[Contribution from the Laboratory of Molecular Structure and Spectra, Department of Physics, The University of Chicago]

Structures of the Halogen Molecules and the Strength of Single Bonds[1]

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The relatively low bond energy of F_2 can reasonably be understood in terms of an accumulation of non-bonded repulsions, and the higher values for the heavier halogens in terms of d hybridization. The latter should impart pronounced multiple-bond character to the "single" bond in Cl_2, Br_2 and I_2. Analogous considerations apply to other first-row and higher-row atom conventional single bonds, and give a reasonable explanation of the relatively greater tendency of first-row than of higher-row atoms to form conventional multiple bonds. In connection with the discussion of Cl_2, it is shown how the use of "unnaturally" small d orbitals can be legitimate and important in p-d hybridization.

Introduction and Conclusions

It is well known that N–N, O–O and F–F bonds are markedly weaker (bond energies are smaller, and bond distances relative to atomic radii are larger) than P–P, S–S, Cl–Cl and analogous higher-row single bonds.[2] On the other hand first-row multiple bonds are well known to be relatively strong, as is shown for example by the existence of gaseous O_2 and N_2 in contrast to the greater stability of single-bonded solids for elementary sulfur and phosphorus. These phenomena have been discussed and it has been suggested that d orbital hybridization may strengthen the higher-row single bonds, but no really satisfactory theoretical explanation has been given.[2a]

The problem is usually formulated as that of explaining the abnormal weakness of first-row single bonds, in particular for F_2.[3a] In the writer's view, however, the weakness of the first-row single bonds is readily understandable, and it is the *strength* of the higher-row single bonds which needs to be explained. In the present paper, by a somewhat detailed comparative discussion of the electronic structures of F_2 and Cl_2, it will be shown to be reasonable that the greater strength of the "single" bond in Cl_2 can be understood as a consequence of pronounced partial multiple bond character made possible by d hybridization. Similar reasoning is applicable to the fifth and sixth column single bonds.

These conclusions depart from the *tacit assumption* customary in defining standard single-bond covalent radii,[3b] that "single" bonds between *like* atoms (*e.g.*, Si–Si, P–P, S–S, Cl–Cl) are truly single. It is of course a familiar idea[3b] that partial multiple-bond character may account for bond lengths shorter than sums of standard covalent radii in the case of single bonds between *unlike* atoms (*e.g.*, Si–Cl, P–Cl, S–Cl).

Granting the correctness of the conclusions above, the greater propensity of first-row than of higher-row atoms to form multiple bonds becomes understandable. For if "single" bonds are truly single for first-row atoms but are partially multiple for higher-row atoms, the *relative* stability of overtly multiple bonds is greater in the former case.

Electronic Structure of the Fluorine Molecule

The MO (molecular orbital) electron configuration of F_2 may be written as

$$(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(2\sigma_u)^2(3\sigma_g)^2(1\pi_u)^4(1\pi_g)^4(3\sigma_u)^0 \quad (1)$$

The MOs $1\sigma_g$ and $1\sigma_u$ correspond to inner-shell (atomic 1s) electrons. Of the valence-shell MOs, the last one, the highly antibonding $3\sigma_u$, is unoccupied. The existence of F_2 as a stable molecule, as compared with the non-existence of Ne_2, may be thought of as due to the *absence* in F_2 of the pair of $3\sigma_u$ electrons which would be present in Ne_2. The forms of the valence-shell MOs in (1) are, in LCAO approximation, as follows (if slight admixings of 1s AOs into $m\sigma_g$ and $n\sigma_u$ are neglected)

$$\left.\begin{aligned} m\sigma_g &= (\sigma_{ma} + \sigma_{mb})/[2(1 + S_{m\sigma})]^{1/2} \\ n\sigma_u &= (\sigma_{na} - \sigma_{nb})/[2(1 - S_{n\sigma})]^{1/2} \\ r\pi_u &= (\pi_{ra} + \pi_{rb})/[2(1 + S_{r\pi})]^{1/2} \\ s\pi_g &= (\pi_{sa} - \pi_{sb})/[2(1 - S_{s\pi})]^{1/2} \end{aligned}\right\} \quad (2)$$

