469. *The Electronic Orbitals, Shapes, and Spectra of Polyatomic Molecules. Part IV.* Tetratomic Hydride Molecules,* AH_3.

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The orbitals of planar and pyramidal AH_3 molecules are correlated. A figure is plotted to indicate whether a given orbital rises or falls in energy as the HAH angle is increased. This is used to explain and predict (i) the shapes and (ii) the spectra of AH_3 molecules. In their ground states, AH_3 molecules containing not more than 6 valency electrons should be planar, and molecules containing 7 or 8 should be pyramidal.

Electronic Orbitals of AH_3 *Molecules.*—The symbols used to describe the orbitals possible for a planar AX_3 molecule (D_{3h} symmetry) are as follows:

	Operation			
Symbol	C_3	$C_2(y)$	σ_h	$\sigma_v(y)$
a_1'	+	+	+	+
a_1''	+	+	−	−
a_2'	+	−	+	−
a_2''	+	−	−	+
e'	Two-fold degenerate orbitals		+	
e''			−	

The z axis is taken as passing through atom A and as being perpendicular to the molecular plane. C_3 denotes a rotation by 120° about this axis. $C_2(y)$ denotes a rotation by 180° about one of the A–H lines. σ_h denotes a reflection in the molecular plane. $\sigma_v(y)$ denotes a reflection in a plane containing the z-axis and one of the A–H lines. + and − denote, respectively, that the wave function does not or does change sign when subjected to the symmetry operation in question. The signs in the last column are fixed by the signs in the first three; the last column is therefore redundant, but is included to facilitate comparison with the symbols for pyramidal molecules. The symbol e is used for all two-fold degenerate orbitals. Single and double primes denote, respectively, orbitals that are symmetric and anti-symmetric with respect to reflection in the molecular plane.

The symbols used to describe the orbitals possible for a pyramidal molecule AX_3 (C_{3v} symmetry) are as follows:

Symbol	C_3	$\sigma_v(y)$
a_1	+	+
a_2	+	−
e	Two-fold degenerate orbitals	

The z axis passes through atom A and is perpendicular to the plane of the three H atoms. C_3 and $\sigma_v(y)$ have the same meanings as before. Note that an a_2'' orbital of the planar molecule becomes an a_1 orbital of the pyramidal molecule, a_1' becomes a_1, a_1'' becomes a_2, and a_2' becomes a_2.

The lowest-energy electronic orbitals possible for a planar AH_3 molecule may be

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* Part III, preceding paper.

described as follows : (i) Three orbitals binding the H atoms to the central atom. Each of these may, for discussions of molecular shape, be regarded as localized in a particular A–H distance and formed by the in-phase overlap of a hydrogen 1*s* valency and an sp^2 hybrid valency of A. All three orbitals are symmetric with respect to reflection in the molecular plane. For discussions of spectroscopic transitions involving these orbitals, however, they must be regarded as non-localized. When so regarded, molecular symbols become appropriate. The equivalent, non-localized orbitals may be obtained as in-phase or out-of-phase combinations of one orbital with the other two (see Fig. 1). The group of three equal orbitals is then split. The first type of combination results in a single a_1' orbital. The second results in two degenerate e' orbitals, the two-fold degeneracy arising essentially from the two-fold symmetry of the potential field. The non-localized orbitals are described further below. (ii) An orbital localized on atom A, closely resembling a pure *p* orbital of A whose axis is perpendicular to the molecular plane. This orbital is of species a_2'' and is non-bonding. (iii) Three orbitals each anti-bonding in each A–H distance and symmetric with respect to reflection in the molecular plane. They are of species $\bar{a}_1'$, $\bar{e}'$, $\bar{e}'$, and are formed by the out-of-phase overlap of atomic orbitals on A with the H 1*s* atomic orbitals. The bars are added to the usual group symbols to denote the anti-bonding character. The lowest of the three is $\bar{a}_1'$. In it the three H orbitals are in-phase and the orbital is therefore bonding between the H atoms. The three H 1*s* orbitals overlap out-of-phase with the A *s* orbital. A radial node is thus present (see Fig. 2). In the $\bar{e}'$ orbitals two of the H 1*s* orbitals are in-phase with each other, the third being out-of-phase. These orbitals are therefore anti-bonding, as a net effect, between the H atoms; and therefore lie above $\bar{a}_1'$ which, although, like the $\bar{e}'\bar{e}'$ orbitals, is A$\longleftrightarrow$H anti-bonding, is also H$\longleftrightarrow$H bonding.

