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Correlation between the ^{19}F absolute nuclear magnetic shielding and its temperature dependence in the fluoromethanes

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Absolute nuclear shieldings for ^{19}F are compared with the temperature dependence in the zero-pressure limit obtained from N.M.R. studies of fluoromethanes in the gas phase. From the correlation between these quantities and between absolute shielding and N.M.R. isotope shifts, it is concluded that σ_e, the ^{19}F shielding at the equilibrium configuration and $(\partial\sigma/\partial\Delta r_{CF})_e$, the change in nuclear shielding with CF bond extension, are correlated, $(\partial\sigma/\partial\Delta r_{CF})_e$ being more negative for smaller σ_e. A similar correlation is deduced for $(\partial\sigma/\partial\Delta r_{CO})_e$ and ^{13}C shielding.

1. INTRODUCTION

Vibrational and rotational effects on the nuclear shielding in a molecule lead to changes of the nuclear resonance frequency with temperature and with isotopic substitution. These observable effects can be understood by considering the nuclear shielding as an electronic property which depends on the relative positions of the nuclei such that its value changes with displacements from the equilibrium molecular configuration. An expansion of the nuclear magnetic shielding as a power series in displacement coordinates q_i about the value σ_e, at equilibrium

$$\sigma = \sigma_e + \sum_i (\partial\sigma/\partial q_i)_e q_i + \sum_{i,j} (\partial^2\sigma/\partial q_i\,\partial q_j)_e q_i q_j + \dots \tag{1}$$

can be used to describe these changes. The nuclear magnetic shielding is a very sensitive index of the electronic environment and derivatives with respect to displacements $(\partial\sigma/\partial q_i)$, are a measure of this sensitivity. The expectation values $\langle q_i \rangle$, $\langle q_i q_j \rangle$ are different for different rotational–vibrational states of the molecule, and for different isotopic forms. These differences result in shifts in the nuclear resonance frequency with temperature and with isotopic substitution. There are also temperature-dependent intermolecular effects on nuclear shielding but these are density-dependent and can be studied separately. When the resonance frequencies observed in the gas phase are corrected for these intermolecular effects, the remaining temperature dependence, in the zero-pressure limit, is that of the thermal average isotropic nuclear shielding characteristic of a molecule, $[\sigma_0(T) - \sigma_0(300\,\mathrm{K})]$.

2. NUCLEAR SHIELDING IN FLUOROMETHANES

In the course of gas-phase studies we have obtained the temperature dependence of the nuclear magnetic shielding in the zero-pressure limit for a variety of nuclei in a large number of molecules. $\sigma_0(T)$ has a non-linear dependence on temperature; shifts which are $-0{\cdot}1$ to $-1{\cdot}9$ ppm over a 50 degree change in temperature (300 K to 350 K) have been observed for ^{19}F in various molecules. [1] A convenient comparison between molecules can be made by noting the magnitude of the temperature coefficient of nuclear shielding $(d\sigma_0/dT)$ at 300 K. In several series of substituted fluoromethanes, we noted that $(d\sigma_0/dT)$ decreases with H substitution and increases with Cl substitution [2]. Since the nuclear shielding itself generally correlates with various substituent effects, we considered the possibility of a correlation between the absolute nuclear shielding, σ_0, and $(d\sigma_0/dT)$ for a small subset of molecules for which comparison may be valid. The fluoromethanes offer such a comparison.

2.1. *Experimental values*

We have measured both the ^{19}F absolute nuclear shielding, σ_0, and its temperature dependence in eleven molecules. The results are shown in table 1. Details of these measurements are given elsewhere [3–6]. Figure 1 shows that there is a general trend of less pronounced temperature dependence with an increase in absolute shielding. Better correlation of these two observables is obtained for molecules related by successive replacement of F, H, or Cl atoms. For each of the series of molecules shown in table 2, the absolute shielding values, σ_0/ppm, are seen to vary in a systematic way with the observed temperature dependence at 300 K, $(d\sigma_0/dT)/10^{-3}$ ppm K^{-1}.

Table 1. Absolute shieldings σ_0, $(d\sigma_0/dT)$ at 300 K, and $^{13/12}C$-induced isotope shifts for ^{19}F nuclei fluoromethanes.