In (2), $m = 2$ or 3, $n = 2$ or 3, $r = 1$, $s = 1$, while σ_{ma}, σ_{mb}, π_{ra}, *etc.*, refer to *normalized* σ or π AOs on the two atoms a and b; $S_{m\sigma}$, $S_r\pi$, etc., are the corresponding overlap integrals, *e.g.*, $S_m\sigma$ is that between σ_{ma} and σ_{mb}. In (2), π here means $2p\pi$ only, and r and s are confined to 1. In (2), σ_{ia} means a hybrid AO of the form

$$\sigma_{ia} = \alpha_i(2s_a) + \beta_i(2p\sigma_a) \quad (3)$$

In eq. 3, $\alpha_i^2 + \beta_i^2 = 1$, of course, but with different values of β (and α) for $m = 2$, $m = 3$, $n = 2$, and $n = 3$; every α_i is assumed to be taken positive, while β_i may then be positive or negative.

The VB (valence-bond theory) analog of (1), if *no hybridization* is assumed, may be written as

$$(1s_a)^2(1s_b)^2(2s_a)^2(2s_b)^2(2p\pi_a)^4(2p\pi_b)^4 2p\sigma_a\cdot 2p\sigma_b \quad (4)$$

with four lone pairs (1s, 2s and two $2p\pi$) on each atom, and one σ bond between two $2p\sigma$ electrons on each atom. The σ bond is weakened by numerous non-bonded repulsions, including both lone-pair:lone-pair and lone-pair:bonding-electron (*e.g.*, $2s_a{}^2$–$2p\sigma_b$) repulsions. Among these repulsions, even the inner-shell:outer-shell repulsions exerted by the 1s electrons are appreciable, but on the other hand there are also appreciable non-bonded attractions.[4]

Returning to the LCAO formulation (1), the direct analog of (4) would be a description in which σ_{2a} and σ_{2b} in the $2\sigma_g$ and $2\sigma_u$ MOs of (1) and (2) are taken as pure 2s, *i.e.*, $\alpha_i = 1$, $\beta_i = 0$ in eq. 3. It would then seem natural to take σ_{3a} and σ_{3b} in

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[1] This work was assisted by the Office of Scientific Research (Air Research and Development Command) under Project R-351-40-4 of Contract AF 18(600)-471 with The University of Chicago.

[2] *Cf.* (a) R. S. Mulliken, This Journal, **72**, 4493 (1950), in particular pp. 4495–7; (b) K. S. Pitzer, *ibid.*, **70**, 2140 (1948).

[3] (a) *Cf. e.g.*, R. T. Sanderson, *J. Chem. Phys.*, **22**, 345 (1954); (b) L. Pauling, *cf.* "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1945.

[4] R. S. Mulliken, *J. Phys. Chem.*, **56**, 295 (1952).

the $3\sigma_g$ (and $3\sigma_u$) MOs as pure $2p\sigma$ ($\alpha_i = 0, \beta_i = 1$ in eq. 3); let us for the moment assume this. After introducing the familiar Coulson LCAO-MO *bond order* concept in a suitably generalized form,[5] (1) and (2) can be made to yield some information about the net over-all bonding effect of the electronic population in F_2. In (1) there are eight bonding electrons (namely, those in the $2\sigma_g$, $3\sigma_g$ and $1\pi_u$ MOs, which have + signs in their LCAO approximations in (2)), and six antibonding electrons (those in $2\sigma_u$ and $1\pi_g$, with − signs in (2)). Since a single pair of bonding electrons constitutes one bond, we may say, with Coulson, that such a pair corresponds to bond order 1.

