FAR ULTRA-VIOLET SPECTRA, IONISATION POTENTIALS, AND THEIR SIGNIFICANCE IN CHEMISTRY

By A. D. Walsh, M.A., Ph.D.

(I.C.I. Research Fellow, University of Cambridge)

Naturally, spectra in the visible region (roughly 7000—4000 A.) were the first to be observed. The development of photography enabled spectra in the " near " ultra-violet (roughly 4000—2000 A.) to be observed, merely by the substitution of a photographic plate for the human eye. Further extension of the spectrum to short wave-lengths met certain difficulties. Historically, therefore, the near ultra-violet region was studied before the far ultra-violet region (roughly 2000—1 A., meeting the region of soft X-rays). Though inevitable, this was in a sense unfortunate, for it is now known that the simplest molecules have their main absorption bands in the far ultra-violet. Hence the great importance of the study of spectra in that region. It is relatively complex molecules that absorb strongly in the near ultra-violet or visible. Consequently, the interpretation of such spectra made little progress until the last two decades, *i.e.*, until after the development of the far ultra-violet region : previous workers were in the position of having to try to interpret relatively complex spectra without the knowledge of simpler spectra which alone could lay the foundations of successful theory.

The Development of Far Ultra-violet Spectroscopy

The development of the far ultra-violet region began with Schumann in the eighteen nineties. Schumann realised that three factors set a limit of *ca.* 2000 A. to the then practice of spectrography. The first was that the oxygen present in the air absorbs strongly at wave-lengths below 2000 A. It was therefore necessary to apply the technique of high vacuum work : the whole spectrograph must be enclosed and evacuated. The second limiting factor was absorption by the material of the prism commonly used to secure dispersion. Schumann partly overcame this by the use of fluorite (CaF_2) for his prisms, and with them he was able to photograph wavelengths well into the far ultra-violet—in fact as far as 1200 A., although he did not know the wave-lengths he was observing because he had no standards. The third limiting factor was absorption by the gelatine universally used in photographic plates to bind the silver halide. Schumann overcame this by employing plates with a film of pure silver bromide on them or with only a very small quantity of gelatine. Such plates are difficult to use because the sensitised film is so readily washed away from the plate surface. Later workers used a normal emulsion with a film of fluorescent oil on the outside : the oil absorbed the short wave-lengths and passed on the energy as longer-wave-length radiation to the silver halide particles—a case of photochemical sensitisation. Still later a process of depositing the silver bromide particles largely on the *surface* (so that light does not have to traverse the gelatine layer to reach them) has been perfected by Ilford and yields very satisfactory plates.

After Schumann, the next great advance was made by T. Lyman in 1906.* Lyman substituted a concave reflection grating for the prism. That had a double advantage. In the first place, it enabled him to observe wave-lengths far beyond the limit set by the absorption of fluorite at 1200 A. ; and secondly, it enabled the calculation by optical theory of the wave-lengths he was observing. Lyman reached 500 A. (he was of course the first to observe the well-known series that bears his name in the spectrum of atomic hydrogen) and, since his time, mainly by the use of more powerful sources, the gap between far ultra-violet and soft X-ray spectra has been entirely closed.

Ultra-violet spectra are well known to result from transitions of electrons from one orbital to another. In order to appreciate the different types of ultra-violet spectra, it is therefore necessary to have some acquaintance with the theory of what electronic orbitals are possible. The next section of this article attempts in very general and simple terms to provide an approach to such a theory. A more detailed account of molecular orbital theory has already appeared in these pages [1] and the present review should be read in conjunction with it.

An Approach to a Theory of Orbitals

The "Fitting-in" of Half Wave-lengths. Experiment has shown that electrons behave as though they had associated with them a wave-length. This wave-length (λ) is given by the formula $\lambda = \boldsymbol{h}/\boldsymbol{mv}$, where $\boldsymbol{h}$ is Planck's constant, $\boldsymbol{m}$ is the mass of the electron, and v is the velocity. The amplitude of the wave motion associated with the electrons being denoted by ψ, since the square of the amplitude of a wave motion is a measure of the intensity of that wave motion, ψ^2 is interpreted as a measure of the probability of finding the electrons : ψ and ψ^2 are, of course, functions of the co-ordinates.

Now suppose we have electrons confined within a one-dimensional space of length l and of uniform potential. What are the possible orbitals they can occupy ? By the terms of the problem, no electrons must at any time be outside the space l. Hence ψ^2 must be zero at all points outside each boundary, *i.e.*, ψ is zero at all points outside each boundary. The possible wave forms with which the electrons may be associated are thus of the types shown in Fig. 1.

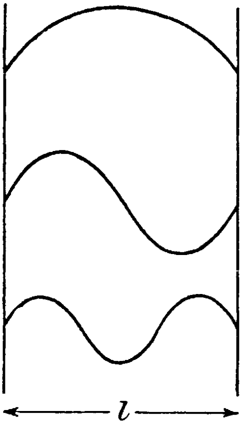


FIG. 1

---

[1] C. A. Coulson, *Quart. Reviews*, 1947, **1**, 144. Chapter III of E. J. Bowen, "The Chemical Aspects of Light", 2nd edtn., Oxford, 1946, will also be found a helpful general reference.

* See his book, "The Spectroscopy of the Extreme Ultra-Violet", Longmans Green & Co., 2nd edition, 1928.

Obviously, the possible wave forms, or orbitals, are obtained by fitting-in half wave-lengths to the available space. This conclusion is quite general.

We need not always draw a diagram. There are mathematical ways of carrying out the fitting-in process which are particularly useful in more complex cases. But it is important to realise that what the mathematics is doing is always fitting-in half wave-lengths to the available space. Obviously, a whole number of half wave-lengths must just equal the length of the available space, *i.e.*, $n\lambda/2 = l$, where $n = 1, 2, 3. \ . \ . \ .$ Each wave-length must always be related to the momentum by the relation $\lambda = h/mv$. Consequently, the kinetic energy

$$= \frac{1}{2}mv^2 = \frac{1}{2m}(mv)^2 = \frac{1}{2m}\cdot\frac{h^2}{\lambda^2} = \frac{n^2h^2}{8ml^2}$$

and the total energy is this quantity added to the uniform potential energy. Thus the energy has only one of a set of values, *i.e.*, is " quantised ", and n is a " quantum number ". This simple case shows that n defines the number of nodes in the wave form of a particular orbital. The result is general—quantum numbers are always to be interpreted as defining in some way the number of nodes in the available space : clearly there will be one for each co-ordinate. Notice that E increases as the quantum number increases and decreases rapidly as the available space increases. In the latter fact lies the fundamental reason for the homopolar bond ; *e.g.*, as two H atoms are brought together the available space for each electron is almost doubled.

Application of Fitting-in Principle to Atoms.—The possible orbitals for atoms will be obtained by fitting-in half wave-lengths to a spherical available space. There may be nodes in radius and also in each of two angles (corresponding to latitude and longitude). Three quantum numbers are thus required. The Pauli principle then allows the electrons to be fed in, two to each possible orbital, starting with those of lowest energy. Such a fitting-in of half wave-lengths to a sphere has been excellently described by W. H. Mills [2] in a review to which the reader is referred.

Certain series of atomic transitions all starting from the same orbital and passing to upper orbitals with successively extra nodes are known as Rydberg series. On a frequency basis, the formula for such a series is

$$\nu_0^n = A - B/(n + m)^2$$

where A and m are specific constants ($m < 1$), B is a universal constant, and n takes integral values. The series found by Lyman in the far ultra-violet spectrum of atomic hydrogen is a special case of such a series.

