Variation of chemical shielding with intermolecular interactions and rovibrational motion. I. ^{19}F nuclei in BF_3, CF_4, SiF_4, and SF_6

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The chemical shifts due to rotational and vibrational motion in CF_4, SiF_4, BF_3, and SF_6 are obtained by extrapolation of ^{19}F resonance frequencies to zero density. The second virial coefficients of chemical shielding, $\sigma_1(T)$, are obtained at the same time from the slopes. It is found that the σ_1 values for these molecules do not depend on temperature nearly as strongly as was previously reported.

The chemical shielding of a nucleus in a gas is dependent on temperature and density. This relationship is commonly expressed in terms of a virial expansion,

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

It is possible to determine both the temperature dependence of chemical shielding in the isolated molecule, $\sigma_0(T)$, and the temperature dependence of the second virial coefficient of chemical shielding, $\sigma_1(T)$, in samples of relatively low density.

$\sigma_1(T)$ depends on intermolecular interactions. In the simplest case of interaction of two spherically symmetric molecules, $\sigma_1(T)$ has the following form:

$$\sigma_1(T)=4\pi\int_0^\infty \sigma(R)e^{-V(R)/kT}R^2\,dR ,$$

where $V(R)$ is the intermolecular potential function. $\sigma(R)$ is the chemical shielding of a nucleus in a molecule in the presence of some other (perturber) molecule at a distance R from it. $\sigma_1(T)$ is obtained by studying samples of sufficiently low density so that the contribution to shielding by terms in ρ^2 or higher order are negligible. The slope of the straight line fitted to observed resonance frequency versus density of perturber gas gives σ_1 for each temperature. The intercepts of such plots likewise vary with temperature and provide information about $\sigma_0(T)$ itself.

$\sigma_0(T)$ is due to anharmonic vibration and centrifugal distortion in the isolated molecule. In a molecule such as xenon, $\sigma_0(T)$ equals a constant due to lack of rotational or vibrational degrees of freedom. The high precision of the temperature and density dependence of the xenon resonance frequency makes possible the extrapolation of the data to zero density of Xe.[1] The residual temperature dependence of the ^{129}Xe signal at zero density is the temperature dependence of the reference substance used.[2] The precisely known temperature dependence of the reference substance allows us to determine the intrinsic temperature dependence of isolated molecules. For example, extrapolation of SiF_4 data to zero density leaves only $\sigma_0(T)$ for SiF_4 combined with the temperature dependence of the reference substance. Having determined the latter to a high degree of precision allows us to find $\sigma_0(T)$ for ^{19}F in SiF_4 by difference.

RESULTS

^{19}F NMR spectra were obtained at 84 MHz on a Bruker HFX-90 variable frequency spectrometer using the pulsed Fourier transform mode. The magnetic field was stabilized on the ^1H resonance signal of a liquid external reference. Temperature regulation, sample preparation and data collection are the same as previously described.[1] Samples ranging in density from 3 to 40 amagats typically required 16 scans except for BF_3 in which the structure due to the ^{10}B and ^{11}B isotopes necessitated taking 64–256 scans.

The NMR resonance frequency is determined over a wide temperature range for given samples of known densities, the results for each sample fit to a polynomial of degree 2 or 3, and the known temperature dependence of the reference substance is removed.[2] From the known densities of the samples we determine σ_1 at different temperatures. Since each sample, regardless of density, contains $\sigma_0(T)$ information, this $\sigma_1(T)$ is used to remove the effect of the density dependence of the gas, and the several independent measures of $\sigma_0(T)$ are combined to yield a statistical "best" value and a standard deviation at each temperature.

While σ_1 becomes smaller with increasing temperature leading to an upfield shift, σ_0 leads to a downfield shift with increasing temperature. Thus, the ^{19}F signal, unlike that of Xe, moves downfield with increasing temperature. This is due to the dominance of the temperature dependence of σ_0 over that of σ_1. The temperature dependence of the reference substance leads to a downfield shift with increasing temperature as well. However, in the ^{19}F case, the downfield shift

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TABLE I. Frequency shifts due to rovibrational motion, $\Delta\nu_0$, and $\sigma_1(T)$ for ^{19}F and BF_3 at 84.679 MHz.

