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Systematic trends in the variation of ^{19}F nuclear magnetic shielding with bond extension in halomethanes

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A modified Urey–Bradley force field using the same set of quadratic constants for all halomethanes, augmented by Morse stretching and Lennard-Jones non-bonded anharmonic force constants, is used to calculate mean bond displacements in two series of halomethanes CF_4, CF_3Cl, CF_3Br, CF_3I and CF_4, CF_3Cl, CF_2Cl_2, $CFCl_3$. The temperature dependence of the $\langle \Delta r_{CF} \rangle^T$ in these molecules is used in a one-parameter fit to the observed temperature dependence of the ^{19}F shielding at the zero-pressure limit, $[\sigma_0(T) - \sigma_0(300)]$. The empirical derivatives $(\partial\sigma^F/\partial\Delta r_{CF})_e$ are then used to calculate the $^{13/12}$C-induced ^{19}F isotope shifts at room temperature. The calculated isotope shifts are in satisfactory agreement with experimental values. The derivatives are: $(\partial\sigma^F/\partial\Delta r_{CF})_e = -1180$, -1630, -1850, -1950, -2000, and -2400 ppm Å^{-1} respectively for CF_4, CF_3Cl, CF_3Br, CF_3I, CF_2Cl_2, and $CFCl_3$. The CF_3X molecules exhibit a nearly linear plot of $(\partial\sigma^F/\partial\Delta r_{CF})_e$ vs. σ_e. For the series $CF_{4-n}Cl_n$ the derivative varies linearly with n. For the series CF_3X, $X = F$, Cl, Br, I, the derivative of the isotropic shielding varies linearly with the component of the shielding tensor which is perpendicular to the XCF plane and that which is along the C–F bond direction.

1. INTRODUCTION

The temperature dependent chemical shifts in the N.M.R. spectra of gases arise from a combination of the intrinsic temperature dependence of nuclear shielding in an 'isolated' molecule and the temperature dependence of the effects of intermolecular interactions. Thus, the nuclear shielding in a pure gas may be written in a virial expansion as follows [1]:

$$\sigma(T, \rho) = \sigma_0(T) + \sigma_1(T)\rho + \sigma_2(T)\rho^2 + \dots \quad (1)$$

The first term arises from the variation with temperature of the populations of the rotational and vibrational states, each one of which has a different characteristic average shielding. With measurements in the linear (in density) regime, the observed shifts can be corrected for the intermolecular contributions $\sigma_1(T)\rho$ so that $\sigma_0(T) - \sigma_0(300\text{ K})$ is obtained. This is mathematically equivalent to extrapolation to a pressure which is low enough that collisional deformation of the molecules no longer contributes to σ, however there are still sufficient collisions to provide averaging over the rovibrational states of the molecule. For ^{19}F this temperature dependence is relatively large and has been measured in several electronic environments [2, 3]. The temperature dependence of $\sigma_0(T)$ can be interpreted in terms of products of electronic and dynamic factors [4]:

$$\sigma_0(T) = \sigma_e + \sum_i (\partial\sigma/\partial\Delta r_i)_e \langle\Delta r_i\rangle^T + \dots . \tag{2}$$

The purely electronic factors σ_e, $(\partial\sigma/\partial\Delta r_i)_e$, and higher derivatives, can be calculated theoretically by considering the nuclear magnetic shielding at the equilibrium configuration and at small displacements away from equilibrium. There are a limited number of such studies, all of which have been carried out on molecules with few electrons [5]. The mean bond displacements $\langle\Delta r_i\rangle^T$, and the mean square amplitudes $\langle\Delta r_i \Delta r_j\rangle^T$ depend on masses and the derivatives of the potential energy surface of the molecule, which in turn depend also on electronic structure. The dynamic factors $\langle\Delta r_i\rangle^T$, etc., can be calculated as a function of temperature for the molecule of interest, using force fields which have been obtained from rotational and vibrational spectra of the molecules. A corollary observation is that of the N.M.R. isotope shift: the change in the nuclear shielding due to isotopic replacement of an atom in the molecule. This is interpreted with the same theoretical treatment; the dynamic factors for isotope shifts are the differences between mean bond displacements $[\langle\Delta r_i\rangle^* - \langle\Delta r_i\rangle]$ and mean square amplitudes of isotopomers [4].

While these observations and their interpretation are of specific interest to N.M.R. spectroscopists, they are of more general interest as a prototype of rovibrational averaging effects on molecular electronic properties. Fortunately, it is possible in N.M.R. spectroscopy to make very precise measurements of a quantity which is very sensitive to changes in electronic environment. Nuclear magnetic shielding is a molecular electronic property which is a sensitive index of the chemical bond and which varies with nuclear displacements from the equilibrium molecular configuration leading to observable changes in the resonance frequency. These changes are more easily observable with increasing magnetic field. Technical developments in the latter during the past 15 years have improved the magnitude of observed frequency shifts by a factor of about 6 and the measurement sensitivity by about two orders of magnitude. Thus, we have an electronic property for which the experiments are easier to carry out than the theoretical calculations. Therefore, it is useful to gain theoretical understanding from noting the general trends in the empirical values of purely electronic quantities such as $(\partial\sigma/\partial\Delta r)_e$, which can be derived from a comparison of the mass and temperature dependence of the observable with the mass and temperature dependence of the dynamic factors.

