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Variation of Nuclear Magnetic Shielding of ^{19}F with Intermolecular Interactions and Rovibrational Motion in Fluoroethanes

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The density and temperature dependence of ^{19}F shielding in CF_3CH_3, CF_2HCH_3, CF_3CF_3, and CF_3CF_2Cl is reported in the following form: $\sigma(T, \rho) = \sigma_0(T) + \sigma_1(T)\rho + \cdots$. The temperature dependence of $\sigma_0(T)$, the ^{19}F nuclear magnetic shielding in the limit of the isolated molecule, is due to rovibrational averaging and is more pronounced for F in the fluoroethanes than in comparable electronic environments in fluoromethanes. Intermolecular effects on shielding due to binary molecular interactions are studied in dilute gas, and the excess shielding in the liquid phase due to many-body contributions is obtained from gas-to-liquid shifts. Pairwise interactions lead to deshielding in all ^{19}F environments; the deshielding effect is greater for molecules with more hydrogens. In liquid, many-body interactions lead to increased shielding so that the ^{19}F nucleus in the liquid phase is somewhat less deshielded than might be expected from extrapolation of the gas-phase results to liquid densities.

The ^{19}F nucleus is an excellent probe of electronic environment because it is a sensitive nucleus and its chemical-shift range is quite reasonable, giving large frequency shifts. Its unique position in all molecules is as a nucleus at the periphery of the molecule, making it a very useful probe of both intermolecular interactions and rovibrational effects on nuclear shielding. As a peripheral atom it is structurally more exposed to intermolecular interactions. As a nucleus in a bond to only one other atom, the fluorine electronic environment changes to a greater extent upon approach of a neighbor molecule or upon bond extension than a nucleus in a more symmetrical environment. In a systematic study of the effects of intermolecular interactions and intramolecular dynamics on ^{19}F nuclear shielding we have studied several fluoromethanes (*1*), fluoroethylenes, (*2a*), and some representative fluoroethanes (CF_3CF_2Cl, CF_3CH_3, CF_2HCH_3, and CF_3CF_3).

The nuclear magnetic shielding, in a gas of modest density, can be written in a virial expansion,

$$\sigma(T, \rho) = \sigma_0(T) + \sigma_1(T)\rho + \sigma_2(T)\rho^2 + \cdots, \qquad [1]$$

the density dependent terms being due to intermolecular interactions. $\sigma_1(T)$, the second virial coefficient for shielding, is a measure of the extent to which shielding

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is affected by pairwise interactions between molecules, which is determined by measuring the resonance frequencies of ^{19}F nuclei in several gas samples of known densities as a function of temperature. In the zero-density limit, we obtain $[\sigma_0(T) - \sigma_0(300\text{ K})]$ which is the temperature dependence of a rovibrationally averaged shielding in the "isolated molecule."

Samples were prepared from the degassed (by freeze–thaw) molecular system obtained from Matheson and PCR Chemicals. The sample tubes were 5 cm long containing about 0.2 ml and fit into standard 5 mm NMR tubes. The volumes were calibrated and a known amount of gas sealed off under liquid nitrogen. The NMR spectra of the individual samples were taken at 84.6 MHz on a Bruker 21 kG spectrometer which is a combination of a high-resolution HFX-90 and a BKR-322S pulse spectrometer with a Nicolet data acquisition system. The lock substance is an external reference (whose absolute temperature-dependent shielding has been previously determined) contained in the annular space between the NMR tube and the 3.9 mm o.d. sample tube. The resonance frequency from 380 K to temperatures at and below the liquefaction temperature of the sample was obtained for each gaseous sample using a previously calibrated variable temperature unit with a precision of ±0.2°. The upper temperature limit is due to the boiling point of the lock substance, toluene-d_8. Data analysis includes fitting the resonance frequency vs T by a polynomial of appropriate order for the quality of the data obtained. From such curves obtained at several densities in the range 3–25 amagat we are able to extract $\sigma_1(T)$. The gas-to-liquid shifts are measured from the signal of the equilibrium vapor and the liquid in the same spectrum.

