470. *The Electronic Orbitals, Shapes, and Spectra of Polyatomic Molecules. Part V.* Tetratomic, Non-hydride Molecules,* AB_3.

By A. D. WALSH.

The procedure developed in previous papers of this series is applied to tetratomic, non-hydride molecules, AB_3. A correlation diagram is plotted between the orbitals possible for planar AB_3 molecules and those possible for pyramidal molecules. This enables a discussion to be given of the shapes of such molecules, and comments to be made on their reactivities and spectra. AB_3 molecules containing $\ngtr 24$ valency electrons are planar in their ground states. Molecules containing 25 or 26 valency electrons should be pyramidal in their ground states, the BAB angle decreasing with increase in the number of electrons. Molecules containing 24 valency electrons should be pyramidal in their first excited states. The ground states of molecules containing 28 valency electrons should be planar or nearly planar.

Orbitals of Non-hydride, AB_3 *Molecules.*—The lowest-lying possible orbitals for a planar AB_3 molecule may be approximately described as follows. (i) Three *s* lone-pair orbitals, one on each of the B atoms. In known AB_3 molecules, B is usually of high electronegativity, greater than that of A. To a first approximation, therefore, these *s* orbitals may be supposed so tightly bound that they hardly interact with each other or with other orbitals. They remain essentially atomic in character and vary little in binding energy as the BAB angle is varied. (ii) Three bonding orbitals. Regarded as localized orbitals, they are formed from sp^2 hybrid valencies of A overlapping in-phase with *p* valencies of the B atoms that point towards atom A. Regarded as non-localized orbitals, they are of species a_1', e', e', as described for AH_3 molecules. (iii) Three orbitals which are approximately *p* lone-pair orbitals, one on each of the B atoms. The axis of each of these *p* orbitals lies in the molecular plane and perpendicular to the adjacent B–A line. The orbitals are approximately non-bonding because the B atoms are far apart. They form

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* Part IV, preceding paper.

non-localized orbitals as indicated in Fig. 1. Two of the orbitals are degenerate and of species e'. They have a net slight bonding effect between the B atoms. The third orbital is of species a_2' and is slightly anti-bonding in each B–B distance; it therefore is of slightly higher energy than the e' orbitals. (iv) Four orbitals built from p orbitals, on the A and the three B atoms, which have their axes perpendicular to the molecular plane (see Fig. 2). The lowest-energy orbital of these has all four p orbitals overlapping in-phase. It is of species a_2'' and is bonding in each A–B and B–B distance. The next two orbitals each have a nodal plane perpendicular to the molecular plane and passing through atom A. They are degenerate, the two-fold degeneracy arising from the two independent and mutually perpendicular possible settings of the above nodal plane. Their species symbol is thus e''. They have a net anti-bonding effect between the B atoms and are A$\longleftrightarrow$B non-bonding. The fourth orbital has the p orbital on atom A overlapping out-of-phase with each of the p orbitals on the B atoms. It is of species a_2'' and is anti-bonding in each A–B distance but bonding between the three B atoms. To denote its A$\longleftrightarrow$B anti-bonding character it is written $\bar{a}_2''$. The fact that B usually has a higher electronegativity than A means that the first three orbitals are more localized on the B atoms than on A, while the fourth orbital is more localized on atom A. The argument is the same as that used in Part II in the discussion of the localization of orbitals. The bonding or anti-bonding properties of the orbitals in (iii) and (iv) suggest that the order of decreasing binding energy is $a_2''e'e'e''e''a_2'$, followed by $\bar{a}_2''$. (v) Three orbitals which are built by the out-of-phase overlap of an orbital on A with an appropriate group orbital compounded from the three B p orbitals whose axes lie along the A–B lines. In the lowest of these (species a_1') the three B p orbitals overlap in-phase with each other but out-of-phase with a central s orbital on A. The orbital is anti-bonding in each A–B distance and is therefore written $\bar{a}_1'$. It corresponds to the $\bar{a}_1'$ orbital described for AH_3 molecules, and is more localized on A than on the B atoms.

