Variation of nuclear magnetic shielding with intermolecular interactions and rovibrational motion. IX. ^{19}F in $F_2C{=}CH_2$ and $F_2C{=}CF_2$

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The effects of intermolecular interactions on ^{19}F nuclear magnetic shielding in $CF_2{=}CF_2$ and $CH_2{=}CF_2$ have been measured in the pure gas at modest densities (7–35 amagat). For $CH_2{=}CF_2$ other measurements by Wisman in 50–150 amagat gas samples agree with our results, and the slopes of the shielding vs density plots are identical within experimental error. The entire set of data for the gas phase and including 170–380 amagat in the liquid phase show a nonlinear behavior, deshielding with increasing density by -0.0152 ppm amagat^{-1} for the low density gas and somewhat less deshielding for the liquid. The temperature dependence in the limit of zero pressure is also reported here: $\sigma_0(T) - \sigma_0(300) = -4.066\times10^{-3}(T\text{-}300)\text{-}1.69\times10^{-5}(T\text{-}300)^2$ ppm for F in $CH_2{=}CF_2$ (which is very similar to that previously reported for $O = CF_2$) and $-8.127\times10^{-3}(T-300)\text{–}2.09\times10^{-5}(T-300^2)$ppm in $CF_2{=}CF_2$.

Our continuing studies of the effects of intermolecular interactions and rovibrational averging on ^{19}F nuclear magnetic shielding include the substituted flouroethylenes $CF_2{=}CFX$ in which there are three separate probe nuclei in the molecules with X = H, Cl, Br, I. This work is reported elsewhere.[1] A natural member of this series is $CF_2{=}CF_2$ in which all flourines are equivalent, and for comparison $CH_2{=}CF_2$, as well. This paper involves the temperature and density dependent studies on $CF_2{=}CF_2$ and $CH_2{=}CF_2$ and comparison with $O{=}CF_2$ which is isoelectronic with the latter.

^{19}F FT NMR spectra were taken at 84.7 MHz of sealed gas samples ~0.2 ml volume, 3.9 mm o.d., 2.2 mm i.d. containing 7–35 amagat $CH_2 = CF_2$ or 7–20 amagat $CF_2{=}CF_2$ in a 5 mm NMR sample tube. The CD_3 signal of toluene-d_8 in the annular region provided field stabilization. The temperature dependence of this signal has been previously determined. Temperature regulation to ± 0.2 deg over the range 220–380 K was provided by a previously calibrated variable temperature system. The gases were obtained from PCR Chemicals.

The *AA 'XX'* spectra for $CH_2{=}CF_2$ have been analyzed previously in the pure liquid and in various solvents.[2] For the purpose of this experiment we needed only the center of the multiplet pattern. Our typical data for $CH_2{=}CF_2$ are shown in Fig. 1. The temperature dependence of the resonance frequency is independent of density. The frequency differences between the curves characteristic of the different samples is independent of temperature. Thus, we see that σ_1 has no measurable temperature dependence. This is not the case in $CF_2{=}CF_2$. In the latter the curves get closer together as the temperature is increased. We did not observe $CF_2{=}CF_2$ beyond 350 K since it is known to polymerize.

When the density dependent parts have been subtracted out, and the temperature dependence of the lock substance is taken into account, the resonance frequencies of the gas in the zero-pressure limit (that is, characteristic of the independent molecule) are obtained. These are shown in Fig. 2 and described with quadratic functions of temperature in Table I.

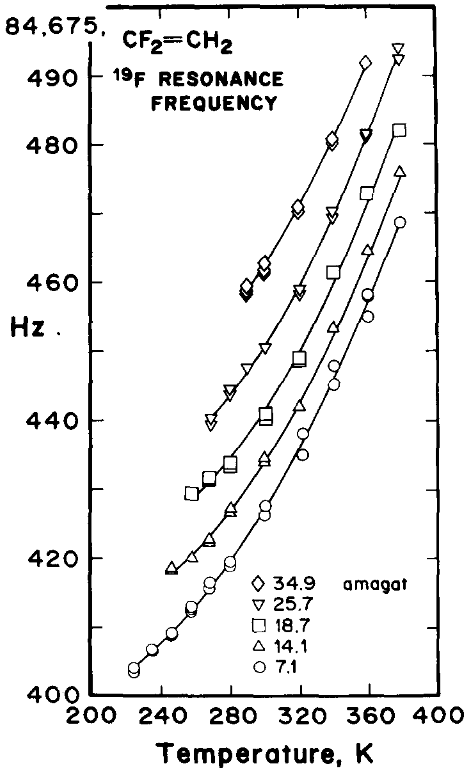

FIG. 1. ^{19}F resonance frequencies for the center of the A multiplet in the *AA 'XX'* spectrum of $CH_2{=}CF_2$. The dependence on density is a linear one over this range.

