ) observed by Lewis and Biegeleisen<sup>35</sup> is in agreement with our interpretation.

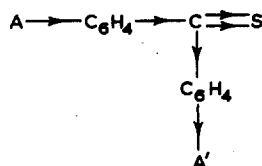


XXVII

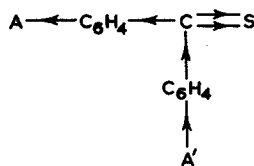


XXVIII

The examples of the thiobenzophenone derivatives (cf. Table 3) were chosen to illustrate the same point. Again, the spectra of mono-*p*-substituted derivatives show two *K*-bands corresponding to the two excited states XXIX and XXX ( $A = \text{Ph}, \text{OH}, \text{NMe}_2$ ;  $A' = \text{H}$ ), whereas *pp'*-disubstituted derivatives ( $A' = A$ ) are responsible for only one band of higher intensity, both excited states now being equivalent.



XXIX



XXX

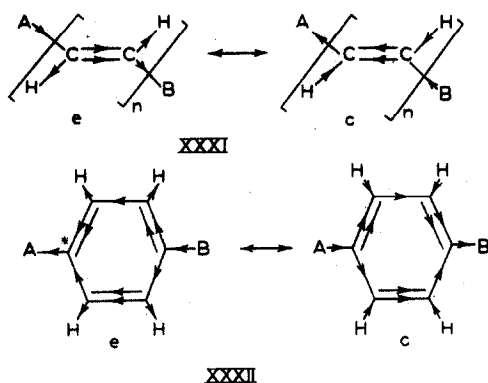
### 5. *K*-BANDS OF ETHYLENE AND BENZENE

The preceding analysis shows that the excited state responsible for the *K*-band of ethylene or any other absorbing system can be represented by XXXI (*e*, "effective" and *c*, "complementary"). It is noteworthy that although ethylene ( $A = B = \text{H}$ ;  $n = 1$ ) is symmetrical in the ground state, according to this view this is no longer true for the (four possible equivalent) excited states. Similarly, the (six possible equivalent) excited states responsible for the *K*-band of benzene ( $A = B = \text{H}$ ) at approximately 2030 Å are represented by XXXII (*e* and *c*), again indicating some

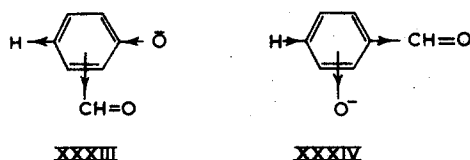
<sup>34</sup> A. Burawoy *Ber. Dtsch. Chem. Ges.* **64**, 473, 1635 (1931).

<sup>35</sup> G. N. Lewis and J. Biegeleisen *J. Amer. Chem. Soc.* **65**, 2102 (1943).

distortion of the electronic system. The effective electron migration in the two branches of the benzene system towards the same (starred) carbon atom is unavoidable. This results in an appreciable destabilisation which should account for the as yet unexplained, most characteristic fact that the *K*-band appears at appreciably shorter wavelengths than that of 1:4-dimethylbutadiene (2270 Å), cyclohexa-1:3-diene (2560 Å) and similar compounds.



As recently shown,<sup>10,24,28</sup> in agreement with this interpretation, the *K*-bands of mono-substituted benzene derivatives such as diphenyl, azobenzene, benzaldehyde, nitrosobenzene, and nitrobenzene (XXXII, A = Ph, N:N.Ph, CH:O, N:O, NO<sub>2</sub>, B = H) are only slightly displaced to longer wavelengths on introduction into the branching *ortho* and *meta* positions of substituents such as the amino, hydroxyl, and thiol groups which have very appreciable effects in the terminal *para* position (B = NH<sub>2</sub>, OH, SH). This is also illustrated in Table 4 for the effect of methyl, chlorine, methoxyl and charged oxygen substituents on the *K*-band of benzaldehyde.



