Theoret. chim. Acta (Berl.) 1, 209—221 (1963)

McGill University, Montreal 2, P. Q. Canada
University of Cincinnati, Cincinnati 21, Ohio, USA

Orbital Electronegativities and the Determination of *s* and *d* Hybridization in Various Halides from Nuclear Quadrupole Resonance Frequencies

By

M. A. WHITEHEAD and H. H. JAFFÉ

The use of Orbital Electronegativities in the interpretation of NQR results for various halides is discussed, and an attempt to determine the amount of *d* hybridization in σ and π bonding is made. The ionic characters are assessed.

Die Anwendung von auf Einelektronenzustände bezogenen Elektronegativitäten zur Interpretation der Kernquadrupolresonanzfrequenzen verschiedener Halogenide wird diskutiert. Es wird versucht, den Anteil von *d*-Hybridisierung in σ- und π-Bindungen zu bestimmen. Der Ionencharakter der Bindungen wird abgeschätzt.

On discute l'emploi des électronégativités d'orbitales dans l'interprétation des fréquences de résonance quadrupolaire nucléaire pour des halogénures et on essaie de déterminer la contribution de l'hybridation *d* dans les liaisons σ et π. On fait une estimation du degré d'ionicité des liaisons.

Earlier reports have covered the relationships 1. between nuclear quadrupole resonance frequencies and the hybridization of halogen atoms, with energy match considerations included, and 2. between the orbital electronegativity and the valence state of atoms [*22*, *23*]. The present paper deals with the relationship between the quadrupole measurements and the orbital electronegativity.

In the case of mono- and di-halide molecules it was established [*22*] that hybridization on the halogen with the less stable atomic orbital accounted well for the observed quadrupole frequency for either nucleus in the molecule, and resulted in a better match in the energies of the combining orbitals, corroborating GORDY's original views [*6*]. It was further shown [*22*, *23*] that the possibility that the *d* orbitals of the halogens were involved in bonding was rendered quite probable, particularly in the case of *BrCl* [*23*, *24*].

In the previous work the valence state ionization potentials were used for the energy of the orbitals on the atoms, but it subsequently appeared that orbital electronegativity was a better approximation to orbital energy and this will be used in this paper.

On the basis of Molecular Orbital Theory, COULSON [*1*, *2*] has shown that the energy of the atomic orbitals combining should be approximately equal. The energy he considered was given by

$$E_i = \int \psi_i \overset{\circ}{\boldsymbol{H}} \psi_i \, d\tau$$

where ψ_i is an orbital function of the atom i and $\overset{\circ}{\boldsymbol{H}}$ is the adjusted Hartree-Fock

Operator. Thus for a strong bond between two atoms A and B,

$$E_A \simeq E_B \tag{1}$$

that is

$$\int \psi_a \overset{\circ}{\boldsymbol{H}} \psi_a \, d\tau \simeq \int \psi_b \overset{\circ}{\boldsymbol{H}} \psi_b \, d\tau$$

It was for this energy that the ionization potential was considered a sufficiently accurate measure.

MULLIKEN [16] has defined the Electronegativity of an atom as

$$\chi = 1/2 \; [EA + IP] \tag{2}$$

where EA and IP are the electron affinity and ionization potential of the atom respectively, and he holds [17] that this electronegativity as a good measure of E_i [16], hence

$$\chi_i \simeq E_i \tag{3}$$

Thus in this new form the theory states: *In order to form a strong bond, the orbital electronegativities of the combining atomic orbitals should be approximately equal — the strongest molecular bond is formed when two atomic orbitals have equal orbital electronegativities.* It is this approach which is used, and applied to the dihalides originally considered, and also to the symmetric polyhalides of group 3 (B), 4 (C, Si, Ge, Sn) and 5 (P, As) and the mixed halides of carbon.

In the interpretation of nuclear quadrupole results [6, 21, 22, 23] the ratio of the frequency of the atom in the molecule, eQq_M, to that of the free atom, eQq_A, is defined as ϱ, where

$$\varrho = eQq_M / eQq_A \tag{4}$$

In the theory of TOWNES and DAILEY [3, 4, 21] this ratio is related to the ionic character of a bond, i, and the amount of s hybridization in the atomic orbital, $\underset{=}{s}$ by the equation*

$$\varrho = (1 - \underset{=}{s})\,(1 \pm i) - \pi \tag{5}$$

where π allows for any π bonding between the p orbitals of the atom and the available π orbitals in the molecule; the $\underset{=}{s}$ and i apply to the σ bond only. The use of d orbitals is not considered and in a compound such as CCl_4 this is justifiable as the d orbitals are quite high in energy [12] and consequently unsuitable for bonding. To a first approximation, again perfectly true in CCl_4, π bonding may be ignored since the carbon has no orbitals to accept p_π electrons from the halogens.

In the diatomics, the ionic character i was defined, following GORDY [5], as

$$i = 1/2 \, |\chi_A - \chi_B| \tag{6}$$

where χ_A and χ_B were the orbital electronegativities [19, 7] of the bonding atomic orbitals of the two atoms A and B of the diatomic molecule AB.

The latest work on electronegativities [10, 8] has allowed a more rigorous approach to the definition of ionic character which supports the definition due to GORDY but removes from it any dependence on NQR results. ICZKOWSKI [10] and subsequently HINZE [8] defined electronegativity from

$$E(n) = K + an + bn^2 + cn^3 \cdots$$

where $E(n)$ is the energy of the valence state of n electrons, and a, b, c, etc.