T	$\Delta\nu_0$, Hz rel to 300 K	SD[a]	σ_1, Hz/amagat	SD[b]
290	−1.01	0.81	1.606	0.145
300	0	0.68	1.585	0.150
310	1.25	0.57	1.566	0.154
320	2.73	0.47	1.545	0.159
330	4.45	0.40	1.527	0.164
340	6.41	0.33	1.508	0.166
350	8.61	0.24	1.489	0.168
360	11.04	0.21	1.471	0.173
370	13.71	0.28	1.453	0.173
380	16.62	0.42	1.435	0.178
390	19.76	0.59	1.418	0.178
400	23.14	0.81	1.401	0.178
410	26.76	1.09	1.384	0.178

[a] This includes the standard deviation of the temperature dependence of the reference substance *p*-xylene. Note that the average error is 1.9% of the total shift observed.

[b] This indicates the precision with which the absolute magnitude of σ_1 is known. Most of the error is due to density errors. The temperature dependence of σ_1 is somewhat more precisely known since the frequencies and temperatures can be measured with good precision.

TABLE III. Frequency shifts due to rovibrational motion, $\Delta\nu_0$, and $\sigma_1(T)$ for ^{19}F in SF_6 at 84.698 MHz.

T	$\Delta\nu_0$, Hz rel to 300 K	SD[a]	T	σ_1, Hz amagat	SD[b]
280	−19.54	1.19	275	1.693	0.156
290	−10.00	0.89	285	1.691	0.142
300	0	0.77	295	1.681	0.131
310	10.45	0.81	305	1.662	0.123
320	21.35	0.85	315	1.637	0.117
330	32.71	0.85	325	1.603	0.111
340	44.53	0.79	335	1.562	0.106
350	56.79	0.65	345	1.512	0.102
360	69.51	0.61	355	1.455	0.098
370	82.69	0.83	365	1.391	0.096
380	96.32	1.39	375	1.318	0.099
390	110.40	1.80	385	1.238	0.107

[a] This includes the standard deviation of the temperature dependence of the reference substances, ^{1}H of ditrifluoromethyl benzene and *p*-xylene. Note that the average error is 0.5% of the total shift observed.

[b] This indicates the precision with which the absolute magnitude of σ_1 is known. Most of the error is due to density errors. The temperature dependence of σ_1 is somewhat more precisely known since the frequencies and temperatures can be measured with good precision.

due to the reference is relatively small, only 7% to 25% that due to σ_0.

The results are shown in Tables I to IV and Fig. 1. They are the first values reported for ^{19}F nuclei. In practice we are able to measure not the absolute magnitudes but only differences in chemical shielding. Thus, when we refer to measurements of $\sigma_0(T)$ we really mean measurements of frequency shifts with temperature in the limit of zero pressure, $\Delta\nu_0$ (as shown in Hz in Tables I to IV), or field shifts expressed in ppm, $(\langle\sigma\rangle^T - \langle\sigma\rangle^{T_0})$, where T_0 is some fixed temperature. We choose $T_0 = 300$ K. In Table V is a summary of $(\langle\sigma\rangle^T - \langle\sigma\rangle^{300})$. ^{1}H shifts are of the order of 2.6×10^{-4} to 0.0018 ppm/deg,[3,4] whereas the ^{19}F shifts we observed in these molecules range from 0.0013 to 0.012 ppm/deg.

The chemical shift due to rovibrational motion is seen to be largest for SF_6 and smallest for BF_3, vary-

TABLE II. Frequency shifts due to rovibrational motion, $\Delta\nu_0$, and $\sigma_1(T)$ for ^{19}F in SiF_4 at 84.679 MHz.

T	$\Delta\nu_0$, Hz rel to 300 K	SD[a]	σ_1, Hz/amagat	SD[b]
270	−9.78	0.55	1.782	0.034
280	−6.50	0.55	1.730	0.038
290	−3.24	0.48	1.682	0.042
300	0	0.55	1.640	0.046
310	3.21	0.70	1.602	0.048
320	6.41	0.77	1.569	0.049
330	9.58	0.77	1.540	0.048
340	12.72	0.70	1.517	0.047
350	15.85	0.51	1.498	0.046
360	18.95	0.52	1.484	0.044
370	22.03	0.63	1.474	0.044
380	25.08	1.18	1.470	0.045
390	28.11	1.51	1.470	1.045

[a] This includes the standard deviation of the temperature dependence of the reference substances, ^{1}H of ditrifluoromethyl benzene and *p*-xylene. Note that the average error is 1.6% of the total shift observed.