The spectra of the *m*- and *o*-formylphenoxide ions show two *K*-bands at approximately 2600 Å and 2460 (2300) Å respectively, which correspond to the *K*-bands of benzaldehyde (2445 Å) and of the phenoxide ion (2374) Å, i.e. to the excited states indicated by XXXIII and XXXIV. This is characteristic of numerous *m*- and *o*-disubstituted benzene derivatives. A detailed discussion of this matter and of the problem of the theoretically possible normal excited states of a molecule rather than those detectable by the favourable positions and intensities of the corresponding absorption bands is outside the scope of this paper.

Theoretical (mathematical) treatments and discussions of the spectrum of benzene, based on its regular hexagon structure and the simplifying consideration of the  $\pi$  electrons only, have led to the assignment of the 2000 Å band to a forbidden

<sup>28</sup> A. Burawoy and J. T. Chamberlain *J. Chem. Soc.* 3734 (1952).

TABLE 4.—MAXIMA OF *K*- AND *B*-BANDS OF SUBSTANCES; X.C<sub>6</sub>H<sub>4</sub>.CH:O IN ETHANOL

| X                 |                    | <i>K</i> -band |                                   |                          | <i>B</i> -band |            |            |
|-------------------|--------------------|----------------|-----------------------------------|--------------------------|----------------|------------|------------|
|                   |                    | <i>P</i> -     | <i>m</i> -                        | <i>o</i> -               | <i>P</i> -     | <i>m</i> - | <i>o</i> - |
| H                 | $\lambda_{\max}$ Å |                | 2,445                             |                          |                | 2,805      |            |
|                   | $\epsilon$         |                | 13,000                            |                          |                | 1,250      |            |
| Me <sup>27</sup>  | $\lambda_{\max}$   | 2,550          | 2,482                             | 2,495                    | 2,800†         | 2,894      | 2,925      |
|                   | $\epsilon$         | 12,500         | 11,000                            | 12,500                   | —              | 1,350      | 1,700      |
| Cl                | $\lambda_{\max}$   | 2,544          | 2,442                             | 2,489                    | 2,800†         | 2,920      | 2,980      |
|                   | $\epsilon$         | 16,000         | 12,500                            | 10,000                   | —              | 1,300      | 1,600      |
| OMe <sup>10</sup> | $\lambda_{\max}$   | 2,765          | 2,525                             | 2,528                    | —*             | 3,087      | 3,210      |
|                   | $\epsilon$         | 15,500         | 9,500                             | 10,500                   | —              | 3,000      | 4,550      |
| O <sup>-</sup>    | $\lambda_{\max}$   | 3,323          | (i) 2,610†                        | 2,613                    | —*             | 3,598      | 3,790      |
|                   | $\epsilon$         | 28,000         | (i) 6,000<br>(ii) 2,404<br>19,000 | 6,300<br>2,310<br>16,000 | —              | 2,400      | 6,400      |

\* *B*-band not observed being masked by *K*-band.

† Inflection.

transition or to a Rydberg transition.<sup>18,20,38,39</sup> However, its identification as a *K*-band (involving an allowed transition of the *N-V* type) is unambiguously established by the very considerable experimental evidence based on the study of the effect of substituents and is already widely accepted by experimentalists.<sup>10,32,40</sup> (For the assignment of the 1800 Å band of benzene to a Rydberg transition, compare references 20, 39, 41).

#### 6. QUALITATIVE EFFECT OF PERTURBATION DUE TO RESONANCE

In view of the difficulty, if not impossibility of a quantitative mathematical treatment of the complex excited states under discussion, it is fortunate that the effect of the perturbation resulting from resonance is qualitatively clear. It corresponds to a change of the effective nuclear charges (the ionisation potentials and electron affinities respectively) in the observed excited states. Thus, the arrows suggested to indicate the individual unperturbed excited states of an absorbing system and the direction of the effective charge migration obtain an additional qualitative, but significant meaning. They can be taken to indicate the ("time-averaged") change of the effective nuclear charges due to the resonance and the resulting stabilisations or destabilisations respectively of the normal excited state.

