468. *The Electronic Orbitals, Shapes, and Spectra of Polyatomic Molecules. Part III.** HAB *and* HAAH *Molecules.*

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The electronic orbitals possible for bent and linear HAB and HAAH molecules are correlated. Whether or not a given orbital becomes more or less weakly bound as the molecule is changed from the bent to the linear form is discussed. The results are used to interpret the shapes and spectra of HAB and HAAH molecules and radicals. HAB molecules containing 10 or less valency electrons should be linear in their ground states. Molecules with 10—14 electrons should be bent in their ground states. 16-Electron HAB molecules should be linear again.

HAAH molecules containing 10 valency electrons should be linear in their ground states. Those containing 12 electrons should be bent but planar (*cis-* and *trans*-forms). Those containing 14 electrons should be bent and non-planar. The spectra of the isoelectronic molecules HCN and C_2H_2 are particularly discussed; the first excited state of each should be non-linear.

Orbitals of HAB *Molecules.*—The lowest-energy orbitals of a linear HAB molecule may be approximately described as follows, on the assumption that they are built solely from *s* and *p* atomic orbitals: (i) An *s* orbital on B. It is assumed that this plays no direct part in the binding of A to B and remains largely unchanged whatever the HAB angle. (ii) A σ orbital binding the H and the A atom. It is built from an H 1*s* and an A *sp* hybrid valency. (iii) A σ orbital binding the B and the A atom. It is assumed to be built from an A *sp* hybrid valency and a B pure *p* valency. (iv) A π orbital binding the B and the A atom. It is built by the in-phase overlap of *p* orbitals on A and B. It is two-fold degenerate; and, since in many HAB molecules B is of greater electronegativity

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* Part II, preceding paper.

than A, it is usually more localized on B than on A. (v) A $\bar{\pi}$ orbital that is anti-bonding between A and B. It is built by the out-of-phase overlap of p orbitals in A and B. It is two-fold degenerate and, by the arguments of Part II, usually more localized on A than on B. (vi) A σ orbital built by the out-of-phase overlap of an orbital on A with a B $p\sigma$ and the H 1s valency. It will usually be more localized on A than on B or H. It is analogous to the $\bar{\sigma}_g$ orbital described in Part II and therefore is assumed to be built from an s orbital of A.

The lowest-energy orbitals of a bent HAB molecule, in addition to the s lone-pair orbital on B, can be approximately described as follows: (i) An a' orbital binding the H and the A atom. When the HAB angle is 90°, the orbital is built from an H 1s and an A pure p valency. (ii) An a' orbital binding the A and the B atom. In the 90° molecule, it is built by the in-phase overlap of pure p valencies on A and B, pointed towards each other. In Fig. 1 the orbitals of the bent and the linear HAB molecules are correlated. Clearly, the two bonding a' orbitals must become the two σ orbitals; and, as explained in Parts I and II, the a'–σ curves must fall from left to right. (iii) An a'' orbital binding the A and the B atom and built by the in-phase overlap of a p orbital on A and a p orbital on B, the axes of these p orbitals being perpendicular to the molecular plane. Clearly, this orbital must become one of the bonding π orbitals in the linear molecule. There is no reason why it should change appreciably in binding energy as the HAB angle changes. It is therefore represented in Fig. 1 by a horizontal straight line. (iv) An a'' orbital that is built by the out-of-phase overlap of p orbitals on A and B, their axes being perpendicular to the molecular plane. It is anti-bonding between A and B, and becomes one of the anti-bonding $\bar{\pi}$ orbitals in the linear molecule. Like the other a'' orbital, there is no reason why its binding energy should change appreciably as the HAB angle changes. It is therefore represented in Fig. 1 by a horizontal straight line. (v) An $\bar{a}'$ orbital analogous to the $\bar{a}_1{}'$ orbital of Part II. By analogy with the latter, when the HAB angle is 90°, the orbital is built from a pure p_z orbital on A overlapping out-of-phase with a B pa' and the H 1s valency. The z-axis lies in the plane of the molecule and bisects the HAB angle. The orbital is usually predominantly localized on A. As the apex angle increases, the orbital tends towards the $\bar{\sigma}$ orbital of the linear molecule. Since it is largely a p orbital of A in the 90° molecule, but an s orbital of A in the linear molecule, it is represented in Fig. 1 by a line that falls steeply from left to right. (vi) An orbital which in the 90° molecule is a pure s lone pair orbital on A. It is of species a', here written $a's_A$. As the HAB angle changes towards 180° the orbital becomes increasingly built from a p orbital of A whose axis lies in the molecular plane. It is therefore represented in Fig. 1 by a line that rises steeply from left to right. Being localized largely on A, it tends to become one of the $\bar{\pi}$ (rather than one of the π) orbitals of the linear molecule. As the HAB angle approaches 180° it becomes, to some extent, A$\longleftrightarrow$B anti-bonding. If the $\bar{\sigma}$ lies slightly lower than the $\bar{\pi}$ orbital, the $a's_A$ orbital curve will actually lead to the $\bar{\sigma}$ rather than to the $\bar{\pi}$ orbital. There is every expectation, however, that this is not so and that $\bar{\sigma}$ lies above $\bar{\pi}$. In the diatomic molecules isoelectronic with HAB molecules (*e.g.*, N_2 isoelectronic with HCN) the analogous $\bar{\sigma}$ orbital certainly lies above the analogous $\bar{\pi}$ orbital. Moreover, analysis (see below) of the spectrum of C_2H_2 (also isoelectronic with HCN) fits well with the assumption that $\bar{\pi}$ lies below $\bar{\sigma}$. For these reasons and also on grounds of simplicity Fig. 1 is drawn with $\bar{\sigma}$ above $\bar{\pi}$. (vii) An a' orbital which in the 90° molecule is a nearly pure p orbital on B whose axis lies in the molecular plane but perpendicular to the A–B line. It probably has a sufficiently different binding energy from the $a's_A$ orbital (or to the two bonding a' orbitals) for little interaction to occur. As the HAB angle increases towards 180°, this a' orbital interacts more and more with the orbital which at 90° is $a's_A$ because the latter becomes increasingly built from a p orbital of A. This interaction increases the binding energy of the present a' orbital. In other words, the present a' orbital becomes increasingly A$\longleftrightarrow$B bonding as the apex angle increases and is represented in Fig. 1 by a line that descends from left to right. At 180° the orbital becomes one of the bonding π orbitals.