Molecular Spectra

We may divide molecular electronic spectra into intra- and extra-valency shell transitions.[3] The first are those involving the lower energy

---

[2] Presidential Address, *J.*, 1942, 457.

[3] R. S. Mulliken and C. A. Rieke, *Rep. Prog. Physics*, 1941, **8**, 231. Any writer on molecular spectra is so heavily indebted to the work of R. S. Mulliken that it is almost impossible to give a full list of acknowledgments. In the selected references given here will be found details of the many other important papers he has published.

and can be considered as taking place largely within the nuclear framework. In order to discuss them we shall use the " fitting-in principle " to determine the possible orbitals between which transitions may take place. In general, the available space is simply the region between and slightly to either side of the nuclei at the ends of a bond. It is formed by the overlap of just two atomic probability pictures. In conjugated compounds, however, a so-called $2p$ atomic orbital [see ref. (1)] on a particular carbon atom overlaps as much with its neighbour on one side as with its neighbour on the other : consequently the " $2p$ " available space is *inevitably* not localised around one inter-nuclear distance but extends over the whole conjugated chain. On excitation, the available space for any electron increases ; but for the purposes of a conceptual scheme, for low excitation energy, we shall usually neglect this.

Extra-valency shell transitions comprise those transitions taking place between orbitals whose dimensions are considerably greater than those of the nuclear framework. In terms of the Bohr theory, these are orbitals only reached from the ground state by absorption of high energy. In considering them, particularly for very highly excited orbitals, we may consider the nuclear framework as approximating to a point. In other words, we shall expect to find the same relations between transitions to these high-energy orbitals as are found between atomic transitions. The upper orbitals may again be considered by applying the fitting-in principle to a spherical available space. In particular, we shall expect to find series of transitions fitting the above Rydberg series formula for atoms.

Obviously, such a series of transitions converges, as n increases, to a limit given by $\nu_0^n = A$, which limit is the ionisation potential. Three such series[4] for acetaldehyde are shown in Fig. 2. Their convergence, all to the same limit, can be clearly seen ; and at the limit, continuous absorption can be seen to commence, corresponding to the fact that there is no restriction on the kinetic energy with which the electron is ejected. Since spectroscopic measurements can be made with considerable precision, extrapolation to the limit may give a very accurate value for the ionisation potential. In this case for acetaldehyde it is 10·2265 ± 0·0007 v.* The stated limits of error always represent the maximum divergence of the measurements from the Rydberg formula, the first few bands (which are expected not to fit) being neglected for this purpose.

Application of Fitting-in Principle to Olefins.—Olefins have two orbitals normally occupied in the C=C bond. Intuitively one feels that if an orbital is such that electrons in it tend to concentrate in the bond, it is bonding. Conversely, if they tend to avoid the bond centre it is *antibonding.* Since the available space for the C=C orbitals must extend a little to either side of the C atoms, possible orbitals are (*a*), (*b*), etc. These

---

[4] A. D. Walsh, *Proc. Roy. Soc.*, 1946, *A*, **185**, 176.

* Values of ionisation potentials given in this review differ from the previously published values because they have been recalculated with the use of the most recent value of the electronic charge.

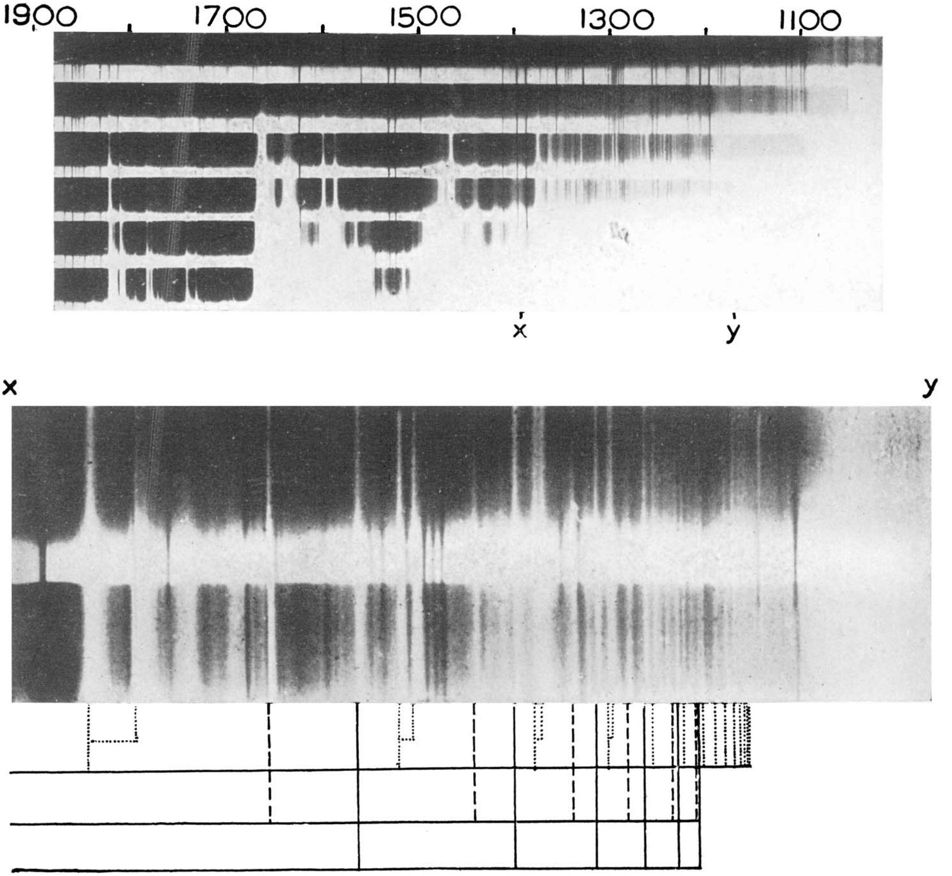


FIG. 2

The spectrum of acetaldehyde.

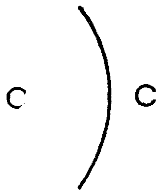
(*Reproduced by permission from* Proceedings of the Royal Society, 1946, *A*, **185**, 176.)

represent graphs of ψ plotted in a direction parallel to the CC axis. Since ψ^2 gives the probability-of-finding picture, clearly (*a*) is a bonding orbital

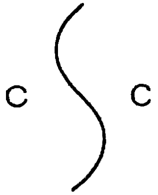
(*a*)

(*b*)

and (*b*) is an anti-bonding orbital. The high strength of the C=C bond implies that both the normally occupied orbitals are of the bonding type, *i.e.*, type (*a*). Considering the available space in a direction at 90° to the CC axis the two lowest energy orbitals are (i) and (ii). The first of these



(i)



(ii)

is called a σ orbital and the second a π orbital. The first is axially symmetrical, the second has a node along the CC axis and is not axially symmetrical.* Clearly, the two orbitals we shall expect to be normally occupied in the C=C bond will be (*a*)(i) and (*a*)(ii).