A sufficient number of zero-pressure limit measurements have become available so that some general trends can be discerned. These measurements are most easily done with the ^{19}F nucleus which exhibits large shifts of nuclear shielding with temperature because fluorine is an end atom in all molecules, a unique position which is associated with both a non-symmetrical electronic environment (and thus a large paramagnetic shielding term sensitive to nuclear displacement) and large amplitudes of vibrational motion.

One general observation is that ^{19}F nuclei in all electronic environments tend to become deshielded as the temperature increases, i.e. $(d\sigma_0/dT) < 0$. This is true for ^{19}F bonded to carbon [2], as well as to other atoms [3]. We have interpreted this behaviour in several systems by calculations of the mean bond displacement directly involving the observed nucleus, $\langle \Delta r \rangle^T$, which increases with temperature. The observed temperature dependence of the shielding can therefore be explained by a decrease in shielding with bond extension, i.e., $(\partial\sigma/\partial\Delta r)_e < 0$. This is in agreement with results of *ab initio* theoretical calculations of shielding as a function of small displacements from the equilibrium molecular configuration.

In addition to the general deshielding with increasing temperature, there are some interesting trends recently observed in the fluoromethanes: (*a*) The magnitude of the temperature dependence $|(d\sigma_0/dT)_{300}|$ is smaller when the ^{19}F nucleus is attached to carbon bearing hydrogen, and decreases as more hydrogens substitute fluorine atoms [2 (c)]. (*b*) $|(d\sigma_0/dT)_{300}|$ is greater when the ^{19}F is attached to carbon bearing chlorine, and increases as more chlorines displace fluorine atoms [2 (c)]. (*c*) These trends are observed in fluoroethanes as well as fluoromethanes [6]. (*d*) For fluoromethanes there is a general correlation between $(d\sigma_0/dT)$ and the absolute shielding, σ_0: The less shielded nuclei have a more pronounced temperature dependence [7]. These trends are intriguing. It is not immediately obvious whether they are due in part to systematic differences in the dynamic averaging upon substitution, or due to systematic differences in the electronic effects. In this paper, we examine the effect of substitution (trends (*b*) and (*d*)) by performing dynamic calculations for two series of molecules: CF_4, CF_3Cl, CF_2Cl_2, $CFCl_3$ and CF_4, CF_3Cl, CF_3Br, CF_3I. By comparison of the calculated temperature dependence of the mean bond displacements with the experimental temperature dependence of the nuclear magnetic shielding, we can obtain the purely electronic factor $(\partial\sigma^F/\partial\Delta r_{CF})_e$ as an empirical quantity.

2. CALCULATION OF MEAN BOND DISPLACEMENTS AND CORRELATION WITH N.M.R. OBSERVATIONS

Comparisons of the empirical derivatives $(\partial\sigma^F/\partial\Delta r_{CF})_e$ for a series of molecules can be meaningful only if they are obtained with the same calculations using directly comparable anharmonic force fields. A review by Duncan shows that uniquely determined general harmonic force fields (GHFF) are available for only selected molecules [8]. Unfortunately, the fluoromethanes (except for CH_3F and CF_4) do not fall into this category. However, the Urey–Bradley model force field, which has found its greatest application in the calculation of vibration frequencies of halogenated molecules, is a suitable approach to this problem. It is especially useful in our application because the UB force constants show a remarkable degree of transferability. This means that we will be able to use the exact same set of UB force constants for all the fluoromethane molecules to be compared, a feature which makes the UB approach specially suitable for our purpose. We have recently completed an interpretation of the ^{19}F shielding in the OCF_2 molecule with the UB model [4 (f)]. In OCF_2, a force constant study has shown that the UB model with 7 independent constants is almost perfectly compatible with the GHFF (10 independent constants) determined from frequencies, frequency shifts, Coriolis constants, centrifugal distortion and inertial defect data [9]. Therefore, we are confident in applying the same approach to the tetrahalomethanes.

There is no available information on vibrational frequencies of isotopically-related halomethanes. However, in adopting a transferable set of UB force constants, the richness in the variety of molecules for which fundamental frequencies are available (18 halomethanes of the type CX_4, CX_3Y, CX_2Y_2 and CX_2YZ) allows the determination of a limited number of force constants while reproducing three times the number of observed frequencies [10]. We use this set by Ngai and Mann exclusively.