FIG. 1. (*Choice of positions for nodal plane not unique.*)

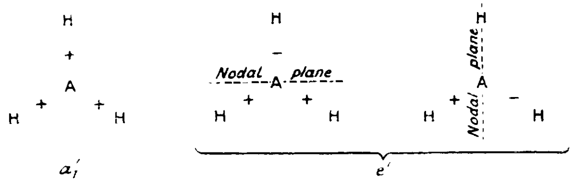
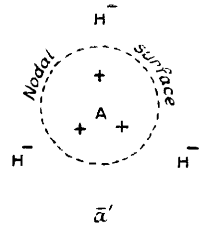


FIG. 2.



For a pyramidal AH_3 molecule in which each HAH angle is 90°, the lowest-energy orbitals may be described as follows : (i) Three bonding orbitals. Each may be regarded as localized in a particular A–H distance and formed by the in-phase overlap of a hydrogen 1*s* orbital and a pure *p* orbital of A. With equal validity the orbitals may be regarded as non-localized and formed from combinations of the three localized orbitals. The non-localized orbitals comprise a single a_1 orbital (in-phase overlap of all three localized bonding orbitals) and two degenerate *e* orbitals (out-of-phase overlap of one of the localized bonding orbitals with the other two). Obviously, these three orbitals become the a_1' and two e' orbitals of the planar molecule. Since the localized orbitals are built from pure *p* orbitals of A in the 90° AH_3 molecule, but from sp^2 hybrid orbitals of A in the planar molecule, they become (as explained in previous papers of this series) more tightly bound as the HAH angle increases from 90° to 120°. For reasons made explicit below, the non-localized orbitals also become more tightly bound as the HAH angle increases. (ii) An orbital localized on atom A, closely resembling a pure *s* orbital of A. This is a non-bonding orbital of species a_1. Clearly, it must become the a_2'' orbital of the planar molecule. As the HAH angle increases from 90° to 120° the orbital becomes very much less strongly bound since it changes from an *s* to a *p* atomic orbital. (iii) Three anti-bonding orbitals of species $\bar{a}_1$, $\bar{e}$, $\bar{e}$, which become the anti-bonding $\bar{a}_1'$, $\bar{e}'$, $\bar{e}'$ orbitals of the planar molecule.

The various non-localized orbitals of the molecule can also be obtained by a procedure similar to that used in Part I. We form first the three possible combinations of the H 1*s* wave functions. These may be chosen as $1s_1 + 1s_2 + 1s_3$, $1s_1 - 1s_2$, and $1s_1 + 1s_2 - 1s_3$.

For simplicity the coefficients properly belonging to these orbitals are omitted. To form such H_3 group orbitals automatically takes account of the symmetry of the molecule. The components from which the non-localized molecular orbitals are built may then be written as follows :

Component	Symbol for C_{3v} symmetry	Symbol for D_{3h} symmetry	Component	Symbol for C_{3v} symmetry	Symbol for D_{3h} symmetry
$1s_1 + 1s_2 + 1s_3$	a_1	a_1'	p_z	a_1	a_2''
$1s_1 - 1s_2$ $1s_1 + 1s_2 - 1s_3$	e	e'	p_x p_y	e	e'
s_A	a_1	a_1'			

Components of the same species may be "mixed" to form the actual molecular orbitals. In doing so, however, we bear in mind the principle (see Part I) that when the HAH angle is 90° the s_A orbital must be kept separate from the other A orbitals. The a_1–a_1' bond orbital is thus built from an in-phase combination of $1s_1 + 1s_2 + 1s_3$ and p_z in the 90° molecule but of $1s_1 + 1s_2 + 1s_3$ and s_A in the planar molecule. Because of the change from p_z to s_A the orbital becomes more tightly bound as the HAH angle increases. The *ee*–*e'e'* bond orbitals are built from an in-phase combination of $\left.\begin{matrix} 1s_1 - 1s_2 \\ 1s_1 + 1s_2 - 1s_3 \end{matrix}\right\}$ and $\left.\begin{matrix} p_x \\ p_y \end{matrix}\right\}$ in both 90° and planar molecules. There is thus no hybridization-change in the contributing A valencies as the HAH angle changes. The orbitals however are anti-bonding between the H atoms and therefore by principle (iii) given in Part I become more tightly bound as the HAH angle increases. The $\bar{a}_1$–$\bar{a}_1'$ orbital is built from an out-of-phase combination of $1s_1 + 1s_2 + 1s_3$ and p_z in the 90° molecule but (necessarily because of its symmetry) from $1s_1 + 1s_2 + 1s_3$ and s_A in the planar molecule. This orbital therefore becomes more tightly bound as the HAH angle increases; it is the analogue of the orbital which in AB_2 molecules causes the trihalide ions to have linear or nearly linear ground states. The $\bar{e}\bar{e}$–$\bar{e}'\bar{e}'$ orbitals are built from out-of-phase combinations of the $\left.\begin{matrix} 1s_1 - 1s_2 \\ 1s_1 + 1s_2 - 1s_3 \end{matrix}\right\}$ and $\left.\begin{matrix} p_x \\ p_y \end{matrix}\right\}$ components in both 90° and planar molecules. They are anti-bonding between the H atoms and therefore become more tightly bound the further the H atoms are apart. The a_1–a_2'' orbital represents a pure *s*-orbital of A in the 90° molecule and a pure p_z orbital of A in the planar molecule; it therefore becomes less and less tightly bound as the HAH angle increases.