Since the second of these is an overtone of the first, it will be of higher energy, *i.e.*, the electrons in the π orbital will be more weakly bound than those in the σ orbital. Consequently, the first ionisation potential of the C=C bond will be π^{-1} in type and the lowest energy transition will be of an electron from (ii)(*a*) to (ii)(*b*). A transition in which an electron passes from one orbital to another of precisely similar type except that it has one or more extra nodes in the direction along the chain of nuclei is called an $N \rightarrow V$ transition.[5] N stands for the normal or ground state, V for the upper state. Clearly, V has a greater anti-bonding nature relative to N.†

---

[5] R. S. Mulliken, *J. Chem. Physics*, 1939, **7**, 20.

* Ref. (1) will make this point clearer.

† For a single bond comprised by the overlap of two atomic orbitals whose amplitude functions are ψ_A and ψ_B, the bonding orbital may be described as $\psi_A + \psi_B$ and the upper orbital as $\psi_A - \psi_B$. The V state has one electron in each, their spins being opposed. In a treatment of molecular structure initiated by Heitler and London, two electrons interact to give either attraction (with their spins opposed) or repulsion (when their spins are parallel). The first corresponds to two electrons in the orbital $\psi_A + \psi_B$, the second to one electron in $\psi_A + \psi_B$, and one (of parallel spin) in $\psi_A - \psi_B$: *i.e.*, the V state has no counterpart in the Heitler–London theory. However, the simple Heitler–London theory is known to neglect the influence of ionic states.[7] Consequently, the V state is interpreted on that theory as *ionic* in nature.

For a single bond, therefore, the length should be greater in state V than in N; so that, by the Franck–Condon principle, the transition should cover a broad wave-length region with a slow rise to maximum intensity.

We are now in a position to interpret the main features of the electronic spectrum of ethylene. This occurs in the far ultra-violet and has been photographed by W. C. Price and W. T. Tutte.[6] It begins with a region of absorption stretching from 2000 A. to beyond 1600 A. (maximum, 1630 A.). This is identified as the $N \longrightarrow V$ transition (ii)(a) to (ii)(b). In the ground state the lack of axial symmetry of the π bond holds the molecule rigid, so that *cis-* and *trans*-disubstituted ethylenes are possible. In the V state one π electron is in an antibonding orbital and one remains in the bonding orbital. Consequently, their effect largely cancels and the C=C bond is free to twist. Probably it takes up a most stable position when the two CH_2 groups are at 90° to each other [8]—perhaps as the two CH_3 groups of ethane probably adopt a staggered configuration. It is not therefore surprising that *cis-trans*-conversions may be brought about by absorption of light of wave-length below 2000 A.

At $\sim$ 1700 A., and especially in the high-energy region beyond 1400 A., bands occur which can be fitted into Rydberg series and lead to the first ionisation potential of $10{\cdot}50 \pm 0{\cdot}03$ v. Discrete absorption is possible because, whatever excited state the π electrons enter, there is always a strong, unchanged, σ bond holding the molecule together—if dissociation occurred, the spectrum would be continuous, since there is no restriction on the kinetic energy with which the products of dissociation separate. With CH_3 substitution, the π^{-1} ionisation potential decreases. The reason for this [cf. ref. (8), p. 268] probably lies, at least partly, in the electron-releasing properties of CH_3 causing increase of electron density in the C=C bond, with consequent increase of electron repulsion.

Application to Acetylenes.—For a particular CC available space, clearly there are two orbitals of type (ii) above, since there are two mutually perpendicular directions both at 90° to the bond axis. In the normal state of the acetylene molecule, in addition to the σ bonding orbital, both these π bonding orbitals are filled. The two π orbitals combine to give a probability picture that is axially symmetrical about the CC line. This is a point not generally appreciated—that, in distinction to the old idea of the C≡C bond as containing three rigid "rods", according to wave-mechanical theory, free rotation is possible in the ground state about the C≡C bond.*

---

[6] *Proc. Roy. Soc.*, 1940, *A*, **174**, 207.

[7] See A. Maccoll, *Quart. Reviews*, 1947, **1**, 36.

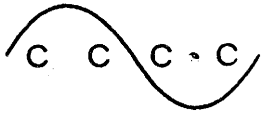
[8] R. S. Mulliken, *Rev. Mod. Physics*, 1942, **14**, 265.

* Thus it has been given as an argument against "hyperconjugation" [for the meaning of this term, see ref. (1)] between the electrons of the CH_3 groups and the C≡C bond in CH_3—C≡C—CH_3 that it ought to cause "double-bond character", whereas the C–C bonds actually show less resistance to twisting than in ethane. This particular argument is not valid, because the effect of the hyperconjugation would be to cause what should be called, not "slight double bond", but "slight triple bond" character, *i.e.*, to cause the slight occupation of extra orbitals in the C–C that, added together, are axially symmetrical.

The spectrum of acetylene was photographed by W. C. Price.[9] It has a wide region of absorption between 2000 A. and 1550 A. which is probably to be interpreted as $N \longrightarrow V$ in type like the ethylene absorption in a similar region. At shorter wave-lengths, bands so sharp as to resemble the lines of atomic transitions can be fitted into two Rydberg series proceeding to the π^{-1} ionisation potential of 11·41 ± 0·01 v. The π electrons of acetylene are thus more tightly bound than those of ethylene. This again is a point not generally appreciated. It can be simply interpreted as follows. Replacement of two CH bonds in C_2H_6 by a CC π bond to give C_2H_4 means that strongly-bound electrons are replaced by weakly-bound ones. Consequently, the electron density at each carbon atom is decreased and a stronger hold is permitted by each atom on its other valency electrons. There is always a balance between the strengths of the various bonds attached to an atom, as a result of the repulsion between the various pairs of electrons. In other words, the CH bonds of C_2H_4 are stronger than those of CH_4, while the σ CC bond of C_2H_4 should be stronger than the σ CC bond of C_2H_6. Replacement of a further pair of CH bonds in C_2H_4 to give the second π bond of C_2H_2 must mean that the CH and original π bonds become stronger than the corresponding bonds of ethylene : *i.e.*, the electrons in each π bond of C_2H_2 are held more tightly than those in the π bond of C_2H_4.

Application to Open, Conjugated Chains.—In buta-1:3-diene [see ref. (1)] the σ electrons are all regarded as occupying orbitals localised in a particular CC or CH bond. The π-type electrons are regarded as occupying orbitals extending over the whole carbon chain. The length of the available space being taken as somewhat greater than the length of the whole carbon chain, possible π orbitals are (a'), (b'), (c'), and (d') : (a') is bonding in all the bonds, (b') is anti-bonding in the central CC bond, (c') is anti-bonding in the two outer CC bonds, (d') is anti-bonding in all the CC bonds. There are four π electrons in the molecule (one from each atom), so that the occupied orbitals are (a') and (b'). Of course the diagrams are to be taken as representing orbital *types* only—ψ would only have the smooth form

(a')



(b')

(c')

(d')

---

[9] *Physical Rev.*, 1935, **47**, 444.

shown if the available space was one of uniform potential: in fact, it is a space of periodic potential and the more precise ψ graph must have superimposed upon the diagrams the pattern of the periodic potential. Nevertheless, as a conceptual basis for orbital theory, diagrams such as (a')—(d') are of great value.