Molecule	σ_0/ppm	$10^3(d\sigma_0/dT)$/ppm K^{-1}	$^1\Delta^{19}F(^{13/12}C)$/ppm
CFH_3	471·0 [1]	−1·515 [2]	−0·072 [11] (−0·067) [10]
CF_2H_2	339·1 [3]	−2·89 [2]	−0·115 [11] (−0·143) [10]
$CFHCl_2$	276·3 [3]	−5·92 [2]	−0·156 [12]
CF_3H	274·1 [1]	−4·75† [5]	−0·126 [11] (−0·133) [10]
CF_2HCl	267·4 [1]	−4·86 [2]	
CF_4	259·0 [1]	−5·01 [6]	−0·118 [11] (−0·105) [10]
CF_3Cl	224·4 [1]	−6·78 [5]	−0·152 [10]
CF_3Br	213·8 [1]	−7·75† [5]	−0·152 [10]
CF_2Cl_2	202·6 [1]	−9·06 [2]	−0·164 [12]
CF_3I	199·6 [3]	−9·25 [4]	−0·149 [12] (−0·132) [10]
$CFCl_3$	195·7 [3]	−11·65 [2]	−0·194 [12] (−0·192) [10]

† The temperature dependences reported in [5] have been corrected:

$$[\sigma_0(T)-\sigma_0(300)]/\text{ppm} = CF_3H\colon -4{\cdot}75\times10^{-3}(T-300)-1{\cdot}79\times10^{-5}(T-300)^2,$$

$$CF_3Br\colon -7{\cdot}75\times10^{-3}(T-300)-7{\cdot}03\times10^{-6}(T-300)^2,$$

$$CF_3CF_3\colon -11{\cdot}37\times10^{-3}(T-300)-3{\cdot}42\times10^{-6}(T-300)^2.$$

Table 2. Systematic trends in the absolute shielding and its temperature dependence in related molecules.

Series	Molecule	σ_0/ppm	$(d\sigma_0/dT)/10^{-3}$ ppm K^{-1}
1	CFH_3	471·0	−1·515
	CF_2H_2	339·1	−2·89
	CF_3H	274·1	−4·75
	CF_4	259·0	−5·01
2	CF_4	259·0	−5·01
	CF_3Cl	224·4	−6·78
	CF_2Cl_2	202·6	−9·06
	$CFCl_3$	195·7	−11·65
3	CF_2H_2	339·1	−2·89
	CF_2HCl	267·4	−4·86
	CF_2Cl_2	202·6	−9·06
4	CFH_3	471·0	−1·515
	$CFHCl_2$	276·3	−5·92
	$CFCl_3$	195·7	−11·65
5	CF_3H	274·1	−4·75
	CF_4	259·0	−5·01
	CF_3Cl	224·4	−6·78
	CF_3Br	213·8	−7·75
	CF_3I	199·6	−9·25

2.2. *Discussion*

The interpretation of the observed temperature dependence of nuclear magnetic shielding is no different from that of any other molecular electronic property. It is determined by two surfaces: (1) the nuclear magnetic shielding surface which is a multi-dimensional function of the molecular configuration, and (2) the potential energy surface which determines the vibrational wavefunctions. The nuclear positions and their displacements Δr, or the normal coordinates, q_i, as well as any electronic property which depends on nuclear positions are averaged over the second surface. We can write the average nuclear shielding σ_0 in terms of the thermal average normal coordinates:

$$\sigma_0(T) = \sigma_e + (\partial\sigma/\partial q_i)_e\langle q_i\rangle^T + (\partial^2\sigma/\partial q_i^2)_e\langle q_i^2\rangle^T + \dots, \tag{2}$$

$\sigma_0(T)$ is the absolute nuclear shielding characteristic of a rovibrationally-averaged molecule at a given temperature. If we consider only the most important terms, after suitable transformation from normal coordinates to internal coordinates, (2) becomes

$$\sigma_0(T) = \sigma_e + (\partial\sigma/\partial\Delta r_{CF})_e\langle\Delta r_{CF}\rangle^T + \dots, \tag{3}$$

so that the observed temperature coefficient is

$$(d\sigma_0/dT)_{300} = (\partial\sigma/\partial\Delta r_{CF})_e(d\langle\Delta r_{CF}\rangle^T/dT)_{300} + \dots. \tag{4}$$

The additional terms which are not shown in (4) involve higher derivatives of the shielding, bond angle deformations, etc. The leading term in $(d\sigma_0/dT)$ is the product of two factors: one is strictly a parameter of the shielding surface and the other depends on a dynamic average over the potential energy surface.