<sup>27</sup> E. A. Braude and F. Sondheimer *J. Chem. Soc.* 3754 (1955). For data in hexane solution.

<sup>28</sup> H. Sponer, G. P. Nordheim and E. Teller *J. Chem. Phys.* 8, 455 (1940); A. L. Sklar and M. Goepfert-Mayer *J. Chem. Phys.* 6, 645 (1938).

<sup>29</sup> V. J. Hammond, W. C. Price, J. P. Teegan and A. D. Walsh *Disc. Faraday Soc.* 9, 53 (1950).

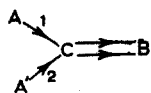
<sup>40</sup> G. N. Lewis and M. Calvin *Chem. Rev.* 25, 303 (1939); A. D. Walsh *Ann. Rep. Chem. Soc., London* 44, 39 (1947).

<sup>41</sup> W. C. Price and A. D. Walsh *Proc. Roy. Soc. A* 191, 22 (1947).

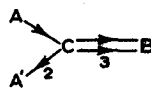
In the excited state of the hydrogen molecule VI, the arrows indicate an increase of the effective nuclear charge (and ionisation potential) at one hydrogen atom and decrease of the effective nuclear charge (and its electron affinity) at the other as compared with those in the unperturbed states, both factors destabilising the normal excited state, whereas in the triplet state VIII the opposite effects occur, corresponding to stabilisation. Similarly, in ethylene, combining for convenience each electron pair as a unit, the state IX, corresponding to the *K*-band, is less stable and state XII, corresponding to the *R*-band, is more stable than the (combined) "unperturbed" state involving one excited electron pair only, which is in agreement with the appearance of *R*-bands at longer wavelengths. (This is only valid for simple compounds, since substituents, very considerably and to a different degree, modify the energy levels corresponding to *R*- and *K*-bands.)

Again, the arrows representing the unperturbed excited states of the electrons of the terminal groups A—C and C—B of ethylene or any other more complicated absorbing system (XXI) indicate an increase of the electron density at C<sub>-A</sub> and a decrease at C<sub>-B</sub>, i.e. a reduction of the ionisation potential at the former and increase of the electron affinity at the latter, both resulting in stabilisation.

Finally, the principle that the observed excited state is more stable if an electron migration towards a nucleus is accompanied by recession of the other electrons (including those in a side-chain), indicates that the destabilisation resulting from a reduced electron affinity as in XXXV (migration of 1 and 2 towards C) is considerably greater than any resulting from an increased ionisation potential as in XXXVI (migration of 2 and 3 from C). Qualitatively, this is just what could be expected, since the interacting part orbitals in the former case are much closer (in space) than in the latter.



XXXV



XXXVI

## 7. *R*-BANDS

Earlier investigations<sup>1,3</sup> have already shown that the apparently complex observations related to *R*-bands can be reduced to two simple generalisations:

(a) Substituents of the chromophoric double bonds have most characteristic effects on *R*-bands which are qualitatively similar to those of substituents (in a side-chain) of an absorbing conjugated system on *K*-bands. The examples shown in Table 3 have been chosen to illustrate this analogy. Again, a methyl group causes a blue-shift, a phenyl group only a moderate red-shift which is only insignificantly enhanced by a diphenyl group, an amino or hydroxyl group or the charged oxygen atom blue-shifts which are particularly strong on direct substitution.

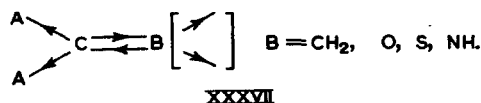
(b) *R*-bands are displaced to shorter wavelengths by influences (solvent effect, proton addition) which increase the polarity of the absorbing system.