To each possible orbital there corresponds an energy level. A π energy level diagram is therefore as in Fig. 3, the symbol $\underline{\|}$ representing a pair of electrons in the normal state. Clearly, there are four possible $N \rightarrow V$ transitions as shown. If we apply the formula for the energy levels, $E = n^2h^2/8ml^2$, which we deduced above, for the $N \rightarrow V_1$ (*i.e.*, the longest wave-length) transition of butadiene, n changes from 2 to 3 (instead of 1 to 2 in ethylene) and the length of the available space is rather less than twice the length in ethylene. Consequently the $N \rightarrow V$ transition for ethylene involves an energy $(4 - 1)h^2/8ml^2 = 3h^2/8ml^2$, whereas the $N \rightarrow V_1$ transition for butadiene involves $\approx (9 - 4)h^2/8m(2l)^2 = \frac{5}{4}.\frac{h^2}{8ml^2}$. This treatment is, of course, very crude, for it uses a formula strictly only applicable to a space of uniform potential, but it illustrates very well (a) that the first $N \rightarrow V$ transition for butadiene involves much less energy than that for ethylene, and (b) that the reason for this is the increase in available space for the π electrons of butadiene relative to those of ethylene. As we pass to hexatriene it is easily shown that the first $N \rightarrow V$ transition needs even less energy. The energy level diagram is now as Fig. 4 and the various π-type orbitals are readily drawn.

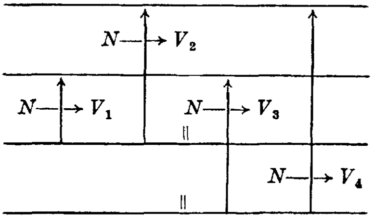


FIG. 3

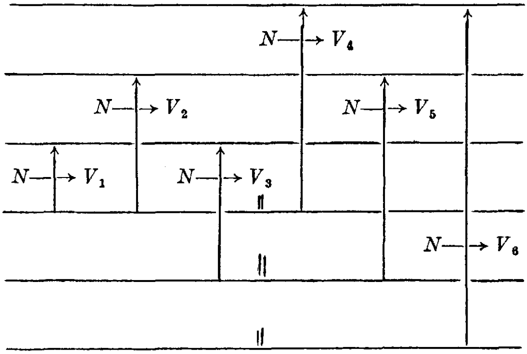


FIG. 4

These results are general. The greater the available space, *i.e.*, the greater the length of the conjugated chain, the further to long wave-lengths lies the first $N \rightarrow V$ absorption. Obviously, this explains the connection of colour with extensive conjugation. Moreover, thinking on classical lines, the greater the possible amplitude of the electrons set into oscillation by the absorption of light energy, the more intense the absorption—so that, as the available space increases for the π electrons, not only does $N \rightarrow V_1$ move to longer wave-lengths, but it also increases in intensity. One has here the twin bases for a theory of colour in dyes.

In butadiene[10] the first $N \rightarrow V$ absorption occurs around 2100 A. Short vibrational progressions show the increased anti-bonding nature of the upper state.* In hexatriene[11] the first absorption is at 2500 A. Short vibrational progressions are again present. The second region of absorption in butadiene around 1750–1700 A. is identified as $N \rightarrow V_2$. At shorter wave-lengths Rydberg series are found, leading to a first ionisation potential (9·07 v.) which, as we should expect, is lower than that for ethylene. For hexatriene the first π^{-1} ionisation potential has the still lower value 8·26 v. The changes of energy level of the occupied orbitals are shown in Fig. 5.[11a] The mean energy per π electron decreases as conjugation increases, *i.e.*, the whole system becomes more stable, although the most weakly bound electrons are ever higher in energy. A consequence is that if conjugation can occur it will. With increase in the number of —C═C— units, a process of division of energy levels takes place. The same process occurs when two H atoms are brought together and the original " 1s " level splits into bonding and anti-bonding levels [" $\sigma(1s)_g$ " and " $\sigma(1s)_u$ " : see ref. (1)]. If the number of —C═C— units is large, there results a large number of levels very close together : *i.e.*, the original sharp π energy level of C_2H_4 becomes a π energy *band*. This enables us to see why the π electrons of graphite occupy an energy band. Similarly, metals have electronic energy *bands* because of the repetition of many identical units.

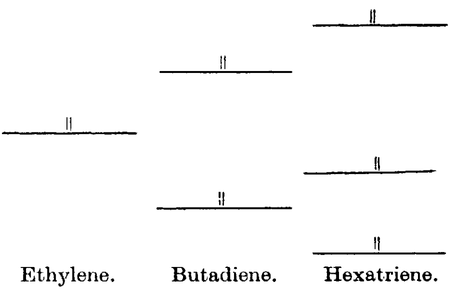


FIG. 5

The same consequences of conjugation occur as one passes from acetylene to diacetylene. But the tighter binding of the π electrons in acetylene means that we shall expect them to conjugate less completely, *i.e.*, remain more localised in their original C≡C bond than do the π electrons of C═C. In agreement, the decrease in first ionisation potential from ethylene to butadiene (10·50 to 9·07 v.) is much more than the corresponding decrease from acetylene to diacetylene (11·41 to 10·79 v.[12]).

---

[10] W. C. Price and A. D. Walsh, *Proc. Roy. Soc.*, 1940, *A*, **174**, 220.

[11] *Idem, ibid.*, 1946, **185**, 182.

[11a] E. Hückel, Paper at International Conference on Physics, London, 1934.

[12] W. C. Price and A. D. Walsh, *Trans. Faraday Soc.*, 1945, **41**, 381.

* At first sight, one might expect the higher V states to show lower vibrational frequencies than the V_1 state : they are more " anti-bonding ". To expect this, however, is to forget that, in practice, as excitation increases, the " available space " increases, *i.e.*, though the higher states have more nodes they are more attenuated. What is important is the number of nodes in relation to the compactness of the orbital. A σ anti-bonding orbital is more anti-bonding than a π if the two have much the same excitation energy ; but if the former lies far above the latter—as is commonly true—then in practice it may produce *less* bond weakening than the latter : an example occurs with acetaldehyde. Similarly, the experimental fact is that the vibrational frequencies for butadiene actually increase as one passes from V_1 to higher V states.

Of the two occupied π orbitals in butadiene, (a') has an anti-node in the central CC bond, while (b') has a node ; (b'), however, is the higher-energy orbital and therefore to be thought of as occupying a greater available space, *i.e.*, to be more diffuse, so that the repulsion represented by the node is somewhat attenuated. Consequently, (b') only partly cancels the effect of (a') in the central C–C and there is some residual double-bond character. The result is that forms cis- *and* trans- *with respect to the conventional single bond* should be possible. To distinguish these forms from the more usual geometrical isomers, R. S. Mulliken [8] has called them *s-cis-* and *s-trans-*forms. He has shown [13] that selection rules make the $N \rightarrow V_1$ transition for the *s-trans*-form allowed but the $N \rightarrow V_2$ forbidden ; whereas for the *s-cis*-form both are allowed. Now the region identified as $N \rightarrow V_1$ in butadiene is considerably stronger than that identified as $N \rightarrow V_2$. In consequence, butadiene gas at room temperature is believed to be predominantly *s-trans* with a smaller proportion of *s-cis*-molecules. The strong Rydberg series leading to 9·07 v. are naturally identified as belonging to the *s-trans*-molecules. Is there any trace of the expected weaker series converging to the first ionisation limit of *s-cis*-butadiene ? It was difficult to answer this until electron-impact data indicated the existence of another ionisation potential at $\sim$ 8·7 v. Careful search in the spectrum [14] then made it possible to pick out a weak, but definite, Rydberg series converging to a limit of 8·75 v. The spectroscopic observations thus provide strong evidence for the existence of two forms of butadiene gas at room temperature. Confirmatory evidence comes from thermodynamic studies.[15]

For hexatriene, *cis-* and *trans*-forms as well as *s-cis-* and *s-trans*-forms should be possible. The spectroscopic observations give evidence of their existence,[11] but the problem of their identification is too complex to be solved with certainty at present.