The symmetry of the molecules considered here varies from T_d to C_1. However, the equilibrium FCF or FCX bond angles do not deviate greatly from tetrahedral, they range from 108 to 111° [7]. The equilibrium C–F bond is between 1·33 and 1·38 Å [7]. The extent of mixing of the CF bond stretch with other internal coordinate displacements in the A_1 vibrational modes varies from one molecule to the next, depending on the symmetry and the masses of the substituents. Nevertheless, the vibrational frequency associated most closely with the CF bond stretch is between 1060 and 1100 cm^{-1} in all these molecules, except in CF_4 in which it is 908 cm^{-1} [8]. From these similarities, we expect that the dynamic averaging will not be drastically different from one fluoromethane to another. Since the series of molecules have very nearly the same CF stretching frequency and have very nearly the same geometry, the $\langle\Delta r_{\mathrm{CF}}\rangle^T$ functions are probably very similar in shape for this series of molecules. If the thermal averages, $[\langle\Delta r\rangle^T - \langle\Delta r\rangle^{300}]$ are, indeed, nearly the same for all the molecules being compared here, then the observed variation in $d\sigma_0/dT$ can be attributed primarily to the variation of $(\partial\sigma/\partial\Delta r)_e$. The absolute shielding at room temperature, $\sigma_0(300)$, differs by only a few ppm from σ_e, the shielding at the equilibrium configuration. Thus, figure 1 indicates a correlation between two purely electronic quantities, σ_e and $(\partial\sigma/\partial\Delta r_{\mathrm{CF}})_e$, the differences in dynamic averaging being responsible for most of the scatter. The plot indicates a more negative $(\partial\sigma/\partial\Delta r_{\mathrm{CF}})_e$ for the less shielded (smaller σ_e) nucleus.

Another N.M.R. observable which is related to dynamic averages on the shielding surface is the isotope shift. The chemical shift induced by ^{13}C-substitution of the carbon bonded to the observed ^{19}F nucleus (a one-bond isotope shift) is given by:

$$\begin{aligned} {}^1\Delta^{19}\mathrm{F}(^{13/12}\mathrm{C}) &= \sigma_0(^{12}\mathrm{CF}) - \sigma_0(^{13}\mathrm{CF}) \\ &= (\partial\sigma/\partial\Delta r_{\mathrm{CF}})_e[\langle\Delta r_{^{12}\mathrm{CF}}\rangle^{300} - \langle\Delta r_{^{13}\mathrm{CF}}\rangle^{300}] + \dots \end{aligned} \tag{5}$$

In (5) we again have a leading term which is a product of an electronic factor and a quantity which depends on the dynamic average over the potential energy

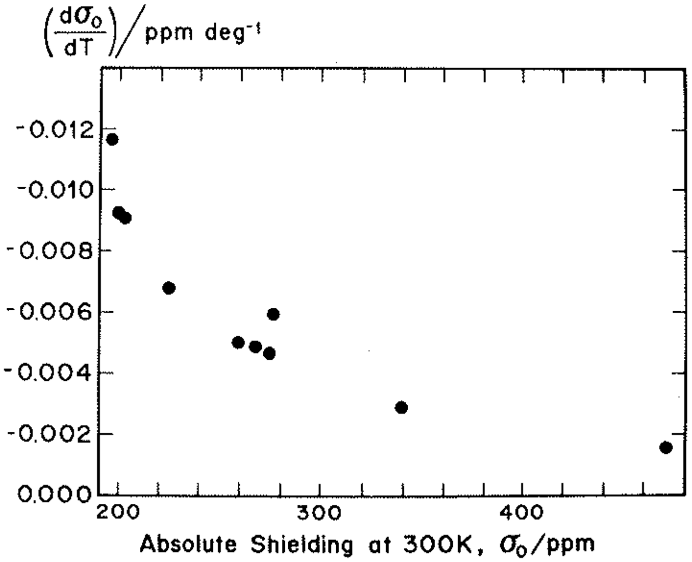

Figure 1. Correlation between absolute ^{19}F shielding in the isolated molecule and the temperature coefficient of the shielding at 300 K.

