Nuclear Magnetic Shielding of Fluorine in the Fluorides of the Elements

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Nuclear magnetic shielding parameters for the (spin-paired) binary fluoride molecules and ions vary periodically with the atomic number of the central atom. The diamagnetic term σ_d has been calculated by Flygare's method, and experimental values of σ_p for 17 binary fluorides have been obtained from spin-rotation interaction constants (with Ramsey's and Flygare's equations) and from the shielding anisotropy for some linear molecules. These values of σ_p agree with those obtained by substracting σ_d(calc.) from the resultant shielding referred to an absolute scale, and σ_p has been obtained in this way for the remaining molecular fluorides and complex ions. The term σ_d increases periodically with the number of electrons in the molecule, but the resultant shielding follows the larger and more irregular variations in σ_p; $|\sigma_p^F|$ increases sharply across the Row of the central atom for the typical elements and also for the transition metals with empty d (t_{2g}) orbitals. Fluorine is highly shielded, however, in the d^6 hexafluoride molecules and ions, possibly because of circulations of the $\pi^* \rightarrow \sigma^*$ type which contribute positive terms to σ_p in ClF. The increase in $|\sigma_p^F|$ across the Row of the central atom is ascribed to increasing imbalance of the fluorine $2p$ electrons with increasing covalency, to the increase in $\langle r^{-3}\rangle_{2p}$, and to the tendency of $(\Delta E)^{-1}$ to increase. Down the Group of the central atom $|\sigma_p^F|$ tends to increase with $(\Delta E)^{-1}$, against the tendency of $\langle r^{-3}\rangle_{2p}$ to decrease (for the typical elements), although there are important anomalies which may show the influence of the radius term. Near the bottom of the later Groups the increase in $|\sigma_p^F|$ is slowed or reversed. Periodic correlations for other nuclei such as ^{13}C show corresponding patterns of variation in σ_p and these are evident also in ^{1}H shielding. The periodic correlation shows the basis of the familiar relation between fluorine shielding and electronegativity of the central atom and of the important exceptions to this relation.

THE difficulties in calculating the paramagnetic term σ_p in nuclear magnetic shielding are well known, both the molecular term defined by Ramsey [1] and that defined by the local-term approximation.[2] The diamagnetic term σ_d, however, is a ground-state term and Flygare's equations [3] now provide a simple and reliable method of calculation which dispenses even with wavefunctions (the free-atom values being available in tables), so that values are readily obtainable over the range of the Periodic Table. Now also experimental values of the paramagnetic term are increasingly becoming available for simple molecules from measurements of the spin-rotation interaction constants C_i, by molecular-beam electric or magnetic resonance methods,[4,5] and microwave spectroscopy,[6] with computer analysis of complex spectra. When an isolated molecule rotates the circulations of the valence electrons 'deshield' the nuclei and in favourable circumstances the 'deshielding' σ_p is measurable as magnetic hyperfine structure of the nuclear spin resonance or of the rotational spectrum. This σ_p is equal to the paramagnetic term which is opposed by the Lamb term in conventional n.m.r. spectroscopy. The derivation of σ_p from spin-rotation constants C_i has been given by Ramsey [4,5] for linear molecules and by Flygare [7] for symmetric- and spherical-top molecules. An absolute measure of the paramagnetic term can be obtained also from the shielding anisotropy $\Delta\sigma$ in linear molecules (for which $\sigma_p^{\parallel}$ is zero) and methods for this are increasingly becoming available, as mentioned below. Reasonably accurate values for σ_p have now been given or are accessible from published measurements of C_i or $\Delta\sigma$ for upwards of 17 binary fluorides.

For the simple binary hydrides [8] absolute values of the molecular (Ramsey) shielding constants σ_d and σ_p, obtained as above, were found to vary periodically in relatively simple fashion with the atomic number of the heavy atom. The variation of the resultant shielding σ is somewhat more complex, this being the algebraic sum of σ_d and σ_p. In the fluorides, the variation of all three terms, shown in the Figures, is more complex again, because of the extra electron shell on fluorine and the larger variety of valence states for the ligand.