FIG. 1. (*The choice of form for the* e' *orbitals is not unique.*)

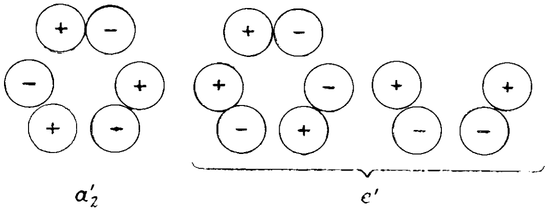
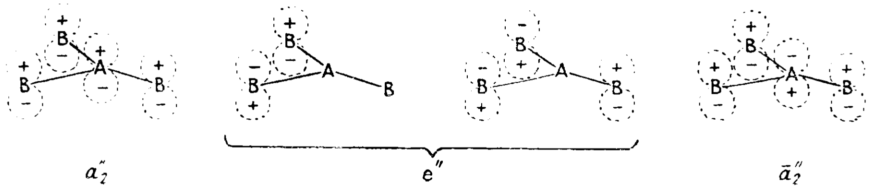


FIG. 2. (*The forms of the* e'' *orbitals are not unique.*)

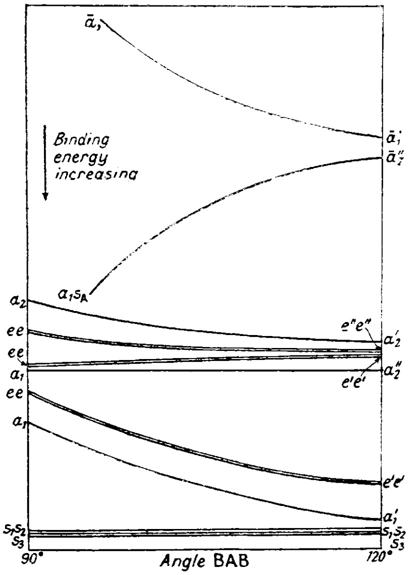


The $\bar{a}_2''$ orbital corresponds to the a_2'' orbital described for AH_3 molecules. Whereas the latter was non-bonding, however, the former is anti-bonding. In AH_3 molecules the a_2'' undoubtedly lies well below the $\bar{a}_1'$ orbital. In non-hydride AB_3 molecules the anti-bonding character of $\bar{a}_2''$ causes it to become of higher energy relative to the other orbitals. It is therefore uncertain in AB_3 whether $\bar{a}_2''$ or $\bar{a}_1'$ lies the higher. The point is exactly analogous to the question whether $\bar{\pi}_u$ or $\bar{\sigma}_g$ lies the lower for a linear AB_2 molecule (Part II).

The lowest-lying orbitals for a pyramidal AB_3 molecule in which the BAB angle is 90° may be approximately described as follows. (i) Three s lone-pair orbitals, one on each B atom. These remain essentially atomic in character and vary little in binding energy as the BAB angle is varied. In Fig. 3, which correlates the orbitals of pyramidal and planar

AB_3 molecules,* they are therefore represented by three horizontal lines close together. (ii) Three bonding orbitals. Regarded as localized orbitals, these utilize pure p valencies of A. Regarded as non-localized orbitals, they are of species a_1, e, e and are represented by lines that fall from left to right in Fig. 3, as described for AH_3 molecules. (iii) Six approximate lone-pair p orbitals, two on each B atom and each of axis perpendicular to the adjacent A–B line. Since these orbitals are approximate lone-pair orbitals they are represented in Fig. 3 by lines that remain fairly close together whatever the angle BAB. Moreover, as the angle changes, they involve no changing hybridization of A valencies. Whether they increase or decrease in binding energy as the BAB angle increases is therefore determined by whether they are B$\longleftrightarrow$B anti-bonding or bonding respectively [principle (iii) of Part I]. These p orbitals may be separated into two groups; those whose axes lie in the plane of the three B atoms and those whose axes do not. Consider the former first. The non-localized combinations of the lone-pair orbitals are of species e, e, a_2, corresponding to the e', e', a_2' group of the planar molecule. The e, e orbitals are weakly bonding between the B atoms as a net effect. They therefore are more tightly bound when the B atoms are close together (angle BAB = 90°) than when far apart (angle BAB = 120°), and are represented in Fig. 3 by lines that rise from left to right. The a_2 orbital is anti-bonding between the B atoms. It is therefore more tightly bound in the planar molecule and is represented by a line that falls from left to right.

FIG. 3.