But what is the bond order for a pair of antibonding electrons? Coulson would presumably say −1, but this does not properly represent the effect of such a pair on bond strength. As the writer has pointed out[4,5] the bonding power (or resonance contribution to the bonding energy) for a pair of electrons in an MO expressed as in (2) should be approximately proportional to

$$S/(1 + S) \text{ and } -S/(1 - S)$$

for a bonding and an antibonding MO, respectively. If so, and if the bond order is called 1 for a bonding pair, then for a corresponding antibonding pair it is

$$-(1 + S)/(1 - S) \qquad (5)$$

The excess of negative bond order over 1 can be shown[4,6] to be the counterpart in MO theory of the non-bonded repulsions between lone pairs in VB theory. The total bond order for the seven pairs of valence-shell electrons in (1) is then

$$4 - (1 + S_s)/(1 - S_s) - 2(1 + S_\pi)/(1 - S_\pi) = 0.54 \qquad (6)$$

after putting in the values[2a] $S_s = 0.11$ and $S_\pi = 0.05$. The resulting crudely computed bond order of 0.5 gives some insight into why the bond strength for F_2 should be exceptionally low.

A more thorough discussion would consider several additional points,[4] of which three will be mentioned here. (1) The S values just given are based on Slater AOs, whereas[2a] using the more accurate self-consistent-field AOs, S_π would be more like 0.12, and the bond order for F_2 computed by (6) would fall to only 0.2. (2) Our assumption made above that $3\sigma_g$ can be constructed from pure $2p\sigma$ if $2\sigma_g$ is made from pure 2s is not justified, but instead there must be *forced hybridization*[6] in $3\sigma_g$, of such a nature as to *decrease* the bond order of the pair of electrons in $3\sigma_g$. Forced hybridization in LCAO-MO theory corresponds to the non-bonded repulsion between lone pairs and bonding electrons (or between different σ bonding electrons) in VB theory. (3) "Spontaneous" or ordinary s-pσ hybridization must diminish somewhat the antibonding action of the $2\sigma_u$ electrons.

The essential qualitative aspects of the preceding discussion may be summed up from the MO viewpoint as follows. In F_2, as described by configuration (1), there are four bonding (two σ and two π) and three antibonding (one σ and two π) pairs of electrons. Because the antibonding effect of an antibonding pair exceeds the bonding effect of a corresponding bonding pair, and because of forced hybridization, the resultant bond strength is much less than that of a normal single bond due to a single bonding pair. However, s-pσ hybridization slightly alleviates the antibonding effect of one of the antibonding pairs ($2\sigma_u$).

Electronic Structure of the Chlorine Molecule

Turning now to Cl_2, the MO electron configuration may be written as follows for the valence-shell electrons

$$\cdots (4\sigma_g)^2(4\sigma_u)^2(5\sigma_g)^2(2\pi_u)^4(2\pi_g)^4 \qquad (7)$$

The same eq. (2) as for F_2 are valid for the forms of the MOs but eq. 3 is replaced[7] by

$$\sigma_{ia} = \alpha_i(3s_a) + \beta_i(3p\sigma_a) + \gamma_i(3d\sigma_a) \qquad (8)$$

$$\pi_{ja} = \alpha_j(3p\pi_a) + \beta_j(3d\pi_a) \qquad (9)$$

In contrast to F_2, where it seems certain that it is negligible, 3d hybridization in Cl_2 may well be important, especially since it must affect practically every one of the valence-shell MOs in such a way as to strengthen the bonding.

There is spectroscopic evidence on Cl_2 and Cl_2^+ which affords some information about the bonding properties of the $2\pi_u$ and $2\pi_g$ MOs in Cl_2. The ionization potential of Cl_2 for removal of a $2\pi_g$ electron is 11.48 volts.[8] From this information together with the known dissociation energy of Cl_2 (2.476 e.v.) and the ionization potential of the Cl atom (13.01 volts), it follows that the dissociation energy of Cl_2^+ is 4.01 e.v.[8] Thus removal of a $2\pi_g$ electron very considerably strengthens the bonding. From this we may conclude that the $2\pi_u$ and $2\pi_g$ electrons in Cl_2 are far from being non-bonding, but are very decidedly bonding and antibonding, respectively. Further information is obtained[9] from what is a very probable, although not absolutely certain, interpretation of the spectrum of Cl_2^+. This shows two $^2\Pi$ states, one 2.57 e.v. above the other, of which the lower one is probably the $^2\Pi_g$ ground state of Cl_2^+, with one $2\pi_g$ electron missing from configuration (7), and the upper one probably the $^2\Pi_u$ state corresponding to one $2\pi_u$ electron missing from (7). The interatomic distances r_e and vibration frequencies ω_e are as follows: Cl_2, $r_e = 1.99$ Å., $\omega_e = 565$ cm.$^{-1}$; Cl_2^+ $^2\Pi_g$, $r_e = 1.89$ Å., $\omega_e = 645$ cm.$^{-1}$; Cl_2^+ $^2\Pi_u$, $r_e = 2.29$ Å., $\omega_e = 569$ cm.$^{-1}$. These data again indicate that the $2\pi_g$ MO is markedly antibonding, the $2\pi_u$ MO strongly bonding, in Cl_2. The foregoing facts show that the two Cl atoms interpenetrate and interact strongly in Cl_2, conditions which favor hybridization.

