The Solvent Dependence of Fluorine Chemical Shifts. Part II.[1] Anisotropic and Polar Solvents

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The ^{19}F chemical shifts of a number of fluorinated compounds have been measured in anisotropic and polar solvents, and thence the gas to solution chemical shifts obtained for these systems. For the non-polar fully fluorinated solutes studied (CF_4, C_4F_8, C_6F_{14}) these gas to solution shifts are shown to agree with the van der Waals mechanism and to result from a product of solvent (S^v) and solute (S^u) contributions. This also allows the solvent anisotropic contribution to be obtained. For benzene and carbon disulphide these are -0.25 and $+0.5$ p.p.m. comparable with those obtained from [1]H n.m.r. studies. The polar solutes in these solvents deviate from this formulation indicating more specific effects. In the case of the polar solvents large systematic upfield deviations from the solvent × solute contributions are observed for the other solutes. These deviations. which may be defined as the electric field contribution are shown to depend on the solvent dielectric constant but to have no relationship with the solute dipole moment. Previous interpretations of ^{19}F polar solvent shifts in terms of a time independent electric field dependence plus a reaction field model are shown to be inadequate. It is suggested that the dipolar fields of the solvent molecules may contribute directly to these large shifts *via* the $\langle E^2 \rangle$ mechanism.

In Part I [1] the ^{19}F chemical shifts of a number of fluorine-containing molecules including all the common referencing compounds, were measured in a variety of non-polar solvents. These results provided a conversion table for these reference compounds and were also used to characterise the van der Waals contribution (σ_w) to [19]F

[1] Part I, R. J. Abraham, G. R. Bedford, and D. F. Wileman, *J.C.S. Perkin II*, 1973, 1027.

chemical shifts. This contribution was shown to be a function of the screening of the fluorine nuclei in the solute by the electrons on the neighbouring atoms.

In this paper we report similar results for anisotropic and polar solvents, in order to extend the conversion Table of Part I to all common solvents and also to characterise the solvent anisotropic (σ_a) and electric field (σ_E) contributions to fluorine chemical shifts.

[19]F Chemical shifts have recently been the subject of a comprehensive review [2] but the only previous detailed investigations of the effect of polar solvents on ^{19}F chemical shifts have been due to Ager and Phillips,[3] Emsley and Phillips,[4] and Taft and his co-workers [5-7] all

These authors suggested that the large van der Waals term was now affecting the shifts. Taft and his co-workers [5,6] measured meta- and para-substituted fluorobenzenes relative to fluorobenzene itself and interpreted the solvent shifts as due to changes in the resonance and inductive contributions of the solvent. Recently, however, they have completely revised their previous interpretations.[7] All these studies suffer from the disadvantage of using internal references and being restricted to fluoroaromatic compounds. It seemed therefore of interest to study in detail the effects of polar solvents on the ^{19}F shifts of simple aliphatic fluorocarbons, and also for comparison, some fluoroaromatic compounds.

TABLE 1

Solvent volume susceptibilities (χ_v), solvent nos. (S^v), refractive indices (n), and dielectric constants (ε) for polar and anisotropic solvents

				Solvent			
	CS$_2$	C$_6$H$_6$	CDCl$_3$	CH$_2$ClCH$_2$Cl	(CH$_3$)$_2$CO	CH$_3$CN	DMSO
$-\chi_v \times 10^{-6}$ c.g.s.	(0.68)	0.562	0.729	0.758	0.461	0.571	0.627
a	0.68	0.611	0.740		0.460	0.534	
S^v	5.60	5.22	5.56	5.48	4.64	4.88	6.52
n [a]	1.6255	1.5011	1.4433	1.4448	1.3588	1.3441	1.479
ε [a]	2.64	2.28	4.81	10.65	20.7	34.5 [b]	46.6 [c]
$(\varepsilon - 1)/(\varepsilon + 1)$	0.451	0.390	0.655	0.828	0.908	0.944	0.957

[a] ' Handbook of Chemistry and Physics,' Chemical Rubber Co., Cleveland, 49th edn.   [b] J. Timmermans, ' Physico-chemical Constants of Pure Organic Compounds,' 1965.   [c] E. M. Kosower, ' An Introduction to Physical Organic Chemistry,' Wiley, London, 1968.