The effects of intermolecular interactions are expressed in the virial expansion of the nuclear magnetic shielding as

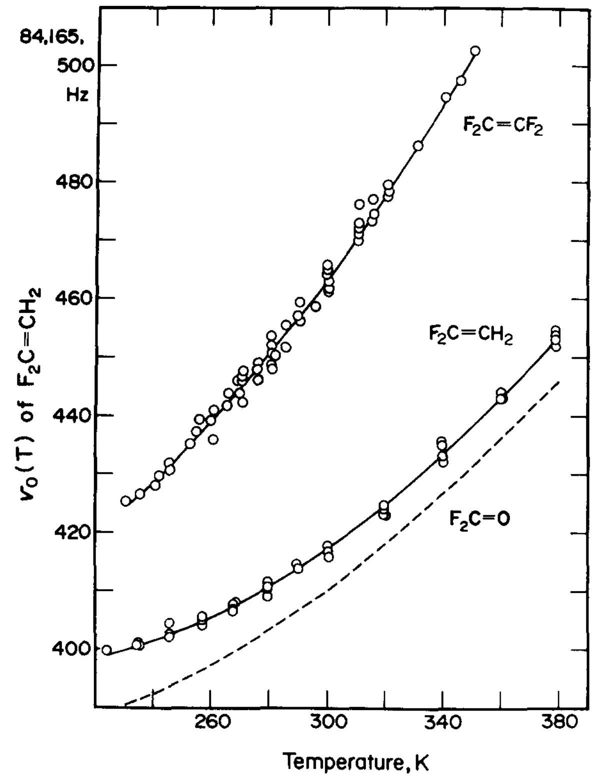

FIG. 2. The temperature dependence of the ^{19}F resonance frequencies (shown in Fig. 1 for $CH_2{=}CF_2$) after the density dependent part and the lock solvent temperature dependence have been removed.

the coefficients of the linear and higher powers of density:

$$\sigma(T,\rho) = \sigma_0(T) + \sigma_1(T)\rho + \sigma_2(T)\rho^2 + \cdots.$$

In our NMR measurements in the gas phase we have generally kept our sample densities to below 40 amagat in order to obtain $\sigma_1(T)$. The results are shown in Table II for $CF_2{=}CF_2$ and $CH_2{=}CF_2$.

Our results for σ_1 of ^{19}F in $CH_2{=}CF_2$ interacting with itself agrees with that of Wisman.[3] Ours is 15.22 ± 0.57 ppb amagat^{-1}, independent of temperature, and Wisman's value is 15.2 ± 1.4 in the same units. Both values include the bulk susceptibility contribution, σ_{1b} (see Table II). This agreement is remarkable, especially when we consider that our data were obtained in 7–35 amagat samples whereas Wisman's were taken in 50–150 amagat gas samples. In Fig. 3 we have combined our gas phase results with those of Wisman for the gas at 305 K and his liquid phase data at 293–303 K, with ours for the liquid at 210–260 K. It is possible to put all these results on one plot for $CH_2{=}CF_2$ because we have found no measurable temperature dependence in σ_1. From Fig. 3 we arrive at several conclusions. One is that the intermolecular effects give a linear plot nearly up to the critical density (146 amagat.) This is reassuring. In previous studies we have always limited our measurements to densities below 40 amagat and sometimes below 10 amagat in order to make observations in the regime where the shielding is linearly dependent on density. We see that we easily satisfy that condition for $CH_2{=}CF_2$. Secondly, the many-body effects which become important at high densities appear to be opposite in sign to the two-body effects; the shielding vs density plot exhibits some deviation from linear behavior even in the gas phase. The fit to a quadratic function of density, $\sigma - \sigma_0 = \sigma_1\rho + \sigma_2\rho^2$, gives $\sigma_1 = -0.0154$ ppm amagat^{-1} and $\sigma_2 = +4.401\times10^{-6}$ ppm amagat^{-2}. This is similar to

TABLE I. Temperature dependence of the ^{19}F nuclear magnetic shielding in the zero-pressure limit.