The calculation of the mean bond displacements $\langle \Delta r \rangle$ follows the method described in detail elsewhere [4 (f)], an application of Bartell's modified UBFF to molecular types with a central atom and mean bond angle displacements which do not contribute significantly to the temperature dependence of the average shielding [11]. Both conditions are satisfied by tetrahedral molecules. The only additional UB parameter is the internal tension [12]. In Bartell's method, the UB quadratic force constants are augmented by Morse anharmonic stretching and cubic force constants for non-bonded interactions. The vibrational contribution to the mean bond displacements $\langle \Delta r_{CF} \rangle$ and $\langle \Delta r_{CX} \rangle$ are expressed in coupled linear equations in the mean square amplitudes and the parameters of the force field. Their temperature dependences are contained in the coth $(hc\omega_i/2kT)$ factors.

For our calculations we used the best available bond distances, mostly from microwave investigations [13]. However, we assumed tetrahedral angles for all the molecules. (The effect of assumed tetrahedral angles on calculated frequencies is negligibly small [14].) Our calculated frequencies using the set of Ngai and Mann UB force constants with more accurate bond distances are in satisfactory agreement with the observed fundamental frequencies, with deviations smaller than ±3 per cent for every molecule.

The Morse parameters in the anharmonic terms for bond stretching are calculated using Herschbach and Laurie's exponential functions [15]. With different bond lengths for C–F bonds in these molecules, the Morse parameter varies somewhat from one molecule to the next. The cubic force constant for non-bonded interactions is calculated from a Lennard–Jones 6–12 function [16] in which the potential parameters were taken from the appropriate noble gases [17]. A Lennard–Jones function has been shown to give good results for halogen–halogen non-bonded interactions [16]. Ngai and Mann's quadratic force constants for non-bonded halogen atoms F_{XX} agree with the second derivative of the Lennard–Jones function for the corresponding X–X noble gas potential, and the mixed terms F_{XY} agree with the second derivatives of the X–Y potential. Therefore, this is a reasonable way of obtaining the cubic UB force constant F^3 for all pairs of non-bonded halogen atoms. Bending anharmonicities are neglected altogether. The contribution of rotation (centrifugal stretching) to mean bond displacements is calculated in the usual way [18].

The results are shown in table 1 and figure 1. The centrifugal stretching is directly proportional to temperature so only the proportionality constants are given. This rotational contribution is 2 to 5 per cent of the mean bond displacement $\langle \Delta r_{CF} \rangle$ at 300 K but gives 11 to 21 per cent of the temperature dependence of $\langle \Delta r_{CF} \rangle^T$. The temperature dependence of $\langle \Delta r_{CF} \rangle$ and $\langle \Delta r_{CCl} \rangle$ are in reasonable agreement with the experimental temperature dependence (by electron diffraction) of the mean bond displacement in CF_4 and CF_3Cl [19]. We note in figure 1 that $\langle \Delta r_{CF} \rangle^T$ in CF_3Cl and CF_3Br are fortuitously nearly identical. This

Table 1. Mean bond displacements and geometry parameters.

	CF_4	CF_3Cl	CF_2Cl_2	$CFCl_3$	CF_3Br	CF_3I
			$\langle \Delta r_{C-F} \rangle 10^3/\text{Å}$			
$T = 200$ K	5·399	5·516	5·694	6·074	5·524	5·590
240	5·516	5·632	5·807	6·192	5·638	5·708
280	5·661	5·773	5·947	6·337	5·777	5·852
320	5·830	5·939	6·110	6·507	5·939	6·020
360	6·021	6·127	6·296	6·701	6·125	6·210
400	6·233	6·336	6·502	6·916	6·330	6·421
$\langle \Delta r_{C-F} \rangle_{rot} 10^3/\text{Å}$	$8·99 \times 10^{-4}$T	$7·39 \times 10^{-4}$T	$5·85 \times 10^{-4}$T	$4·69 \times 10^{-4}$T	$6·62 \times 10^{-4}$T	$6·35 \times 10^{-4}$T
r_e(C–F)/Å	1·317†	1·325‡	1·338§	1·362‖	1·326¶	1·378¶
r_e(C–X)/Å		1·752‡	1·775§	1·754‖	1·923¶	2·144¶

† Jeanotte, A. C., Marcott, C., Overend, J., 1978, *J. chem. Phys.*, **68,** 2076.

‡ Typke, V., Dakkouri, M., Oberhammer, H., 1978, *J. molec. Struct.*, **44,** 85.

§ Kristoff, J. J., Diss. Purdue Univ., 1958, (*Diss. Abs.*, **18,** 1997).

‖ Loubser, J. H. N., 1962, *J. chem. Phys.*, **36,** 2808.

¶ Cox, A. P., Duxbury, G., Hardy, J. A., Kawashima, Y., 1980, *J. chem. Soc. Faraday II*, **76,** 339.