The resonance frequency in CF_3CH_3 is shown (in Fig. 1) to be linear with density, as it should be in the limit of pairwise interactions. The slopes at three selected

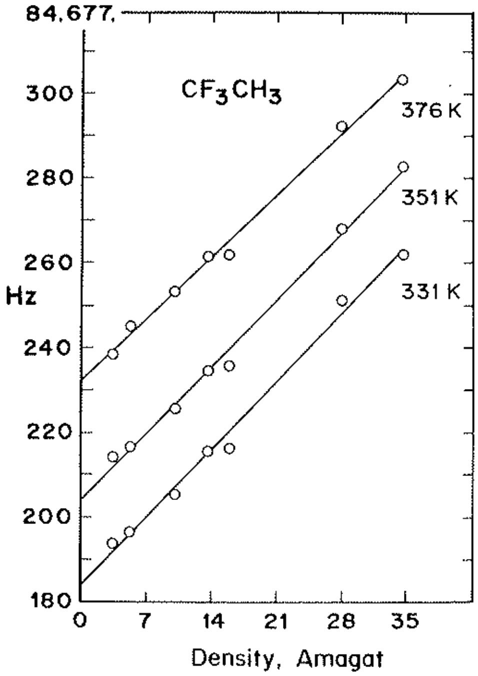

FIG. 1. Typical density dependence of the ^{19}F resonance frequency. The virial coefficient of nuclear shielding, $\sigma_1(T)$ is obtained from the slopes of plots such as these.

temperatures indicate a smaller magnitude of σ_1 at higher temperatures, the usual behavior for intermolecular effects on F nuclei. The bulk susceptibility contribution to σ_1 in this experiment ($\sigma_{1b} = 2\pi\chi/3$) is only a small part of the observed σ_1. The intermolecular interaction effects on shielding are given by ($\sigma_1 - \sigma_{1b}$), shown in Table 1. Pairwise interactions between molecules leads to deshielding for all these ^{19}F environments with greater effects for the somewhat more exposed CF_3 than for the CF_2 in CF_3CF_2Cl, a geometric nuclear site effect (*2b*). Our value of σ_1 for CF_3CH_3 at 350 K, $-(26.2 \pm 1.1) \times 10^{-3}$ ppm amagat^{-1}, agrees with the value reported by Mohanty and Bernstein (*3*), $-(26.4 \pm 1.8) \times 10^{-3}$. The temperature dependence of σ_1 which we report here ($+0.056 \times 10^{-3}$ ppm amagat^{-1} deg^{-1}) is different from theirs ($d\sigma_1/dT = +0.32 \times 10^{-3}$ ppm amagat^{-1} deg^{-1}). However, the latter is obtained from absolute values of σ_1 at two temperatures, each of which has a sizable error. Our measurements are obtained from the temperature-dependent resonance frequencies for each sample through the range of temperatures indicated in the tables, which allows us to obtain the T dependence of σ_1 with better precision than the accuracy of the absolute value of σ_1 at any one temperature. The error in the latter is entirely dominated by uncertainties in the density which do not significantly affect the temperature dependence of σ_1.

The previously reported isotope shift in σ_1 (*3*) for $CF_3C(H/D)_3$ is unusually large and doubtful. It appears to have been obtained from separate samples of CF_3CH_3 and CF_3CD_3. An isotope shift in σ_1 should be measured by observing both molecules in the same sample, otherwise the difference in σ_1 could be largely dominated by different density errors in separate samples. We made no attempt to measure the isotope shift on σ_1, which is expected to be negligibly small on the basis of our calculated -4×10^{-5} ppm amagat^{-1} shift in σ_1 between CHD_3 and CH_4 (*2a*).