RESULTS AND DISCUSSION

The resultant ^{19}F shielding, $\sigma(\delta)$, plotted as open squares in the Figures, was obtained by referring the chemical shift δ, measured relative to $CFCl_3$, to Hindermann and Cornwell's absolute scale.[9] This they based on Weiss's measurement [10] of the fluorine spin-rotation constant C_i^F in HF (g) and on their own accurate measurements of chemical shifts for fluorine reference standards relative to HF (g).[11,12] In opposition to the convention for absolute shielding, σ, but in accord with

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[6] C. Townes and A. Schawlow, 'Microwave Spectroscopy,' McGraw-Hill, 1955, ch. 8; W. Gordy and R. L. Cook, 'Microwave Molecular Spectra,' Interscience, 1970, sections 9.7 and 11.4.

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[10] R. Weiss, *Phys. Rev.*, 1963, **131**, 659.

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Absolute values of the nuclear magnetic shielding parameters for fluorine in the binary fluorides of the elements. The negative sign in the column headings $-C_i$ and $-\sigma_p$ is to be noted. Numbers in parentheses are uncertainties (in units of the last digit) given by the original authors. The parameters and their derivation are explained in the text; $\sigma(C^{19}FCl_3)$ is 189 p.p.m.[9] To reduce the total number of references, shifts are referred where possible to compilations. (g), (l), and (s) refer to the state of the compound; (l) is written for pure liquids or solutions. Solutions in water or anhydrous HF are given as (aq) or (HF). In some compounds (SF_4, halogen fluorides, *etc.*) in which the fluorines are stereochemically distinguishable these may be described as axial or equatorial, or by numbers in parentheses, *e.g.* ClF_3 has one unique fluorine (1) and a pair equally shielded (2).

	σ_d(calc.)		$-C_i^F$		$-\sigma_p$(obs.)	σ_T	δ		$\sigma(\delta)$	$-\sigma_p(\delta)$
Molecule	p.p.m.	Ref.	kHz	Ref.	p.p.m.	p.p.m.	p.p.m.	Ref.	p.p.m.	p.p.m.
HF (g)	482	9	307.6 (1.5)	9, 10,	63	20, 410 *	−221	9, 11	410	72
				17	67	415				
^{6}LiF (g)	492	13	37.3 (3)	18	115	377				
LiF (s)							−218	*a*	407	
BeF_2 (g)	528	14								
$[BeF_4]^{2-}$ (aq)	609						−178	*b*	367	242
BeF_2 (s)							−189	36	378	
BF_3 (g)	583			17	256	327	−138	9	327	256
$[BF_4]^-$ (pent.)	618						−150	*b*	339	279
CF_4 (g)	631	19	6.85 (35)	17, 19	373	258	−70	9	259	372
NF_3 (l)	599						145	*b*	44	555
$[NF_4]^+$(HF)	615						215	*c*	−26	641
F_2O (l)	562	14					248	*b*	−59	621
F_2 (g)	530	13	157.4 (3)	12, 17, 20	756	−226	422	9, 12	−233	763
				31	750	−220				
^{23}NaF (g)	524		2.2 (2)	21, 22	73	451				
NaF (s)							−218	*d*	407	
MgF_2 (s)	551				170		−193	33	382	170
$[AlF_4]^-$ (aq)	702						−153	*e*	342	360
$[AlF_6]^{3-}$ (s)	707						−179	*a*	368	339
α-AlF_3 (s)							−180	*a*	369	
SiF_4 (g)	655		2.42 (8)	17, 19	285	370	−174	9	363	292
$[SiF_6]^{2-}$ (aq)	721						−127	34	316	405
$[SiF_6]^{2-}$ (s)	721						−149	*a*	338	383
PF_3 (l)	634			17			−34	*b*	223	398
PF_5 (l)	703						−76	*b*	265	438
$[PF_6]^-$ (aq)	734						−65	39	254	477
							−71	*f*	260	477
(s)	734						−74	*a*	263	471
SF_6 (g)	747		4.6 (1.0)	5	585	162	49	9	140	607
SF_4 (l) (eq)	681						71	*b*	118	563
(ax)	665						118	*b*	71	594
^{35}ClF (g)	569	3	−22.67 (3)	23	−62	631	−448	9	637	−68
ClF_3 (g) (1)	643						13	9	176	467
(2)	626						139	9	50	576
ClF_5 (l) (1)	712						247	*b*	−58	770
(4)	693						412	*b*	−223	916
$[ClF_6]^+$ (HF)	739						388	*g*	−200	940
^{39}KF (g)	553		10.69 (7)	24	230	323				
(s)							−130	*a*	319	
CaF_2 (s)							−104	33	293	
$[ScF_6]^{3-}$ (aq)	723						−71	*f*	260	463
ScF_3 (s)							−45	*a*	234	
$[TiF_6]^{2-}$ (aq)	729						75	34, *f*	114	615
$[NiF_6]^{2-}$ (HF)	800						−320	*h*	509	291
ZnF_2 (s)	630				337		−202	33	391	337
$[GaF_n(OH_2)_{6-n}]^{(3-n)+}$	784						−142	*i*	331	453
GaF_3 (s)							−187	*a*	376	
$[GaF_6]^{3-}$ (s)	784						−129	*a*	318	466
GeF_4 (g)	744		1.88 (8)	19	370	374				
(l)	744						−178	*b*	367	377
$[GeF_6]^{2-}$ (aq)	818						−123	34	312	−506
AsF_3 (g)	715			25						
(l)	715						−41	*b*	229	486
AsF_5 (l)	786						−66	39	255	531
$[AsF_6]^-$ (aq)	803						−60	39	250	553
SeF_4 (l)	750						64	39	125	686
SeF_6 (l)	827						51	39	128	689
BrF_3 (l) (1)	732						−38	*b*	227	505
(2)	700						−23	*b*	212	488
BrF_5 (l) (1)	810						142	39	52	758
(4)	784						272	39	−83	867
KrF_2 (l)	672						50	*j*	139	533
^{85}RbF (g)	624		10.37 (14)	26	347	277				
(s)							−107	*a*	296	
SrF_2 (s)							−83	33	272	
YF_3 (s)							−79	*a*	268	
ZrF_4 (s)							19	*a*	170	
$[ZrF_6]^{2-}$ (aq)	801						−3	34	192	609
(s)	801						−9	*a*	198	603