---

* $\underset{=}{s}$ is used throughout this paper for what has previously been designated s^2

are energy coefficients. It can be shown [*10*] that only the n and n^2 terms are large. The electronegativity χ is defined as

$$\chi = \frac{dE(n)}{dn} = a + 2bn$$

while the ionic character is defined as the *charge transfer* which makes the electronegativities of the bonding orbitals identical

$$\chi_A^* = \chi_B^{*\star}$$

The system is electrically neutral, with two valence electrons,

$$n_B^* = 2 - n_A^*$$

but

$$a_A + 2b_A n_A^* = a_B + 2b_B n_B^*$$

hence

$$a_A + 2b_A n_A^* = a_B + 2b_B\,(2 - n_A^*)$$

so that if the ionic character is defined as

$$i = (n_A^* - 1)$$

then

$$i = \frac{\frac{1}{2}\left|\chi_A - \chi_B\right|}{(b_A + b_B)}\,,\ \text{for } \chi_A = a_A + 2b_A$$

This makes i a dimensionless quantity, since $\left.\frac{\partial E(n)}{\partial n}\right|_{n=1}$ and b are energies, and with $b_A + b_B = 1$ energy unit this reduces to equation (6). The assessment of b_A and b_B is not expressable in terms of electronegativity difference, but nevertheless it appears that Gordy's original definition (6) is the most reasonable at present available. The actual value of i will be altered by the denominator $(b_A + b_B)$ and absolute values may shift for the s character, but the change should not be significant.

In a polyatomic molecule, a new complication arises since the orbital electronegativity of the central atom will depend on the atoms or groups to which it is bonded. In order to account for this environmental factor, the method of KAGARISE [*11*] and of LAGOWSKI [*13*] is followed, in which the electronegativity of a central atom — say carbon — toward one of its neighbours is adjusted for the presence of all other neighbours by a correction calculated from their electronegativity, giving what will be called an *effective electronegativity*, χ^{eff}. This procedure has been quite successful in the correlation of infrared and NQR results [*15*], and has been theorectically justified [*8*].

The Method

It is desired to use equation (5), omitting the last term (π), to solve for i and $\underline{s}$. The ionic character i is assumed to be given by Gordy's relation [*6*]. The relation between orbital electronegativity of a hybrid χ_0^{hyb} and the individual orbital

---

$\star$ The starred quantities refer to the polarized diatomic system, the unstarred ones to the separate neutral atoms electronegativities of the pure s, and p orbitals, χ_0^s and χ_0^p, was found to be a simple linear relation [7]:

$$\chi_0^{\text{hyb}} = \underline{s}\,\chi_0^s + (1-\underline{s})\,\chi_0^p \tag{7}$$

In recalculating the halides in the F, H and D cases and in the XCN cases, the χ_0^{eff} of the F, H and D was assumed to be pure unhybridized χ_0, while in the CN group the χ_0^{eff} of the C orbital towards the halogen was taken as 2.6 to bring it into line with the previous paper [22]. Hence in the A-X halides

$$\left(\frac{\chi_0^s}{2}-\frac{\chi_0^p}{2}\right)\underline{s}^2-\left(\frac{\chi_0^s}{2}-\chi_0^p+1+\frac{\chi_0^A}{2}\right)\underline{s}+\left(1+\frac{\chi_0^A}{2}-\frac{\chi_0^p}{2}\right)-\varrho=0$$

where A has no quadrupole moment. But in $BrCl$ and ICl where both halogens show a resonance we have

$$\varrho_{Cl} = (1-\underline{s}_{Cl})\,(1-i) \tag{5a}$$

$$\varrho_{X} = (1-\underline{s}_{X})\,(1+i) \tag{5b}$$

where i is given by (6) and χ_0^{hyb} for Cl and X are given by (7). This can be solved either by initially assuming a value for $\underline{s}_{Cl}$ or $\underline{s}_X$ and calculating the corresponding $\underline{s}_X$ or $\underline{s}_{Cl}$ and recalculating till $\underline{s}_{Cl}$ and $\underline{s}_X$ remain constant, or by the following procedure:

Rearranging and adding (5a) and (5b) to eliminate i,

$$\varrho_{Cl}\,(1-\underline{s}_X)+\varrho_X\,(1-\underline{s}_{Cl}) = 2\,(1-\underline{s}_X)\,(1-\underline{s}_{Cl}) \tag{5c}$$

$\underline{s}_X$ can be expressed in terms of $\underline{s}_{Cl}$, ϱ_{Cl} and ϱ_X. Thus (5a) becomes a cubic in $\underline{s}_{Cl}$, giving three real roots, only one of which is chemically acceptable and yields a reasonable value of $\underline{s}_X$ when substituted in (5c).