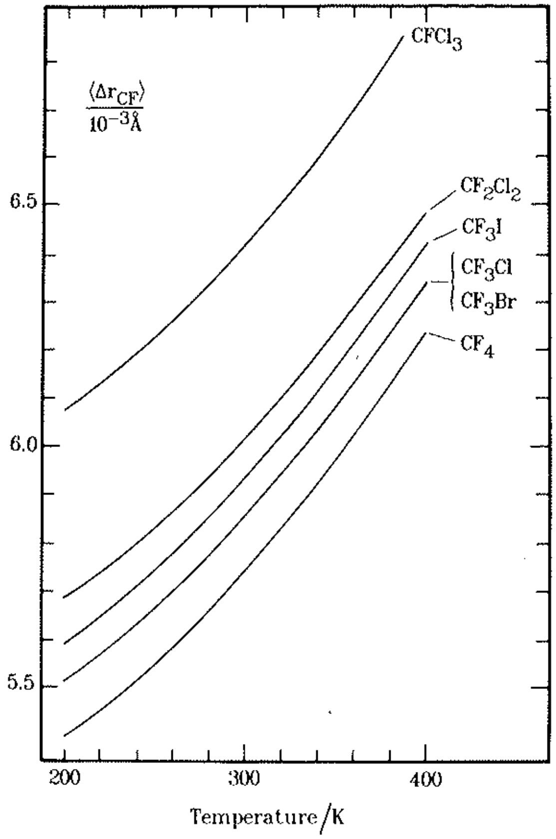

Figure 1. Mean C–F bond displacements in halomethanes.

comes about because the vibrational contribution to $\langle \Delta r_{CF}\rangle$ in CF_3X increases monotonically in the sequence F to I whereas the rotational contribution decreases.

We assume that the observed temperature dependence of the shielding can be expressed as follows:

$$\sigma_0(T) \simeq \sigma_e + (\partial\sigma^F/\partial\Delta r_{CF})_e\langle\Delta r_{CF}\rangle^T. \tag{3}$$

Here, only the mean bond displacement of the bond involving the observed nucleus is included. That is, we neglect $(\partial\sigma^F/\partial\Delta r_{CF'})_e$ and $(\partial\sigma^F/\partial\Delta r_{CX})_e$ as well as any contribution due to bond angle deformation. For a one-parameter fit, we also neglect terms in the second derivatives of shielding. In figure 2, we show the extent to which the experimental $[\sigma_0(T) - \sigma_0(300)]$ functions [2] can be fitted to the temperature dependence of $\langle\Delta r\rangle^T$, as in equation (3), with a single parameter. The empirical parameters, the shielding derivatives $(\partial\sigma^F/\partial\Delta r_{CF})_e$ are shown in table 2. Here the experimental values of $(d\sigma_0/dT)_{300}$ are also shown for comparison, although the experimental data over the entire temperature range shown in figure 2 was used for fitting, not just the slope at 300 K. The value of $(\partial\sigma^F/\partial\Delta r_{CF})_e$ for CF_4, -1180 ppm Å^{-1} is comparable to that obtained earlier, -1115 ppm Å^{-1}, with a different force field [4(d)]. The derivatives shown in table 2 are probably good to only 10 per cent in absolute magnitudes because of the approximations used. However, the relative values within the set of molecules

Table 2. Comparison with N.M.R. observables.

	$\sigma_0(300)$† ppm	$\sigma_0(300) - \sigma_e$ ppm	$10^3(d\sigma_0/dT)_{T=300}$† ppm deg^{-1}	$(\partial\sigma/\partial\Delta r_{CF})_e$ ppm Å^{-1}	$10^4[\langle\Delta r_{12_{CF}}\rangle - \langle\Delta r_{13_{CF}}\rangle]_{T=300}$/Å	$^1\Delta^{19}F(^{13/12}C)$/ppm	
						Calc.	Obs.
CF_4	259·0	−6·8	−5·01 ± 0·07	−1180	0·70	0·083	0·111 ± 0·005
CF_3Cl	224·4	−9·5	−6·78 ± 0·18	−1630	0·79	0·129	0·144 ± 0·005
CF_3Br	213·8	−10·8	−7·75 ± 0·14	−1850	0·81	0·151	0·144 ± 0·005
CF_2Cl_2	202·6	−12·0	−9·06 ± 0·25	−2000	0·90	0·180	0·168 ± 0·01
CF_3I	199·6	−11·5	−9·25 ± 0·16	−1950	0·84	0·163	0·154 ± 0·005
$CFCl_3$	195·7	−15·4	−11·65 ± 0·44	−2400	1·0	0·240	0·194 ± 0·01

† [20]. ‡ [2].