Molecule	σ_p(calc.) p.p.m.	Ref.	$-C_I^F$ kHz	Ref.	$-\sigma_p$(obs.) p.p.m.	σ_T p.p.m.	δ p.p.m.	Ref.	$\sigma(\delta)$ p.p.m.	$-\sigma_p(\delta)$ p.p.m.
$[NbF_6]^-$ (MeCN)	808						101	39	88	720
MoF_6 (l)	840						278	39	−89	929
$[PdF_6]^{2-}$ (HF)	866						−351	*h*	540	326
AgF (s)							−266	*j*	455	
							−318	*a*	507	
CdF_2 (s)							−198	33	387	
^{115}InF (g)	703		18.77 (10)	27	510	193				
InF_3 (s)							−215	*a*	404	
$[SnF_6]^{2-}$ (aq)	901						−156	*b*	345	556
(s)	901						−164	*a*	353	548
SbF_3 (l)	767						−53	*b*	242	525
$[SbF_6]^-$	902						−109	39	298	604
TeF_4 (l)	817						−26	39	215	602
TeF_6 (l)	889						−56	*b*	245	644
IF_5 (l) (1)	880						14	*b*	175	705
(4)	859						59	*b*	130	729
$[IF_6]^+$ (s)	912						*ca.* 60	*f*	130	782
$[IF_6]^-$ (soln.)	896						1, −114	*f*	188, 303	708, 593
IF_7 (l) (2)	938						170	*b*	19	913
(5)	929						170	*b*	19	913
XeF_2 (s)	745			32	(*ca.* 200	*ca.* 550)				
(HF)	745						258	*b*	−69	814
XeF_4 (HF)	813						440	*b*	−251	1 064
XeF_6 (l)	886						546	*b*	−357	1 243
^{133}CsF (g)	691		14.94 (6)	28	536	155				
(s)							−10	*a*	29	
BaF_2 (s)							−11	33	200	
LaF_3 (s)							8	*a*	181	
CeF_4 (s)	817						−181	*a*	370	
HfF_4 (s)							−43	*a*	232	
$[HfF_6]^{2-}$ (s)	948						−39	*a*	228	720
(aq)	948						−44	34	233	715
$[TaF_6]^-$ (HF)	954						35	*f*	154	800
WF_6 (l)	1 004						166	39	23	981
ReF_7 (l)	1 026						347	*b*	−158	1 184
$[PtF_6]^{2-}$ (HF)	1 010						−364	*h*	553	457
(s)	1 010						−329	*a*	518	492
HgF_2 (s)							−197	33	386	
^{205}TlF (g)	836		17.89 (15)	29	679	157				
ThF_4 (s)							89	*a*	100	
$[PaF_6]^-$ (HF)	1 043						131	*k*	58	985
$[PaF_7]^{2-}$ (HF)	1 039						−136	*k*	325	714
UF_6	1 045						746	*l*	−557	1 602

