549. *Excited States of Acetylene. Part I. Possibilities of Interaction between σ-Bond Hybridisation and π-Electron Excitation with Resulting Changes of Shape during Transitions.*

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In π-electron excitations of unsaturated molecules, the lowest orbitals available to receive the promoted electron, supposing the σ-bond structure to remain unaltered, may interpenetrate so strongly with occupied σ-orbitals neighbouring the centre of unsaturation, that energetically lower promotions can be realised at the cost of a changed σ-bond hybridisation. The result is a gross change of shape on excitation, as is illustrated by a preliminary consideration of the case of acetylene. An unappreciated prevalence of such changes may be the reason why so few upper states of polyatomic molecules have as yet been characterised.

THE study of lower excited states, and thus of potentialities for electronic deformation in normal states, of those molecules which are parent forms of the distinctive units of unsaturation in organic chemistry, should logically be taken in the order, ethylene, acetylene, benzene, to deal first with the range of cases in which the only unsaturated element is carbon. However, the reverse order of attack on these three molecules has been found the more practical, because it is the order of increasing difficulty, and thus better permits the necessary process of self-education.

Before the present, already briefly reported, study of acetylene (*Nature*, 1952, **169**, 1101), the only fully established assignment of a near-ultra-violet transition of any molecule of more than two atoms to a well-characterised upper electronic state was that of the B_{2u}–A_{1g} transition of benzene. It happens that for benzene the excited (B_{2u}) state is of exactly the same shape and very nearly the same size as the normal (A_{1g}) state. Perhaps this has been a historical disadvantage: for one of the reasons why only one electronic band-system of a polyatomic molecule has yet been successfully analysed—only one upper state characterised—may be that analysis has too often been attempted under the preconception that the upper state would be something like the lower in form: the Franck–Condon principle has been interpreted as implying that major changes of shape on excitation are unlikely. On the other hand, Mulliken suggested that an upper state of a simple molecule may differ in form from the lower, when he pointed out that the near-ultra-violet band-system of carbon disulphide is too complicated to represent a transition from a linear ground state to a linear upper state. He worked out the band-structures that could result from the excitation of a linear triatomic molecule to a bent upper state; but the actual upper state involved in the carbon disulphide transition was not elucidated (*Phys. Review*, 1941, **59**, 873; **60**, 506).

The need for keeping in view the possibility of a gross change of form, essentially a change of σ-orbital hybridisation, when one is attacking the analysis of a near-ultra-violet band-system of a π-electron molecule such as acetylene, is indicated by the following elementary considerations—these impressed themselves on us during our study of data herewith presented, but (as one of us discovered in a conversation in Dunedin in August 1952) were independently evolved in purely theoretical work by Dr. F. A. Johnson, who up to that moment had known nothing of this investigation.

The normal acetylene molecule is linear ($D_{\infty h}$ in the notation of symmetry theory), and its highest occupied orbitals are those of the unsaturation shell, that is, the two equivalent bonding orbitals π_u, one of which is schematically represented in Fig. 1 at (*A*). Supposing that the molecule retains its linear shape on excitation, the lowest unoccupied orbital into which an electron from a π_u orbital could be lifted is that obtained by introducing a central nodal surface normal to the internuclear line, the antibonding π_g orbital, represented in Fig. 1 at (*B*). There must be much steric repulsion between any electron occupying this orbital and the electrons of the C–H bonds. An even worse position would arise, if we should try to promote a π_u electron to the antibonding σ_u orbital, which also has a nodal plane across the middle of the molecule, but is concentrated about the molecular axis, mainly outside the C–C span, with the result that an occupying electron would be very strongly interpenetrated with the C–H-bond electrons. Faced with these more or less difficult alternatives, the molecule might well find it more energetically economical so to alter its σ-bond hybridisation that orbitals for the reception of the excited electron are made available which lie considerably further out of the way of the C–H bonds.