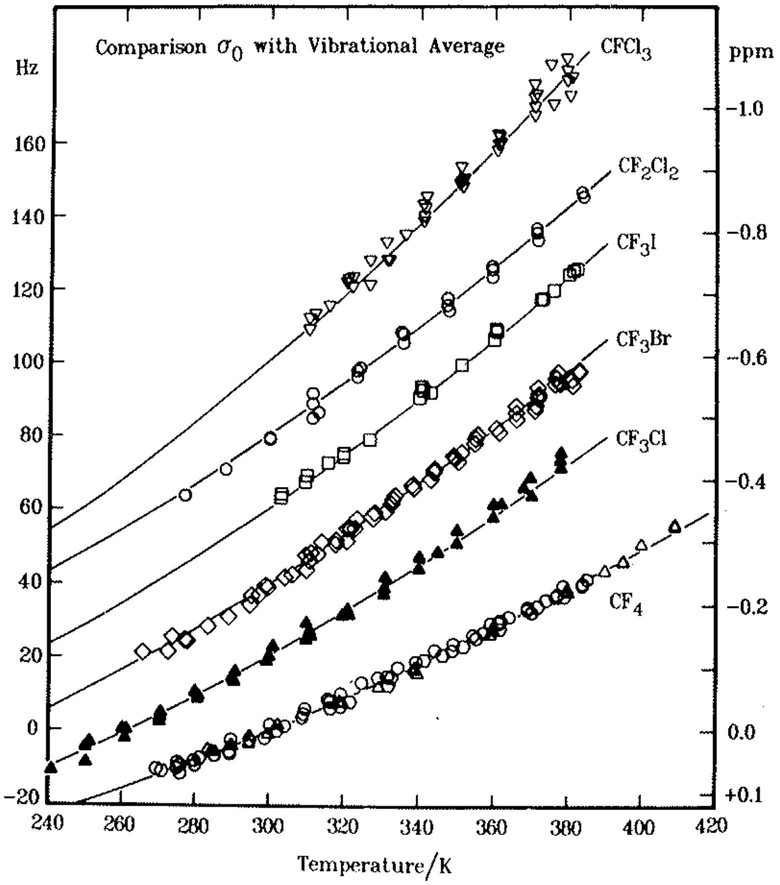

Figure 2. Comparison of experimental temperature dependence at 84·67 MHz of the ^{19}F nuclear resonance frequency in the 'isolated molecule' limit with the calculated temperature dependence using $[\sigma_0(T) - \sigma_0(300\,\mathrm{K})]^{\mathrm{calc}} = (\partial\sigma/\partial\Delta r)_e[\langle\Delta r\rangle^T - \langle\Delta r\rangle^{300}]$.

are more precisely known than this. We used a set of UB quadratic force constants which is internally consistent in reproducing fundamental frequencies of all [18] halomethanes, not just the ones included in the present study [10]. We obtained the anharmonic non-bonded force constants from a Lennard–Jones functional form with parameters r_0 and ε for pairs of rare gas molecules which form an internally consistent set, compatible with the comprehensive collection of spectroscopic, bulk transport, and scattering data for all pairs of rare gases examined by Kestin [17]. With the empirical $(\partial\sigma^{\mathrm{F}}/\partial\Delta r_{\mathrm{CF}})_e$ we also obtain an estimate of $[\sigma_0(300) - \sigma_e]$, the rovibrational correction to the nuclear shielding, shown in table 2. This correction is applied to the observed absolute shielding [20] to give the shielding at the equilibrium configuration, σ_e. The latter estimates are in error by the amount contributed by the terms in $(\partial^2\sigma/\partial\Delta r^2)_e$ and higher derivatives which have not been included.

Using the same dynamical calculations and the shielding derivatives found consistent with the temperature dependence in the zero-pressure limit, we calculate the $^{13/12}$C-induced ^{19}F isotope shifts. We assume that we can express this isotope shift by

$$\sigma(^{12}\mathrm{CF}_n X_{4-n}) - \sigma(^{13}\mathrm{CF}_n X_{4-n}) \simeq (\partial\sigma^{\mathrm{F}}/\partial\Delta r_{\mathrm{CF}})_e[\langle\Delta r_{^{12}\mathrm{CF}}\rangle - \langle\Delta r_{^{13}\mathrm{CF}}\rangle]. \quad (4)$$

The calculated isotope shifts are compared with the experimental values we obtained from gas phase spectra in table 2. The latter agree with previously published liquid phase results [21] within experimental error. We find that the calculated and observed N.M.R. isotope shifts in these series of molecules roughly follow the relative order of the temperature dependence observed in the zero-pressure limit.

The isotope shift calculation is more approximate than that of the temperature dependence of σ_0. The mass dependence of the C–F bond due to $^{13/12}$C substitution is more dependent on the nature of the force field than substitution at an end atom. There are undoubtedly some deficiencies arising from the use of a UB force field and in the neglect of bending anharmonicity, which may affect the $^{13/12}$C dependence of the mean C–F bond displacement. In addition, the contribution to the isotope shifts of terms in the higher derivatives are not necessarily negligible, whereas their contributions to the temperature dependence are expected to be negligible. This is based on Ditchfield's findings in diatomic molecules, using first up to sixth derivatives of nuclear shielding obtained from *ab initio* calculations [5 (d)]. Our calculated isotope shifts are in substantial agreement with experiment; the small differences may be attributed to the neglected terms in the higher derivatives. These neglected terms also lead to some error in the determination of σ_e from σ_0.