* With vibrational corrections.[9]

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I.U.P.A.C. (1972) recommendations, the chemical shift σ is taken here as positive downfield. Ideally the shielding constants should refer to the gaseous molecule, but for compounds for which no measurements on the gas have been reported the gas–liquid and gas–solid shifts are expected to be small enough to be ignored for the present purposes. As the Table shows, there is even some measure of agreement between ^{19}F shifts in complex anions in solution and in the solid state (the measurements quoted for complex fluorides are as far as possible for ionic solids, *e.g.* with a larger alkali-metal cation). Until recently the measurement of shifts in solids was subject to considerable error (which was often understated) because of dipolar broadening, but the work of Waugh and others with multiple-pulse techniques is now furnishing accurate values (± 1 p.p.m.) such as those quoted for BeF_2, NaF, MgF_2, CaF_2, ZnF_2, SrF_2, CdF_2, BaF_2, and HgF_2.

The diamagnetic term σ_d, plotted as closed squares in the Figures, is Ramsey's molecular term [1] and values have been given for HF,[9] LiF,[13] BeF_2,[14] F_2O,[14] and F_2.[13] For all the other molecules and complex, ions σ_d was calculated by Flygare's method [3] (which gives values agreeing within 1 or 2 p.p.m. with *ab initio* values where these have been calculated). Bond lengths and angles were taken from the Chemical Society's Tables or from the literature,[15] and the free-atom value of σ_d^F was taken as 470.7 p.p.m. (480.2 p.p.m. for F^-).[16] The gauge origin is at the nucleus in question.

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[14] S. Rothenberg and H. F. Schaefer, *J. Amer. Chem. Soc.*, 1973, **95**, 2095 and refs. therein.

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The paramagnetic term σ_p(obs.), plotted as closed circles in the Figures, was calculated where necessary from the spin-rotation constants C_i^F (by Ramsey's or Flygare's equations) given in the Table. As the Table shows, these values of σ_p(obs.) agree reasonably well with values of $\sigma_p(\delta)$ obtained by subtracting σ_d(calc.) from the resultant shielding $\sigma(\delta)$ derived from the chemical shift δ. Because of this good agreement, $\sigma_p(\delta)$ was plotted in the Figures (as open circles) for those molecules and ions for which σ_p has not been measured directly; σ_T values for the resultant shielding are the sum of σ_p(obs.) and σ_d(calc.).

Spin-rotation constants C_i^F have been measured, mostly by molecular-beam electric resonance, for the following molecules (some of the references are to derived values of σ_p): HF,[9,10,17] LiF,[18] BF_3,[17] CF_4,[17,19] F_2,[12,17,20] NaF,[21,22] SiF_4,[17,19] PF_3,[17] SF_6,[5] ClF,[23] KF,[24] GeF_4,[19] AsF_3,[25] RbF,[26] InF,[27] CsF,[28] and ^{205}TlF.[29] Vibrational effects have been neglected in the calculation of σ_p. The Table follows Ramsey's sign convention which defines C_i by the Hamiltonian $\mathscr{H} = -\boldsymbol{h}C_i\boldsymbol{I}\,.\,\boldsymbol{J}$ (microwave spectroscopists usually define C_i with the opposite sign). All the measured spin-rotation constants for fluorine are negative except for ClF, which thus, unusually, has an antiparamagnetic σ_p. This has been explained by Cornwell[30] and also by Santry in terms of a $\pi^* \rightarrow \sigma^*$ electronic circulation which is dominated by the chlorine terms, because both orbitals are antibonding and chlorine is the less electronegative element.