TABLE 2

[19]F Chemical shifts (p.p.m. upfield [a]) of some fluoro-compounds in anisotropic and polar solvents, corrected for bulk susceptibility

			Solvent							
			Anisotropic		Polar					
	Solute		CS$_2$	C$_6$H$_6$	CDCl$_3$	CH$_2$ClCH$_2$Cl	Me$_2$CO	MeCN	Me$_2$SO	Gas
(1)	CF$_2$Br$_2$	(−8.00)	0.53	1.93	0.81	1.67	4.01	3.77	4.98	5.73
(2)	CFCl$_3$	(0.00)	−0.75	0.06	−0.63	−0.15	0.89	1.04	−0.03	5.12
(3)	CF$_2$ClBr	(0.00)	−1.05	0.23	−0.74	−0.08	1.76	1.57	1.79	4.64
(4)	CF$_3$Cl	(5.00)	0.84	1.93	1.19	1.61	2.82	2.80	1.55	7.17
(5)	CFCl$_2$CFCl$_2$	(66.00)	0.56	1.63	1.18	1.49	2.46	2.44	1.75	5.65
(6)	CF$_3$CCl$_3$	(81.00)	−0.35	0.79	0.47	0.58	1.39	1.26	−0.22	6.04
(7)	CF$_3$CHClBr	(75.00)			0.90	0.98	1.82	1.69	−0.32	7.38
(8)	C$_6$H$_5$CF$_3$	(62.00)		0.86	0.85	0.72	1.39	1.25	−1.02	7.68
(9)	sym-C$_6$F$_3$Cl$_3$	(111.00)	−0.54	2.82	1.36	2.00	3.90	3.95	2.59	8.12
(10)	C$_6$F$_6$	(161.00)	−1.03	2.18	0.96	1.56	3.85	3.60	1.63	9.73
(11)	α	(80.00)	0.55	1.40	0.80	0.89	1.78	1.52	c	6.33
(12)	β n-C$_6$F$_{14}$	(126.00)	−0.55	0.53	−0.06	0.05	0.80	0.44	c	4.37
(13)	γ	(122.00)	0.36	1.34	0.71	0.88	1.55	1.27	c	4.73
(14)	C$_4$F$_8$	(133.00)	0.32	1.63	1.00	1.02	2.11	1.68	−0.20	7.85
(15)	CF$_4$	(61.00)	−0.05 [b]	1.09	0.30	0.51	1.61	1.34	−0.88	7.76 [b]

[a] Relative to CFCl$_3$ in CFCl$_3$ as 0.00 p.p.m.   [b] Taken from W. T. Raynes and M. A. Raza, Mol. Phys., 1971, **20**, 555.   [c] Insoluble.

using fluoroaromatic compounds as solutes. Emsley and Phillips measured the solvent shifts of a number of fluorinated benzenes and pyridines from C$_6$F$_6$ as internal reference, and concluded that these shifts were due to the solute reaction field for polar solutes. This reaction field term was shown by Cooper et al. not to apply to the solvent shifts of some simple fluorobenzenes in which the measured fluorine atom had two ortho-hydrogen atoms.[8]

There has been no previous study on the σ_a contribution to fluorine solvent shifts.

EXPERIMENTAL AND RESULTS

The experimental method and details were as reported previously.[1] In some instances where the perfluoro-solutes were of limited solubility in the polar solvents spectral accumulation using a Varian CAT 1024 accessory was necessary to observe the signals. The ^{19}F chemical

[2] J. W. Emsley and L. Phillips, Progr. N.M.R. Spectroscopy, eds. J. W. Emsley, J. Feeney, and L. H. Sutcliffe, Pergamon Press, Oxford, Vol. 7, 1971.

[3] I. R. Ager and L. Phillips, J.C.S. Perkin II, 1972, 1975.

[4] J. W. Emsley and L. Phillips, Mol. Phys., 1966, **11**, 437.

[5] R. W. Taft, E. Price, I. R. Fox, I. C. Lewis, K. K. Anderson, and G. T. Davis, J. Amer. Chem. Soc., 1963, **85**, 709.

[6] R. W. Taft, E. Price, I. R. Fox, I. C. Lewis, K. K. Anderson, and G. T. Davis, J. Amer. Chem. Soc., 1963, **85**, 3146.