Fig. 1 shows the eight lowest-lying intra-valency-shell orbitals. A ninth, highest, is also possible but is not needed for the purposes of this paper; see also the comments on this point in Part I.

Shapes of HAB *Molecules.*—The lowest five orbital curves in Fig. 1 either fall from left to right or are horizontal. One therefore expects that HAB molecules containing 10 or less valency electrons will be linear in their ground states. HCN, containing 10 valency electrons, is an example. The hypothetical molecules HBO and HBeF should also be linear. The HCO radical, however, containing 11 valency electrons, has to have one electron in the $a's_A$–$\bar{\pi}$ orbital. By analogy with NO_2 (see Part II), the radical should therefore possess an apex angle in its ground state appreciably less than 180°. A spectrum has been attributed to HCO which we discuss below in relation to the shape of the radical. The 12-electron radical HON or HNO (which has been postulated as an intermediate in the photochemical decomposition of nitrites; see, *e.g.*, Thompson and Dainton, *Trans. Faraday Soc.*, 1937, **33**, 1546) must in its ground state have two electrons in the $a's_A$–$\bar{\pi}$ orbital. It should therefore possess a ground-state apex angle appreciably less than that for HCO. The HO_2 radical, with 13 valency electrons, should also be non-linear with an apex angle in the ground state not much less than that of HNO. Of 14-electron molecules, HOCl and HOBr are almost certainly bent molecules in the ground state, in accord with expectations from Fig. 1.

FIG. 1.

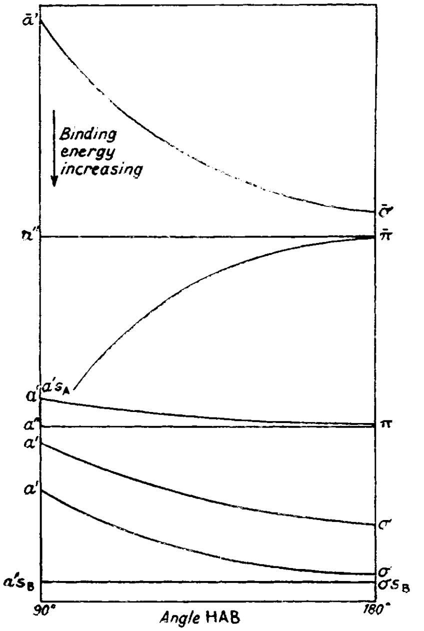
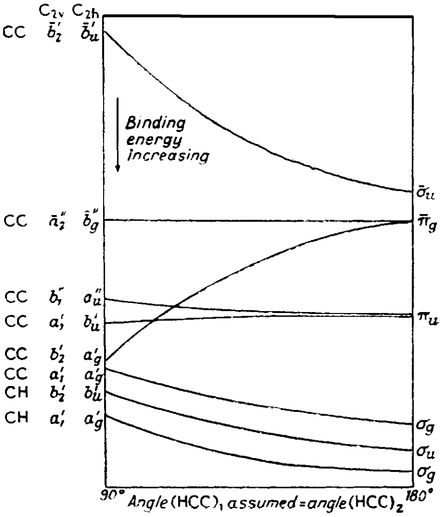


FIG. 2.