The shielding anisotropy, $\Delta\sigma^F$, has been measured in the linear molecules F_2 and XeF_2 from lineshapes for the solids. For F_2,[31] although variation in the diamagnetic term was as usual neglected, correction for $\Delta\sigma_d$ (given as -75 p.p.m. by Gierke and Flygare[3]) gives a value of σ_p(obs.) from $\Delta\sigma$ which agrees well with those from the spin-rotation constant and the chemical shift (Table). For XeF_2,[32] the authors note that their value of $\Delta\sigma^F$ is much smaller than those previously calculated from localised-orbital models, and speculate that this may be due to positive contributions to σ_p, *e.g.* from $\pi^* \rightarrow \sigma^*$ excitation as in ClF. However, the reported anisotropy in the fluorine shielding gives a value for $-\sigma_p$(obs.) which, even after correction for $\Delta\sigma_d$ (some 400 p.p.m.), is still several hundred p.p.m. smaller than the value estimated from the chemical shift [contrast the good agreement between σ_p(obs.) and $\sigma_p(\delta)$ for ClF]. This value for σ_p(obs.) is given in the Table but has not been plotted in the Figures.

Accurate values for the ^{19}F shielding-tensor elements have been determined (by multiple-pulse methods)[33] for MgF_2 and ZnF_2, which have similar tetragonal structures containing linear FMF groupings. The Table gives values for σ_p(obs.) which have been recalculated from the reported $\Delta\sigma^F$ (the authors determined σ_p by use of an average energy chosen to fit the trace of the shielding tensor).

The Periodic Correlation.—Fluorine-19 shieldings for molecular species, mostly with lower oxidation states of the central atom, are plotted in Figure 1 against the atomic number Z of the central atom so as to show the periodic relations. In the second Row, we see that σ_d^F increases across the Row with Z, but also increases and then decreases with the number of fluorine ligands (*i.e.* with the total number of electrons in the molecule) in the sequence LiF, BF_3, CF_4, NF_3, F_2O, and F_2. The discontinuity between CF_4 and NF_3 is discernible also in the resultant shielding σ and in the paramagnetic term σ_p. In the corresponding plot for the proton shielding,[8] on the other hand, σ_d increases steadily with Z across the Row of the Periodic Table despite the increase and then decrease in the number of hydrogen atoms, because of the small number of electrons on them and because the electrons on the central atom are closer to the proton in question.

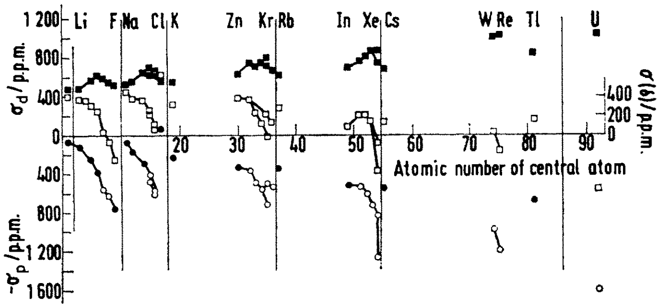

FIGURE 1 Fluorine-19 shielding parameters for the binary fluorides (molecular species) plotted against the atomic number of the central atom. The key for all the Figures is as follows: σ_d(calc.) for molecular fluorides (■) and fluoro-anions (▲); $\sigma(\delta)$ for molecular fluorides (□) and fluoro-anions (△); σ_p(obs.) (●); and $\sigma_p(\delta)$ for molecular fluorides (○) and fluoro-anions (×)

In the third Row of the fluoride plot in Figure 1, σ_d rises in the sequence NaF, MgF_2, SiF_4, and PF_5, but there

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is a dip at SF_4 and also at PF_3, values for both fluorides of phosphorus having been plotted. For the higher fluoride compared to the lower, both σ_d and $|\sigma_p|$ are larger, and this is a general observation. As to the resultant ^{19}F shielding, this is higher in the higher oxidation state for the fluorides of Group 5 and 6 elements, but is higher for the lower fluorides of the halogens or xenon. The positive contribution to σ_p in ClF has been mentioned. Figure 1 shows the shielding anomaly at ClF in the third Row; it could be claimed that the paramagnetic term for ClF begins the sequence evident in the fourth Row. Here, in the diamagnetic term for ZnF_2, GeF_4, AsF_3, SeF_4, BrF_3, and KrF_2, there is a dip at AsF_3 and again at BrF_3 and KrF_2; BrF_5 is also plotted. In the fifth Row σ_d rises in the sequence InF, SbF_3, TeF_4, and IF_5, then rises for XeF_6 or falls for XeF_2.