TABLE 1

The Observed Second Virial Coefficient of ^{19}F Nuclear Magnetic Shielding in Various Gases, $\sigma_1(T)$ and ($\sigma_1 - \sigma_{1b}$) for Interaction between Like Pairs of Molecules (in ppb amagat^{-1})

Molecule	T (K)	$\sigma_1(T)$	χ (10^{-6} cm^3/mol)[a]	σ_{1b}	($\sigma_1 - \sigma_{1b}$) at 340 K
CF_3CH_3	330–380	$-(26.44 \pm 1.10)$ $+ 5.62 \times 10^{-2}$ (T-340)	−39.7	−3.71	−22.73
CF_2HCH_3	330–380	$-(22.85 \pm 1.34)$ $+ 1.02 \times 10^{-1}$ (T-340)	−36.3	−3.39	−19.46
$C\mathit{F}_2ClCF_3$	340–380	$-(23.27 \pm 1.38)$ $+ 6.85 \times 10^{-2}$ (T-340)	−60.5	−5.65	−17.62
$C\mathit{F}_3CF_2Cl$	340–380	$-(24.28 \pm 1.41)$ $+ 8.03 \times 10^{-2}$(T-340)	−60.5	−5.65	−18.63
CF_3CF_3[b]	270–380	$-(17.44 \pm 0.80)$ $+ 2.41 \times 10^{-2}$(T-300)	−49.8	−4.65	−16.21

[a] Calculated from Pascal's constants and in good agreement with values calculated by J. A. Beran and L. Kevan, *J. Phys. Chem.* **73**, 3860 (1969), using Haberditzl's method: for CF_2HCH_3, −36.9; for CF_3CF_2Cl, −65.0; and for CF_3CF_3, −52.5.

[b] C. J. Jameson, A. K. Jameson, and H. Parker, *J. Chem. Phys.* **70**, 5916 (1979).

TABLE 2

Temperature Dependence of ^{19}F Nuclear Resonance at 84.67 MHz in the Liquid Phase and in the Vapor in Equilibrium with It[a]

Molecule	T_0 (K)	$\nu_{\text{LIQ}}(T)$[b]			$\nu_{\text{VAP}}(T)$[b]			$(\sigma_{\text{LIQ}} - \sigma_{\text{VAP}})(T)$				Bulk susc. contrib (ppm)[c]		
		T (K)	a_1	$10^3\ a_2$	T (K)	b_1	$10^3\ b_2$	T (K)	c_0	$10^2\ c_1$	$10^4\ c_2$	d_0	$10^2 d_1$	$10^4 d_2$
CF_3CH_3	300	220–310	−1.529	−5.49	258–320	2.242	1.66	258–310	−4.648	4.45	2.61	−0.892	0.570	0.403
CF_2HCH_3	300	227–310	−0.563	—	280–328	1.148	1.54	280–310	−5.035	2.02	1.79	−1.016	0.402	0.202
CF_2ClCF_3	300	190–320	−0.429	−1.02	228–340	1.930	8.63	230–320	−3.301	2.81	1.14	−0.978	0.583	0.233
CF_3CF_2Cl	300	190–320	−0.811	−1.97	228–340	1.795	7.85	230–320	−3.530	3.08	1.16	Same as above		
CF_3CF_3	250	230–275	−1.128	−1.42	230–275	1.725	17.56	230–275	−3.651	3.37	2.24	−0.941	0.594	0.287

[a] The experimental data can be adequately described by the following functions valid only in the temperature ranges indicated: $\nu_{\text{LIQ}}(T) = \nu_{\text{LIQ}}(T_0) + a_1(T - T_0) + a_2(T - T_0)^2$ (Hz); $\nu_{\text{VAP}}(T) = \nu_{\text{VAP}}(T_0) + b_1(T - T_0) + b_2(T - T_0)^2$ (Hz); $(\sigma_{\text{LIQ}} - \sigma_{\text{VAP}})(T) = c_0 + c_1(T - T_0) + c_2(T - T_0)^2$ (ppm). The gas-to-liquid shifts due to bulk susceptibilities are shown in the same functional form, for the same range of temperatures.