Molecule	T, K	$[\sigma_0(T) - \sigma_0(300)]$, ppb
$CF_2{=}CF_2$	230–350	$-8.127(T-300) - 2.09\times10^{-2}(T-300)^2$
$CF_2{=}CH_2$	225–380	$-4.066(T-300) - 1.69\times10^{-2}(T-300)^2$
$O{=}CF_2$[a]	230–380	$-4.332(T-300) - 1.3465\times10^{-2}(T-300)^2$

[a] Reference 6.

TABLE II. The observed second virial coefficient of ^{19}F nuclear magnetic shielding, $\sigma_1(T)$ and $(\sigma_1 - \sigma_{1b})$ for interaction between like pairs of molecules, all in ppb/amagat.

Molecule	$CF_2{=}CH_2$	$CF_2{=}CF_2$
T, K	290–380	270–320
$\sigma_1(T)$	$-(15.22\pm0.57)$[a]	$-(17.79\pm1.96)$ $+5.25\times10^{-2}(T-300)$
χ, 10^{-6} cm^3/mol	-25.0[b]	-31.7[b]
σ_{1b}	-2.34	-2.96
$(\sigma_1 - \sigma_{1b})$ at 300 K	-12.9	-14.8

[a] Wisman reported $-(15.2\pm1.4)$ ppb/amagat (Ref. 3).

[b] Calculated from Pascal's constants, in good agreement with values calculated by J. A. Beran and L. Kevan (Ref. 5) using Haberditzl's method: for $CF_2{=}CH_2$ -28.7 and for $CF_2{=}CF_2$ -36.9×10^{-6} cm^3/mol.

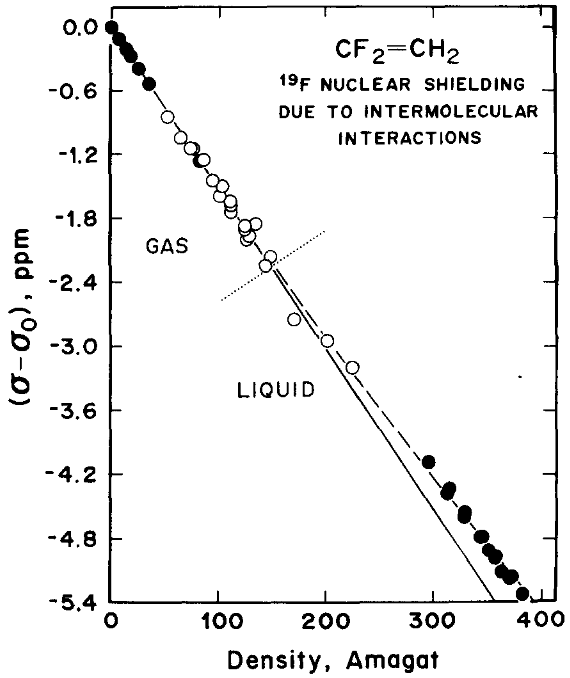

FIG. 3. The density dependence of the ^{19}F nuclear shielding. The filled circles are from this work, the open circles are from Wisman (Ref. 3). There was no observable temperature dependence of σ_1 obtained from the low density data shown in Fig. 1. Wisman's gas data taken at 305 K. The liquid data were taken at 293–303 K (Wisman) and 220–280 K (this work). The slope of the straight line is -0.01522 ppm amagat^{-1}. Densities of the liquid were obtained from Landolt–Bornstein, Vol IV 4 a. The critical point is 303.3 K, 146 amagat.

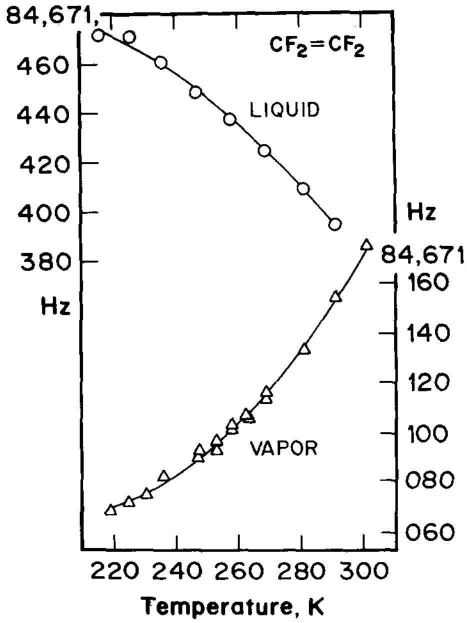

FIG. 4. ^{19}F resonance frequencies in the vapor in equilibrium, with liquid $CF_2{=}CF_2$, observed simultaneously.