[7] R. T. C. Brownlee, S. K. Dayal, J. L. Lyle, and R. W. Taft, J. Amer. Chem. Soc., 1972, **94**, 7208.

[8] M. A. Cooper, H. E. Weber, and S. L. Manatt, J. Amer. Chem. Soc., 1971, **93**, 2369.

shifts of 12 fluoro-compounds were measured from an external $CFCl_2CFCl_2$ reference, and the shifts then corrected for the solvent bulk susceptibility (χ_v) determined as previously from n.m.r. measurements at two field orientations [1] at 40 °C. The χ_v values for the solvents used are given in Table 1 and compared with the literature values (at 20 °C). Considerable differences are apparent for the anisotropic solvents benzene and acetonitrile, probably due to a large temperature dependence of the susceptibility in these compounds.

Referencing the shifts to the scale with $CFCl_3$ solute in $CFCl_3$ solvent as 0·00 p.p.m. gives the values shown in Table 2. The format of Table 2 is identical to the analogous Table for non-polar solvents [1] and the results can be used in a similar fashion. Thus consideration of the vertical columns enables the internal ^{19}F chemical shifts of these compounds relative to $CFCl_3$ to be determined and also allows easy interconversion between reference scales. Horizontal values show the solvent effects after correcting for solvent bulk susceptibility and it is the interpretation of these that is we wish to discuss. To this end we have included in Table 2 the values of the gas-phase chemical shifts for these fluoro-compounds as obtained previously.[1]

DISCUSSION

Anisotropic Solvents.—The anisotropic contribution (σ_a) to the observed solvent shift arises from the variation with direction of the diamagnetic susceptibility (χ) of the solvent molecules. According to Buckingham *et al.*[9] this contribution is given for cylindrical solvents by equation (1) where $\chi_\parallel$ and $\chi_\perp$ are susceptibilities parallel and

$$\sigma_a = -n(\chi_\parallel - \chi_\perp)(3\cos^2 0 -1)/3R^3 \qquad (1)$$

perpendicular to the solvent axis, 0 is the average orientation of the resonant nucleus relative to the axis of the solvent molecule, R is the distance of separation, and n is the number of molecules in the relevant range.

The solvents CS_2 and C_6H_6 have values of $(\chi_\parallel - \chi_\perp)$ of -5×10^{-29} and -9×10^{-29} c.g.s. respectively[9] and should give rise to upfield (*i.e.* negative σ_a) for C_6H_6 $(\theta \ ca. \ 0°)$ and low field shifts for CS_2 $(\theta \ ca. \ 90°)$.

The calculation of these anisotropic shifts has been refined considerably since this early work.[10-12] However, these more sophisticated calculations do not affect the general argument.

The ^{19}F chemical shifts from the gas phase of a non-polar fluoro-compound in CS_2 and C_6H_6 will be due to just the van der Waals (σ_w) and anisotropy (σ_a) contributions, assuming no complex formation. (In this case also we may take σ_E as zero.)

Thus the observed low field shift (δ) is given by equation (2). The van der Waals contribution σ_w

$$\delta = \sigma_w + \sigma_a \qquad (2)$$

may be expressed as a product of two constants, S^u and S^v, which are functions of solute and solvent respectively.[1] Equation (2) now becomes (3)

$$\delta = S^u \cdot S^v + \sigma_a \qquad (3)$$

The values of S^u for the fluoro-compounds in Table 2 have been obtained previously[1] and therefore plotting these against δ should yield a straight line of gradient S^v and intercept σ_a. The results for C_6H_6 solvent using the data for the non-polar fluoroalkane solutes of Table 2 $(\alpha, \ \beta, \ \text{and} \ \gamma \ \text{fluorines of} \ C_6F_{14}, \ CF_4, \ C_4F_8)$ are shown in Figure 1(a). This figure shows that a very good linear correlation exists as predicted by equation (3). The intercept gives the anisotropy contribution for benzene as $-0·25$ p.p.m. This has the correct sign as predicted from solvent molecular shape considerations (*i.e.* upfield) and the value is also fairly close to that determined
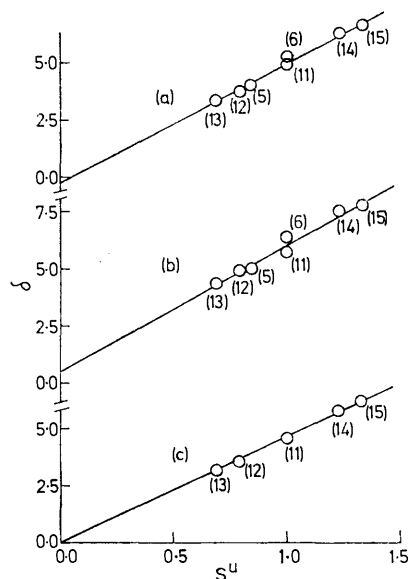