[b] These have not been corrected for the slight temperature dependence of the lock substance, toluene-d_8.

[c] Calculated by $(2\pi/3)\chi(\rho_{\text{LIQ}} - \rho_{\text{VAP}})(T)$ using χ values given in Table 1, liquid and vapor densities from Landolt-Bornstein, Vol. 4, Pt. 4a, 6th ed., and from W. H. Mears, R. F. Stahl, S. R. Orfeo, R. C. Shair, L. F. Kells, W. Thompson, and H. McCann, *Ind. Eng. Chem.* **47,** 1449 (1955).

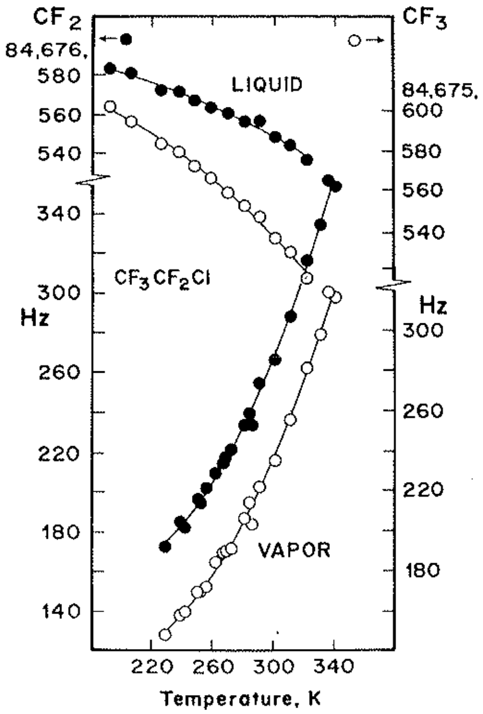

FIG. 2. Typical liquid and equilibrium vapor data.

Another method of observing intermolecular effects on shielding is by measurements of gas-to-liquid shifts (Table 2). We show an example of this type of data in Fig. 2. The temperature dependence due to rovibrational averaging ($\sigma_0(T)$) subtracts out in taking ($\sigma_{\text{LIQ}} - \sigma_{\text{VAP}}$) ($T$). Therefore, only the temperature dependence of the intermolecular effects (binary and higher order) on shielding (and the bulk susceptibility contribution) are observed. The observed gas-to-liquid shifts vary with temperature as shown in Fig. 3, primarily because the density of the liquid varies with temperature. The gas-to-liquid shifts corrected for bulk susceptibility contributions can be compared directly with the ($\sigma_1 - \sigma_{1b}$) from the dilute gas-phase measurements by calculating an "effective σ_1" for the liquid, σ_1^{eff}, from ($\sigma_{\text{LIQ}} - \sigma_{\text{VAP}}$)($T$)/($\rho_{\text{LIQ}} - \rho_{\text{VAP}}$)($T$). In Table 3, we note that the values of σ_1^{eff} are in the same relative order as σ_1 in this series of molecules. $|\sigma_1^{\text{eff}}|$ increases as the system approaches densities greater than the critical density (*2a*). A more appropriate comparison of ($\sigma_1^{\text{eff}} - \sigma_1$) for different molecules at the same reduced densities (ρ/ρ_{crit}), (rather than at the same temperature) shows that the differences ($\sigma_1^{\text{eff}} - \sigma_1$) are in the same relative order as in Table 3. The discrepancy between the dilute gas and liquid intermolecular effects on shielding arises from the many-body terms which contribute in the liquid phase. The many-body effects increase the ^{19}F nuclear shielding, that is, they are opposite in sign to the two-body effects, and are largest for fluoroethanes with hydrogens. This is consistent with our findings in other systems containing fluorine. The net effect is that the ^{19}F nucleus in the liquid phase is somewhat less deshielded than might be expected from extrapolation of the dilute gas-phase results to liquid densities. We also find that the difference between σ_1^{eff} and σ_1 is larger for the fluoroethanes than for the fluoromethanes. We have no explanation for this.