Considering now the remaining three B p orbitals: these give rise to a_1, e, e orbitals corresponding to the a_2'', e'', e'' group of the planar molecule. The e, e or e'', e'' orbitals have a net anti-bonding effect between the B atoms. They are therefore represented in Fig. 3 by lines that fall from left to right. The a_1 or a_2'' orbital is bonding between the B atoms and might therefore be expected to rise from left to right in Fig. 3. On the other hand, it probably changes from being built almost solely from B orbitals in the 90° molecule to being built increasingly also from an A p orbital as the BAB angle increases, *i.e.*, it increases in A$\longleftrightarrow$B bonding character. As a result, the orbital may vary comparatively little with change of angle and has been represented in the Figure by a horizontal line. In any case, however, the variation in the a_2'', e'', e'' or a_2', e', e' group will be small compared with the variation in the a_1', e', e' group. (iv) An orbital that is approximately an s orbital on atom A. It is of species a_1 (written a_1s). As the BAB angle increases, this orbital rises steeply in energy, as in AH_3, because it becomes more and more built from a p orbital of A. In AB_3, in addition, it becomes more and more A$\longleftrightarrow$B anti-bonding, tending to approach the $\bar{a}_2''$ orbital of the planar molecule. (v) An orbital of species a_1 (written $\bar{a}_1$) which is anti-bonding in each A–B distance and corresponds to the $\bar{a}_1'$ orbital of the planar molecule. It is built from an s orbital of A in the planar molecule, but from a p_z orbital of A in the 90° molecule and is therefore represented in Fig. 3 by a curve that falls steeply from left to right. If $\bar{a}_1'$ for the planar molecule lies below $\bar{a}_2''$, the steep curve from the a_1s orbital will lead eventually to $\bar{a}_1'$. Otherwise, curves of the same species would cross. Similarly, the curve from the $\bar{a}_1'$ orbital would then lead not to the $\bar{a}_1'$ but to the $\bar{a}_2''$ orbital.

Shapes of AB_3 *Molecules.*—Of the twelve lowest orbital curves in Fig. 3, all but two either fall to right or remain roughly constant in energy. The two that rise only

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* For clarity, Fig. 3 (like Fig. 1 of Part IV) is over-simplified. Thus the a_1s_A and *ee* bonding orbital curves probably cross (see Part VII). Crossings (or avoided crossings) would complicate the diagram, but need not upset the basic ideas of this paper.

do so slightly. One therefore has a strong expectation that AB_3 molecules containing 24 or less valency electrons will be planar. This is borne out by the facts (see Table). A molecule with 25 or 26 valency electrons, however, has to have one or two electrons, respectively, in the $a_1s\text{–}\bar{a}_2''$ or $\bar{a}_1'$ orbital. This means that such molecules can be expected to be pyramidal, the BAB angle being less for a 26- than for a 25-electron molecule. There appears to be only one example of a 25-electron molecule, *viz.*, ClO_3 which, although probably pyramidal, has an unknown OClO angle. 26-Electron molecules are all pyramidal as expected, the BAB angle being ~100°. As with triatomic molecules, one notices the importance of pure number in determining the shape of a molecule. The Table includes a few B_2AC molecules because a correlation diagram very similar to Fig. 3 (except that no orbitals are now degenerate) should apply to such molecules (see following papers). The linkage of shape with number of valency electrons should therefore be the same for B_2AC as for AB_3 molecules.

Shapes of tetratomic AB_3 (*and some* B_2AC) *molecules.*

No. of valency electrons	Molecule					Shape
24		CO_3^{--}		NO_3^-		Planar
		SO_3		NO_2Cl		
		BF_3		BO_3^{3-}		
		BCl_3		InI_3		
		BBr_3		$GaCl_3$		
		$COCl_2$		$GaBr_3$		
		$COBr_2$		$CSCl_2$		
25		ClO_3				Pyramidal
26	IO_3^-	PF_3	104°	SbI_3	~99°	
	ClO_3^-	PCl_3	100° 6′	$BiCl_3$	~100°	
		PBr_3	101°	$BiBr_3$	100°	
		PI_3	100°	$SOCl_2$: ∠ClSCl	114°	
		$AsBr_3$	100°	∠ClSO	106°	
		AsI_3	100°	$SOBr_2$: ∠BrSBr	96°	
		$AsCl_3$	98° 25′	NF_3 : 102° 9′		

The values given are the BAB angles where known. Except for NF_3, PCl_3, and $AsCl_3$, they are quoted from Allen and Sutton, *Acta Cryst.*, 1950, **3**, 46. The value for NF_3 comes from a micro-wave determination by Sheridan and Gordy (*Phys. Review*, 1950, **79**, 513). The values for PCl_3 and $AsCl_3$ come from micro-wave determinations by Kisliuk and Townes (*J. Chem. Phys.*, 1950, **18**, 1109).

The 22-electron hypothetical molecule CO_3 should be planar and paramagnetic. The 23-electron molecule NO_3 (Sidgwick, "The Chemical Elements and their Compounds," Oxford Univ. Press, 1950, Vol. I, pp. 691—692) should also be planar.