In the tetrahalides the χ_0^{hyb} for the central atom is taken as the effective orbital electronegativity, which is, in a compound $CABDE$, for the CE bond, (the C orbital forming the bond with E) the appropriate hybrid orbital electronegativity of C, corrected by 1/6 of the difference of this quantity and the appropriate orbital electronegativities of A, B and D:

$$\begin{aligned}\chi_0^{\text{eff}}(C) &= \chi_0^{\text{hyb}}(C)+\frac{1}{6}\,[\chi_0^{\text{hyb}}(A)-\chi_0^{\text{hyb}}(C)]+\frac{1}{6}\,[\chi_0^{\text{hyb}}(B)-\chi_0^{\text{hyb}}(C)]+\\ &\quad+\frac{1}{6}\,[\chi_0^{\text{hyb}}(D)-\chi_0^{\text{hyb}}(C)]\\ &= \frac{1}{2}\,\chi_0^{\text{hyb}}(C)+\frac{1}{6}\,[\chi_0^{\text{hyb}}(A)+\chi_0^{\text{hyb}}(B)+\chi_0^{\text{hyb}}(D)]\end{aligned} \tag{8}$$

Combining equations (5), (6), (7) and (8) one then obtains (the subscripts $_0$ and superscripts $^{\text{hyb}}$ will be dropped, *all electronegativities* being understood to be *orbital electronegativities*. and to apply to hybrid orbitals unless otherwise superscripted by s or p to indicate pure s or p orbital electronegativities):

$$\begin{aligned}\varrho &= (1-\underline{s}_E)\left\{1+\frac{1}{2}\,[\chi^{\text{eff}}(C)-\chi(E)]\right\}\\ &= (1-\underline{s}_E)\left\{1+\frac{1}{4}\,\chi(C)+\frac{1}{12}\,[\underline{s}_A\,\chi^s(A)+(1-\underline{s}_A)\,\chi^p(A)+\underline{s}_B\,\chi^s(B)+\right.\\ &\quad+(1-\underline{s}_B)\,\chi^p(B)+\underline{s}_D\,\chi^s(D)+(1-\underline{s}_D)\,\chi^p(D)]-\frac{1}{2}\,\underline{s}_E\,\chi^s(E)\\ &\quad\left.-\frac{1}{2}\,(1-\underline{s}_E)\,\chi^p(E)\right\}\end{aligned} \tag{9}$$

where the various $\underline{s}_A$ etc. are the amounts of *s* character of the different atoms A, B, C, D and E. Since the present paper deals with tetrahalide compounds for which only a single *NQR* frequency is known, only one of these $\underline{s}$ values, $\underline{s}_E$, can be obtained. Thus, some decision must be made about the others.

In the case of the totally symmetric compounds MX_4, there is no problem; all the $\underline{s}_X$ are necessarily equal, because of symmetry, and the compounds, which are all known to be tetrahedral, must consequently be sp^3 hybridized (as long as *d* orbital effects are ignored), so that $\underline{s}_M = 0.25$. In the less symmetric types of compounds CXY_3 and CX_2Y_2, there is no a priori reason why all C orbitals should be exactly sp^3; however, the experimental bond angles are generally rather close to tetrahedral [*23*], and as such no other type of hybridization could uniquely be derived, even if it were assumed that the orbital necessarily points in the bond direction (orbital following). Consequently pure tetrahedral hybridization was assumed for all these compounds. When either X or Y was hydrogen, no allowance for its hybridization was needed, since hydrogen utilizes only $1s$ orbitals. Also when X or Y was fluorine, no *s* hybridization was used; F was assumed to use a pure $2p$ orbital, in agreement with the conclusion reached earlier that hybridization of F is energetically unlikely [*22*]. In the trihalides of the group 3 and group 5 elements, the valence angles deviate considerably from tetrahedral, and the hybridization was determined, assuming orbital following as the only readily available approach. With a bond angle of 120° in BCl_3, $\underline{s}_B = 0.333$; in PCl_3 with an angle of 100°, $\underline{s}_P = 0.148$, and in $AsCl_3$ (103°), $\underline{s}_{As} = 0.184$.

In the treatment of the trihalides, of course, equation (9) is slightly modified, since one of the ligand atoms is omitted.

For the various types of compounds, then, equation (9) simplifies considerably, to give in each case a quadratic equation in the single quantity $\underline{s}$ which is to be evaluated. The resulting quadratics are readily obtained. (Appendix p. 220).

In these equations, $\underline{s}$ is the only unknown; the ϱ are experimentally measured quantities taken from the literature. All orbital electronegativities are taken from work in this Laboratory [*7*], and are reduced to the PAULING scale. All the equations are simple quadratics in $\underline{s}$, giving two real solutions. Of the two, only solutions in the range $0 < \underline{s} < 1$ have physical significance; always at least one, and in general only one, of the solutions was found to lie in this range, so that no problems of arbitrary or intuitive choice of the desired root arose. Once $\underline{s}$ is obtained in this way, it is readily substituted into equation (7) to give χ_0^{hyb} and this in turn into equation (6) to give i.

Results and Discussion

The recalculated results (Tab. 1) for the monohalides and interhalogen compounds show no appreciable change from those given previously [*22*]. However, the molecules DBr and DI now yield results for the halogen hybridization, whereas previously they failed. The molecules ICN, $BrCl$ and ICl still fail to give reasonable results. Thus in $BrCl$ the possible results for chlorine are + 0,69 *s* or — 0.049 s character, corresponding to + 1.89 *s* or — 0.036 *s* character for the bromine. This is not unexpected. If the equation (5b) allows for *d* character in the σ bond then

$$\varrho_X = (1 - \underline{s}_X + d_X)(1 + i)$$

while (7) becomes, to a first approximation

$$\chi_0^{\text{hyb}} = \underline{s}\,\chi^s + (1-\underline{s}-\underline{d})\,\chi^p + \underline{d}\chi^d$$

The only reasonable result therefore is that involving $-0.049\,s$ character for chlorine and $-0.035\,s$ character for bromine, since $1.89\,s$ character is impossible! The minus result for chlorine is to be expected when the occurrence of d character is ignored, since for X (Br or I) the s_X is actually $(s_X - d_X)$ and the whole s character of the bromine or iodine is consequently masked. Thus the hybrid electronegativity will be far too small, and the apparent ionic character too large. The chlorine will then give an apparently negative s hybridization in order to satisfy the cubic equation and equation (5a).