FIGURE 1 Variation of ^{19}F chemical shift from gas phase (δ) with solute no. (S^u) in the solvents: (a) C_6H_6; (b) CS_2; and (c) MeCO (solutes numbered as in Table 2)

for σ_a for benzene from ^{1}H shifts, *i.e.* $-0·43$;[10] $-0·5$ p.p.m.[11]

Two further conclusions may be drawn from these results. First, following from the linearity of the graph, the σ_a value for benzene appears to be constant over a large range of solute sizes. The solute molar volumes range from >60 (CF_4) to 210 ml $(n-C_6F_{14})$. In the case of proton solvent shifts Rummens[13] found the benzene σ_a value had a very small dependence on solute size being inversely proportional to the sixth root of the molar volume.

A dependence on solute size of this order would not be detected in our work, nor probably in any ^{19}F solvent shifts owing to the 'swamping' of the anisotropy term by the σ_w contribution.

Secondly we note that when the other fluoro-compounds are included in Figure 1(a) considerable deviations are found, particularly for polar and aromatic solutes (*e.g.* $CF_2Br_2, C_6H_5CF_3, C_6F_6$). This suggests that

[9] A. D. Buckingham, T. Schaefer, and W. G. Schneider, *J. Chem. Phys.*, 1960, **32**, 1227.
[10] R. J. Abraham, *Mol. Phys.*, 1961, **4**, 369.

[11] J. K. Becconsall, *Mol. Phys.*, 1968, **15**, 129.
[12] J. C. Schug, *J. Phys. Chem.*, 1966, **70**, 1816.
[13] F. H. A. Rummens, *J. Amer. Chem. Soc.*, 1970, **92**, 3214.

some 'specific' interactions occur between these fluoro-solutes and benzene. The situation may be analogous to that found in proton chemical shifts (ASIS) where benzene produces large upfield shifts of the solute protons in polar and aromatic solutes.[14] We note that benzene and C_6F_6 can form a 1 : 1 solid complex [15] and also other investigations have found evidence of complex formation in solution.[16,17]

The same procedure applied to the CS_2 solvent shifts gives the plot shown in Figure 1(b) which again is a good linear plot with an intercept equivalent to an anisotropic shift of ca. 0·5 p.p.m. This value is in the predicted direction (i.e. downfield) but is larger than would be expected from the values found for proton shifts, e.g. 0·14;[10] 0·05 p.p.m.[18]

in this case in total contrast to the proton solvent effects it is the second term in equation (4) which is dominant. Thus the support for the first term in equation (4) provided by proton studies is not directly relevant to ^{19}F studies.

Theoretically, the shielding constant tensor may always be expressed to the second power in the instantaneous electric field at the nucleus concerned. However in the normal use of equation (4) σ_E is the measured isotropic chemical shift resulting from averaging over all molecular orientations and E_z and E^2 are average values obtained very often by reaction field theory. In this averaging process a basic assumption has been made which we are questioning. This will be returned to later.

TABLE 3

Residual solvent shifts after correcting for σ_w

	Solute	μ/D [a]	Residual upfield shift				
			$CDCl_3$	CH_2ClCH_2Cl	Me_2CO	$MeCN$	$DMSO$
(1)	CF_2Br_2	(0·66)	0·47	1·26	2·78	2·77	5·57
(2)	$CFCl_3$	(0·45)	0·25	0·65	0·78	1·19	1·89
(3)	CF_2ClBr	(0·5) [b]	0·29	0·87	1·85	1·91	3·80
(5)	$CFCl_2CFCl_2$	(0·31) [c]	0·14	0·39	0·66	0·84	1·51
(9)	sym-$C_6F_3Cl_3$	(0)	0·41	0·95	1·77	2·13	2·88
(4)	CF_2Cl_2	(0·51)	0·19	0·52	0·80	1·05	1·62
(10)	C_6F_6	(0)	0·29	0·71	1·64	1·78	2·46
(8)	$C_6H_5CF_3$	(2·86)	−0·10	−0·33	−0·68	−0·53	−0·81
(7)	$CF_3CHClBr$	(1·13) [c]	0·03	0·01	−0·13	0·02	−0·07
(6)	CF_3CCl_3	(0·47) [c]	−0·01	0·02	−0·01	0·10	0·26