Application to Cyclic Molecules

(a) *Cyclic Dienes :* cyclo*Pentadiene,* cyclo*Hexadiene.*—These two dienes are examples of dienes that are, perforce, *s-cis.* Their spectra illustrate very well the differences of *s-cis-* from *s-trans*-dienes. In *s-trans*-butadiene the $N \rightarrow V_1$ is considerably stronger than the $N \rightarrow V_2$ absorption. In *cyclo*pentadiene and *cyclo*hexadiene, however, the first region of absorption $(N \rightarrow V_1)$ is decidedly weaker than the second $(N \rightarrow V_2)$, in agreement with the theoretical selection rules. Also, both regions of absorption occur at considerably longer wave-lengths than in *s-trans*-butadiene. This shift to lower energy is paralleled by the lowered ionisation potentials found [16] (8·4 v. for *cyclo*hexadiene, 8·62 v. for *cyclo*pentadiene : cf. 9·07 v. for *s-trans*-butadiene). Obviously, a large part of the ionisation potential

---

[13] *J. Chem. Physics*, 1939, **7**, 121.

[14] T. M. Sugden and A. D. Walsh, *Trans. Faraday Soc.*, 1945, **41**, 76.

[15] J. G. Aston, G. Szasz, H. W. Woolley, and F. G. Brickwedde, *J. Chem. Physics*, 946, **14**, 67.

[16] W. C. Price and A. D. Walsh, *Proc. Roy. Soc.*, 1941, *A*, **179**, 201.

lowering is due to the *s-cis*-arrangement of the double bonds, since it occurs also in *s-cis*-butadiene. It is probably due to the fact that the repulsion represented by the node in (b') (p. 79) must be more intense in an *s-cis*- than in an *s-trans*-form, since the two outer CC bonds [in which the electrons of (b') spend nearly all their time] are closer together in the former than in the latter. Consequently, the energy level (χ_2) corresponding to (b') lies higher in energy in the *s-cis*-form, so that its ionisation potential is reduced and the $N \rightarrow V_1$ and $N \rightarrow V_2$ transitions are shifted to long wave-lengths. The energy level (χ_1) of the other occupied orbital (a') should not be much changed between the two forms; * and, indeed, electron-impact data, which clearly indicated the existence of two χ_2 ionisation potentials for ordinary butadiene gas, gave no indication of two χ_1 ionisation potentials differing markedly. The result is that the *total* π electronic energy in *s-cis*- must be greater than in *s-trans*-butadiene ; so that, if, as is probable, the other electrons have much the same energy in both forms, *s-cis* must be the higher in energy.[17] This conclusion fits pleasingly with the thermodynamic studies.[15] At low temperatures butadiene is entirely *s-trans*. As the temperature rises, the proportion of *s-cis* increases. Similarly, glyoxal prefers to exist in the *s-trans*-form.[18, 19]

Probably the weak $N \rightarrow V_1$ absorption expected for *s-cis*-butadiene in ordinary butadiene gas lies at rather longer wave-lengths than that (~2100 A.) for *s-trans* ; but the strength of the latter plus its spread to long wave-lengths with increasing pressure make it difficult to observe the former. However, the weak absorption in the 2400—2200 A. region has been found to be strongly temperature-dependent,[20] increasing with temperature. This is evidence that the *s-cis* $N \rightarrow V_1$ transition is located in the region 2400—2200 A. as compared with 2200—2000 A. for *s-trans*, 2400—2200 A. for *cyclo*pentadiene, and 2600—2300 A. for *cyclo*hexadiene. These locations fit nicely with the observed sequence of first ionisation potentials.

(b) *Cyclic Trienes : Benzene.*—In benzene the π electrons occupy orbitals that extend over the whole hexagon. The possible π orbitals are obtained

---

[17] A. D. Walsh, *Nature*, 1946, **157,** 768.

[18] *Idem, Trans. Faraday Soc.*, 1945, **42,** 66.

[19] J. E. LuValle and V. Schomaker, *J. Amer. Chem. Soc.*, 1939, **61,** 3520.

[20] R. S. Rasmussen, D. D. Tunnicliff, and R. B. Brattain, *J. Chem. Physics*, 1943, **9,** 432.

[21] R. S. Mulliken, *J. Chem. Physics*, 1939, **7,** 339.

* An effect that may be important here is that, in the *s-cis*-form, the $2p$ atomic orbitals on the end C atoms will overlap slightly (corresponding to part of the idea of Dewar-type structures), so that the available space partakes slightly of the nature of an endless (circular) chain.

*cyclo*Pentadiene and *cyclo*hexadiene should also show the phenomenon of " hyperconjugation ", *i.e.*, continuation to some extent of the conjugated chain through the CH_2 groups just as through the O atom in furan. A CH_2 group electronically resembles an oxygen atom, from which it can be regarded as arising by pulling out protons from the nucleus. There is no doubt that this effect must occur, but it is probably less important than was earlier thought.[21]

by fitting-in half wave-lengths to the two-dimensional available space.* The lowest orbital (χ_1) has no nodes in the available space. The next has a nodal line passing through the ring centre. There are in fact two such orbitals (χ_2 and χ_3) of equal energy, their nodal lines being at 90°. The second arises from the need not to favour any particular atom in the symmetrical ring: it has a node, as we proceed round the ring, where the first has an anti-node and *vice versa.* These orbitals are the analogues of the *p* orbitals that arise for a spherical available space, and together they combine to give a probability picture that has hexagonal symmetry. The next orbital (χ_4) has two nodal lines at 90°, *i.e.*, four amplitude regions of alternating sign. By itself this would not give an even probability round the ring; but by taking a second such orbital (χ_5) with its nodal lines rotated through 45° relative to χ_4 (*i.e.*, giving a node, as we proceed round the ring, where χ_4 had an anti-node and *vice versa*), it is possible—taking the two in combination—to preserve the hexagonal symmetry: χ_4 and χ_5 are thus of equal energy. They are the two-dimensional analogues of the *d* orbitals that are possible for a spherical available space. The next orbital has three nodal lines all passing through the ring centre and with angles of 60° between them: this affects all the bonds equally and is thus the only one of its kind.

There are six π electrons in benzene, so the normal state has the configuration $\chi_1{}^2\ \chi_{2,\ 3}{}^4$; $N \longrightarrow V$ transitions are possible by taking an electron from $\chi_{2,\ 3}$ and putting it in $\chi_{4,\ 5}$. There are clearly four such transitions [22] (assuming no change of multiplicity), according to whether we take an electron from χ_2 or χ_3 and whether we put it in χ_4 or χ_5. At first sight these would be of equal energy, but *interaction* of the electrons results in three transitions of different energy appearing, one being twofold. The first is responsible for the well-known 2600 A. absorption system, the second for bands between 2000 and 1800 A., and the third (the twofold one) for intense absorption at 1790 A.[23] An empirical fact is that the 2000—1800 A. transition in benzene moves much further to long wave-lengths when a side chain is conjugated with the ring than does the transition at 1790 A. in benzene.[24] Rydberg series [25] for both the $\chi_{2,\ 3}$ (limit 9·240 ± 0·005 v.) and the χ_1 electrons (limit 11·7 ± 0·3 v.) have been observed.