The total bonding power of the $4\sigma_g$ and $5\sigma_g$ MOs

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[5] R. S. Mulliken, *J. chim. phys.*, **46**, 675 (1949), Sec. 21, eq. 145b and following discussion.

[6] R. S. Mulliken, *J. Chem. Phys.*, **19**, 912 (1951), and 1955 paper in *J. Chem. Phys.*

[7] Eqs. (8) and (9) neglect forced hybridization which mixes in $1s_a$, $2s_a$ and $2p\sigma_a$ into σi_a and $2p\pi_a$ into πj_a. This need not be considered in a qualitative discussion, except to note that it corresponds to the inner-shell:outer-shell repulsions of VB theory.

[8] Private communication from K. Watanabe, who also finds similar results for Br_2 (10.31 volts) and I_2 (8.82 volts). Electron impact work by Morrison and Nicholson (*J. Chem. Phys.*, **20**, 1021 (1952)) gave 11.80, 10.91 and 9.42 volts for Cl_2, Br_2 and I_2, respectively.

[9] See Elliott and Cameron, *Proc. Roy. Soc.*, (*London*), **164A**, 531 (1938) regarding Cl_2^+. Also G. Herzberg, "Spectra of Diatomic Molecules," Second Edition, D. Van Nostrand Co., New York, N. Y., 1950.

in (7), taken together, must be somewhat increased, and the antibonding power of $4\sigma_u$ considerably decreased, by dσ hybridization, the coefficients in eq. 8 adjusting themselves so as to minimize the total energy. Very likely more important, the *bonding* power of $2\pi_u$ must be *strengthened*, by admixture of $3d\pi$ with positive β/α in (9), causing increased overlapping of π AOs of the two atoms, while the *antibonding* power of $2\pi_g$ must be *weakened* by admixture of $3d\pi$ with negative β/α in (9), causing decreased overlapping.

It thus appears reasonable that a markedly increased net bonding due to d hybridization, somewhat reinforced by consequent increased s-pσ hybridization brought about by decreased bond distance, may account for the high bond energy of Cl_2 as compared with F_2. Inherently stronger pσ bonds,[2a] and greater spontaneous s-pσ hybridization because of lower s → p promotion energy, may also have helped. It should be noted that this result must have been obtained against the opposition of fairly strong inner-shell: outer-shell repulsions,[2] which must be even more important in Cl_2 than in F_2.

The degree of d hybridization need not necessarily be very great, since[10] "a little hybridization goes a long way." One might like to deduce the amount of pπ-dπ hybridization from the spectroscopic information cited above, but after some consideration, the writer feels that too many factors are involved to permit reliable conclusions. Nevertheless, the effects of hybridization can be better visualized by talking in terms of definite numbers, and for this purpose the following may be offered as rather wild guesses: F_2, 2% s-pσ hybridization[4]; Cl_2, 10% s-pσ and 3% s-dσ hybridization (*i.e.*, 10% promotion $s^2p\sigma \rightarrow s(p\sigma)^2$ and 3% $s^2 \rightarrow sd\sigma$, and 5% pπ-dπ hybridization (*i.e.*, 5% promotion $p\pi^2 \rightarrow p\pi d\pi$). This would correspond to mean atomic populations of $1s^2\ 2s^{1.98}\ 2p\sigma^{1.02}\ 2p\pi^4$ for F in F_2 and $1s^2\ 2s^2\ 2p^6\ 3s^{1.87}\ 3p\sigma^{1.10}\ 3p\pi^{3.90}\ 3d\sigma^{0.03}\ 3d\pi^{0.10}$ for Cl in Cl_2. The population just given for Cl_2 would correspond in VB theory to 10% triple (or 5% quintuple, or 20% double) bond character due to π bonding. In addition, it would involve 6% excess σ bond order (*i.e.*, 0.03 of an extra s and of an extra dσ bond, or 0.06 of a strong extra s-dσ hybrid σ bond).

