475. *The Electronic Orbitals, Shapes, and Spectra of Polyatomic Molecules. Part X.* A Note on the Spectrum of Benzene.*

By A. D. Walsh.

The reasons are discussed for the appearance of numerous non-totally symmetrical vibration frequencies in the near-ultra-violet spectrum of benzene. On the basis of conclusions reached in Part IX * and on the assumption that changes of restoring forces in the first excited states of benzene relatively to the ground state are similar to those in the first excited state of ethylene relatively to its ground state, a large number of such vibrational modes might be expected in the benzene spectrum.

There has been much study of the first singlet–singlet absorption and fluorescence transitions of benzene (see, especially, Garforth, Ingold, and Poole, *J.*, 1948, 406). As a result, the vibrational structure is now well-established and it is generally accepted that (*a*) the transition is an electronically forbidden one, (*b*) the upper state is either ${}^1B_{2u}$ or ${}^1B_{1u}$, (*c*) the transition is made allowed by an e_g^+ vibration. There has also been a vibrational analysis of the first triplet→singlet emission spectrum (Shull, *J. Chem. Phys.*, 1949, **17**, 295). The upper state in this emission is either ${}^3B_{1u}$ or ${}^3B_{2u}$. In these spectra progressions occur in the totally symmetrical, breathing, vibration of the hexagon. The occurrence of these progressions is explained as due to an expansion of the hexagon in the upper state (Garforth, Ingold, and Poole, *J.*, 1948, 508; Craig, *J.*, 1950, 2146). Numerous other vibrations appear in the spectra; but hitherto there appears to have been no attempt to explain *why* they appear. The fact that one of them (*e.g.*, an e_g^+ vibration for the singlet–singlet transition) enables the electronically forbidden transition to appear is of course no explanation of why it appears.

The fundamental reason for the appearence of these vibrations must be that they occur in response to a change in restoring forces consequent upon the electronic excitation. Alternatively, they may be supposed to occur in response to a change of geometry in the equilibrium form of the upper state relatively to the ground state; but if this viewpoint is adopted then the departure from D_{6h} symmetry in the upper state must be supposed sufficiently small for classification of the levels according to the symmetry operations appropriate to the D_{6h} class to retain its importance.† The situation is very like that in the near-ultra-violet absorption of formaldehyde (Part VI, *J.*, 1953, 2306) where the conclusion was reached that the upper state had a shape sufficiently different from that of the ground state to cause the appearance of certain vibrations, but sufficiently close to C_{2v} symmetry for formulations in terms of symbols appropriate to the latter symmetry to remain important.

In Part IX we concluded that, in the first excited state of the C_2H_4 molecule, (i) the C–C bond should be lengthened, (ii) the $-C\!<$ groups should be twisted relatively to each other, (iii) each C atom should probably move out of the mirror plane bisecting the HCH angle of the other CH_2 group, and (iv) the arrangement of the three bonds about each C atom should become pyramidal; and probably (v) the CH bonds should lengthen and (vi) the angles between the three bonds attached to either C atom should not remain equal. Conclusion (iii) may be thought of as a tendency of the $-C\!<$ groups to rotate about axes perpendicular to their planes. The fundamental hypothesis of the present paper is that tendencies to change of length and arrangement of the bonds about any C atom should be present in the first excited states of benzene similar to those in the first excited state of ethylene. The excited orbital in the ${}^{3,1}B_{1u}$, the ${}^{3,1}B_{2u}$, and the ${}^1E_u^-$ states mentioned here is similar in certain respects to that of the first excited state of ethylene.

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* Part IX, preceding paper.

† Change of shape of the benzene molecule on excitation should be much less than the change of shape of the ethylene molecule on similar excitation because (*a*) in benzene only one "π"-electron out of six is excited compared with one of two for ethylene and (*b*) the ring form of the benzene molecule restricts, *e.g.*, twisting of the bonds.