[a] Values of dipole moment taken from 'Handbook of Chemistry and Physics' Chemical Rubber Co., Cleveland, 49th edn. [b] Estimated. [c] Values calculated from the observed dielectric constant using the Halverstadt–Kumler equation (I. F. Halverstadt and W. D. Kumler, *J. Amer. Chem. Soc.*, 1942, **64**, 2988).

The polar and aromatic solutes (as for benzene) deviate significantly from this line which again may indicate more specific interactions in these cases.

The solvent numbers for CS_2 and benzene obtained from the gradient of the lines in Figure 1(a) and (b) are given in Table 1.

Polar Solvents.—The electric field contribution to the chemical shift was first calculated by Pople and Marshall [19] for a hydrogen atom, and later extended by Buckingham [20] to the particular case of a C–H system. In this the proton chemical shift is given by equation (4)

$$\sigma_E = -AE_z - BE^2 \qquad (4)$$

where A and B are constants characteristic of the C–H bond, E is the electric field, and E_z the component along the bond. Many subsequent investigations have confirmed the general validity of this equation for *C–H bonds* and a number of these have used equation (4) together with reaction field theory to calculate the effect of polar solvents on solute proton chemical shifts.[9,10] Usually in these studies the E^2 term is found to be small (it is often ignored).

Equation (4) and the reaction field model have been assumed to apply also to ^{19}F solvent shifts. However

We therefore wish to isolate the electric field contribution to the solvent effects of Table 2 without recourse to equation (4). In general, the chemical shift of a fluorinated solute in any solvent from the corresponding gas phase value, after correction for the solvent bulk susceptibility, is given by equation (5). On the assumption

$$\delta = \sigma_w + \sigma_E + \sigma_a \qquad (5)$$

that σ_E vanishes for non-polar solutes (see later) equation (5) reduces to equations (2) and (3).

Thus a plot of δ *versus* S^u for non-polar solutes in a polar solvent should be a straight line of gradient S^v and intercept σ_a.

The results found for acetone as solvent [illustrated in Figure 1(c)] confirm these predictions. The gas to solvent shifts of CF_4, C_4F_8, and the α, β, and γ fluorine atoms of n-C_6F_{14} all correlate linearly with S^u. The line has essentially zero intercept (i.e. σ_a ca. 0). Similar results (not shown) were obtained for the other polar solvents of Table 2 all having essentially zero intercepts.

The gradients of these lines are thus equal to the solvent number S^v and these values are given in Table 1.

To test whether the solvent numbers so obtained are a

[14] P. Laszlo, *Progr. N.M.R. Spectroscopy*, eds. J. W. Emsley, J. Feeney, and L. H. Sutcliffe, Pergamon Press, Oxford, Vol. 3, 1967.
[15] C. R. Patrick and G. S. Prosser, *Nature*, 1960, **187**, 1021.
[16] D. V. Fenby and R. L. Scott, *J. Phys. Chem.*, 1967, **71**, 4103.
[17] W. A. Duncan, J. P. Sheridan, and F. L. Swinton, *Trans. Faraday Soc.*, 1966, **62**, 1090.
[18] H. J. Bernstein, 4th International Symposium on Magnetic Resonance, I.U.P.A.C. Butterworths, London, 1972, p. 79.
[19] T. W. Marshall and J. A. Pople, *Mol. Phys.*, 1958, **1**, 199.
[20] A. D. Buckingham, *Canad. J. Chem.*, 1960, **38**, 300.

measure of the van der Waals interactions in these solvents the S^v values were plotted (not shown) against the function of the solvent refractive index $n^2 - 1$. This function was found to give a reasonable correlation with the S^v values for non-polar solvents.[1] The polar solvents obey the same relationship and this supports the above treatment and also shows that the van der Waals interactions are dominant for these non-polar solutes in polar solvents.