(c) *Pyrrole, Thiophen, and Furan.*—In molecules such as pyrrole, thiophen, and furan, a 2*p* atomic orbital is present on the N, S, or O atom and has an axis parallel to that of the 2*p* orbitals on the carbon atoms. In addition, two electrons from the N, S, or O have to be accommodated in the orbitals constructed from the hetero-atom 2*p* orbital. The degree to which this 2*p* orbital completes the ring for the π available space must depend upon the

---

[22] R. S. Mulliken, *J. Chem. Physics*, 1939, **7,** 353; cf. ref. (7), pp. 38, 39.

[23] W. C. Price and A. D. Walsh, *Proc. Roy. Soc.*, 1947, *A*, **191,** 22.

[24] A. D. Walsh, *ibid.*, p. 32; *Trans Faraday Soc.*, 1946, **42,** 62.

[25] W. C. Price and R. W. Wood, *J. Chem. Physics*, 1935, **3,** 439.

* "Two-dimensional", because, as long as we are dealing with π electrons, the fitting-in process concerns essentially only two directions. Hence we speak of nodal "lines" instead of nodal "planes". These terms should cause no confusion.

electronegativity of the atom. If the electronegativity is very high, the $2p$ orbital may be thought of as very contracted relative to the carbon $2p$ orbitals, *i.e.*, little conjugation of the hetero-atom electrons with the CC π electrons takes place, the former remain as a lone pair, and the latter are much as in *s-cis*-dienes. If the electronegativity is much lower, *i.e.*, close to that of carbon, full conjugation will take place and the ring available space will be completed for the π electrons. The system will be very much like benzene, the hetero-atom with its pair of electrons replacing one of the C=C groups with its pair of π electrons. Such a case is known as " homocyclic " conjugation.[21]

Of N, S, and O, S has the lowest electronegativity and O the greatest. The lone pair of S, indeed, resembles closely the π electrons in ethylene. Thus their ionisation potential in hydrogen sulphide is 10·47 v. as compared with 10·50 v. for the π^{-1} ionisation potential in ethylene. Consequently, S can replace a group —CH=CH—, without fundamental alteration of molecular orbitals. It is found, for example, in fungicides and other highly specific biological reagents that this replacement can be made without loss of activity.[26] Consequently, we expect thiophen to have a strong resemblance to benzene. It is well known that, chemically, this is so true that they can only be separated with difficulty. Thiophen then might be expected to be a case of nearly homocyclic conjugation : it has a sextet of π electrons and its orbitals and transitions should be very similar to those of benzene. It has a region of absorption from 2600 to 2200 A. which, according to G. Milazzo,[27] probably corresponds to the benzene 2600 A. region, a second system,[27] possibly corresponding to the benzene 2000—1800 A. region, and a third, intense region of absorption around 1800—1750 A.[16] as has benzene. In pyrrole the occurrence of conjugation between the C=C and N electrons is evidenced by the only feebly basic character of the substance : but this conjugation is likely to be less than in thiophen. Indeed, no system corresponding to the benzene 2600 A. region has yet been discovered with pyrrole. On the other hand, in *N*-methylpyrrole the well-known electron-releasing properties of a methyl group make the N atom effectively less electronegative, so that approach should be made towards the benzene and thiophen spectra. G. Milazzo [28] has obtained the spectrum of *N*-methylpyrrole at wave-lengths above 2000 A. and shown the appearance of a region between 2600 and 2250 A. probably corresponding to the benzene 2600 A. transition.

However, the interpretation of the spectra of pyrrole, thiophen, and furan is still very uncertain and incomplete. One would expect, for example, furan to show least tendency to homocyclic conjugation, but some of its spectroscopic features [16] agree surprisingly with the theoretical characteristics that have been deduced for homocyclic conjugation.[21]

Application to Triatomic Molecules.—The molecule CO_2 is linear. In it, we must regard the C atom as like the C atoms in acetylene, *i.e.*, forming

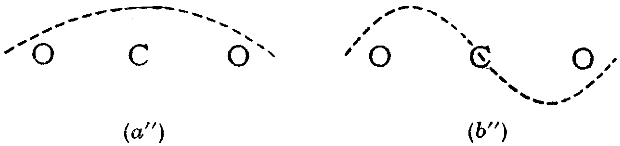
---

[26] J. C. McGowan, private communication ; H. Erlenmeyer, E. Berger, and M. Leo, *Helv. Chim. Acta*, 1933, **16**, 733.

[27] Private communication.

[28] *Gazzetta*, 1944, **74**, 152.

two hybrid valencies in line and having two pure $2p$ valencies mutually at 90°, and at 90° to the line of the hybrid valencies. The $2p$ valencies overlap sideways with corresponding valencies on the O atoms. π bonds in each of two planes at 90° result, and the π available space is taken as the whole length of the molecule [cf. the description given in ref. (1), p. 169]. Fundamental and first overtone π orbitals, as (a'') and (b''), are then possible.



(a'') (b'')

The anti-bonding orbital (b'') will be largely localised round the oxygen atoms, since its amplitude at the C atom is zero. The distance apart of the O atoms makes it only weakly anti-bonding, almost non-bonding. Eight electrons have to be fed into the possible π orbitals. Four go into two orbitals as (a''), mutually at 90°. Four go into two orbitals as (b''), also at 90°. In addition there are eight other " outer " electrons—a $2s$ lone pair on each O atom and two electrons in each of the two, localised, σ, C–O bonds.

The most weakly bound electrons are those in orbitals (b''). Therefore the minimum ionisation potential (at $13{\cdot}79 \pm 0{\cdot}01$ v.[29]) corresponds to the removal of an electron from an orbital largely localised round the oxygen atoms. The first overtone π orbitals are fully occupied, and the lowest empty orbital is an anti-bonding one of σ type. The longest wave-length absorption bands ($\sim$ 1600 A.) are therefore interpreted on these views as due to a transition of one of the π electrons localised round the oxygen atoms to an anti-bonding σ orbital.

The molecule SO_2 is bent. Localised σ bonds are formed by endwise overlap of S and O $2p$ valencies. The bent configuration means that sideways overlap of the $2p$ orbitals on the O atoms not only takes place with an S $2p$ orbital but also with each other. That is, the π available space may be regarded as a closed ring and the possible π orbitals are similar to those in benzene—one with no nodes as we pass round the ring and two (not actually of equal energy, since SO_2 is not completely symmetrical) each with two nodes in the ring. Six electrons can thus be accommodated in the low-lying π orbitals. In addition to these and to the σ bond orbitals, there are $2s$ lone pairs on each atom and $2p$ lone pair orbitals (with axes in the ring plane) on each O atom. A total of twenty electrons can be accommodated. A linear triatomic molecule of similar atoms, as we have seen, can only accommodate easily *sixteen* electrons. This is the basis of the rule which states that triatomic molecules not containing hydrogen are linear if they contain sixteen or less " valency " electrons, and bent if more. Up to sixteen electrons, a linear molecule is more stable because it can provide orbitals with not more than one node in the atomic chain, whereas a bent

---

[29] W. C. Price and D. M. Simpson, *Proc. Roy. Soc.*, 1939, *A*, **169**, 501.

configuration uses π orbitals with two nodes in the (ring) atomic chain. Beyond sixteen electrons, the bent molecule is the more stable because it can still provide low-lying π orbitals whereas the linear form has only highly anti-bonding σ orbitals available.