Table 1[f]. *Recalculated ionic characters and hybridization of the dihalides*

Compound			Orbital Electronegativities		Orbital Hybridization	Orbital Electronegativity		Bond Ionic Character
A	B	ϱ	χ_0^s	χ_0^p	$\underline{s}$	χ_0^{hyb}	χ_0^{eff}	i
F				3.90				
	Cl	1.33[a]	5.69	2.95	0.048	3.08		0.40
F				3.90				
	Br	1.41[a]	5.93	2.61	0.067	2.82		0.54
H			2.21					
	Cl	0.49	5.69	2.95	0.074	3.15		0.47
D			2.21					
	Cl	0.50[b]	5.69	2.95	0.069	3.14		0.47
D			2.21					
	Br	0.69	5.93	2.61	0.107	2.97		0.38
D			2.21					
	I	0.80[c]	5.06	2.51	0.050	2.64		0.22
CN							2.6[e]	
	Cl	0.60[a]	5.69	2.95	0.147	3.35		0.38
CN							2.6[e]	
	Br	0.74[d]	5.93	2.61	0.140	3.08		0.24

[a] DAILEY, B. P.: J. physic. Chem. 57, 490 (1953).
[b] LIVINGSTON, R.: J. physic. Chem. 57, 496 (1953).
[c] ALLEN, H.: J. physic. Chem. 57, 501 (1953).
[d] SCHAWLOW, A. L.: J. chem. Physics 22, 1211 (1954).
[e] Taken as 2.6 to keep results in line with previous paper. See Ref. 22.
[f] Compare with W. GORDY, Ref. 6, p. 18.

These results support the qualitative assessments of GORDY, although he preferred to conclude that neither s nor d character was in fact involved. This is however untenable, since as previously shown [*23*, *24*], hybridization is necessary to explain that $\varrho_{Br}\ \varrho_{Cl} > 1$.

a) The Tetrahalides of C, Si, Ge and Sn

The results for the symmetric tetrahalides of C, Si, Ge and Sn are given in Tab. 2 and for the unsymmetric carbon tetrahalides in Tab. 3.

As most detailed data are available for carbon compounds, these will be discussed more fully, and the conclusions will then be applied to the tetrahalides of the other elements. As chlorine in CCl_4 is successively substituted by fluorine the orbital electronegativity towards chlorine is increased, and in order to match this the chlorine has to increase its hybridization; at the same time the increasing electronegativity of the carbon orbital means its contraction, so the amount of *s* needed for the best overlap is decreased; thus while the absolute amount of hybridization increases with substitution, the rate of increase tails off; in order to match electronegativities there is a simultaneous charge transfer *from* the chlorine *to* the central carbon, decreasing the ionic character of the bond.

Table 2[j]. *Ionic Character and Hybridization in the Symmetric Tetrahalides*

Compound			Orbital Electronegativities[b]		Orbital Hybridization	Orbital Electronegativities		MX Bond Ionic Character
MS_4		ϱ[a]	χ_0^s	χ_0^p	$\underline{\underline{s}}$	χ_0^{hyb}	χ_0^{eff}	i
C					0.25[c]	2.51		
	Cl	0.746[d]	5.69	2.95	0.097	3.21	2.86	0.174
	Br	0.83[e]	5.93	2.61	0.069	2.84	2.68	0.08
	I	0.929[i]	5.06	2.51	0.004	2.52	2.52	0.002
Si					0.25[c]	2.32		
	Cl	0.372[d, f]	5.69	2.95	0.371	3.92	3.14	0.408
	Br	0.46[e]	5.93	2.61	0.315	3.66	2.99	0.335
	I	0.580[i]	5.06	2.51	0.262	3.18	2.75	0.215
Ge					0.25[c]	2.59		
	Cl	0.467[d]	5.69	2.95	0.323	3.82	3.21	0.31
	Br	0.54[e]	5.93	2.61	0.286	3.56	2.97	0.295
	I	0.587[i]	5.06	2.51	0.293	3.26	2.92	0.169
Sn					0.25[c]	2.52		
	Cl	0.439[d, f]	5.69	2.95	0.338	3.87	3.19	0.338
	Br	0.50[e, g]	5.93	2.61	0.307	3.63	3.08	0.275
	I	0.594[e, h, i]	5.06	2.51	0.278	3.22	2.87	0.177

[a] The ϱ are calculated from averaging the eQq_M which when the frequencies differ by less than 2% are not considered as due to chemical inequivalence of the atoms.

[b] The electronegativities are given in Pauling units from the Mulliken electron volt scale using [7] $\chi_{\text{Pauling}} = (\chi_{\text{Mulliken}} - 1.23)\ 0.168$.

[c] Assumed because of symmetry.