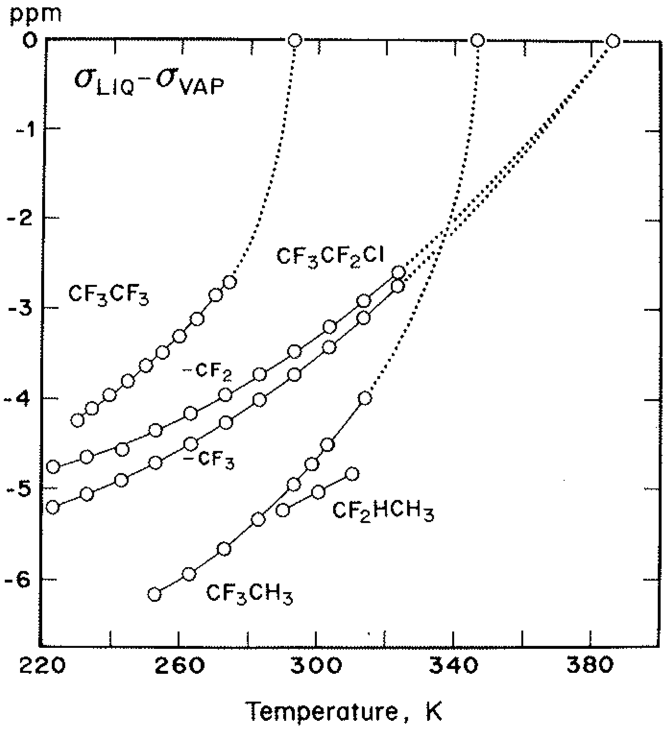

FIG. 3. The ^{19}F gas-to-liquid shifts in the fluoroethanes. The curves approach zero at the critical temperature and are described by quadratic functions of temperature in Table 2. Critical temperatures are from Landolt-Bornstein, Vol. 4, Pt. 4a.

In the binary collision model of the intermolecular effects on shielding by Raynes, Buckingham, and Bernstein (*4*), $(\sigma_1 - \sigma_{1b})$ correlates with the electric dipole polarizability since the van der Waals contribution to σ_1 in this model is proportional to $\alpha I\langle r^{-6}\rangle$. However, the polarizabilities for this set of molecules ($\alpha = 44.7$, 44.3, 64.5, and 46.0×10^{-25} cm^3, respectively, for CF_3CH_3, CF_2HCH_3, CF_3CF_2Cl, and CF_3CF_3) (*5*) are not in the same relative order as the measured $(\sigma_1 - \sigma_{1b})$. The magnitudes of $(\sigma_1 - \sigma_{1b})$ are greater for molecules with more hydrogens, similar to

TABLE 3

Comparison of the Effects of Intermolecular Interactions on Shielding in the Dilute Gas, $(\sigma_1 - \sigma_{1b})$ and in the Liquid $(\sigma_1^{\text{eff}} - \sigma_{1b})^a$

Molecule	T_{crit}	T	$(\sigma_1 - \sigma_{1b})$	$(\sigma_1^{\text{eff}} - \sigma_{1b})$	diff
CF_3CH_3	346.3	320	−23.857	−14.591	+9.3
CF_2HCH_3	386.7	320	−21.496	−13.395	+8.1
CF_2ClCF_3	386.5	330	−18.305	−12.411	+5.9
CF_3CF_2Cl	386.5	330	−19.433	−13.486	+5.9
CF_3CF_3	292.7	270	−13.34	−11.75	+1.6
		250	−14.26	−13.39	+0.9

[a] All in ppb amagat^{-1}.

our early findings that ^{129}Xe has a larger σ_1 in CH_4 than in CF_4, despite the greater polarizability of the latter (*6*).