Shapes of AH_3 *Molecules*.—Fig. 3 shows a qualitative correlation diagram between the orbitals of the pyramidal and the planar AH_3 molecules. The three lowest-energy curves all descend from left to right. One therefore expects AH_3 molecules containing six or less valency electrons to be planar. BH_3 and the carbonium ion CH_3^+ supply examples. Evidence exists that the ion CH_3^+ prefers a planar form (see Bartlett and Knox, *J. Amer. Chem. Soc.*, 1939, **61**, 3184). On the other hand, a molecule such as NH_3 or OH_3^+, containing eight valency electrons, has to place two electrons in the a_1–a_2'' orbital whose curve in Fig. 3 rises steeply from left to right. It is to be expected, therefore, that the ammonia molecule should be pyramidal. The actual value of the HAH angle in AH_3 molecules containing eight valency electrons naturally varies somewhat with the nature of A. From NH_3 to PH_3 to AsH_3 to SbH_3 the angle decreases by some 15° ($\angle$HNH = 106° 47′; Herzberg, "Infra-red and Raman Spectra," van Nostrand, New York, 1945 : $\angle$HPH = 93° 50′, $\angle$HAsH = 91° 35′, $\angle$HSbH = 91° 30′; Nielsen, *J. Chem. Physics*, 1952, **20**, 759). The decrease could be plausibly attributed to a smaller drop from left to right of the *ee*–*e'e'* and a_1–a_1' curves as the size of atom A increases.

It has often been suggested that the CH_3 radical is planar. The radical has, however, seven valency electrons, one of which has to occupy the a_1–a_2'' orbital. According to Fig. 3, therefore (cf. NO_2), it is unlikely that the radical is planar in its ground state.* It should have a HCH angle intermediate between 120° and the HNH angle of the ground state of NH_3.

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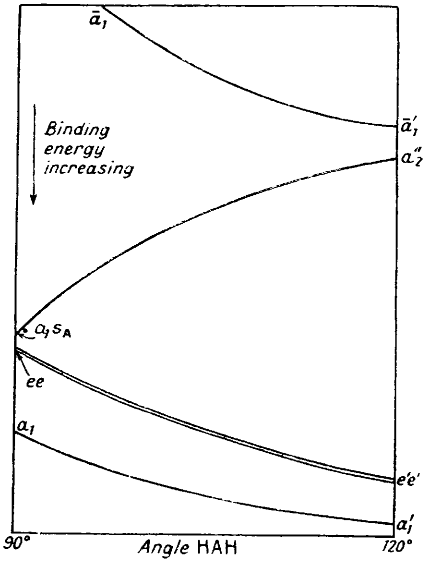
* Linnett and Poë (*Trans. Faraday Soc.*, 1951, **47**, 1033) have also arrived at the conclusion that the CH_3 radical is not planar.

However, even in NH_3 the potential barrier to inversion is not very high (2076 cm.$^{-1}$). In CH_3 this potential barrier should be considerably less. Inversion is likely to be so easy a process, therefore, that experiments to determine the presence or absence of optical activity in a product CRR′R″Y formed from an optically active compound CRR′R″X *via* a reaction involving the free radical CRR′R″ will not distinguish the planarity or otherwise of the radical.

When BH_3 forms the co-ordination complex OC ⟶ BH_3, the electrons donated to the BH_3 enter the a_1–a_2'' orbital, so that the BH_3 group becomes pyramidal (Gordy, Ring, and Burg, *Phys. Review*, 1950, **78**, 512).

According to Fig. 3, AH_3 molecules containing 10 valency electrons should be planar or nearly planar. Unfortunately, no such molecules (*e.g.*, FH_3) are known to exist—a fact which is understandable in view of the anti-bonding properties of the $\bar{a}_1$–$\bar{a}_1'$ orbital which would have to be occupied in the ground state of a 10-electron molecule.