In addition to the $^{13/12}$C-induced isotope effect on ^{19}F shielding, two-bond isotope shifts have been reported for the series $CF^{35}Cl_{3-n}{}^{37}Cl_n$ [20]. Brey *et al.* found a shift of approximately $-0{\cdot}007$ ppm per $^{37/35}$Cl substitution for the ^{19}F shielding at 230 K, at which temperature best resolved spectra were obtained [22]. The two-bond isotope shift involves at least two important contributions. The first is a small secondary effect on the C–F bond in question due to isotopic substitution at a C–Cl bond, detected by the change in ^{19}F shielding with C–F bond extension. The second term involves a larger primary effect on the C–Cl bond length, detected by the change in the ^{19}F shielding with neighbouring bond extension, $(\partial\sigma^F/\partial\Delta r_{CCl})_e$. Using our estimate for $(\partial\sigma^F/\partial\Delta r_{CF})_e \simeq -2400$ ppm Å^{-1}, we find that the change in the C–F bond contributes not more than 60 per cent of the total observed isotope shift. Including primary and secondary changes in the C–Cl bonds we calculate (by the method used in [4 (g)]) a derivative for the ^{19}F shielding with respect to the neighbouring bond extension.

$$(\partial\sigma^F/\partial\Delta r_{CCl})_e \simeq -70\,\mathrm{ppm\,Å^{-1}}.$$

This derivative has the same sign as $(\partial\sigma^F/\partial\Delta r_{CF})_e$, i.e. extension of a remote bond with temperature also promotes a deshielding of the observed nucleus. We calculated the isotope shift at 300 K as well, in an attempt to reproduce the observations of Brey *et al.* for this system. We do not find a significant temperature dependence as postulated. We believe that their reported temperature dependence is only an apparent one, mostly due to better resolved spectra (narrower lines) at 230 K than at 300 K.

There are relatively few calculations of σ_e for ^{19}F with which we may compare our results. For CF_4 and CF_3Cl, the ^{19}F shielding calculated with a double valence-split basis using Ditchfield's GIAO scheme yields 287·8 [23] and 281·4 ppm [24] for CF_4 and 260·1 ppm [24] for CF_3Cl, to be compared with our 265·8 and 233·9 ppm respectively.

3. Discussion

The studies of the temperature dependence of ^{19}F nuclear shielding in the zero-pressure limit and the present calculations on the series of related halomethanes were conducted with the expectation of finding some degree of transferability of $(\partial\sigma/\partial\Delta r_{CF})_e$ for the halomethanes. Instead, we find that the derivative $(\partial\sigma^F/\partial\Delta r_{CF})_e$ varies substantially from one halomethane to another. Indeed the temperature dependence of $\langle\Delta r_{CF}\rangle^T$ is nearly the same (4·0 to $4{\cdot}2 \times 10^{-6}$ Å deg^{-1} in the range 200 to 400 K), so that the differences in the temperature dependence directly reflect differences in $(\partial\sigma^F/\partial\Delta r_{CF})_e$. The $^{13/12}C$-mass dependence of $\langle\Delta r_{CF}\rangle$ at a given temperature changes systematically with substitution, $([\langle\Delta r_{^{12}CF}\rangle - \langle\Delta r_{^{13}CF}\rangle] = 0{\cdot}70$ to $1{\cdot}0 \times 10^{-4}$ Å), in the same relative order as the observed isotope shifts. Thus, the observed changes in the isotope shifts along the members of the series can be attributed to the changes in both the dynamic and electronic terms, whereas the changes in the temperature dependence can be attributed to variation of the purely electronic terms. The most interesting result is the correlation that we find between two purely electronic quantities, the empirical shielding derivatives $(\partial\sigma^F/\partial\Delta r_{CF})_e$ and the absolute nuclear shielding σ_e for each series of halomethanes considered here (figure 3 (*a*)).