[d] Livingston, R.: J. physic. Chem. **57**, 496 (1953).

[e] Schawlow, A. L.: J. chem. Physics **22**, 1211 (1954).

[f] Dehmelt, H. G.: J. chem. Physics **21**, 380 (1953).

[g] Shimamura: J. Sci. Hiroshima Univ. **17 A**, 383 (1954).

[h] Kojima, Tsukada, Ogawa and Shimauchi: J. chem. Physics **21**, 2237 (1953).

[i] Robinson, H., H. G. Dehmelt and W. Gordy: J. chem. Physics **22**, 511 (1954).

[j] Compare the results in Ref. 6, p. 18.

With the hydrogen substitution, however, increased hydrogen substitution for chlorine in CCl_4 decreases the χ_0^{eff} (C), increasing the mismatch with the pure *p* of the chlorine, but the bonding sp^3 carbon orbital is expanded by substitution of *H* for *Cl*, so that chlorine *s* hybridization is needed to improve overlap; this increases the χ mismatch; the compromise arrived at is a decreasing amount of hybridization, sufficient to give directional character to the *p* orbital, and increasing charge transfer to match the χ and the space distribution. Both hybridization and charge transfer are energetically unfavourable and only the increased binding energy due to good overlap and good electronegativity match make them worthwhile. Work at present going on in this Laboratory permits us to assess the change in χ with charge, and preliminary results substantiate the above interpretations.

Lucken [*14*] has suggested that if the *C-Cl* bond is the same in the $CH_X Cl_{4-X}$ series then in a plot of ionic character against hybridization, Fig. 1, the points should fall on a smooth curve or a straight line. As is apparent, there is a distinct break at CCl_4 for the hydrogen and fluorine lines. If the hydrogen line is assumed "normal", then the fluorine curve is "abnormal".

Table 3. *Ionic Character and Hybridization in Unsymmetrical Carbon Tetrahalides*

Compound			Orbital Electronegativities		Orbital Hybridization	Orbital Electronegativities		CCl Bond Ionic Character
		ϱ^b	χ_0^s	χ_0^p	$\underset{=}{s}$	χ_0^{hyb}	χ_0^{eff} (C)	i
M C					0.25[f]	2.51		
$\frac{X_3}{Cl}$	$\frac{Y}{\;}$ F	0.719[b]	5.69	2.95 3.90	0.143 0.0[f]	3.33 3.9	3.01	0.161
Cl	H	0.698[b]	5.69 2.21	2.95	0.079 1.0	3.16 2.21	2.68	0.242
$\frac{X_2}{Cl}$	$\frac{Y_2}{\;}$ F	0.701[c]	5.69	2.95 3.90	0.174 0.0[f]	3.42 3.9	3.12	0.152
Cl	H	0.656[d]	5.69 2.21	2.95	0.061 1.0[f]	3.11 2.21	2.50	0.301
$\frac{X}{Cl}$	$\frac{Y_3}{\;}$ F	0.694[d, e]	5.69	2.95 3.90	0.193 0.0[f]	3.47 3.9	3.19	0.140
Cl	H	0.620[d, e, f]	5.69 2.21	2.95	0.043 1.0[f]	3.06 2.21	2.36	0.352

[b] Livingston, R.: J. chem. Physics **19**, 803, 1434 (1951).
[c] Akon, C. D., and T. Iredale: J. chem. Physics **34**, 340 (1961).
[d] Hooper, H. O., and P. J. Bray: J. chem. Physics **33**, 334 (1960).
[e] Hooper, H. O., and P. J. Bray: Brown University, Rhode Island. Pamphlet (1960).
[f] Assumed values, see text.

Lucken postulated for these compounds that the fluorine p_z and antibonding *C-Cl* σ^* orbital overlap. This feed-in of electrons from the fluorine increases the ionic character of the bond and consequently decreases the frequency. The hyperconjugative double bonding forces the carbon to appear more electronegative than the mere inductive effect via the σ bonds.

It is impossible to distinguish between these views. However, if we assume that the second effect is true, then it is possible to estimate its size. If the line for the $CH_X Cl_{4-X}$ is extended through CCl_4, the fluorine compounds would be expected to fall on this line. The ϱ from these "assessed" i and s, ϱ_{ass}, on subtracting from the experimental results yields the hyperconjugative π bonding.

If the relationship between the amount of s hybridization on the chlorine in the F compounds is plotted against the ionic character then three straight lines are obtained. These are plotted on Fig. 1 and are seen to cut the extension of the hydrogen "normal curve". The cuts are

$CFCl_3$	$0.13i$	$0.11\underline{\underline{s}}$
CF_2Cl_2	$0.09i$	$0.12\underline{\underline{s}}$
CF_3Cl	$0.05i$	$0.13\underline{\underline{s}}$

whence from $\varrho_{Cl} = (1-i)\,(1-\underline{\underline{s}}) - \pi_h^*$
where π_h^* is the hyperconjugative π bonding to the antibonding σ^* by the fluorine p, the π_h^* occurring are

$CFCl_3$	.05
CF_2Cl_2	.10
CF_3Cl	.13

Thus only 5, 10 or 13% of the hyperconjugative effect is needed to bring the fluorine measurements from the "normal" to "abnormal" curve. This is well within the estimates of LUCKEN, and the recent qualitative discussion of this effect by WILLIAMS [*25*].