The temperature dependence of the resonance frequency of the "isolated" molecule, $\nu_0(T)$, is obtained when the observed resonance frequencies are corrected for the density-dependent terms and the temperature dependence of the toluene-d_8 (see Fig. 4). From each of these curves we obtain the $[\sigma_0(T) - \sigma_0(300)]$ functions which are shown in Table 4.

In Fig. 4 we note that with Cl substitution, the $\nu_0(T)$ curves are steeper, $(d\sigma_0/dT)_{300} = -13.14$ ppb deg^{-1} for CF_2Cl and -11.33 ppb deg^{-1} for CF_3 in CF_3CF_2Cl, for example. With H substitution, a smaller T dependence is observed: $(d\sigma_0/dT)_{300} = -10.28$ ppb deg^{-1} for CF_3CH_3 and -11.37 ppb deg^{-1} for CF_3CF_3. These trends were also observed in the fluoromethanes (*1*). The intrinsic temperature dependences

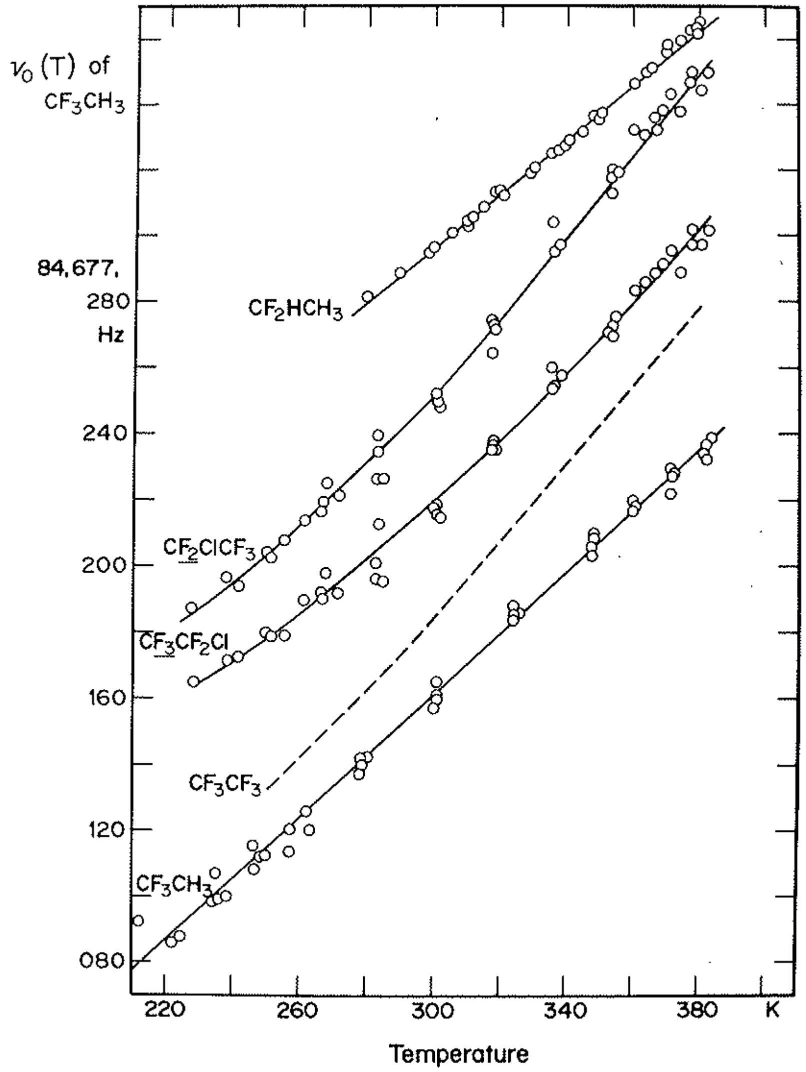

FIG. 4. The ^{19}F resonance frequencies in the zero-pressure limit from which the functions $[\sigma_0(T) - \sigma_0(300\text{ K})]$ given in Table 4 are obtained, compared with CF_3CF_3 from C. J. Jameson, A. K. Jameson, and H. Parker, *J. Chem. Phys.* **69,** 1318 (1978).