One difficult point has been passed over, namely, that the "natural" 3d AO of the free Cl atom corresponds to a much smaller effective nuclear charge Z_{ef}. (about 1.1) than for the 3s and 3p electrons, electrons, and only a small term value (about 1.8 e.v.),[8] hence a very large size, facts which are very unfavorable for hybridization. In many cases where there is d hybridization, a positive charge on the atom concerned increases the d term value and so favors hybridization,[11] but no such effect appears possible in a homopolar molecule like Cl_2. Fortunately it is not necessary in forming hybrid AOs to confine oneself to "natural" AOs. According to the variation principle of quantum mechanics, the individual AOs composing a hybrid AO in a molecule should adjust themselves in any such way as to minimize the total energy. A good example is that of the improvement of the H_2 molecule wave function by using 1s-2pσ hybrid AOs instead of pure 1s AOs. According to Rosen,[12] this is successfully accomplished by hybridizing 2pσ AOs *with* $Z_{ef} = 2.38$ and 1s AOs with $Z_{ef} = 1.19$. This adjustment of the Z_{ef} values makes the 1s and 2pσ AOs about equal in size and so greatly increases their overlap and with this the resonance energy of hybridization. At the same time, however, the promotion energy is increased, since for a "natural" 2pσ AO, for which $Z_{ef} = Z = 1$, the energy is a minimum with respect to variations of Z_{ef}. The increased promotion energy[13] acts as an unfavorable factor, but not enough so to destroy the benefits of increased overlap.

More specifically, let us consider pπ–dπ hybridization in the $2\pi_u$ bonding and $2\pi_g$ antibonding MOs of Cl_2 (*cf.* eq. 2, 9). The overlap integral S_π between two Cl atom hybrid AOs π_a and π_b of the form given in eq. 9 is

$$S_\pi = \int \pi_a \pi_b dv = \alpha^2 S_{p\pi} + 2\alpha\beta S_{p\pi,d\pi} + \beta^2 S_{d\pi}$$

where $S_{p\pi} = \int 3p\pi_a \cdot 3p\pi_b dv$, $S_{p\pi,d\pi} = \int 3p\pi_a \cdot 3d\pi_b dv$, $S_{d\pi} = \int 3d\pi_a \cdot 3d\pi_b dv$. Approximately, for $\beta^2 << 1$, hence $\alpha \approx 1$

$$S_\pi \approx S_{p\pi} + 2\beta S_{p\pi.d\pi} \qquad (10)$$

That is, for small amounts of hybridization, S_π is increased above $S_{p\pi}$ approximately in proportion to $\beta S_{p\pi,d\pi}$.

There is good reason[4,5] to believe that the contributions of electrons in the $2\pi_u$ or $2\pi_g$ MOs to the bond energy are roughly proportional to S_π. Now[2a] $S_{p\pi}$ for Cl_2 is about 0.10 or 0.15. If it is supposed that $\beta^2 = 0.025$, corresponding to the "wild guess" above on hybridization in Cl_2, and if β is assumed equal in magnitude for the two π MOs, then $\beta = +0.16$ for the $2\pi_u$ and -0.16 for the $2\pi_g$ MO. Now suppose that $S_{p\pi,d\pi}$ is about 50% greater than $S_{p\pi}$, as seems not unreasonable if the $3d\pi$ AO is taken with a suitable Z_{ef} value (say $Z_{ef} = 4$). Then, for the bonding $2\pi_u$ MO, S_π is about 50% larger, and for the antibonding $2\pi_g$ MO, about half as large, as if these MOs were built from unhybridized $3p\pi$ AOs. The result for the two shells $(2\pi_u)^4(2\pi_g)^4$ in (7) could be a *net bonding effect* as great as if one had two normal unhybridized π bonds alone, as in N_2; whereas without hybridization, the same two shells would give a considerable net antibonding effect. The resultant net gain in bond energy could plausibly be 5 or 6 e.v.