The first excited state of HCN should be bent, just as should be the first excited state of ClCN or CO_2 (Part II). The low-lying excited state of HCO in which the outermost electron lies in the a''–$\bar{\pi}$ or $\bar{a}'$–$\bar{\sigma}$ orbital rather than in the $a's_A$–$\bar{\pi}$ orbital should have an equilibrium form that is linear.

The ground states of 16-electron molecules should be linear once again. The molecule $(HFF)^-$ would thus be expected to be linear. Although the shape of this particular ion is not known, it is of interest that the shape of the isoelectronic ion $(FHF)^-$ is almost certainly linear and symmetrical (Westrum and Pitzer, *J. Amer. Chem. Soc.*, 1949, **71**, 1940).

Reactivity of HAB *Molecules.*—The reactivity of HAB molecules or radicals may be discussed along lines similar to those used in Part II. The HCO radical in its ground state, for example, should have its odd electron largely localized on the C atom. The first excited state of the HCN molecule should have an odd electron largely localized on the C atom and another largely localized on the N atom.

Spectra of HAB *Molecules.*—(1) *Spectrum of* HCN. If triplet $\longleftarrow$ singlet changes are neglected, the longest-wave-length absorption regions of HCN, if the upper state remains linear, should be due to the transitions

$$\cdots (\pi)^3(\pi),\ {}^1\Delta \longleftarrow \cdots (\pi)^4,\ {}^1\Sigma^+ \quad \ldots\ldots \quad (1)$$

$$\cdots (\pi)^3(\bar{\pi}),\ {}^1\Sigma^- \longleftarrow \cdots (\pi)^4,\ {}^1\Sigma^+ \quad \ldots\ldots \quad (2)$$

$$\cdots (\pi)^3(\bar{\pi}),\ {}^1\Sigma^+ \longleftarrow \cdots (\pi)^4,\ {}^1\Sigma^+ \quad \ldots\ldots \quad (3)$$

Transitions (1) and (2) are electronically forbidden, but (3) is allowed. Transition (1) is two-fold degenerate. In fact, one can see from Fig. 1 that two of the transitions should lead to strongly bent upper states and two to linear upper states; and further that it is the two transitions that lie lowest in energy that should lead to the bent upper states. These two will be

$$\cdots (a'')^2(a')(a'),\ {}^1A' \longleftarrow \cdots (\pi)^4,\ {}^1\Sigma^+ \quad \ldots\ldots \quad (4)$$

and

$$\cdots (a'')(a')^2(a'),\ {}^1A'' \longleftarrow \cdots (\pi)^4,\ {}^1\Sigma^+ \quad \ldots\ldots \quad (5)$$

Since, by analogy with atoms and diatomic molecules, ${}^1\Delta$ may be expected to lie lower than ${}^1\Sigma^-$ and ${}^1\Sigma^+$, one may suggest that (4) and (5) correlate with the degenerate transition (1). Transitions (4) and (5) are electronically allowed, though likely to be weak because of the Franck–Condon principle and because of their relation to (1). Transition (2) is likely to be so weak as not to be observed. Transition (3), being of the $V \longleftarrow N$ class, is expected to be intense. All four transitions should lead to a marked increase of C–N length. Transitions (4) and (5) should thus lead to the appearance of both the bending and C–N stretching vibrations in the upper state; transition (3) should lead to the appearance only of the C–N stretching vibration. The magnitude of the stretching frequency should be considerably reduced relatively to that of the ground state. Let us now compare these expectations with the observed spectrum.