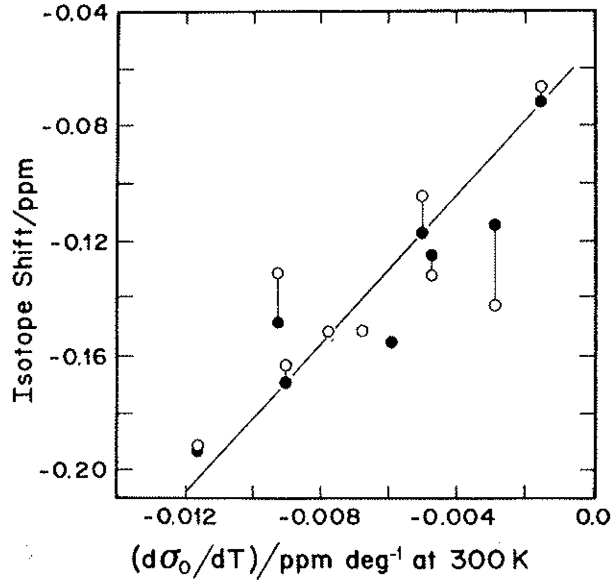

Figure 2. Correlation between $^{13/12}$C-induced isotope shifts in ^{19}F shielding [10–12] and the temperature coefficient of the shielding at 300 K.

surface. The dynamic averages in (4) and (5) correlate with one another in diatomic molecules [9]. On one hand, the heavier isotope has smaller amplitudes of motion than a lighter one on the same potential energy surface. On the other hand, the average amplitude of vibrational motion increases with temperature. In a polyatomic molecule, there will be some correlation of these two dynamic factors if the isotopically substituted mass is an end atom in the structure, as in $\Delta r(C{=}^{18}O)$ compared with $\Delta r(C{=}^{16}O)$. In other molecular structures, the dynamic averages in (3) and (4) may correlate with one another, but not necessarily. When they do correlate, the observed N.M.R. isotope shifts should be related to the observed $(d\sigma_0/dT)$. A plot of literature values of $^1\Delta^{19}F(^{13/12}C)$, the $^{13/12}$C-induced isotope shift in the ^{19}F N.M.R. spectrum vs. our $(d\sigma_0/dT)_{300}$ is shown in figure 2. There is considerable scatter, the data are twenty years old, nevertheless, there is a clear pattern. Thus, we expect the $^{13/12}$C-induced shifts in the fluoromethanes to correlate with σ_0 to the same extent that $(d\sigma_0/dT)$ correlates with σ_0, and indeed, a plot of literature values of $^1\Delta^{19}F(^{13/12}C)$ versus σ_0 of ^{19}F in these compounds is very similar to figure 1.

An analogous correlation between the $^{18/16}$O-induced isotope shift ($^1\Delta^{13}C(^{18/16}O)$) and the ^{13}C chemical shift in various carbonyls has been noted [13]. For this observable the important dynamic average is the mean displacement of the C=O bond. Since the carbonyl stretching frequency is nearly the same for all these organic compounds, and the equilibrium value of r_{CO} is nearly constant, we can expect that $[\langle\Delta r_{C\,^{18}O}\rangle - \langle\Delta r_{C\,^{16}O}\rangle]$ is nearly the same. The observed linear relation of the isotope shift with the ^{13}C shielding indicates a correlation between σ_e and $(\partial\sigma/\partial\Delta r_{CO})_e$ in these related compounds. The slope of this line indicates a more negative $(\partial\sigma/\partial\Delta r_{CO})_e$ for the less shielded nucleus. This is the same correlation which is indicated between $(\partial\sigma/\partial\Delta r_{CF})_e$ and σ_e for ^{19}F in the fluoromethanes in figure 1.

In order to understand the correlation between σ_e and its derivative, $(\partial\sigma/\partial\Delta r_{CF})_e$, we need a model for the F shielding surface in the fluoromethanes.