the nonlinear behavior observed in ^{129}Xe shielding in xenon gas for densities greater than 100 amagat.[4] For Xe, $\sigma_1 = -0.624$ ppm amagat $^{-1}$ and $\sigma_2 = +0.503\times10^{-3}$ ppm amagat^{-2}, if only terms quadratic in density are included to fit data up to 250 amagat. The ratio of σ_2/σ_1 for ^{19}F in $CF_2{=}CH_2$ is 2.8×10^{-4} amagat $^{-1}$ and for Xe it is 8.1×10^{-4} amagat^{-1}. The liquid and its equilibrium vapor have been observed in $CF_2{=}CF_2$. These frequencies are shown in Fig. 4, from which we obtain $(\sigma_{\rm LIQ} - \sigma_{\rm VAP})(T)$. In $CF_2{=}CF_2$ we obtain an "effective σ_1"for the liquid, the ratio $[\sigma_{\rm LIQ} - \sigma_{\rm VAP}]/[\rho_{\rm LIQ} - \rho_{\rm VAP}]$ equals -14.2×10^{-3}, to be compared with $\sigma_1 = -18.8\times10^{-3}$ ppm amagat $^{-1}$, both at 280 K. In Fig. 3 the effective σ_1 is the slope of a line which joins a liquid point with its equilibrium vapor point. ^{19}F in $CH_2{=}CF_2$ also exhibits an effective σ_1 which is smaller in magnitude than the σ_1 for low density gas. We can see in Fig. 3 the $\sigma(\rho)$ function which gives rise to this typical behavior, the deshielding two-body effects dominate until the shielding many-body effects become important. We believe that Fig. 3 may be typical for ^{19}F shielding since we found in nearly all cases that the effective σ_1 is of smaller magnitude than σ_1 at the same temperature.

Wisman observed a sharp break in his plot such as Fig. 3, for densities around the critical density, the straight line breaks off and turns around to higher shielding. He proposed some kind of ordering phenomenon to explain this. It is very likely that his sample densities exceeded the critical density and what he observed was the vapor (in equilibrium with some liquid), with resonance frequencies characteristic of densities lower than the overall prepared densities of the samples.

The value of $(\sigma_1 - \sigma_{1b})$ for interaction between $CF_2 = CF_2$ molecules is comparable to that for $CH_2 = CF_2$ (see Table II). This is not suprising because their electric dipole polarizabilities are comparable (41.7×10^{-25} cm^3 for $CF_2{=}CF_2$ and 40.8×10^{-25} cm^3 for $CH{=}CF_2$).[5] Using the theory of Raynes, Buckingham, and Bernstein,[7] Wisman estimates the van der Waals contribution to the intermolecular effects on shielding is -11.75 ppb amagat^{-1}, in good agreement with -12.9 ppb amagat^{-1}.

The observed temperature dependences of the rovibrationally averaged ^{19}F shielding in the "isolated" molecules are compared to $O{=}CF_2$[6] in Fig. 2. The temperature dependences of $CH_2{=}CF_2$ and $O{=}CF_2$ are very similar. This is not surprising since the CH_2 group is isoelectronic with an oxygen atom. The vibrations involving the $= CF_2$ group are the ones most important to the vibrational averaging of the ^{19}F shielding. The shielding tensors of both molecules have been measured in a molecular beam maser by Kukolich *et al.*[8,9] The shielding components along an axis normal to the CF_2 plane (z) and along the axis in the plane and perpendicular to the double bond (y) are nearly equal in these molecules: 242 and 227 for σ_{zz} and 300 and 281 for σ_{yy} for $CH_2{=}CF_2$ and $O = CF_2$, respectively. The shielding component along the double bond distinguishes the two molecules and is mainly responsible for the chemical shift between them. The rovibrational averaging of the shielding involves motions of the $= CF_2$ group, which mainly affect the σ_{zz} and σ_{yy} components. Therefore, it is not suprising that the functional forms of $[\sigma_0(T) - \sigma_0(300)]$ for these two molecules are very similar.

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