The absorption system of longest wave-length lies between 2000 and 1789 Å (Hilgendorff, *Z. Physik*, 1935, **95**, 781). It is weak and consists of bands with a mean separation of 450 cm.$^{-1}$. It has not yet been properly analysed, but may be attributed to (4) and/or (5). 450 cm.$^{-1}$ may represent the bending frequency (712 cm.$^{-1}$ in the ground state) in the upper state, but the C–N stretching frequency ought to be present also. The second absorption system is much stronger. It begins around 1500 Å and extends to at least 1350 Å (Price, *Phys. Review*, 1934, **46**, 259; Price and Walsh, *Trans. Faraday Soc.*, 1945, **41**, 381). At the long-wave-length end it consists of quite sharp bands which are single-headed and shaded towards the red. The bands steadily increase in intensity up to the shortest-wave-length band at *ca.* 1360 Å. Price reported that the main bands were reproduced very well by the formula

$$\nu = 68{,}645 + 901(v' + \tfrac{1}{2}) - 22(v' + \tfrac{1}{2})^2\ {*}$$

The intensity of the 1500—1350-Å system (a little weaker than the Rydberg bands at shorter wave-lengths) makes it practically certain that it is to be identified as transition (3). The facts that only one vibration frequency appears strongly in the system, that the bands are red-degraded and that there is a slow rise to maximum intensity accord with our expectations for transition (3). The single-headed nature of the bands is also in accord with the expectations for (3), since the bands of (3) should possess no *Q*-branch. Clearly the frequency 901 cm.$^{-1}$ is to be identified as the C–N stretching vibration in the upper state. This vibration has a frequency of 2089 cm.$^{-1}$ in the ground state. The reduction is very great, but proportionately no greater than that known to occur for similar $(\bar{\pi}) \longleftarrow (\pi)$ jumps in, *e.g.*, the N_2 and the O_2 molecule. ω_e for the O_2 molecule drops from 1580 to 700 cm.$^{-1}$ in passing from the $X^3\Sigma_g^-$ to the $B^3\Sigma_u^-$ state. To interpret the 901-cm.$^{-1}$ frequency as the bending vibration ν_2 increased from the value of 712 cm.$^{-1}$ in the ground state would be difficult in view of the fact that only one frequency is strongly involved in the observed absorption—for whether a low-lying upper state is bent or not, it is expected to involve a strongly C$\longleftrightarrow$N anti-bonding orbital; so that while ν_1' might

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* The origin, however, lies at longer wave-lengths than 1457 Å (68,645 cm.$^{-1}$). The bands can be followed to *ca.* 1500 Å (see photograph by Price and Walsh, *loc. cit.*).

occur alone, ν_2' is expected to occur only in association with ν_1'. Observation and theory agree in assigning a linear upper state to the 1500—1350-Å system.

(2) *Spectrum of* HCO. The longest-wave-length absorption of the HCO radical should be due to one of the transitions

$$\cdots (a''),\ {}^2A'' \longleftarrow \cdots (a'),\ {}^2A' \qquad . \ . \ . \ . \ . \ . \ . \quad (6)$$

$$\cdots (a')(a')^2,\ {}^2A' \longleftarrow \cdots (a')^2(a'),\ {}^2A' \qquad . \ . \ . \ . \ . \quad (7)$$

Both are allowed transitions, (6) with polarization perpendicular to the molecular plane, (7) with polarization in the molecular plane. Transition (6) should cause an increase in apex angle (to a linear upper state), (7) a decrease. Transition (6) would be better formulated as

$$\cdots (\bar{\pi}),\ {}^2\Pi \longleftarrow \cdots (a'),\ {}^2A' \quad . \ . \ . \ . \ . \ . \ . \ . \quad (8)$$

Transition (7) should cause a particular increase of C–O distance, but (8) would probably also cause an increase. Both transitions should therefore involve both the bending and a stretching vibration.