TABLE 4

Temperature Dependence of the ^{19}F Nuclear Magnetic Shielding in the Zero-Pressure Limit

Molecule	T (K)	$[\sigma_0(T) - \sigma_0(300)]$ (ppb)
CF_3CH_3	215–380	$-10.27\ (T\text{-}300)$
CF_2HCH_3	300–380	$-10.77\ (T\text{-}300)$
CF_2ClCF_3	228–380	$-13.14\ (T\text{-}300) - 1.44 \times 10^{-2}\ (T\text{-}300)^2$
CF_3CF_2Cl	228–380	$-11.33\ (T\text{-}300) - 5.9 \times 10^{-3}\ (T\text{-}300)^2$
CF_3CF_3[a]	250–380	$-11.37\ (T\text{-}300) - 3.42 \times 10^{-3}\ (T\text{-}300)^2$

[a] C. J. Jameson, A. K. Jameson, and H. Parker, *J. Chem. Phys.* **69**, 1318 (1978).

of the ^{19}F shielding at room temperature, $-(d\sigma_0/dT)_{300}$ in the fluoroethanes are compared to fluoromethanes in similar electronic environments in Fig. 5. We have previously found that there is a qualitative but clear relationship between $[\sigma_0(T) - \sigma_0(300)]$ and the extent to which the populations of the vibrational degrees of freedom of a molecule can be affected by temperature: the more "low-frequency" modes a molecule has, the greater the temperature dependence of the shielding. Since the temperature dependence of $\sigma_0(T)$ involves sums over terms in $\coth(hc\omega_i/2kT)$, low ω_i modes generally make important contributions to the temperature dependence. In the fluoroethanes, low-frequency torsional vibrations, which are not present in the fluoromethanes, may account for the greater temperature dependence of the former.

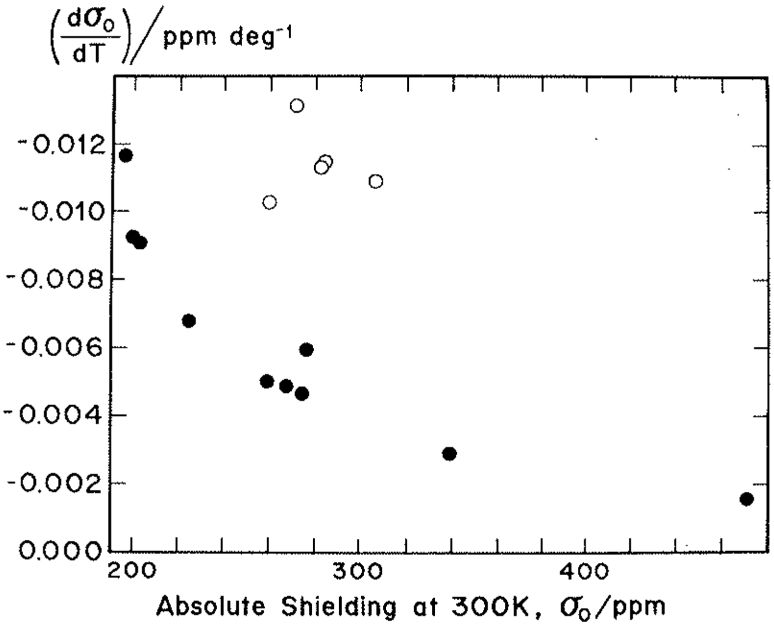

FIG. 5. The ^{19}F nuclei in the fluoroethanes (open circles) have a greater temperature dependence than the ^{19}F nuclei in similar average electronic environments in the fluoromethanes (filled circles). Absolute shielding values taken from C. J. Jameson, A. K. Jameson, and P. M. Burrell, *J. Chem. Phys.* **73**, 6013 (1980) and C. J. Jameson, A. K. Jameson, and J. Honarbaksh, *J. Chem. Phys.* **81**, 1198 (1984).

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