The vibration forms of the benzene molecule are conveniently given by Bailey, Ingold, Poole, and Wilson (*J.*, 1946, 231). Because of (i), we expect the a_{1g}(C) vibration to appear. Because of (v), we expect the a_{1g}(H) vibrations to appear. By making a model in which the arrangement of bonds about any C atom is pyramidal and applying twists to the various C–C links, it is possible to achieve forms which would be reached during the a_{2u}, b_{2g}(C), b_{2g}(H), e_u^+(C), e_u^+(H), and e_g^- vibrations. In other words, because of (ii) and (iv), we expect each of the out-of-plane deformation vibrations of the benzene molecule possibly to appear. Because of (iii), (v), and (vi), we expect in-plane deformation vibrations to appear, *e.g.*, the four e_g^+ modes.

A large number of the possible vibrations of the benzene molecule may therefore appear. This is in accord with the analyses of the spectra that have been carried out. In the first singlet–singlet absorption, for example, the following vibrations have all been identified (Garforth and Ingold, *J.*, 1948, 420): a_{1g}(C), a_{1g}(H), a_{2u}(H), b_{2g}(C), b_{2g}(H), e_g^+(C1), e_g^+(C2), e_g^+(H1), e_u^+(C), e_u^+(H), and e_g^-(H). The e_g^+(H2) vibration appears in the triplet–singlet emission. Which of these vibrations will be particularly prominent or what changes in quantum number may occur for a particular vibration will of course be determined largely by the symmetry of the upper level. Thus at least one e_g^+ vibration is expected to be prominent for a ${}^{e1}B_{1u}$ or ${}^{e1}B_{2u}$ upper state in order that the transition may perturb the nearest electronically allowed transition (${}^1E_u^- \longleftarrow {}^1A_{1g}$); and at least one e_g^+, b_{2g}, or e_g^- vibration is expected to be prominent for a ${}^{e3}B_{1u}$ or ${}^{e3}B_{2u}$ upper state for a similar reason (see Craig, *J. Chem. Phys.*, 1950, **18**, 236). The prominence or otherwise of particular vibrations will also be affected by the exact geometry of the upper state and by the Boltzmann factors for bands originating from vibrating ground states; all the present paper does is to point out that the occurrence of so many vibrational modes is to be expected from the conclusions concerning the shapes of excited molecules reached in earlier papers of this series.

The argument may be reversed: the appearance of all the above vibrations may be taken as evidence for the conclusions of Part IX concerning the changes of shape or the restoring forces controlling the length and arrangement of the bonds about each C atom, in the first excited state of the C_2H_4 molecule relatively to its ground state.

Finally, it is interesting to trace the fundamental reasons for the occurrence of, *e.g.*, the e_g^+ and b_{2g} vibrations. The former occurs for essentially the same reason as the ν_6e vibration occurs in the spectrum of methyl iodide or the ν_5b_2 vibration probably occurs in the spectrum of formaldehyde. This reason can be traced back first to the expectation that a $=\mathrm{C}<$ group or a $-\mathrm{C}\leqq$ group will resemble in certain respects an $\mathrm{O}=\mathrm{C}=$ or $\mathrm{N}\equiv\mathrm{C}-$ group respectively; then to the expectation that the CO_2 and the HCN molecule are bent in their first excited states; next to the expectation that a 4-electron AH_2 molecule is linear but a 5-electron AH_2 molecule bent; and in the last resort to the linkage of the shape of such a molecule with hybridization of the valencies of the central atom and the linkage of valency hybridization with bond strengths and the total potential energy of the molecule. The b_{2g} vibration occurs for essentially the same reason as the $\nu_2a_1$vibration occurs in the spectrum of methyl iodide or the ν_6b_1 vibration in the spectrum of formaldehyde; this reason can also be traced back through the successive papers of this series to the properties of the a_1s–π_u and a_1–σ_g, b_2–σ_u orbitals described in Part I. Put in another way, the fundamental reason for occurrence of these vibrations lies in the need of a molecule to form the strongest possible bonds and yet to keep its *total* potential energy as low as possible. Because of the interactions between electrons these two needs often oppose one another. These considerations should make it clear that attempts to understand the benzene spectrum on the basis of changes in an isolated set of six "π"-electrons are inadequate; one has to consider interactions of all the electrons in the molecule.

LEEDS UNIVERSITY.

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