The so-called "hydrocarbon flame bands" observed between 4100 and 2500 Å (maximum intensity between 3600 and 3000 Å) in the emission spectra of certain flames have been attributed by Vaidya (*Proc. Roy. Soc.*, 1934, *A*, **147**, 513) to the HCO radical. Dyne and Style (*Discuss. Faraday Soc.*, 1947, 159) have obtained the bands in fluorescence by exciting gaseous formaldehyde with light of wave-length in the fluorite region; this supports the identification of the emitter as HCO. The identification is not yet fully proved, but will be provisionally assumed here. Gaydon (" Spectroscopy and Combustion Theory," Chapman and Hall, London, 1948), from a study of the rotational fine structure of the band, has concluded that the emitter is linear or nearly so. The conclusion, if accepted, must be taken as referring to the equilibrium forms of both upper and lower states. Vaidya has classified the bands into two systems, *A* and *B*, which appear under slightly different experimental conditions. The bands of the *B* system are mostly separated from the strongest *A* bands by intervals of about 240 and 154 cm.$^{-1}$. Gaydon, however, doubts the reality of two separate systems, suggesting instead that the *A* and the *B* bands are different heads of the same bands. According to Gaydon, the main vibrational frequencies involved are 1072 cm.$^{-1}$ (in the upper state) and *ca.* 1960 cm.$^{-1}$ (in the lower state). On the other hand, Murphy and Schoen (*J. Chem. Phys.*, 1951, **19**, 1214) have shown that all but five of the bands reported by Vaidya may be expressed in terms of two vibrations, *i.e.*, four frequencies, two in the upper and two in the lower state. These are: $\nu_1' = 1229$ cm.$^{-1}$; $\nu_2' = 1070$ cm.$^{-1}$; $\nu_1'' = 1880$ cm.$^{-1}$; $\nu_2'' = 1538$ cm.$^{-1}$. v_1'' is found to have any value up to 9; v_2'' is always 0 or 1. Comparison of the lower-state frequencies with those of HCHO suggests that ν_1 represents the C═O valency vibration (1744 cm.$^{-1}$ in the ground state of HCHO) and ν_2 represents the CH bending vibration (1503 cm.$^{-1}$ in the ground state of HCHO). If these analyses and the ascription of the bands to HCO are confirmed, the characteristics are not incompatible with the expectations for the reverse of transition (8). The expectations for the reverse of transition (7) would also fit, except for the supposed linearity of the upper state.

Vaidya compares the bands with those of the β-system of the isoelectronic molecule NO. The β emission bands of NO lie in the same region of the spectrum as the hydrocarbon flame bands. (They also reveal closely similar vibrational frequencies, *viz.*, 1038 and 1904 cm.$^{-1}$, but if the Murphy–Schoen identification of the 1070-cm.$^{-1}$ frequency is accepted, its closeness to 1038 cm.$^{-1}$ is fortuitous.) The bands are known to represent a ${}^2\Pi \longleftrightarrow {}^2\Pi$ transition and may be interpreted as involving the jump of an electron from a $(\bar{\pi})$ to a (π) orbital. The parallel, such as it is, would fit better with assignment of the bands to the reverse of transition (7) than to the reverse of transition (8). The supposed long progressions in ν_1'' and the big reduction of ν_1' relative to ν_1'' would fit the reverse of (7) better than the reverse of (8).

The observed bands are, however, not yet proved to be due to HCO; nor is the analysis so far given yet to be accepted without reserve. If the provisional analysis or identity of the emitter should be incorrect, the present remarks will still be of value in predicting the characteristics to be expected for any long-wave-length transitions observed for the HCO radical.

(3) *Spectrum of* HO_2. Although no electronic transition has yet been attributed to HO_2, it is worth noting that the radical should possess at least one low-lying transition. This may be formulated in absorption as

$$\cdots (a')(a'')^2,\ {}^2A' \longleftarrow \cdots (a')^2(a''),\ {}^2A'' \qquad \ldots\ldots \quad (9)$$

It should be an allowed transition with polarization perpendicular to the molecular plane, and should cause an increase of apex angle.

Orbitals and Spectra of HAAH *Molecules.*—The HCN molecule is isoelectronic with C_2H_2. In order to discuss the spectrum of the latter, let us first consider the orbitals appropriate to HAAH molecules as a class. Such molecules may be linear or non-linear. If the latter, but still planar, they may be either *cis* or *trans*. *cis*-Molecules would belong to the C_{2v}, *trans* to the C_{2h} class. The symbols appropriate to the orbitals of the latter are

	C_2^z	σ_h	i		C_2^z	σ_h	i
a_g	+	+	+	b_g	—	—	+
a_u	+	—	—	b_u	—	+	—

where i represents the operation of inversion at the centre of symmetry of C_{2h} molecules. C_2^z represents the operation of rotation by 180° about the z axis which is taken as passing through the centre of symmetry and at right angles to the molecular plane. σ_h represents the operation of reflection in the plane of the molecule. + and —, as usual, imply that the wave function does not or does, respectively, change sign when a particular operation is carried out. The C_{2v} symbols have been defined in Part I. For convenience we shall add single and double primes to the symbols for both classes to denote symmetric and anti-symmetric behaviour with respect to reflection in the plane of the molecule.