It is clearly possible that the linear (sp) hybridisation, which determines the σ-bond framework of the normal acetylene molecule, might change in the direction of plane-trigonal (sp^2) hybridisation, so that bond angles become reduced from 180° towards 120°. The simplest form which such an occurrence could take is that in which the change of hybridisation $sp \longrightarrow sp^2$ is complete, so that the excited acetylene molecule assumes the shape of a normal ethylene molecule from which two hydrogen atoms have been removed: they might be two *trans*- or two *cis*-related hydrogen atoms. In place of each removed hydrogen atom we shall have, in first approximation, a plane-trigonal atomic orbital capable of holding up to two unshared electrons. This is schematically represented in Fig. 1 at (C) and (D), the diagrams illustrating what we may call the *trans*- and *cis*-bent molecules of excited acetylene (in symmetry notation, the C_{2h} and C_{2v} models respectively).

FIG. 1. *Schematic representation of orbitals which may lose or gain an electron in transitions between the normal molecule of acetylene and various possible models of the excited molecule.*

Linear ground state: a bonding π_u orbital. Linear excited state: antibonding π_g orbital.

trans-Bent excited state: sp^2 atomic orbitals constituting nearly non-bonding molecular orbitals. *cis*-Bent excited state: sp^2 atomic orbitals constituting nearly non-bonding molecular orbitals.

For either model, in this first approximation, the two sp^2 atomic orbitals are collectively equivalent to two non-bonding molecular orbitals of identical energy: those of the C_{2h} model will be labelled a_g and b_u, and those of the C_{2v} model a_1 and b_1. The energies of these non-bonding orbitals are expected to lie between that of the bonding π_u orbital and that of the antibonding π_g orbital of the linear molecule. Thus, provided that the σ-bonding is not too much weakened by the hybridisation change, the production of these a and b orbitals of bent states should allow an excitation of lower energy than would the π_g orbital of the normal state of acetylene.

In closer approximation, the sp^2 atomic orbitals must be expected to interact slightly, so that electrons entering them will not be wholly unshared, and the generated molecular orbitals will neither be completely non-bonding nor accurately degenerate. In the C_{2h} model, the orbital we label b_u will be slightly bonding, and the orbital a_g slightly anti-bonding. In the C_{2v} model, orbital a_1 will be weakly bonding and b_1 weakly antibonding.

Such refinements will concern us later; but for the present the broad energetic distinction between the approximately non-bonding orbitals of the bent models, and the strongly bonding and anti-bonding orbitals of the linear model, will justify taking bent states into account as possibilities, when attacking the analysis of near-ultra-violet band-systems of triple-bonded molecules such as acetylene. In our problem we shall take them into account in the broadest way, without preconception as to the quantitative magnitude of any hybridisation change, which has, indeed, to be determined by the analysis. Our subsequent references to the *trans*- and *cis*-bent (or C_{2h} and C_{2v}) models will imply nothing about bond angles, except that they are equal * and less than 180°.

The above discussion restricts attention to planar models of excited acetylene. One can, of course, imagine also three-dimensional models of the excited molecule, *e.g.*, models of symmetry C_2, in which the two bond angles lie in different planes, much as in the usually considered model of the normal state of hydrogen peroxide. However, elementary structural theory does not suggest that models of this character would be represented among the lower excited states of acetylene; and it is only with the lowest excited state that we shall be concerned. In order to produce the above planar models, one π orbital of the normal molecule has to be destroyed: to make a three-dimensional model both π orbitals must become disrupted. Moreover, the hybridisation change needed to produce the three-dimensional molecule must be more drastic than from sp to sp^2; it would have to extend towards sp^3 at least, if not towards p. A preliminary recognition of the improbability of finding a three-dimensional state among the lowest excited states of acetylene is useful, because we have to develop the theory of electronic transitions between models of different shapes sufficiently to provide an adequate basis for the analytical problem undertaken, but, because of the complicated nature of such theory, we do not want to generalise it more than necessary. Therefore, we have approached our problem on the basis of the limited assumption that the relevant excited state, if not linear, will at least be planar : this optimism proved to be justified.

Proceeding from these considerations, we shall next deal with the experimental and the theoretical tools used, and then we shall describe and interpret the first ultra-violet band-system of acetylene, drawing conclusions about the geometrical and dynamical characteristics, and about the electronic constitution, of the excited state of the molecule. For a preliminary indication of these conclusions the Summary of Part IV (p. 2725) may be consulted.

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[*Received, March 23rd*, 1953.]