However, from this must be subtracted the promotion energy required for a 2.5% promotion ($\beta^2 = 0.025$) of the eight Cl atom $3p\pi$ electrons to $3d\pi$ AOs with $Z_{ef} \approx 4$. Promotion of $3p\pi_{Cl}$ to "natural" $3d\pi_{Cl}$ ($Z_{ef} = 1.1$) costs about 12 e.v.; promotion to $3d\pi_{Cl}$ with $Z_{ef} = 4$ might cost roughly twice as much,[14] say 24 e.v.; the total cost for eight $3p\pi$

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(10) R. S. Mulliken, *J. Chem. Phys.*, **19**, 900 (1951).

(11) Craig, Maccoll, Nyholm, Orgel and Sutton, *J. Chem. Soc.*, 332 (1954).

(12) N. Rosen, *Phys. Rev.*, **38**, 2099 (1931).

(13) For the natural *AO*, the mean kinetic potential and total energies are related by $U = -2T$, $E = T + U$. If Z_{ef} (which measures the size of the AO) is altered, T and U change proportionally to Z_{ef}^2 and to Z_{ef}. From this fact, the variation of E with Z_{ef} can be calculated.

(14) This figure is based on ref. 13. The latter is applicable to one-electron atoms, but is approximately correct for non-penetrating excited AOs in many-electron atoms. Since with $Z_{ef} = 4$, $3d_{Cl}$ would become somewhat penetrating, the estimated promotion energy may be rather too large.

electrons would be (8)(0.025)(24) = 4.8 e.v. If there is a gain of say 5.6 e.v. in bonding, there is a profit of 0.8 e.v. All the figures are of course only illustrative, but they indicate that an appreciable net gain in bond energy by pπ-dπ hybridization is not unreasonable.

It should be especially noted that the *gain* in bond energy by hybridization goes linearly with β (*cf.* eq. 10), while the *cost* goes as β^2. Hence if β^2 is sufficiently small the gain will certainly exceed the cost.

Single bonds in Br_2 and I_2 should be strengthened in a way similar to that for Cl_2 by d hybridization, as should also S–S, P–P and other second-row and higher-row single bonds.

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[CONTRIBUTION FROM THE LABORATORY OF MOLECULAR STRUCTURE AND SPECTRA, DEPARTMENT OF PHYSICS, THE UNIVERSITY OF CHICAGO]

Bond Angles in Water-Type and Ammonia-Type Molecules and Their Derivatives[1]

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The factors which may determine the smaller bond angles in the hydrides of the higher-row fifth-column and sixth-column atoms as compared with NH_3 and H_2O, and the much larger energies required to flatten PH_3 and AsH_3 to planar form than for NH_3, are discussed using LCAO molecular orbital and valence bond theory. It is shown that the observed differences can reasonably be understood as a result of d hybridization in the e-type or b_2-type bonding molecular orbitals, together perhaps with smaller nonbonded repulsions between H atoms, in the higher-row hydrides. Significant factors affecting the bond angles in the halides of fifth-column and sixth-column atoms are also surveyed.

Introduction

According to quantum-mechanical valence-bond theory in its simplest form, the bonds in molecules such as H_2O, H_2S, . . ., and their derivatives and NH_3, PH_3, . . ., and their derivatives should make 90° angles with one another for pure p-electron valence. The actual observed angles are usually considerably greater (see Table I for some examples).[2] This fact can be understood qualitatively in terms of partial s, p hybridization, non-bonded repulsions between H (or other substituted) atoms, and other factors.[3,4] However, no adequate explanation seems to have been offered as to why H_2S, H_2Se, . . ., and PH_3, AsH_3, . . ., have angles close to 90° when their first-row analogs H_2O, NH_3 do not,[5,6] nor why the energy required to make NH_3 planar (0.26 e.v.) is so much smaller than for PH_3 (1.3 e.v.) or AsH_3 (1.5 e.v.).[2b] What seems to be a reasonable explanation is presented below. Some discussion of the lack of corresponding differences for substituted compounds (*e.g.*, PF_3 as against NH_3) is also given.