Now the lowest-energy orbitals of a linear HAAH molecule are, in order or decreasing binding energy, σ_g, σ_u, σ_g, π_u, $\bar{\pi}_g$, $\bar{\sigma}_u$. The first two σ orbitals may be thought of as largely localized in the AH bonds. The third and fourth σ orbitals and both the π orbitals are AA orbitals. Whether we correlate the orbitals of the linear molecule with those of a bent C_{2v} (*cis*-)molecule or with those of a bent C_{2h} (*trans*-)molecule, it is easy to see that, just as one of the curves leading to $\bar{\pi}$ in Fig. 1 rises from the bent to the linear HAB molecule, so one of the curves leading to $\bar{\pi}_g$ will rise from the bent to the linear HAAH molecule. This is because the orbital concerned changes from being built from s orbitals of the A atoms in a bent molecule where the HCC angles are 90° to being built from p orbitals of the A atoms in the linear molecule. Further, by a simple application of the principles used in these papers it is not difficult to show that the five lowest orbital curves on a correlation diagram for bent-linear molecules will have their minima on the HCC angle = 180° line. Fig. 2 shows the correlation diagram that one obtains.* In other words, HAAH molecules containing 10 valency electrons should have linear ground states while those containing 11 or 12 valency electrons should have non-linear ground states. The latter might be either *cis* or *trans*. In agreement, the C_2H_2 molecule, possessing 10 valency electrons, has a linear ground state. The HNNH molecule, having 12 valency electrons, would be expected to have a bent ground state, existing in either a *cis*- or a *trans*-form. The correctness of the expectation is strongly supported by the fact that the molecule N_2F_2 is known to have a planar ground state with *cis*- and *trans*-isomers (Allen and Sutton, *Acta Cryst.*, 1950, **3**, 46). From Fig. 2 one would also expect 14-electron molecules to have bent ground states. Such ground states, however, would have the anti-bonding b_g''–$\bar{\pi}_g$ orbital filled; and, in order to relieve the repulsion represented by this anti-bonding orbital, one-half of the molecule would be expected to be twisted through 90° relative to the other, *i.e.*, into a non-planar form. The reason for this twisting has been described earlier (Walsh, *J.*, 1948, 331) and will be referred to again in Part IX. The expectation is strongly supported by the observed shape of the ground state of the H_2O_2 molecule which contains 14 valency electrons.

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* It should be noted that for acetylene, if $\bar{\sigma}_u$ lay below $\bar{\pi}_g$, crossing of the orbital curves leading to these two orbitals would be possible; this is in contrast to the situation in, *e.g.*, AB_2 molecules. However, there is little doubt that $\bar{\sigma}_u$ lies above $\bar{\pi}_g$ for acetylene.

Turning now to the spectrum of C_2H_2, it is clear that the longest-wave-length absorption should lead to a bent upper state, just as with the isoelectronic molecule HCN. The longest-wave-length absorption known consists of very weak, red-degraded bands [$\varepsilon_{\text{max.}} \simeq 0{\cdot}3$ (Platt, Klevens, and Price, *J. Chem. Phys.*, 1949, **17**, 466)] between 2400 and 2100 Å. Kistiakowsky (*Phys. Review*, 1931, **37**, 276) observed bands from 2377 to 2246 Å. Lind and Livingston (*J. Amer. Chem. Soc.*, 1933, **55**, 1036) observed sharply defined bands stretching to shorter wave-lengths. Since this paper was submitted for publication, King and Ingold (*Nature*, 1952, **169**, 1101) have reported that the absorption does lead to a non-linear upper state; that, in fact, the excited state has a planar, centrosymmetric, zigzag form; that the lowest vibrational level lies at 2369 Å; that the upper-state vibration frequencies involved are 1385 (CC stretching) and 1049 cm.$^{-1}$ (opening the HCC angles); and that the transition is polarized perpendicularly to the plane of the bent molecule (implying that the upper state has the symmetry A_u of the C_{2h} class).

What are the detailed expectations concerning the longest-wave-length transition? Neglecting triplet $\longleftarrow$ singlet transitions, we should expect, if the upper state remained linear, the four lowest-energy transitions to be

$$\cdots(\pi_u)^3(\bar{\pi}_g),\ {}^1\Delta_u \longleftarrow \cdots(\pi_u)^4,\ {}^1\Sigma_g^+ \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

$$\cdots(\pi_u)^3(\bar{\pi}_g),\ {}^1\Sigma_u^- \longleftarrow \cdots(\pi_u)^4,\ {}^1\Sigma_g^+ \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

$$\cdots(\pi_u)^3(\bar{\pi}_g),\ {}^1\Sigma_u^+ \longleftarrow \cdots(\pi_u)^4,\ {}^1\Sigma_g^+ \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