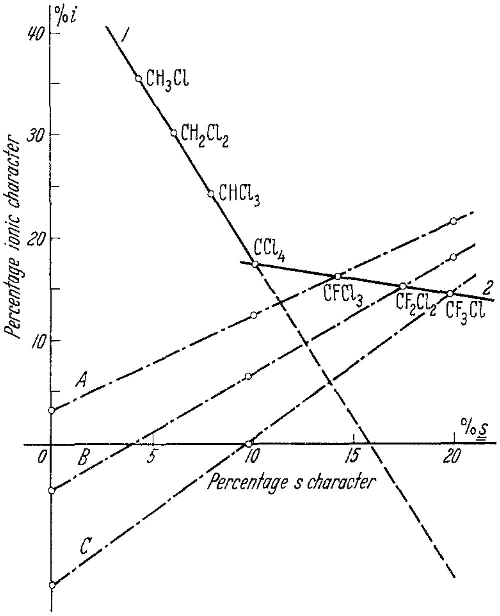

Fig. 1. *The percentage ionic character against percentage s hybridization in the chlorine σ orbital.* Curve 1 represents the "*normal*" curve for the change in ionic character with electronegativity determined from $\chi = \underline{\underline{s}}\,\chi_s + (1-\underline{\underline{s}})\,\chi_p$, and curve 2 the "*abnormal*" curve for the fluorine compounds. A, B and C are the change of i with $\underline{\underline{s}}$ for the compounds $CFCl_3$, CF_2Cl_2 and CF_3Cl and where they cut the extrapolation of curve 1 is the "expected" values for i and $\underline{\underline{s}}$. The deviation from the extrapolated curve 1 to curve 2 is due to π_h* hyperconjugation

When the carbon tetrahalides are considered, the substitution of Cl by Br and I would be expected to follow a smooth sequence similar to those in the polyhalides above, and reflecting the same arguments. The prediction would be that as the series is descended, the $\chi_0^{\text{eff}}\,(C)$ is decreased, the χ_0^p (halogen) is smaller, more nearly matching $\chi_0^{\text{eff}}\,(C)$ and hence the hybridization will smoothly decrease. This would be parallelled by a smooth decrease in the ionic character of the bond. Tab. 2 shows that these decreases do occur, but not very smoothly. Thus the s hybridization suddenly decreases to zero for iodine (0.004) from 7% for bromine and 10% for the chlorine compound. The ϱ show a smooth increase in value, and these together with the χ_0^s and χ_0^p would suggest that iodine would display a decrease in $\underline{\underline{s}}$ *less* than that displayed in going from Cl to Br. The break is no doubt due to the possibility of d character in the σ bond of the halogen in Br and I which masks the actual s hybridization [*24*]; thus it would normally be expected that the sequence Cl, Br and I would show *increased* s character [*20*], since the chlorine χ being the least well matched would be expected to use the least s character, as any s invariably increases the mismatch of the χ_0^{Cl} and χ_0^{eff}. The d character is presumably used to improve overlap, since it offsets the mismatch of χ which would result in increasing s character in the sequence Cl, Br, I, and at the same time is less significant in determining the orbital size, and hence overlap, than the *s* character. The carbon tetrahedral and chlorine *p* orbitals display similar space distribution, chlorine using sufficient *s* to make the overlap a maximum without mismatching the χ severely; in bromine and iodine however the orbitals need to be made considerably more directional to make the overlap a maximum, and invoke *d* character to minimize the χ discrepancy.

The arguments also apply to the deuterium halides in Tab. 1, where the *s* character actually increases from *DCl* to *DBr* and then decreases in going to *DI*.

Table 4

	D	*C*	*Si*	*Ge*	*Sn*
			Change in s Hybridization (%)		
Cl to Br	+3.86	−3.0	−5.6	−3.7	−3.1
Br to I	−5.69	−6.5	−5.3	+0.7	−2.9
			Change in Ionic Character (%)		
Cl to Br	−6.36	−9.4	−7.5	−1.5	−6.3
Br to I	−16.49	−7.8	−12.0	−12.6	−9.8

Table 5. *π-Bond Characters of the Group 4 Tetrahalides*

	From Eqn. (5) and CX_4 Results	From PAULING and DAS and HAHN[a,b]	From GORDY[c]
$SiCl_4$	0.37	0.45 ± 0.12	0.30
$SiBr_4$	0.37	0.60 ± 0.15	0.26
$GeCl_4$	0.28	0.41 ± 0.16	0.14
$GeBr_4$	0.29	0.16 ± 0.06	0.12
GeI_4	0.34	0.11 ± 0.07	0.09
$SnCl_4$	0.31	0.22 ± 0.11	0.09
$SnBr_4$	0.33	0.25 ± 0.08	0.08
SnI_4	0.34	0.21 ± 0.01	0.06

[a] Ref. 18, p. 241. [b] Ref. 4, p. 148. [c] Ref. 6, p. 27.

FCl to *FBr* shows an increasing *s* percentage. Thus all the systems show similar trends to the carbon tetrahalides.