TABLE I

BOND ANGLES IN RH_2, RX_2, RH_3 AND RX_3 MOLECULES

H_2O: 105° 3'	F_2O: 101°	Cl_2O: 110.8°		
H_2S: 92° 16′		Cl_2S: 102°		
H_2Se: ~90°			Br_2Te: 98°	
NH_3: 106° 46′	NF_3: 102° 9′			
PH_3: 93° 18′	PF_3: 102°	PCl_3: 100° 7′	PBr_3: 101°	PI_3: 100°
AsH_3: 91° 30′	AsF_3: 102°	$AsCl_3$: 98° 25′	$AsBr_3$: 101°	AsI_3: 100.5°
SbH_3: 91° 30′		$SbCl_3$: 99.5°	$SbBr_3$: 97°	SbI_3: 98.5°

Fifth-Column Hydrides

The non-localized MO (molecular orbital) structures of hydrides of the type AH_n have been described qualitatively in earlier papers.[7] For NH_3 the structure is

$$\text{Pyramidal NH}_3\text{: } (1a_1)^2\underset{B}{(2a_1)^2}\underset{B}{(1e)^4}(3a_1)^2 \qquad (1)$$

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(1) This work was assisted in part by the Office of Scientific Research, Air Research and Development Command, under Project R-351-40-4 of Contract AF 18(600)-471 with The University of Chicago.

(2) For references on bond angles, *cf.* (a) A. D. Walsh, *J. Chem. Soc.*, 2266 (1953); G. Herzberg, "Infrared and Raman Spectra," Van Nostrand Co., New York, N. Y., 1945; (b) R. E. Weston, THIS JOURNAL, **76**, 2645 (1954); (c) P. Kisliuk, *J. Chem. Phys.*, **22**, 86 (1954).

(3) See D. F. Heath and J. W. Linnett, *Trans. Faraday Soc.*, **44**, 556 (1947), on H_2O; D. F. Heath, J. W. Linnett and Wheatley, *ibid.*, **46**, 137 (1950), on H_2O, H_2S, H_2Se, NH_3, AsH_3, CH_4, etc.; T. Simanouti, *J. Chem. Phys.*, **17**, 245, 734 (1949); D. F. Heath and J. W. Linnett, *ibid.*, **18**, 147 (1950); J. Duchesne and I. Ottelet, *ibid.*, **17**, 1354 (1949); *J. Phys. Rad.*, **11**, 119 (1950). Also ref. 2c.

(4) A. D. Walsh, *J. Chem. Soc.*, 2260 (1953). However, Walsh's assumption that A atom s-pz hybridization is absent in the MOs of AH_2 and AB_2 molecules for a 90° bond angle cannot be accepted.

(5) However, C. A. Burns, Jr., and W. Gordy [*Phys. Rev.*, **92**, 274 (1953)] in order to account for observed asymmetry in nuclear quadrupole coupling in H_2S, have postulated considerable amounts of d as well as s hybridization, and state that qualitative estimates indicate that such hybridization is in harmony with the observed bond angle.

(6) Linnett and Poë (*Trans. Faraday Soc.*, **47**, 1033 (1951)) have emphasized that the bond angles in NH_3 and H_2O approximate to those for tetrahedral hybrid valence, and have made calculations which favor this view (but see T.-Y. Wu, *J. Chem. Phys.*, **22**, 1125 (1954)). Refinement of the same calculations and their extension to PH_3 by Mellish and Linnett (*Trans. Faraday Soc.*, **50**, 657 (1954)), predict close approximation to tetrahedral angles for PH_3 as well as NH_3, in disagreement with what is observed.

(7) R. S. Mulliken, *J. Chem. Phys.*, **1**, 492 (1933); **3**, 506 (1935).