The S^v values in Table 1 may now be used together with the S^u values (from Part I)[1] to estimate the van der Waals contribution to the observed gas to solvent shift of a polar solute in a polar solvent. As the shift is given by equation (6) the residual shift $(\delta - S^u \cdot S^v)$ should be

$$\delta = S^u \cdot S^v + \sigma_E \qquad (6)$$

the electric field contribution. These residual shifts for the remaining ten solutes of Table 2 are given in Table 3 for all the polar solvents investigated here, which are
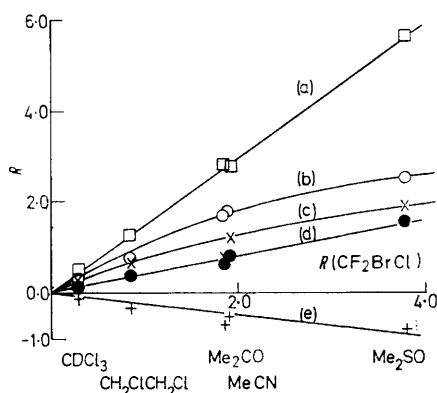

FIGURE 2 Residual shifts (R) of (a) CF_2Br_2; (b) C_6F_6; (c) $CFCl_3$; (d) $CFCl_2CFCl_2$; and (e) $C_6H_5CF_3$ versus those of CF_2BrCl (solvents as indicated)

listed in order of increasing dielectric constant. Table 3 also includes, for comparison, the dipole moments of the solutes. The shifts in Table 3 are all upfield, i.e. the van der Waals interaction $(S^u \cdot S^v)$ predicts larger low-field shifts than are observed.

These residual upfield shifts are of considerable interest. The first question to ask is whether these are a general phenomenon or whether they are the result of specific solvent–solute interactions. Inspection of Table 3 shows that the shifts progressively increase with solvent dielectric constant, which suggests a general effect. This is conclusively confirmed by the treatment of these results in Figure 2, in which the excess shift for the remaining solutes are plotted against the excess shift for CF_2BrCl.* Any general phenomenon would give rise to straight lines or smooth curves, whereas any specific interaction could produce scattered results.

The overwhelming inference from Figure 2 is that the shifts are a general phenomenon. Only in one case do

we find exceptional behaviour and this is for the $CFCl_3$ in acetone value, which deviates ca. 0·5 p.p.m. from the smooth curve for the other solvents. A specific complex in this case is not surprising (cf. the well known chloroform–acetone complex).[10] However, in all the other cases, there is a straight line or smooth curve, suggesting that these shifts all have the same origin.

However, inspection of Table 3 and Figure 2 also shows that these shifts appear to have no relationship whatsoever to the general predictions of equation (4) and the reaction field theory. The solutes C_6F_6 and $C_6F_3Cl_3$ with zero dipole moments give large upfield shifts, the slightly polar solutes $CFCl_2CFCl_2$ and CF_2Cl_2 also give sizeable upfield shifts, but the much more polar solutes $CF_3CHBrCl$ and $C_6H_5CF_3$ give zero and small downfield shifts respectively.

If we consider two similar molecules, undoubtedly the reaction field of $CF_3CHClBr$ is much larger than that of $CFCl_2CFCl_2$ yet in the former case the excess shift is zero for all solvents whilst in the latter there is a large upfield shift.

The results therefore unequivocally lead to the conclusion that the reaction field of the solute is of little or no influence in producing these excess shifts.† This is reinforced by the dependence of these shifts on the dielectric constant of the solvent. The simple reaction field model of a spherical solute cavity predicts a dependence on $(\varepsilon - 1)/(\varepsilon + 1)$. This function (Table 1) only varies from 0·65 ($CDCl_3$) to 0·96 (DMSO) and is very nearly constant for the last three solvents. In contrast the excess shifts in DMSO are an order of magnitude larger than those in $CDCl_3$, and even between acetone and DMSO the shift on average doubles. There is an approximate correlation of these shifts with $\varepsilon^{\frac{1}{2}}$, but this is only approximate (cf. acetone and acetonitrile).