Fluorine-19 shieldings for complex fluoride anions, solid fluorides, and high oxidation states of the central atom are plotted in Figure 2. A striking feature of Figures 1 and 2 is the plunge downfield of the resulting shielding across a Row of the typical elements, following the paramagnetic term. In the corresponding hydride plot,[8] σ_d^H and $|\sigma_p^H|$ increase across the Row in rather symmetrical fashion. The resultant proton shielding very slightly rises then falls across the second Row (from lithium), but in subsequent Rows it rises monotonically, *i.e.* the diamagnetic term 'dominates' although the margin is small. The p electrons on fluorine lead to much more dramatic changes in σ_p. The increasing imbalance of the p electrons with increasing covalency across the Row [2,34] acts to increase $|\sigma_p|$, helped by the increase in $\langle r^{-3}\rangle_{2p}$ and the tendency of $(\Delta E)^{-1}$ to increase. Towards the end of the second Row, the repulsion of lone-pair electrons in NF_3, F_2O, and F_2 tends to decrease the radius term and increase the average-energy term, increasing $|\sigma_p|$. The average-energy approximation breaks down of course for molecules like ClF in which there are significant positive contributions to σ_p.

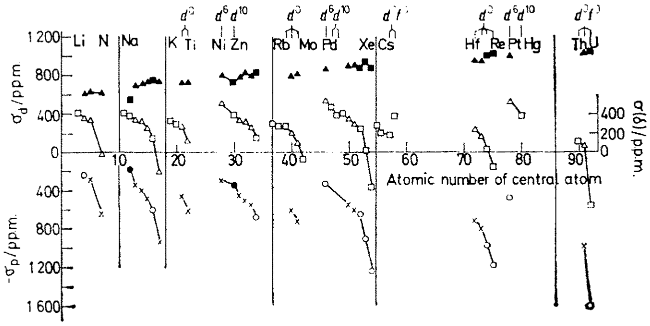

FIGURE 2 Fluorine-19 shielding parameters for the binary fluorides: fluoride anions, solids, and high oxidation states of the central atom

Of the transition-metal fluorides, some remain to be measured, but some of the gaps are due to the compounds being paramagnetic since fluorine is a weak-field ligand. Figure 2 clearly demonstrates the contribution to σ_p when the fluorine p electrons are able to circulate in low-lying d (t_{2g}) orbitals on the metal, as in the d^0 complexes $[TiF_6]^{2-}$, $[ZrF_6]^{2-}$, and $[HfF_6]^{2-}$.[34] There is then a dramatic increase in shielding to the spin-paired d^6 complexes $[NiF_6]^{2-}$, $[PdF_6]^{2-}$, and $[PtF_6]^{2-}$, whether in HF solution or in the solid.[35] {The ^{17}O resonance in $[Co(pd)_3]$ (pd = pentane-2,4-dionate) and the ^{14}N resonances in the hexa-ammines of Co^{III}, Rh^{III}, and Ir^{III} are at similarly high field.} In the d^6 fluorides there is now the possibility of $\pi^* \rightarrow \sigma^*$ circulations on fluorine involving e_g^* orbitals on the metal, perhaps contributing positive terms to σ_p.[35]

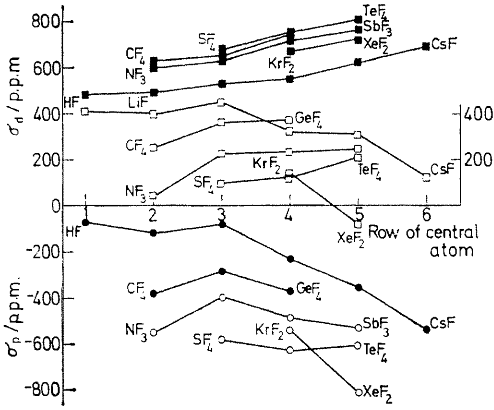

FIGURE 3 Variation in ^{19}F shielding down the Group of the central atom for Groups 0, 1, 4, 5, and 6