One deduces from Fig. 3 that the first excited state of CO_3^{--}, NO_3^-, BF_3, or SO_3 should be pyramidal in its equilibrium form. Relatively to, say, ClO_3 the first excited states of these molecules have one less electron stabilizing the planar form. If ClO_3 is pyramidal, therefore, these excited states should certainly be so. Similarly, when BF_3 forms the co-ordination complex $(CH_3)_2O \rightarrow BF_3$, the electrons donated to the BF_3 have to enter the $a_1s\text{–}\bar{a}_2''$ or $\bar{a}_1'$ orbital, resulting in the BF_3 group becoming pyramidal (see Dunderman and Bauer, *J. Phys. Chem.*, 1946, **50**, 32).

According to Fig. 3, 28-electron molecules should be planar or nearly so. Unfortunately a structure determination has been reported for only one 28-electron molecule, *viz.*, ClF_3, namely, by Allen and Sutton (*loc. cit.*) as a personal communication from Wahrhaftig, so that the evidence for it cannot be critically examined. According to it, ClF_3 is a pyramidal molecule with the ClFCl angle 86·5° ± 1·5°. This is not in accord with expectations from this paper and further evidence is awaited. If it should prove that the molecule is after all far from planar, it must mean that not all the premises upon which the present prediction of near planarity are based apply to ClF_3. The present discussion is confined, for example, to molecules wherein only *s* and *p* atomic orbitals are used, and assumes that the only possible shapes belong to the D_{3h} or the C_{3v} symmetry class.*

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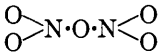
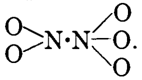
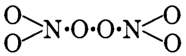
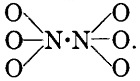
* *Added in Proof.*—ClF_3 has now been reported to be planar (Burbank and Bensey, *J. Chem. Phys.*, 1953, **21**, 602; Smith, *ibid.*, p. 609), in agreement with our expectations. However, it is reported as a slightly distorted T-shaped molecule; this could not have been predicted by our work, which was limited to a consideration of the symmetrical C_{3v} and D_{3h} models only.

Reactivity of AB_3 *Molecules.*—Fig. 3 also enables one to discuss the reactivities of tetratomic molecules. A radical such as NO_3, for example, should have its odd electron in an e'' orbital which, we have argued, is largely localized on the O atoms. We have already seen (Part II) that the odd electron of the NO_2 molecule is localized largely on the N atom. One would expect therefore the structure of N_2O_5 (which is probably formed from $NO_3 + NO_2$) in the gas phase to be  ${}^{O}_{O}\!>\!N{\cdot}O{\cdot}N\!<\!{}^{O}_{O}$ rather than . This is known to be correct (Sidgwick, *op. cit.*).* Similarly, one expects the N_2O_6 molecule to be  ${}^{O}_{O}\!>\!N{\cdot}O{\cdot}O{\cdot}N\!<\!{}^{O}_{O}$ rather than the ethane-like structure . This again appears to be true (Sidgwick, *op. cit.*). The odd electron of the NO molecule lies in an orbital more localized on the N than on the O atom (cf. Part II). It follows that the N_2O_3 molecule is expected to have the structure  $O{\cdot}N{\cdot}N\!<\!{}^{O}_{O}$. Similarly, N_2O_4 (which dissociates to $2NO_2$ rather than to $NO + NO_3$) should have the structure  ${}^{O}_{O}\!>\!N{\cdot}N\!<\!{}^{O}_{O}$ rather than  $O{\cdot}N{\cdot}O{\cdot}N\!<\!{}^{O}_{O}$ or O·N·O·O·N·O. Pauling suggested the second of these because the first violated his " adjacent charge " rule. However, there is now little doubt that the first is correct (Ingold and Ingold, *Nature*, 1947, **159**, 743; Walsh, *J. Chem. Phys.*, 1947, **15**, 688). Sidgwick (*op. cit.*) gives the structure ONONO for the N_2O_3 molecule, but the evidence for this does not appear unambiguous. NO should react with NO_3 to give the molecule  $O{\cdot}N{\cdot}O{\cdot}N\!<\!{}^{O}_{O}$ which could give $2NO_2$. The step $NO + NO_3 = 2NO_2$ may occur in the reaction between NO and O_2 to give (finally) NO_2.

Similar considerations should govern the interaction of PO, PO_2, and PO_3 radicals, and are relevant to an understanding of how P_4 on oxidation produces P_4O_{10} molecules.