Transition (10) would be two-fold degenerate and, like (11), would be electronically forbidden. From Fig. 2, however, it is clear that two of the four transitions should in fact lead to bent upper states. These two will be the two of lowest energy. If the bent upper states are taken to be *trans*, the formulation of the transitions should be

$$\cdots(b_u')(a_u'')^2(a_g'),\ {}^1B_u \longleftarrow \cdots(\pi_u)^4,\ {}^1\Sigma_g^+ \quad . \quad . \quad . \quad . \quad . \quad (13)$$

$$\cdots(b_u')^2(a_u'')(a_g'),\ {}^1A_u \longleftarrow \cdots(\pi_u)^4,\ {}^1\Sigma_g^+ \quad . \quad . \quad . \quad . \quad . \quad (14)$$

Both are electronically allowed. ${}^1\Delta_u$ correlates with ${}^1B_u$ and ${}^1A_u$; ${}^1\Sigma_u^-$ with ${}^1A_u$, and ${}^1\Sigma_u^+$ with ${}^1B_u$. The observed ${}^1A_u \longleftarrow {}^1\Sigma_g^+$ transition is to be identified as (14). Transition (14) is electronically allowed (with polarization along the z axis), but it should be weak partly because of the Franck–Condon principle and partly because of its relation to the forbidden transition (10) or (11). It should weaken the C–C bond as well as reduce the HCC angles and so should arouse both the CC stretching vibration and one of the bending vibrations of the molecule. The CC stretching frequency should be reduced relatively to its ground state value (1974 cm.$^{-1}$). All these expectations accord with the facts.

It is of particular interest that the bending frequency (1049 cm.$^{-1}$) is increased in the excited, relatively to the ground, state. $\nu_4''\pi_g$ of the ground state carries the molecule into the bent, *trans*-form (C_{2h}) and has a value 612 cm.$^{-1}$. This is in accord with the upper state's resembling a C_2H_4 molecule minus two H atoms; for the force constants controlling bending of C–H bonds are known to increase from C_2H_2 to C_2H_4,* a fact readily understandable in terms of the carbon-atom hybridization involved and the spherical symmetry of an *s*-orbital, unlike that of a *p*-orbital.

By analogy with atoms and diatomic molecules, one would expect ${}^1\Delta_u$ to lie lower than ${}^1\Sigma_u^-$ and ${}^1\Sigma_u^+$. In that case the observed ${}^1A_u$ state probably correlates with ${}^1\Delta_u$ rather than ${}^1\Sigma_u^-$; and we should expect to observe two further intra-valency-shell transitions, *viz.*, transition (13) to a bent upper state and (at shorter wave-lengths) transition (12) to a linear upper state. The forbidden transition (11) would probably be too weak to appear. Transition (12), belonging to the $V \longleftarrow N$ class, should be more intense than (13). The latter however, is electronically allowed and polarized in the plane of the bent molecule; it should arouse both CC stretching and HCC bending frequencies. Transition (12) should arouse strongly only the totally symmetrical CC stretching frequency, considerably

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* Linnett, Heath, and Wheatley (*Trans. Faraday Soc.*, 1949, **45**, 833) give the following values $>\!\!-$C–H $0{\cdot}66 \times 10^{-11}$, $=\!C\!<_{\mathrm{H}}$ $0{\cdot}60 \times 10^{-11}$ (in-plane distortion), and $\equiv$C–H $0{\cdot}24 \times 10^{-11}$ erg/radian^2.

reduced from its value of 1974 cm.$^{-1}$ in the ground state. By analogy with HCN, the reduction might be to a value $\simeq$800 cm.$^{-1}$. The frequency should be much less in the $^1\Sigma_u{}^+$ than in the ^1A_u or the ^1B_u state since the a_g'–$\bar{\pi}_g$ orbital loses some of the anti-bonding character which it has in the linear molecule, tending towards a bonding orbital in the 90° bent molecule. On the other hand, Ross (*Trans. Faraday Soc.*, 1952, **48**, 973), as a result of theoretical calculations, has suggested that the observed ^1A_u state correlates with $^1\Sigma_u{}^-$ rather than with $^1\Delta_u$. In that case, the $^1\Delta_u$ state remains linear and transition to it, being forbidden, would probably not be observed; and we should expect to observe only one further intra-valency-shell transition, *viz.*, (13) to a bent upper state correlating with $^1\Sigma_u{}^+$. One difficulty with Ross's suggestion is that it implies that the order of the $^1\Delta$ and the $^1\Sigma$ state is different for C_2H_2 and HCN; if $^1\Delta$ lay above $^1\Sigma$ for HCN, then the upper state of the $^1\Sigma \longleftarrow {}^1\Sigma$ transition, to which the HCN 1500—1350-Å bands undoubtedly correspond, should be bent and it would be difficult to explain why only one frequency appears strongly in the region.