The results in Table 3 thus lead to the remarkable conclusion that although the dielectric constant of the solvent is a major factor in determining these shifts the polarity of the solute (as expressed by its dipole moment) is not a determining factor.

This necessitates a fundamental reappraisal of polar solvent effects on ^{19}F shifts which is beyond the scope of this paper. Here we wish finally to note certain regularities in the data which may give some indication of the mechanism responsible for these phenomena. Thus we note that CF_3CCl_3 and $CF_3CHClBr$ have similar, essentially zero excess shifts which means that these solutes give the same solvent shifts in the solvents as the non-polar solutes used to obtain the S^v values, i.e. CF_4, C_4F_8, and n-C_6F_{14}. Thus the CF_3X compounds ($X = F$, $CHClBr$, CCl_3, C_5F_{11}) and the CCF_2C fragments behave similarly in polar solvents.

This indicates that substituents β to the ^{19}F nucleus under investigation do not play a major role in these excess shifts. This is in direct contrast to the influence of substituents in determining the van der Waals shifts

* To avoid confusion the shifts for CF_2Cl_2 (almost the same as $CFCl_2CFCl_2$), $C_6F_3Cl_3$ (very similar to C_6F_6), $CF_3CHClBr$, and CF_3CCl_3 (zero shifts) are not included.

† The more complex ellipsoidal models of the reaction field [4,10,21] would not seriously affect this argument.

[21] P. Diehl and R. Freeman, Mol. Phys., 1961, 4, 39.

in non-polar solvents (the S^u numbers)[1] in which the β-substituents were implicated due to the Z_i/r_i^2 dependence.

This is confirmed by the order of increasing excess shifts of the other solutes investigated, which is $CFCl_2CFCl_2 \sim CF_2Cl_2 < CFCl_3 < C_6F_6 \sim C_6F_3Cl_3 < CF_2BrCl < CF_2Br_2$. Again we note that substituents geminal to the ^{19}F nucleus are of major importance, that the replacement of C–F by C–C does not affect the excess shift, but that replacement of C–F by C–Cl and particularly C–Br causes very large excess shifts.

The results suggest that the more polarisable the atom geminal to the fluorine the greater will be the upfield shift. The ordering of the geminal atoms of the solute is $F \sim C < Cl < Br$ and this does correspond to the order of the C–X bond longitudinal polarisabilities (1·2, 1·0, 3·2, and 4·6 × 10^{-24} cm^3 for X = F, C, Cl, and Br respectively).[22]

The fact that these excess upfield shifts are related in some way to the bond polarisabilities and *not* to the solute reaction field suggests a possible connection between these shifts and the large downfield shifts due to the van der Waals interactions in non-polar solvents. It is also immediately obvious that these could be related. For any solute in any solvent, the instantaneous electric field at any ^{19}F nucleus $(\bar{E}_T)$ will be given by the vector sum of the contributions from the Van der Waals interactions $(\bar{E}_v)$ and the instantaneous dipolar field of the solvent $(\bar{E}_s)$ [equation (7)].

$$\bar{E}_T = \bar{E}_v + \bar{E}_s \tag{7}$$

Both these contributions average to zero when averaged over all orientations of the solute and solvent molecules, and thus neither contribute to the time independent average field E of equation (4). However, the mean square field $\langle E_T^2 \rangle$ will not average to zero and will contain contributions from both effects. It is this mean square field which plays such an important part in ^{19}F (as distinct from ^1H) solvent effects.

It is an open question as to whether the dipolar field (E_s) actually contributes an upfield shift or merely quenches the van der Waals lowfield shift. In CF_2Br_2 the observed ^{19}F chemical shift in DMSO is only 0·75 p.p.m. to low field of the gas value (Table 2) and this suggests that there will be compounds in which the ^{19}F chemical shift in polar solvents will be to high field of the gas value.

Finally we note also that whatever the mechanism of these shifts the magnitude of this polar effect is very large [*e.g.* CF_2Br_2 in DMSO, 5·6 p.p.m. (Table 3)] considerably greater than previous work based on equation (4) would suggest. This in particular makes the use of internal referencing procedures to evaluate solvent effects in these systems very dubious.

[22] R. J. W. Le Fèvre, *Adv. Phys. Org. Chem.*, 1965, **3**, 50.