The silicon, germanium, and tin tetrahalides would be expected to behave like the carbon cases, if the situation were the same in each compound as in the carbon predecessor. As can be seen from Tab. 4, the *trend* is the same in each group, but the *absolute values*, Tab. 2, *differ* greatly. From both the values of χ and the spacial overlap requirements, such absolute differences are difficult to explain, but the use of metal *d* orbitals as acceptors of halogen p_π electrons would result in just such an overassessment of *s* and *i* character. Thus using equation (5)

$$\chi = (1 - \underline{s})\,(1 + i) - \pi$$

and assuming that $\underline{s}$ and i for any MCl_4, MBr_4 or MI_4 are the same as those in the carbon analogues (an approach suggested by the similarity of the change in hybridization and ionic character in Tab. 4, which suggests some common constant absolute shift in the ionic and *s* characters determined), the π bond orders in Tab. 5 are obtained.

Thus d orbital participation in these compounds is of two kinds. The halogen d orbitals hybridize in the σ bond of the halogen; the metal d orbitals act as unhybridized acceptors for the halogen p_π electrons. There is at the moment no evidence of halogen d_π or metal d_σ involvement.

Very interestingly, these values are all close together, supporting the idea of a common cause. In the elements *Si*, *Ge*, *Sn* there are available *d* orbitals, 3*d*, 4*d* and 5*d* respectively (whereas in carbon $n = 2$, there are no *d* orbitals) which can accept electrons from the halogens to form $p_\pi - d_\pi$ bonds. At this time we have no satisfactory way of assessing the χ of any vacant orbital[*25*]; let us assume for the sake of argument that $\chi \simeq 1/2\ (EA)$ then this assumption suggests an order of magnitude for $\chi_{\mathrm{d\ vacant}} \simeq 0.1$ whence it is difficult to see how the d_π could overlap at all well with the p_π halogen with $\chi_p = 3.5$ (*Cl*); 2.82 (*Br*) or 2.72 (*I*). A more detailed discussion and resolution of this contradiction must await a better understanding of orbital electronegativities of vacant orbitals, which is now under investigation in this Laboratory [*8*]. However, it is comforting to note that the present results are of the same order of magnitude and trend as those obtained [*4*] on the basis of PAULING electronegativity and his interpretation [*18*] of bond lengths. They differ very greatly from the predictions of GORDY [*6*], but this is not surprising in view of his calculated values of effective electronegativity which for the silicon, germanium and tin halides are extremely low. It is also preferable to have no π bonding in the carbon cases where no suitable *d* orbitals occur to allow it, than the π characters stipulated by GORDY.

b) The Trichlorides of B, P and As

The results obtained by use of equation (14) for boron, phosphorus and arsenic trichlorides are shown in Tab. 6. Once again the ionic characters and hybridization of the halides are large, and unexpectedly so, in view of the closeness of the χ_M and $\chi_{\mathrm{halogen}\ p}$ and the lack of *s* character in the metal orbital. It appears that here, too, π bonding is important, in boron using the empty boron p_π orbital and in phosphorus and arsenic the empty *d* orbitals of the central atom. In these cases, however, no assessment of the amount of π bonding was readily possible,

Table 6. *Hybridization and Ionic Character in BCl_3, PCl_3 and $AsCl_3$*

			Orbital Electronegativities		Orbital Hybridization	Orbital Electronegativities		MCl Bond Ionic Character
M	X_3	ϱ	χ_0^s	χ_0^p	$\underline{s}$	χ_0^{hyb}	χ_0^{eff} (M)	i
B					0.33[a]	1.92		
	Cl	0.394[b]	5.69	2.95	0.28	3.72	2.82	0.45
P					0.15[a]	2.58		
	Cl	0.477[c]	5.69	2.95	0.31	3.80	3.19	0.31
As		0.185[d]			0.18[a]	2.82		
	Cl	0.459	5.69	2.95	0.36	3.93	3.37	0.28

[a] From bond angles; see text.
[b] CHIBA, T.: J. physic. Soc. (Japan) **13**, 860 (1958).
[c] Ref. 15.
[d] OGAWA, S.: J. physic. Soc. (Japan) **13**, 618 (1958).

as it was in group four by comparison with the carbon compounds; in these cases again the difference in χ between an empty orbital ($\chi \simeq 0.2$) and the chlorine p ($\chi = 3.152$), seems too large.

It is interesting to note that the assumption of orbital following made above to evaluate hybridization in *As* and *P* is *not* critical. If an alternative extreme assumption were made, that *P* is purely sp^3 (tetrahedrally) hybridized, χ_0^{hyb} (*P*) would be 2.99, $\underline{\underline{s}}$ would be 0.343, instead of 0.314, and i would be 0.275 instead of 0.306. The conclusions are unaltered. If working in the other direction, π character is estimated from known bond lengths [*9*] by the Pauling method [*18*], giving 0.10 for PCl_3 and 0.077 for $AsCl_3$, then this would reduce $\underline{\underline{s}}$ and i to 0.2312 and 0.25 respectively in PCl_3 and to 0.299 and 0.237 respectively in $AsCl_3$, while in BCl_3 it gives 0.35 as the π character corresponding to an $\underline{\underline{s}}$ and i of 0.002 and 0.51 respectively. In the phosphorus and arsenic compounds the results seem more reasonable according to intuitive judgment.

Acknowledgements: The Air Force is thanked for financial support during the course of this research. The authors wish to thank Mr. J. HINZE for his comments.