FIG. 3.



The fundamental reason for the pyramidal shape of an 8-electron molecule may be alternatively stated as follows (cf. Part II). In the ground state of such a molecule, two electrons have to occupy an orbital localized entirely on the central atom. These lone-pair electrons repel the electrons in the A–H bonds. If the molecule were planar they would be in a pure p_z orbital. As a result of the repulsion they move somewhat away from the bond electrons in the $+z$ direction (corresponding to hybridization of the s and the p_z valencies of A). Also as a result of the repulsion, the bond electrons move further away from atom A (corresponding to increasing p-character and consequent reduced electronegativity of the A valencies pointing towards the H atoms). When there are no lone-pair electrons on A the molecule is planar in its ground state. In the ground state of a 10-electron molecule a second lone pair of electrons would have to occupy the second orbital that can be built from s and p_z orbitals of A. A second hybrid orbital of this sort would point in the $-z$ direction and so cause the bond electrons to be subject to as much repulsion from above the molecular plane as from below.

The localization of the orbitals shown in Fig. 3 should be of help in interpreting the reactivity of AH_3 molecules. For example, the two most weakly bound electrons of NH_3 should be localized on the N atom. It is natural, therefore, that NH_3 reacts towards electrophilic reagents at the N atom.

Spectra of AH_3 *Molecules.*—Fig. 3 may be used to discuss the long-wave-length spectra of AH_3 molecules. The intra-valency-shell absorption transition of NH_3 of longest wave-length should be

$$(a_1)^2(e)^4(a_1)(\bar{a}_1),\ {}^1A_1 \longleftarrow (a_1)^2(e)^4(a_1)^2,\ {}^1A_1 \quad . \quad . \quad . \quad . \quad (1)$$

The transition is analogous to the following transition of the N_2 molecule :

$$KK'(\sigma_g2s)^2(\sigma_u2s)^2(\pi_u)^4(\sigma_g2p)(\sigma_u2p),\ {}^1\Sigma_u^+ \longleftarrow KK'(\sigma_g2s)^2(\sigma_u2s)^2(\pi_u)^4(\sigma_g2p)^2,\ {}^1\Sigma_g^+$$

$(\bar{a}_1)$ is anti-bonding between the H_3 group and N, just as (σ_u2p) is N⟷N anti-bonding. For the N_2 molecule the (π_g) orbital lies below the (σ_u2p) orbital. The $(\bar{e})$ orbital corresponds to the (π_g) orbital, but because of its additional H⟷H anti-bonding character is expected to lie above $(\bar{a}_1)$. Transition (1) should lead to an increase of HNH angle (to a nearly planar form) and also of N–H distance. It is an allowed transition, polarized parallel to the symmetry axis. The allowed nature means that only the totally symmetrical vibrations should occur in the upper state. In view of the expected change of both angle and distance, one would expect both the a_1 vibrations to be aroused. The frequencies of both these should be greatly lowered relatively to the ground state. In fact, because of the strongly anti-bonding nature of the upper $(\bar{a}_1)$ orbital the transition may well give rise to continuous absorption. Experimentally, the first absorption region of ammonia occurs from 2167 to 1675 Å ($\lambda_{\max.}$ at *ca.* 1900 Å). Thompson and Duncan (*J. Chem. Phys.*, 1946, **14**, 573) were unable to find an absorption system of longer wave-length, even in tubes 10 m. long with the gas at 1 atmosphere. The absorption consists of diffuse bands which, according to Duncan (*Phys. Review*, 1935, **47**, 822) belong to a single v' progression. The upper state frequency is 878 cm.$^{-1}$. Dixon (*ibid.*, 1933, **43**, 711) had earlier classified the bands with the aid of two upper-state frequencies, *viz.*, 890 and 2720 cm.$^{-1}$. The intensity is such that there is little doubt of the allowed nature of the transition. It follows that the upper-state frequency or frequencies represent one or both of the two a_1, parallel frequencies (*ca.* 950 and 3334 cm.$^{-1}$ in the ground state). The slow rise to a maximum intensity shows that the dimensions of the molecule change considerably in the excitation. It is possible, therefore, that the observed absorption could be interpreted as (1). The high energy of the excitation (origin 46,157 $\pm$ 30 cm.$^{-1}$), however, must mean that it cannot lie far from the Rydberg transition of longest wave-length. The ionization potential of ammonia is known to lie quite low. From unpublished electron-impact data, Sugden finds a value 10·8 v. The region 2178—1675 Å may therefore contain the first Rydberg transition of the molecule. For comparison, one may cite ethylene which has an ionization potential of 10·50 v and a first Rydberg transition at 1744 Å. This Rydberg transition may be formulated as :

$$(a_1)^2(e)^4(a_1)(a_13s),\ {}^1A_1 \longleftarrow (a_1)^2(e)^4(a_1)^2,\ {}^1A_1 \quad . \quad . \quad . \quad . \quad (2)$$