For a few diatomic molecules $\sigma(r)$ is known only over a very small range of values around the equilibrium internuclear separation, r_e. The only $\sigma(r)$ function which is known for a wide range of nuclear configurations is that for ^1H in the H_2^+ molecule, in which $\sigma(r)$ has been calculated accurately for $r = 0{\cdot}015 a_0$ to $22 a_0$ [14]. The function $\sigma(r_{AB})$ for nucleus A in a general diatomic molecule AB is qualitatively similar to $\sigma(r)$ in the H_2^+ molecule. The limiting behaviour is the same: a large diamagnetic shielding appropriate to the united atom formed from $A + B$ at $r_{AB} = 0$, and a diamagnetic shielding appropriate to the free A atom at $r_{AB} = \infty$. As the A and B atoms approach each other from infinite separation, a paramagnetic contribution starts from zero, gives a negative contribution at long range, goes through some minimum value and eventually goes to zero again at $r_{AB} = 0$. Although $\sigma(r)$ proceeds smoothly from $r = 0$ (the He^+ ion) to $r = \infty$ for the H_2^+ molecule, there may be more structure to the short-range ($r \ll r_e$) portion of the $\sigma(r)$ function when atoms possessing core electrons are involved. Ignoring the behaviour of $\sigma(r_{AB})$ at very short distances, the functional form can be assumed to be qualitatively similar to $\sigma(r)$ in the H_2^+ molecule. The form of the ^{19}F shielding surface in the fluoromethanes is not known. The F nuclear shielding varies with C–F bond distance, r_{CF}, the FCX angle, etc., and we envision a $\sigma(r_{CF})$ function in a plane cutting through the shielding surface (keeping angles and all other distances constant). We assume that this function is qualitatively similar to $\sigma(r)$ for a diatomic molecule.

A possible relationship between σ_e and $(\partial\sigma/\partial\Delta r)_e$ is sketched in figure 3. We adopt $\sigma(r_{CF})$ functions of the same form as $\sigma(r)$ for the H_2^+ molecule and sketch the two extreme cases: $CFCl_3$ ($\sigma_0 = 195{\cdot}7$, $d\sigma_0/dT = -11{\cdot}65 \times 10^{-3}$ ppm deg^{-1}, $r_0 = 1{\cdot}362$ Å) and CFH_3 ($\sigma_0 = 471{\cdot}0$ ppm, $d\sigma_0/dT = -1{\cdot}515 \times 10^{-3}$ ppm deg^{-1}, $r_0 = 1{\cdot}382$ Å). In most molecules the ^{19}F nucleus is less shielded than in the free

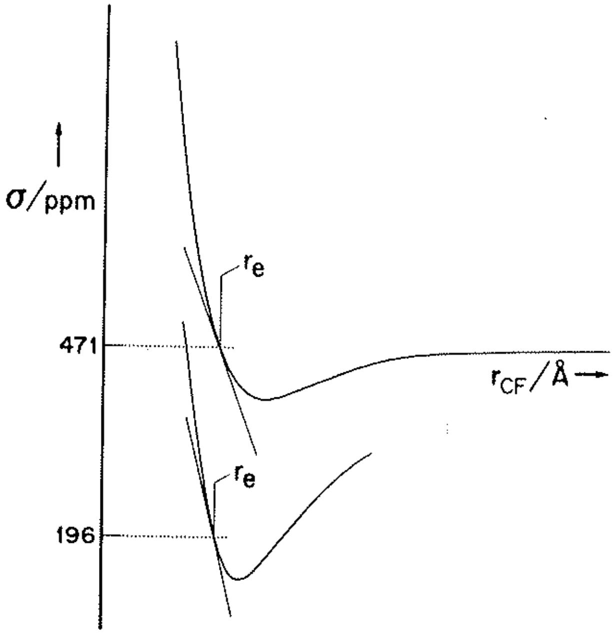

Figure 3. A rough sketch indicating that portion of the ^{19}F shielding surface for fluoromethanes, which shows the variation with r_{CF} keeping all other geometrical variables the same. The limiting value as $r_{CF} \rightarrow \infty$ is 470·71 ppm, the diamagnetic shielding of the free fluorine atom.

F atom (ClF is an exception). Both curves should go to the limiting value of 470·71 ppm which is the diamagnetic shielding of the free F atom. We have made use of the empirically determined negative sign of the derivative $(\partial\sigma/\partial\Delta r)_e$ for ^{19}F in a variety of molecules [15]. Figure 3 indicates a less steep functional dependence on r at the equilibrium configuration, concomitant with greater shielding. In making this sketch we have made no distinction between σ_e and σ_0 (300 K). These undoubtedly differ by a few ppm since the latter involves averaging over displacements away from r_e. We also made no distinction between the true r_e and the r_0 which one obtains from microwave spectroscopy; r_0 is generally greater than r_e by 0·001 Å or so. A similar sketch may be drawn for ^{13}C shielding and r_{CO} in organic carbonyls. Until we have accurate calculations of portions of the nuclear shielding surface for molecules of this size, we can only draw on empirical observations for indications such as these.

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