King and Ingold were unable to follow the bands of transition (14) to their maximum, since the latter lay outside the range observable with a quartz spectrograph. According to Ross (*loc. cit.*) the maximum would probably occur between 1900 and 1650 Å. If this estimate is correct, then, as the following evidence shows, the transition is overlapped by at least one other transition before its maximum is reached.

The Rydberg bands of acetylene start sharply near 1500 Å. To the long-wave-length side of them and to the short-wave-length side of the bands already mentioned, occurs at least one other system. The intervening bands (see photograph by Price and Walsh, *Trans. Faraday Soc.*, 1945, **41**, 381) cover an extensive region from *ca.* 2070 to *ca.* 1550 Å with $\lambda_{\text{max.}}$ at *ca.* 1725 Å. Platt, Klevens, and Price (*loc. cit.*) give $\varepsilon_{\text{max.}}$ for this region as $\simeq$500 compared with a value between 10,000 and 100,000 for the first Rydberg band, but these values are subject to an uncertainty of at least three times. The author's photographs and appearance–pressure data suggest that $\varepsilon_{\text{max.}}$ for the 1725-Å system is not less than 10% of $\varepsilon_{\text{max.}}$ for the first Rydberg band. The comparatively high intensity makes it practically certain that, at least in the neighbourhood of $\lambda_{\text{max.}}$, a $V \longleftarrow N$ transition is involved. In other words, transition (12) is present at least around 1725 Å. In the longer-wave-length portion of the region (2070—1850 Å) the frequency intervals are 1365 and 865 cm.$^{-1}$ (Herzberg, *Trans. Faraday Soc.*, 1931, **27**, 378). By analogy with the 2400—2100-Å bands, these frequencies almost certainly represent CC stretching and HCC bending respectively. The fact that two frequencies are involved almost certainly implies that the upper state is bent; and the absorption may be identified as belonging to transition (13). To be sure, other bands are present weaker than those concerned in the 1365- and 865-cm.$^{-1}$ frequency intervals (Walsh, unpublished results), but these may well represent the expected continuation of the 2400—2100-Å system. Some at least of the bands are red-degraded. The pattern of bands observed in the 2070—1850-Å region stretches some way further to short wave-lengths, but towards 1725 Å it becomes confused and not obviously the same as at longer wave-lengths. A frequency difference of *ca.* 720 cm.$^{-1}$ is noticeable towards the shorter-wave-length end of the region. The diffuseness of the bands, the presence of emission lines in the Lyman continuum used as background in the author's photographs, and the overlapping of bands make both measurement and analysis difficult. While certainty must await a complete analysis of the region, it appears not unlikely that two main transitions are concerned in the 2070—1550-Å region: one that stretches from the 2070—1850-Å region towards shorter wave-lengths and so occupies a very extensive region of the spectrum, and one (more intense) that overlaps this in the neighbourhood of 1725 Å. It is noteworthy that, on intensity data, Platt, Klevens, and Price (*loc. cit.*) show the 2070—1850-Å region as a separate transition about 100 times weaker than that in the 1725-Å region. It appears therefore that $^1\Delta_u$ lies lower than $^1\Sigma_u{}^-$ and $^1\Sigma_u{}^+$; that the 2400—2100-Å bands represent transition to a bent ^1A_u state correlating with $^1\Delta_u$; that the 2070—1850-Å bands represent transition to a bent ^1B_u state correlating with $^1\Delta_u$; * and

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* Herzberg (*loc. cit.*) suggested the bands were due to a $^3\Sigma \longleftarrow {}^1\Sigma$ transition, but this is unlikely

that in the neighbourhood of 1725 Å appears transition (12) [overlapping (13)] to a linear $^1\Sigma_u^+$ upper state, the bands being analogous to the HCN 1500—1350-Å system and presumably involving a single strong progression. The alternative interpretation, based on Ross's suggestion, *viz.*, that the whole 2070—1550-Å region represents one transition appears less likely. The possibility of complications such as the existence of transitions to *cis* upper states should, however, be borne in mind; it would certainly be expected that *cis*- and *trans*-isomers of bent C_2H_2 would exist. It should also be noted that Herzberg (*loc. cit.*) refers to weak continuous absorption setting in at *ca.* 1880 Å; the origin of this is unknown, but may be impurity.

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