We also find that $(\partial\sigma/\partial\Delta r_{CF})_e$ correlates with the ^{13}C–F coupling constants measured in the gas phase, shown in figure 3 (*b*). The latter agree with previously reported liquid phase data [21]. The correlation of $(\partial\sigma^F/\partial\Delta r_{CF})_e$ with the coupling constant $^1J(CF)$ is interesting. No explanation has been offered for the linear relationship originally noted between the ^{13}C–^{19}F coupling constant and the $^{13/12}C$-induced ^{19}F isotope shift in halomethanes [21]. More recently, an analogous linear relation between the ^{31}P–^{17}O coupling constant and the $^{18/16}O$-

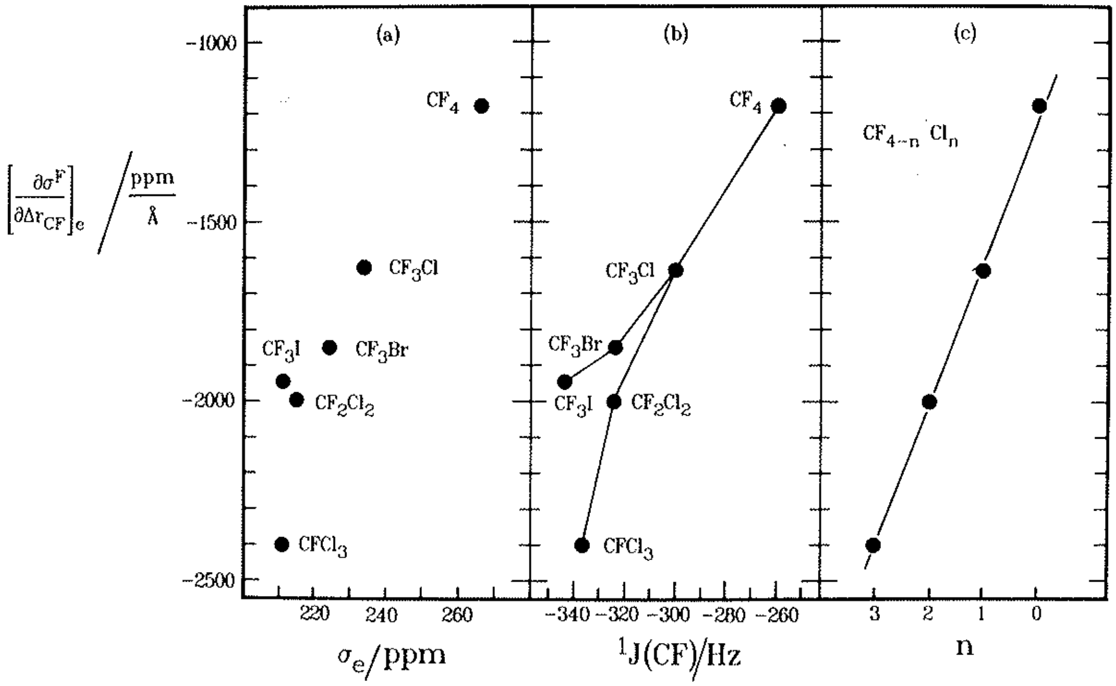

Figure 3. Correlation of the ^{19}F nuclear shielding derivatives with (*a*) the absolute shielding at the equilibrium configuration, (*b*) the ^{13}C–^{19}F coupling spin–spin coupling constant observed in the gas phase, and (*c*) the extent of Cl-substitution.

induced ^{31}P isotope shift has been reported [25]. That the purely electronic part of the isotope shift correlates with the coupling constant in figure 3 (*b*) means that the same changes in electronic distribution which lead to a decrease in the paramagnetic term also leads to a decrease in the coupling constant.

The systematic non-linear variation of $(\partial\sigma/\partial\Delta r_{CF})_e$ with σ_e in the series $CF_{4-n}Cl_n$ reflects the typical sagging curves for chemical shifts with successive substitution of halogens. The curvature disappears when $(\partial\sigma/\partial\Delta r_{CF})_e$ is plotted vs. n for $CF_{4-n}Cl_n$ in figure 3 (*c*). The linear correlation which exists between $(\partial\sigma^F/\partial\Delta r_{CF})_e$ and σ_e in CF_3X as X varies from F through I, and that which exists between $(\partial\sigma^F/\partial\Delta_{CF})_e$ and n in $CF_{4-n}Cl_n$ indicate that it may be possible to predict the value of the shielding derivative for one member of a series of related molecules from the known values of derivatives for other members of the series.

4. CORRELATION WITH THE SHIELDING TENSOR COMPONENTS

Although we have fitted only the isotropic shielding data, it is worthwhile to consider the relationship between the empirical derivatives and the shielding tensor components. The ^{19}F nuclear shielding tensor components for the series CF_4, CF_3Cl, CF_3Br, CF_3I have been obtained by low-temperature rigid lattice studies of CF_3X enclathrated in D_2O [26]. The components of the ^{19}F nuclear shielding tensors in these molecules exhibit systematic changes with X. Although the ^{19}F shielding tensor is not axially symmetric about the C–F bond, the σ_{33} direction lies very close to the C–F bond direction, and this component decreases monotonically in the order F, Cl, Br, I, and in fact increases linearly with the electronegativity of X. The most shielded (σ_{22}) direction lies in the XCF plane perpendicular to the C–F bond and is insensitive to X. The least shielded (σ_{11}) direction is perpendicular to the XCF plane and this component decreases monotonically in the order F, Cl, Br, I, again increasing linearly with the electronegativity of X [26]. The absolute shielding component σ_{22} which does not change with substituent X very likely has a derivative $(\partial\sigma_{22}^F/\partial\Delta r_{CF})_e$ which is independent of substituent X. Figure 4 shows the correlation of the empirical derivatives $(\partial\sigma/\partial\Delta r)_e$ with the other two shielding components.