Appendix

$$MX_4\colon \frac{1}{4}(\chi^s-\chi^p)\underline{\underline{s}}^2-\left[1+\frac{1}{4}\chi^s-\frac{1}{2}\chi^p+\frac{1}{4}\chi(M)\right]\underline{\underline{s}}+1-$$
$$-\frac{1}{4}\chi^p+\frac{1}{4}\chi(M)-\varrho=0 \tag{10}$$

where χ^s and χ^p refer to atom X, and χ (M) refers to the tetrahedral hybrid.

MX_3Y, where X is the element for which the NQR frequency is measured:

$$\frac{1}{3}(\chi^s-\chi^p)\underline{\underline{s}}^2-\left[1+\frac{1}{3}\chi^s-\frac{2}{3}\chi^p+\frac{1}{4}\chi(M)+\frac{1}{12}\chi(Y)\right]\underline{\underline{s}}+$$
$$+1+\frac{1}{4}\chi(M)+\frac{1}{12}\chi(Y)-\frac{1}{3}\chi^p-\varrho=0 \tag{11}$$

with the same definitions, except that χ (Y) is the appropriate hybrid orbital electronegativity of atom Y.

MX_2Y_2, NQR frequency measured for X:

$$\frac{5}{12}(\chi^s-\chi^p)\underline{\underline{s}}^2-\left[1+\frac{5}{12}\chi^s-\frac{5}{6}\chi^p+\frac{1}{4}\chi(M)+\frac{1}{6}\chi(Y)\right]\underline{\underline{s}}+1+$$
$$+\frac{1}{4}\chi(M)+\frac{1}{6}\chi(Y)-\frac{5}{12}\chi^p-\varrho=0 \tag{12}$$

MXY_3 where the NQR frequency of X is known:

$$\frac{1}{2}(\chi^s-\chi^p)\underline{\underline{s}}^2-\left[1+\frac{1}{2}\chi^s-\frac{1}{4}\chi^p+\frac{1}{4}\chi(M)+\frac{1}{4}\chi(Y)\right]\underline{\underline{s}}+1-$$
$$-\frac{1}{2}\chi^p+\frac{1}{4}\chi(M)+\frac{1}{4}\chi(Y)-\varrho=0 \tag{13}$$

MX_3 where now χ (M) is the orbital electronegativity for the hybrid of B, P or As specified in the text.

$$\frac{1}{4}(\chi^s-\chi^p)\underline{\underline{s}}^2-\left[1+\frac{1}{4}\chi^s-\frac{1}{2}\chi^p+\frac{1}{4}\chi(M)\right]\underline{\underline{s}}+1+$$
$$+\frac{1}{4}\chi(M)-\frac{1}{4}\chi^p-\varrho=0 \tag{14}$$

References

[*1*] COULSON, C. A.: Proc. Camb. phil. Soc. **53**, 1367 (1931).

[*2*] — Quart. Rev. **1**, 144 (1947).

[*3*] DAILEY, B. P., and C. H. TOWNES: J. chem. Physics **23**, 118 (1955).

[*4*] DAS, T. P., and E. L. HAHN: Nuclear Quadrupole Resonance Spectroscopy. p. 138. New York — London: Academic Press 1958.

[*5*] GORDY, W., W. V. SMITH and R. F. TRAMBARULO: Microwave Spectroscopy. New York: John Wiley and Sons 1953.

[*6*] — Discussions of Faraday Soc. **19**, 14 (1955).

[*7*] HINZE, J., and H. H. JAFFÉ: J. Amer. chem. Soc. **84**, 540 (1962).

[*8*] —, M. A. WHITEHEAD and H. H. JAFFÉ: (to be published).

[*9*] Interatomic Distances. Spec. Publ. Chem. Soc. No. 11, London 1958.

[*10*] ICZKOWSKI, R. P., and J. L. MARGRAVE: J. Amer. chem. Soc. **83**, 3547 (1961).

[*11*] KAGARISE, R. E.: J. Amer. chem. Soc. **77**, 1377 (1955).

[*12*] KLEMPERER, W.: J. Amer. chem. Soc. **83**, 3910 (1961).

[*13*] LAGOWSKI, J. J.: Quart. Rev. **13**, 233 (1959).

[*14*] LUCKEN, E. A. C.: J. chem. Soc. **1959**, 2954.

[*15*] —, and M. A. WHITEHEAD: J. chem. Soc. **1961**, 2459.

[*16*] MULLIKEN, R. S.: J. chem. Physics **2**, 782 (1934).

[*17*] — J. Chim. physique **46**, 497 (1949).

[*18*] PAULING, L.: The Nature of the Chemical Bond, Cornell U.P. 1960 3rd Edition, p. 224.

[*19*] PRITCHARD, H. O., and H. A. SKINNER: Chem. Rev. **55**, 745 (1955).

[*20*] — and F. H. SUMNER: Proc. Roy. Soc. **A 235**, 136 (1956).

[*21*] TOWNES, C. H., and B. P. DAILEY: J. chem. Physics **17**, 782 (1949).

[*22*] WHITEHEAD, M. A., and H. H. JAFFÉ: Trans. Faraday Soc. **57**, 1854 (1961).

[*23*] — — J. chem. Physics **34**, 2204 (1961).

[*24*] — J. chem. Physics **36**, 3006 (1962).

[*25*] WILLIAMS, J. F. A.: Trans. Faraday Soc. **57**, 2089 (1961).

[*26*] ZEIL, W.: Angewandte Chemie **23**, 751 (1961).

(Received January 3, 1963)