The upper orbital closely resembles a 3*s* orbital of the N atom and the transition is of the same symmetry type as (1). It should cause an increase of HNH angle (because of the removal of an electron from the a_1–a_2'' orbital). Since, however, the upper orbital is non-bonding, the transition should not cause much change of NH length. In other words, it should not have the same tendency as (1) to lead to dissociation of the molecule. It is possible, therefore, that the observed bands in the first absorption region of NH_3 are due to transition (2); but that they are complicated by the presence of transition (1) in the same region. Such an interpretation has the advantage that, if the upper orbital of (1) is repulsive, we could explain the observed diffuseness of the bands by supposing pre-dissociation to occur in the upper state of (2). Photochemical work provides strong evidence that dissociation to NH_2 and H occurs in the absorption. The interpretation would be exactly analogous to that given by us for the first absorption region of the H_2O molecule (Part I, p. 2263). Mulliken (*J. Chem. Phys.*, 1933, **1**, 492; 1935, **3**, 506) has earlier ascribed the 2167—1675-Å system to transition (2). The probability that two transitions are concerned in the system complicates comparison of observed and calculated transition intensities (Thompson and Duncan, *loc. cit.*). Transition (2) might arouse strongly only the $\nu_2(a_1)$ frequency (950 cm.$^{-1}$ in the ground state) and not the $\nu_1(a_1)$ vibration (3334 cm.$^{-1}$ in the ground state), in possible agreement with Duncan's vibrational analysis.

That the first absorption system of NH_3 does cause a change of HNH angle is supported by the appearance of the NH bending vibration in the corresponding absorption region of methylamine (Sponer and Teller, *Rev. Mod. Phys.*, 1941, **13**, 75). The banded absorption of this amine lies between 2500 and 2000 Å and gradually passes into a continuum at shorter wave-lengths.

The first absorption of the PH_3 molecule consists of two or three diffuse bands between 2300 and 2200 Å, followed by continuous absorption from 2200 to beyond 1850 Å (Melville, *Nature*, 1932, **129**, 546; Cheesman and Emeléus, *J.*, 1932, 2847). We suggest that the continuous absorption belongs to transition (1) and the bands to transition (2) [(a_14s) replacing (a_13s)] perturbed by transition (1). The first absorption of AsH_3 and SbH_3 (Cheesman and Emeléus, *loc. cit.*) is continuous and may be ascribed to transition (1), perhaps involving also the appropriate analogue of (2).

The two lowest-energy intra-valency-shell absorption transitions of the CH_3 radical should be

$$\ldots (\bar{a}_1),\ {}^2A_1 \leftarrow \ldots (a_1),\ {}^2A_1 \qquad (3)$$

$$\ldots (e)^3(a_1)^2,\ {}^2E \leftarrow \ldots (e)^4(a_1),\ {}^2A_1 \qquad (4)$$

Both are allowed transitions. Which would be the lower in energy is uncertain. By analogy with NH_3, it is probable that the absorption corresponding to (3) would lie at wave-lengths shorter than 2500 Å. If absorption due to the CH_3 radical is found at wave-lengths above 2500 Å it is probably to be interpreted as (4). Transition (4), however, is likely to be weak, since it corresponds to one that would be forbidden if the radical were planar; and the departure from planarity may not be great. Since the ionization potential of the CH_3 radical is known to be only *ca.* 10·0 v, it is probable that (3) would lie close to the transition

$$\ldots (3sa_1),\ {}^2A_1 \leftarrow \ldots (a_1),\ {}^2A_1 \qquad (5)$$

Transitions (3) and (5) are polarized along the symmetry axis, *i.e.*, along the axis of least moment of inertia. The molecule is a symmetric top and the transitions should give rise to parallel bands. Both should cause an increase of HCH angle. The upper state of both would probably be planar. Transition (3) should cause a big increase of C–H distance. The strongly anti-bonding nature of the upper ($\bar{a}_1$) orbital may cause (3) to give rise to continuous absorption. Transition (4) should give rise to perpendicular bands. It should result in a marked decrease of apex angle and an increase of C–H distance. No electronic spectrum of CH_3 is yet known, but these detailed predictions should help in the search now being undertaken in various laboratories for that spectrum.

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