Since $\widehat{OSO}$ is obtuse, the π orbital (π_1^*) with a nodal line through the S atom is clearly less anti-bonding than that (π_2^*) with a nodal line at 90° to this. The latter is vacant, for SO_2 has only eighteen electrons. The long wave-length bands shown by SO_2 can be naturally interpreted as due to a transition of an electron from π_1^* (weakly $O \longleftrightarrow O$ anti-bonding and localised round the oxygen atoms) to π_2^* ($S \longleftrightarrow O$ anti-bonding). That the transition shows wide vibrational structure and results in a decrease of the angle $\widehat{OSO}$ [30] fits well with this.

Application to Carbonyl Molecules.—The oxygen atom of a carbonyl group possesses a lone pair of $2p$ electrons. These take no part in the bond and may be called non-bonding electrons. The bond has, normally, an occupied σ and an occupied π orbital. Anti-bonding excited orbitals—either σ or π—having a node between the C and O are, of course, possible. An $N \rightarrow V$ transition of, say, the π electrons is thus possible, just as in C_2H_4. We may also have, however, a transition of one of the lone pair, non-bonding, electrons to the π or σ anti-bonding orbitals. A transition of such an electron to an anti-bonding π upper level is known as an $N \rightarrow A$ transition,[31] whereas a transition of such an electron to a σ anti-bonding upper level is called $N \rightarrow B$ in type. Now the first ionisation potential of carbonyl molecules is known (*e.g.*, from the Rydberg bands having very little vibrational structure) to correspond to the removal of one of the oxygen lone pair electrons. Consequently the sequence of decreasing binding energy for the electrons in a carbonyl group is

σ bonding electrons, π bonding electrons, non-bonding electrons

and the $N \rightarrow A$ transition is expected to cause the longest wave-length spectrum. The selection rules require this transition (in contrast to $N \rightarrow V$ and $N \rightarrow B$) to be of low probability.

For simple carbonyl compounds such as aldehydes and ketones the longest-wave-length absorption takes the form of weak bands situated near 2900 A. The 2900 A. systems are therefore interpreted as $N \rightarrow A$ in type. As an example, the light emitted by formaldehyde molecules in the so-called cool flames of hydrocarbon combustion is due to the reverse of such a transition, *viz.*, $A \rightarrow N$.

How are we to distinguish the $N \rightarrow B$ and π $N \rightarrow V$ transitions ? In order to answer this question, consider an energy-level diagram for a simple carbonyl group as shown in Fig. 6. If the $\rangle C{=}O$ group is conjugated with another unsaturated group, our discussion above shows that the most weakly bound π occupied orbital will be raised, and the lowest empty π orbital

---

[30] *Idem, ibid.*, 1938, **165**, 272.

[31] H. L. McMurry and R. S. Mulliken, *Proc. Nat. Acad. Sci.*, 1940, **26**, 312.

lowered. In other words, the $N \rightarrow V$ transition shifts towards longer wave-lengths. There is no reason, however, why the non-bonding $2p$ orbital should be particularly affected by the conjugation. Therefore the $N \rightarrow B$ transition should show comparatively little change with conjugation. We thus have a way of distinguishing the $N \rightarrow V$ and the $N \rightarrow B$ transitions. The $N \rightarrow A$ transition will, like the $N \rightarrow V$ transition, move to long wave-lengths, because its upper state is depressed by the conjugation. This fits nicely with the fact that the longest-wave-length absorption in acraldehyde and crotonaldehyde occurs around 3300 A. instead of 2900 A.

After the 2900 A. system, the next two regions of absorption in formaldehyde occur at 1745 and 1560 A.[32] In acetaldehyde (see Fig. 2) they are at 1800 and 1650 A. respectively.[4] In acraldehyde, regions occur at 1750 and 1935 A. and in crotonaldehyde at 1800 and 2030 A.[33] All these molecules have an absorption system (of similar appearance) in the neighbourhood 1750—1800 A. This transition is therefore identified, in each case, as $N \rightarrow B$ in type. On the other hand, the transition at 1560 A. in formaldehyde and 1650 A. in acetaldehyde apparently corresponds to the region at 1935 A. in acraldehyde and 2030 A. in crotonaldehyde. This transition therefore appears to be the $N \rightarrow V$ one; and indeed, its appearance in acraldehyde and crotonaldehyde is very similar to that of the longest-wave-length transition in olefins. In acetaldehyde and formaldehyde, however, it is certainly overlain by a Rydberg transition.

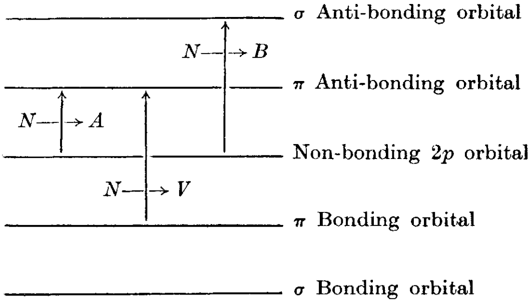


FIG. 6

A transition of $N \rightarrow B$ type can evidently occur in any group AB where A has a lone pair of electrons, even though A and B are joined only by a single, σ, bond—there is no necessity for a double bond. We expect and find (around 1650 A.) such transitions in, for example, alcohols, ethers, and thiols. Similarly, we expect them in the alkyl halides. Thus the continuous absorption shown by methyl iodide around 2600 A. is interpreted as $N \rightarrow B$ in type.[34] The upper orbital, especially, being σ (*i.e.*, compact) in type, is strongly anti-bonding, so that in state B the bonding is seriously weakened (though it must be remembered that in state B there are still two electrons in a bonding orbital). It is not therefore surprising that methyl iodide is known to dissociate to $CH_3 + I$ in its continuum of absorption. In groups containing a double bond the dissociation is less likely to occur since state B has now one electron in an anti-bonding orbital as against four in bonding ones. $N \rightarrow A$ transitions also produce weakened bonding:

---

[32] W. C. Price, *J. Chem. Physics*, 1935, **3**, 256.

[33] A. D. Walsh, *Trans. Faraday Soc.*, 1945, **41**, 498.

[34] R. S. Mulliken, *Physical Rev.*, 1942, **61**, 277.

e.g., the C=O valence vibration has a frequency of 1187 cm.$^{-1}$ in the formaldehyde 2900 A. bands as against 1750 cm.$^{-1}$ in the ground state.

Bond Polarity in Carbonyl Molecules, especially CO_2 *and* CO.—An important factor that will affect the location of $N \rightarrow A$, $N \rightarrow B$, and $N \rightarrow V$ transitions is the magnitude of the polarity in the $>C=O$ bond. Obviously, as the $>\overset{\delta+}{C}=\overset{\delta-}{O}$ bond polarity increases there will be increasing repulsion between the electrons of the bond and the non-bonding oxygen electrons, *i.e.*, both the lone-pair and the bonding electrons will become more weakly bound. This means that all three transitions, $N \rightarrow A$, $N \rightarrow B$, and $N \rightarrow V$, move to longer wave-lengths (it being assumed, as is reasonable, that the outlying upper orbital is less subject to the repulsion). Reversing the argument, by studying one of these transitions in simple molecules we can arrange the molecules in an order of ascending carbonyl polarity.[35]

By arranging carbonyl molecules in order of decreasing lone-pair orbital ionisation potential we have another way of establishing a broad order of carbonyl-bond polarity. This has been attempted for a fairly extensive list of molecules.[35, 36] A particularly interesting point is the way in which CO_2 fits into this list as a carbonyl molecule of very low bond polarity. The very low bond polarity is not surprising, for the linearity of the molecule means we must regard its C atom as in a similar valency condition to those of acetylene [37, 38] and the strong electron-attracting powers of an acetylenic C atom are indicated by the tendency of acetylene to act like an acid or by the high dissociation constant of $CH{:}C{\cdot}CO_2H$ relative to $CH_2{:}CH{\cdot}CO_2H$. The competition of two oxygen atoms for the electrons of one carbon atom in CO_2 must also reduce the bond polarities.