Spectra of AB_3 *Molecules.*—By the Franck–Condon Principle, since the first excited states of such molecules as CO_3^{--}, NO_3^-, BF_3, or SO_3 should be non-planar, one expects the longest-wave-length electronic transitions of these molecules to occupy a wide region of the spectrum. This is true of, *e.g.*, SO_3, which has a long-wave-length transition extending from 3000 to beyond 2200 Å. A further reason lies in the increase of A–B length that will occur in the transition. The $\bar{a}_2''$ and the $\bar{a}_1'$ orbital are both so highly $A \longleftrightarrow B$ anti-bonding that it is not surprising that all the known spectra of 26-electron molecules are continuous. The spectra of PCl_3, PBr_3, $AsCl_3$, $SbCl_3$, and $BiCl_3$ (Sponer and Teller, *Rev. Mod. Phys.*, 1941, **13**, 75) supply examples.

The SO_3 absorption referred to above consists of weak, diffuse, bands superimposed on a continuous background. We suggest that the bands and the continuous background are to be interpreted as due to two transitions which may both be formulated

$$\cdots(a_2)(a_1),\ {}^1A_2 \longleftarrow \cdots(a_2')^2,\ {}^1A_1' \qquad . \quad . \quad . \quad . \quad . \quad (1)$$

corresponding to the two transitions

$$\cdots(a_2')(\bar{a}_2''),\ {}^1A_1'' \longleftarrow \cdots(a_2')^2,\ {}^1A_1' \qquad . \quad . \quad . \quad . \quad . \quad (2)$$

and

$$\cdots(a_2')(\bar{a}_1'),\ {}^1A_2' \longleftarrow \cdots(a_2')^2,\ {}^1A_1' \qquad . \quad . \quad . \quad . \quad . \quad (3)$$

Both (2) and (3) are forbidden; (2) should lead to a pyramidal and (3) to a planar upper state. In agreement the absorption is not very strong, ε slowly increasing from a very low value at 3000 Å to about 100 at 2150 Å (Fajans and Goodeve, *Trans. Faraday Soc.*, 1936, **32**, 511). It should be noted, however, that the peak of the absorption lies at some unknown wave-length below 2150 Å. The banded part of the absorption appears to begin at about 2700 Å, but the bands have only been measured below 2500 Å. They are separated by an approximately constant frequency difference of

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* In the solid state, N_2O_5 is known to be NO_2^+,NO_3^- (Grison, Eriks, and de Vries, *Acta Cryst.*, 1950, **3**, 290).

430 cm.$^{-1}$. The probable interpretation of this is that it represents either the symmetrical stretching or the symmetrical bending vibration (both of species a_1 for a pyramidal upper state, or a_1' and a_2'' respectively for a planar form) of the upper state. In the ground state the a_1'- and the a_2''-vibration have frequencies of 1069 and 653 cm.$^{-1}$ respectively (Gerding and Lecomte, *Physica*, 1939, **6**, 737). The bands have a curious flat-topped structure (see Figure given by Fajans and Goodeve, *loc. cit.*). Indeed, 430 cm.$^{-1}$ really refers to the measured separations of the minima (which alone are sharp) between the bands. No explanation of this band shape has yet been given.

The 23-electron NO_3 molecule is known to give rise to absorption bands between 7100 and 5000 Å (see Jones and Wulf, *J. Chem. Phys.*, 1937, **5**, 873). The extinction coefficient is quite high (~2000 at $\lambda_{\text{max.}}$ which is ~6650 Å). This suggests the identification (see Fig. 3)

$$\cdots (e')^3(a_2')^2,\ {}^1E' \longleftarrow \cdots (e')^4(a_2'),\ {}^1A_2' \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Now (4) is an allowed transition, the molecule being planar in the equilibrium forms of both combining states. Not surprisingly, therefore, the bands are quite different from those of SO_3, being comparatively sharp and narrow. Moreover, the very long wave-length of this NO_3 absorption system is in accord with the discussion above and with the closeness of the binding energies of the orbitals a_2'', e'', e'' and e', e', a_2' in Fig. 3. If (4) is assumed to be correct, the bands should turn out under higher dispersion to be perpendicular in type. Since the (e') and (a_2') orbitals concerned are respectively $O \leftrightarrow O$ bonding and anti-bonding, the main vibrational frequency involved should be the a_1' totally symmetrical stretching vibration of the upper state.

The absorption shown by dilute aqueous solutions of nitrates (a rounded peak between 3000 and 2500 Å with ε ~7; Sponer and Teller, *loc. cit.*; Katzin, *J. Chem. Phys.*, 1950, **18**, 789) is probably to be interpreted as transition (1) of the nitrate ion, more or less perturbed by the adjacent solvent and cations.

LEEDS UNIVERSITY. [*Received, May 15th*, 1952.]