The interpretation of the electron transition responsible for *R*-bands (see XII) advanced in this paper accounts for these observations\*:

(a) The two electron pairs of a double bond can be compared with the two

\* In principle, this does not exclude the triplet state X which would allow for a slightly modified analysis.

branches of a substituted absorbing conjugated system responsible for *K*-bands. The substituents will not only modify the polarity of the double bond in the ground state, but (like side-chain substituents of systems responsible for *K*-bands) also participate in the transition. The direction of the effective electron migration is, again, towards the substituents (A), in agreement with the principle that by far the most stable excited state is obtained if a charge migration towards a nucleus is accompanied by a recession of all other participating electrons (cf. e.g. XXXVII).



(b) An increase of the polarity of the double bond will correspond to an electron shift in both bonds. This will stabilise the "effective" part orbitals of the unperturbed states involving the excited electrons of one bond, but destabilise those of the other bond and, thus, reduce their degree of interaction. In the absence of any quantitative analysis, no prediction of the resultant effect is possible. However, what should be more important, the stabilisation arising from the interaction of the electron pair of the double bond migrating towards C with that of a C—A bond, both being shifted (as the polarity of the system increases) against the direction of the effective electron migration, will certainly be reduced. This will enhance (or, if opposing, mask) the former effect and, thus, be mainly responsible for the blue-shift of the *R*-band. A more detailed discussion of the (physically) rather complex effect of substituents on the position of *R*-bands will require systematic investigations not yet available or, if possible, a semi-quantitative mathematical analysis of the matter.

#### 8. BENZENOID-(B<sup>21</sup>-) BANDS

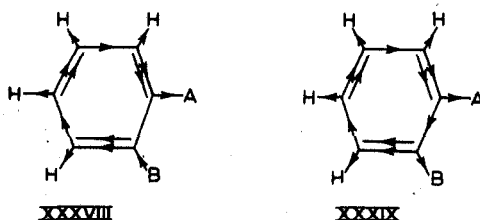
As recently pointed out, the *B*-bands originate in the same type of electronic transition as the *K*-bands, but correspond to electronic migrations around the conjugated system formed by all three benzene double bonds.<sup>24</sup> This is supported by an analysis of the spectra of disubstituted benzene derivatives which shows that substituents in *ortho* position to each other are now terminal groups of the absorbing system. Thus, in contrast to the *K*-bands, the (in many cases masked) *B*-bands of diphenyl, azobenzene, benzaldehyde, nitrosobenzene, and nitrobenzene are strongly displaced to longer wavelengths on introduction of an amino, hydroxyl or thiol group into the *ortho* position, whereas in the branching *meta* and, in particular, in the *para* position these substituents have much smaller effects.

This is also shown by the spectra of the substituted benzaldehydes reported in Table 4, again chosen to illustrate simultaneously the different behaviour of the *K*-bands, in which case the *para* position is terminal and the *meta* and *ortho* positions are branching. The *B*-bands of the *para* substituted benzaldehydes are partly or completely masked by the *K*-bands of higher intensity, but a comparison of the spectra of benzaldehyde and of *p*-methyl-, *p*-chloro-, and *p*-methoxy-benzaldehyde respectively indicates that these substituents are responsible for slight hypsochromic shifts (for the similar effect of the *p*-methoxy group in 2:4-dimethoxy-1-nitrosobenzene, cf. reference 24, Fig. 1).

The excited state of disubstituted benzene derivatives corresponding to a *B*-band



can, thus, be described by XXXVIII. That of mono-substituted benzene derivatives such as phenol or aniline ( $B = OH, NH_2$ ;  $A = H$ ) should be similar, but the possibility of a slightly modified excited state XXXIX for benzene itself and derivatives such as nitrobenzene or benzaldehyde ( $A = H, NO_2, CH:O$ ;  $B = H$ ) cannot be experimentally excluded and, indeed, may be more likely. The generally lower intensity of the  $B$ -bands ( $\epsilon, \sim 100-7000$ ) as compared with that of the  $K$ -bands ( $\epsilon, \sim 5000-200000$ ) is accounted for by the smaller transition moments due to the charge migration around the benzene ring.



Although this interpretation of the  $B$ -band transition is well supported by experimental evidence, a more detailed analysis of the complex effect of substituents cannot be given briefly.