[b] This indicates the precision with which the absolute magnitude of σ_1 is known. Most of the error is due to density errors. The temperature dependence of σ_1 is somewhat more precisely known since the frequencies and temperatures can be measured with good precision.

TABLE IV. Frequency shifts due to rovibrational motion, $\Delta\nu_0$, for ^{19}F in CF_4 at 84.268 MHz.

T	$\Delta\nu_0$, Hz rel to 300 K	SD[a]
270	−12.07	1.33
280	−8.18	0.91
290	−4.15	0.71
300	0	0.58
310	4.28	0.58
320	8.70	0.60
330	13.24	0.63
340	17.92	0.61
350	22.72	0.53
360	27.65	0.51
370	32.72	0.37
380	37.91	0.45
390	43.24	0.70
400	48.69	1.07
410	54.28	1.55

[a] This includes the standard deviation of the temperature dependence of the reference substances, ^{1}H of ditrifluoromethyl benzene and *p*-xylene. Note that the average error is 0.9% of the total shift observed.

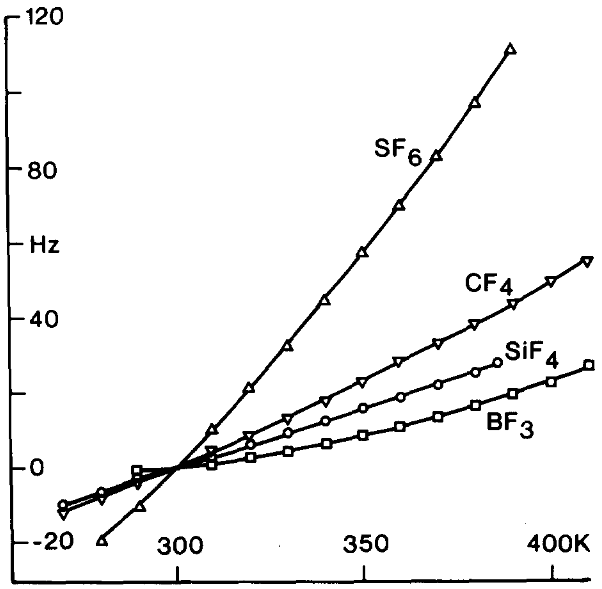

FIG. 1. Frequency shifts with temperature for ^{19}F in the isolated molecules of SF_6, CF_4, SiF_4, and BF_3, at 84.3 MHz for CF_4, and 84.7 MHz for the others.

ing by an order of magnitude for this set of molecules. To what extent this is due to large differences in the ^{19}F chemical shielding function or to differences in the dynamic states of the molecules is still to be determined. The relative precision of these results is a great improvement over those reported for ^{1}H shifts.[3,4] The main reason for this is that unlike ^{1}H shifts the ^{19}F shifts due to rovibrational motion are much larger than the frequency shifts due to the temperature dependence of the reference.

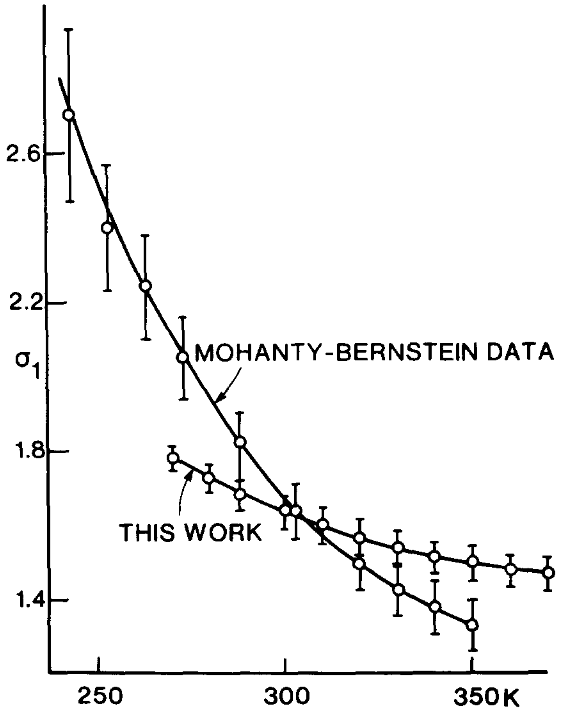

FIG. 2. A comparison of the σ_1 for SiF_4 obtained in this work with that of Mohanty and Bernstein (Ref. 5) both in Hz/amagat at 84.7 MHz.