The continuity of CO_2 with carbonyl compounds in the usual sense, however, is at first sight surprising, in view of the molecular orbital picture given above. Yet the continuity seems to be the experimental fact. Apart from the bond properties (length, energy and force constant) of CO_2 fitting very well with those expected for a carbonyl bond of the polarity indicated by its ionisation potential, the term values (*i.e.*, the energy differences ot the electronic states from the ionisation limit) are closely similar to those for formaldehyde, acetone, etc. (see table in ref. [39]). This must mean that the electron being excited in all these molecules has closely similar characteristics. In formaldehyde and acetone it is accepted to be one of a $p\pi$ lone pair on the O atom, with a C=O double bond as neighbour. Hence CO_2 must presumably contain a lone pair with such a bond as a neighbour.

This can be understood at once if we say CO_2 is well represented by the valence-bond picture O=C=O. It is not so obvious if we adopt the molecular orbital picture of p. 86. The two pictures are not so different, however, as appears at first sight [cf. ref. (40)]. Thus, on the valence-bond picture, the π orbital localised in one C–O distance is at 90° to the π orbital localised in the

---

[35] A. D. Walsh, *Trans. Faraday Soc.*, 1947, **43,** 158.
[36] *Idem, ibid.*, 1946, **42,** 56.
[37] *Idem, J. Amer. Chem. Soc.*, 1946, **68,** 2408.
[38] *Idem,* Faraday Society Symposium, " The Labile Molecule ", September, 1947.

other: but each π bond has a $p\pi$ lone pair, of axis in the same plane, on the O atom not actually concerned in that π bond. Now it is a general rule [41] that such a situation means repulsion between the π electrons and those in the parallel lone-pair orbital. Repulsion in both planes is thus involved. The weakly anti-bonding orbitals of the molecular orbital picture are the analogue of the repulsion in the valence-bond picture. Moreover, the anti-bonding electrons of the former are largely localised round the O atoms—they are " lone-pair " electrons although they have a probability of being found on either of the O atoms. Still again, each of the two bonding π orbitals in the molecular-orbital picture has two electrons giving bonding in each of the two bonds, *i.e.*, they can be regarded as two half bonds in each C–O distance. Each CO bond is thus a double bond—one σ and two half π bonds, with weak repulsion superimposed. This is just the picture on the valence-bond model.

Nevertheless, on the above molecular-orbital picture, it *is* rather surprising that CO_2 should fit so well into the carbonyl series. If the molecular-orbital picture has to be modified it will almost certainly be because of neglect of repulsion between the electrons in the different orbitals. There must be repulsion between the electrons in the two perpendicular π orbitals, for instance. It may be that this is sufficiently great to cause the wave forms of p. 86 to be modified to localised orbitals and reconciled with the valence-bond model. In particular, it is more than probable that the anti-bonding π orbitals should be modified to atomic orbitals localised round a particular O atom.[40] Mulliken has pointed out that the peculiarities of the mathematical formulation of these orbitals make this change less important than it appears at first sight.[40]

The compilation of an order of carbonyl-bond polarity revealed some significant correlations. As the bond polarity increased, so the bond-stretching force constant and the bond energy decreased, while the bond length increased. The total variation in these quantities is large and the bond polarity appears the most important parameter determining them, though other factors no doubt play a part also.

Carbon monoxide also fits the carbonyl series arranged in order of bond polarity.[39] It comes right at the top of the series, *i.e.*, on the basis of its ionisation-potential at 14·55 v. it has almost zero bond polarity. This agrees with the very low observed dipole moment. Its properties are just about those we should expect for an almost non-polar carbonyl bond; and the term values of the Rydberg transitions leading to the 14·55 v. ionisation potential are closely similar to those for CO_2, $H\cdot CHO$, $CH_3\cdot CHO$, etc. Carbon monoxide therefore appears to have a carbonyl double bond with a lone pair of oxygen electrons, rather than the triple-bond structure that has often been suggested. A clue to the structure is probably to be found in the fact that as the carbonyl-bond polarity decreases so the bond strengthens. Carbon monoxide therefore naturally adjusts itself to have as low a dipole moment as possible. This it can do by virtue of the flexibility of C atom

---

[39] L. H. Long and A. D. Walsh, *Trans. Faraday Soc.*, 1947, **43**, 342.
[40] R. S. Mulliken, *J. Chem. Physics*, 1935, **3**, 720.

valencies that comes from the possibility of various degrees of hybridisation of 2*s* and 2*p* atomic orbitals.[38] Probably the C atom is near the acetylenic condition. It has a lone pair in a hybrid orbital, it forms a σ C–O bond with an electron in the other hybrid orbital, and it forms a π C–O bond with an electron in a pure 2*p* orbital. It does not seem unreasonable that the oxygen lone-pair electrons prefer to remain largely in an O 2*p* orbital rather than to occupy to any great extent the C 2*p* orbital. The low polarity is due partly to the hybrid C orbital having a high electronegativity and partly to this being so tightly bound that it permits the C to hold its *p* orbitals more tightly, as explained before (p. 79). The low dipole moment, high bond energy, low bond length, and high stretching-force constant may thus all be naturally connected.

The *reasons* for the weakening of carbonyl bonds with increasing polarity have been discussed elsewhere.[41] The polarity weakening may be traced in many other classes of bonds,[42] though it is often overlaid by other effects.

Ionisation Potential Data in General

The ionisation potentials of lone-pair electrons are much the most extensively known. Such electrons may be referred to as " atomic " rather than " molecular ". Their transitions frequently appear line-like in type, enabling precise measurement and comparatively easy fit into Rydberg series. In contrast, excitation of strongly bonding (*e.g.*, σ) electrons inevitably tends to cause dissociation with consequent diffuseness of absorption. Many ionisation potentials of non-bonding orbitals are thus known with precision, a smaller number known for weakly bonding (*e.g.*, π) orbitals, and comparatively few known for strongly bonding orbitals ; [43] the values in the last case coming usually from electron-impact, rather than spectroscopic work.

The advent of this new body of knowledge about electrons in molecules, being both extensive and precise, should have an important relevance for many aspects of molecular structure theory. Some beginnings in applying the data to chemical problems have been reviewed elsewhere.[44] Applications to spectroscopic problems will be found scattered through the papers by R. S. Mulliken.

[41] A. D. Walsh, *J.*, in the press.

[42] *Idem, Trans. Faraday Soc.*, 1947, **43**, 60.

[43] For a list of ionisation potentials so far determined, see T. M. Sugden, A. D. Walsh, and W. C. Price, *Nature*, 1941, **148**, 372 ; W. C. Price, *Chem. Reviews*, 1947, **41**, 257.

[44] A. D. Walsh, Victor Henri Memorial Vol., Desoer, Liége, in the press ; see also A. D. Walsh, *Ann. Reports*, 1947, in process of publication.