#### 9. CONCLUSION

The wave-mechanical resonance characteristic for the excited states of all poly-electronic systems involves a complicated fluctuation ("time-averaged" distribution) of the transition energy. In this sense, it represents a definite physical phenomenon which is absent in ground states. Although the mathematical method of approach is similar, this has, as a phenomenon, nothing in common with the well-known applications of the valence-bond method to the interpretation of the stability of ground states. Thus, the latter may be accounted for without reference to "resonance", whereas excited states cannot.

Already, for this reason, the stability of an excited state cannot and does not show a simple relationship to that of the corresponding ground state.<sup>6\*</sup> This also represents the justification for the present interpretation which considers the energy difference between the ground and normal excited states only, the energy of the former always being taken as zero (for a related discussion of this matter, cf. Simpson<sup>4b</sup>).<sup>†</sup>

In the well-known simplifying, but in the author's view unjustified, application of the conception of resonance among several valence-bond structures to the (non-mathematical) interpretation of the constitutive changes in molecular structures, the contribution to the resonance hybrid of the various, often arbitrarily chosen, idealised ("unperturbed") states has been assumed to be a function of their relative stability and taken as a measure of the ensuing resonance (stabilisation) energy, the unknown magnitude of the resonance integrals not being considered. It should, therefore, be emphasised that in the present interpretation of *excited states*, the

\* This follows already from the fact that the positions of the individual absorption bands of any particular substance are affected differently on introduction of a substituent or by a change of solvent.

† A classical analogue would be a system of coupled harmonic oscillators at rest (ground state) and in their normal modes of vibration (excited states).

<sup>4b</sup> W. T. Simpson *J. Amer. Chem. Soc.* 77, 6164 (1955).

degree of interaction generally does not coincide with the contribution of the unperturbed excited states to the hybrid; that it may cause destabilisation as well as stabilisation, and that there is no freedom of choice once the electron migration of the transition is experimentally established.

The theoretical analysis outlined in this paper shows that the empirical conclusions derived from systematic experimental investigations of electronic spectra, when based on molecular structures built up of localised bonds only, can be consistently accounted for with the help of well-established wave-mechanical principles. It offers a qualitative, but very detailed understanding of electronic spectra of complicated polyatomic organic molecules<sup>5,6</sup> not attainable by mathematical treatments aiming at quantitative evaluations of spectroscopic data.‡

The interpretation of electronic perturbations in an *excited state* as a wave-mechanical resonance phenomenon owed its success and justification to the ability to account qualitatively for the previously unexplained experimental fact that the He atom forms two systems of energy levels and for perturbations observed in atomic spectra in general, rather than to its quantitative aspect. This is also true for Mulliken's fundamental analyses of the structures and electronic spectra of simple molecules.

Similarly, an analytical approach to the complicated problems related to the electronic spectra of more complex polyatomic molecular structures, e.g. more detailed wave-mechanical formulations or mathematical analyses of principles possibly based on simple models, should make a greater contribution to the understanding of these problems than attempts at speculative mathematical evaluations of spectral data. The present qualitative analysis, which has taken into account all known relevant data, is accessible to experimental test and may serve as a guide for further systematic investigations, should offer a useful basis.

If not otherwise stated, the spectra of the carbonyl compounds are new determinations obtained with a Hilger E3 quartz spectrograph fitted with a Spekker photometer, those of the thiobenzophenone derivatives with a Hilger Uvispek Photoelectric Spectrophotometer. The latter have been selected from an unpublished extensive investigation carried out by Dr. P. Brocklehurst. This and the help given by Dr. A. R. Thompson in the preparation of this paper are gratefully acknowledged.

‡ In this connection, reference should be made to the very detailed, critical and significant, analysis of the mathematical approach and its limitations to the problems of molecular structures and, in particular, of excited states by Kauzmann.<sup>43</sup>

<sup>43</sup> W. Kauzmann, *Quantum Chemistry*, pp. 375-478. Academic Press, New York (1957).