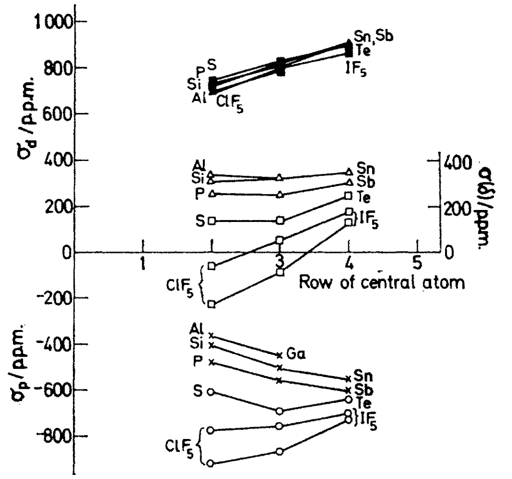

FIGURE 4 Variation in ^{19}F shielding down the Group of the central atom in hexafluoride ions and molecules, and halogen pentafluorides

Figures 3 and 4 show the variation in shielding parameters down the Group of the central atom for corresponding compounds, so far as these have been measured. (Figure 2 shows some irregularities, due to ions and molecules with different oxidation states of the central atom being plotted on the same axes.) The diamagnetic term increases with increase in the number of electrons, and the increment is particularly large from the fluorides of the third Row to those of the post-transition elements of the fourth (Figure 3): contrast σ_d for the alkali-metal

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fluorides. The resultant shielding follows the larger and less regular changes in the paramagnetic term. The irregularities are perhaps due to the opposing influences of the $(\Delta E)^{-1}$ term, which increases, and $\langle r^{-3}\rangle_{2p}$ which decreases down the Group of the typical elements.

The quantity $|\sigma_p|$ tends overall to increase down the Group following $(\Delta E)^{-1}$, but is particularly large for fluorides of the elements of the second Row which have small atoms (with only two inner electrons). The fall in $|\sigma_p|$ from the second to the third Row, and the increase thereafter down the Group, is shown in Figure 3 for the alkali-metal fluorides, and is evident also in the recent measurements of the solid difluorides of the main-Group 2 elements.[33,36] The same pattern can be seen in the corresponding periodic correlations for other nuclei, ^{13}C for example.[37] In the hydride plot,[8] $|\sigma_p{}^H|$ increases monotonically down a Group; but symmetrically with $\sigma_d{}^H$, the increments are larger from the first Row to the second and from the third to the fourth (for post-transition elements).

A further irregularity, shown clearly in Figure 4, is the decrease in $|\sigma_p|$ towards the bottom of Groups 6 and 7, and the reduced increment in $|\sigma_p|$ towards the bottom of Groups 4 and 5, so that the resultant shielding increases. This tendency is evident also in ^{1}H and ^{13}C shielding.[8,37] It is particularly marked in the higher fluorides of later Groups, and so is not an effect of change in molecular shape across the Row (Figure 4). From the evidence of KrF_2 and XeF_2, Group 0 seems to be exceptional compared with the preceding Groups (Figure 3).

The Figures show the basis for the well known electronegativity correlation in ^{19}F shielding,[2,30,38] *i.e.* that the latter tends to decrease with increasing electronegativity of the ligand, and covalency of the bond, as across the Row of the typical elements. They illustrate also well known exceptions to this rule, such as the tendency for the shielding to decrease down the Group of the central atom, as its electronegativity decreases (for typical elements). Thus the Group 2 difluorides are largely ionic, but the ^{19}F resonances in the solids cover about one third of the chemical-shift range, *ca.* 600 p.p.m., considered to represent the transition from purely ionic (F^-) to purely covalent (F_2) bonding;[33,36,38] SrF_2 and CF_4 have similar fluorine shifts but very different ionicities.

Another well known exception to the electronegativity correlation is the lower ^{19}F shielding in the transition-metal hexafluoride anions of Groups 4A [34] and 5A [39] and the hexafluorides of Group 6A,[39] compared with corresponding compounds of the typical elements of Groups 4—6, although the main-Group elements are expected to be the more electronegative. Here, too, the Group 2 measurements [33,36] provide a new example, since the ^{19}F shielding is higher in the sub-group (Zn, Cd, and Hg; d^{10}) difluorides than in the difluorides of the alkaline-earth metals, which are the more electropositive. These examples are not of course anomalous in the general theory of nuclear magnetic shielding, as we have seen. But even for closely analogous compounds, electronegativity arguments must be used with care since σ- (and π-) inductive effects may alter σ_d, and the radius and energy terms in σ_p, in a complex fashion.

The periodic correlation has been found to be useful for detecting errors in the reported shifts (*e.g.* in the compilations, in these times of change in sign convention).

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