Let us consider a possible explanation for this correlation. The paramagnetic part of the shielding tensor can be deduced from the observed individual components and translated to absolute shielding values via the absolute ^{19}F shielding scale based on HF [20]. In $\sigma = \sigma^d + \sigma^p$, for nucleus N, the diamagnetic part can be calculated by the Gierke and Flygare method to within a few ppm [27]:

$$\sigma_{av}^d \simeq \sigma_{av}(\text{free atom}) + (e^2/3mc^2) \sum_{N'} Z_{N'}/r_{NN}.$$

In this model, the effect of bond displacement of the diamagnetic shielding in CF_3X molecules comes from the terms $(\partial/\partial\Delta r_{CF})[Z_C/r_{CF} + Z_X/r_{XF} + 2Z_F/r_{FF}]$. Ditchfield has shown [5 (d)] that in diatomic molecules the component of the shielding tensor along the direction of the bond is less sensitive to bond extension. This component has no paramagnetic contribution, thus, $(\partial\sigma^d/\partial\Delta r)_e$ must be less important than $(\partial\sigma^p/\partial\Delta r)_e$ for diatomic molecules. It can be inferred from this that the paramagnetic contributions to shielding are more sensitive than the diamagnetic contributions to C–F bond extension in the CF_3X molecules.

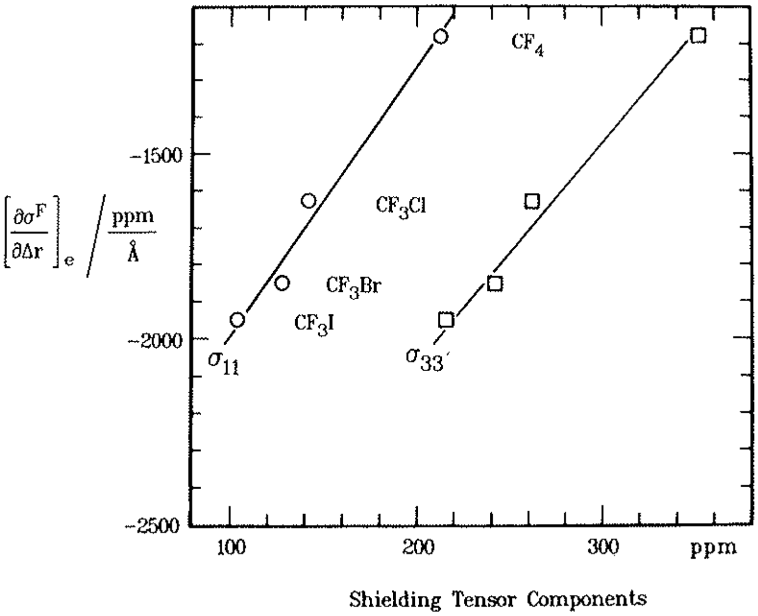

Figure 4. Comparison of the individual components of the ^{19}F shielding tensor in CF$_3X$ (from [25]) with the nuclear shielding derivatives in these molecules. The σ_{11} direction is perpendicular to the XCF plane, the σ_{33} direction lies very close to the C–F bond direction. (σ_{22} is nearly independent of X.)

By examining the paramagnetic components of the ^{19}F shielding tensor, the systematic change in $(\partial\sigma^F/\partial\Delta r_{CF})_e$ with X can be interpreted as follows: The paramagnetic term depends on mixing of magnetic-dipole-connected states or molecular orbitals. The integrals which appear in the mixing coefficient fall off more sharply than r^{-1} (so is more strongly dependent on bond displacement than the diamagnetic term). The mixing coefficients are inversely related to the energy difference between the mixed states. The derivatives $(\partial\sigma_{11}^F/\partial\Delta r_{CF})_e$ and $(\partial\sigma_{33}^F/\partial\Delta r_{CF})_e$ vary with X due to the changes in the energy gap $(2p_y \rightarrow \sigma_{CX}^*)$ associated with X substitution, and also because the integrals between σ_{CX}^* and F$_{2p_y}$ vary with X. (The magnitude of the integrals increase with the size of X.) Both factors increase the magnitude of the paramagnetic term. As X is changed from F through I, the same variation of electronic factors which leads to larger negative σ^p also leads to larger negative $(\partial\sigma^p/\partial\Delta r_{CF})_e$. This and the relatively smaller derivatives of the positive diamagnetic terms lead to the correlation of $(\partial\sigma/\partial\Delta r_{CF})_e$ with the individual components σ_{11} and σ_{33}, (figure 4) and with the isotropic average absolute shielding σ_e (figure 3 (*a*)).

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