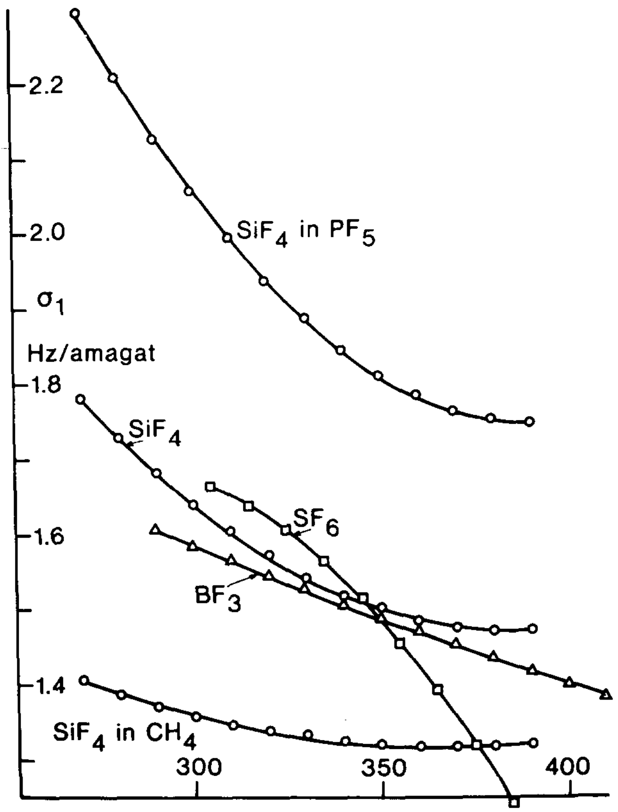

FIG. 3. Second virial coefficient of ^{19}F chemical shielding, σ_1, as a function of temperature for pure SiF_4, BF_3, and SF_6 and for SiF_4 in CH_4 and PF_5.

In the course of the above analysis we obtain $\sigma_1(T)$ even though it is not our prime concern. The σ_1 results are shown in Tables I to IV and in Figs. 2 and 3. The best temperature dependent data on ^{19}F in the literature seemed to be that of Mohanty and Bernstein in which great care was taken to eliminate bulk susceptibility variations by using a single sample tube for all measurements.[5] We compare our $\sigma_1(T)$ for ^{19}F in pure CF_4, SF_6, and SiF_4 with these data. An example of the comparison is shown in Fig. 2 for SiF_4 data. The great disparity between our work and the work which we had considered as the standard for comparison was unexpected. The difference seems to be that Mohanty and Bernstein's sample geometry allowed the sample tube to project out of the dewared region in the variable temperature probe. Thus, there were two regions at different temperature. Since the pressure must be a constant throughout the tube, there developed a density difference in the two temperature regions—neither density being the nominal overall density! The validity of the data of Mohanty and Bernstein has recently also been questioned by Rummens.[6] He points out that the large derivatives of σ_1 with respect to temperature in Mohanty and Bernstein's results are very difficult to explain theoretically. If we use a simple model based on 50% of the sample tube being at the dewared temperature and 50% at room temperature, and allow for no mixing between the two regions, then we can account

TABLE V. Temperature dependence of ^{19}F shielding in ppm, expressed as field shifts in the form of a function $a_0+a_1\tau+a_2\tau^2$ in which $\tau=T-300$.

	$\langle\sigma\rangle^T-\langle\sigma\rangle^{300}$, ppm			$\sigma_1(T)$, ppm/amagat		
Molecule	$10^2\,a_1$	$10^5 a_2$	Molecular pair	$10^2\,a_0$	$10^5\,a_1$	$10^7\,a_2$
BF_3	−0.1334	−1.3990	BF_3, BF_3	−1.8722	+2.3753	−0.1940
CF_4	−0.5007	−0.7722	CF_4, CF_4	−1.1549		
SF_6	−1.2073	−2.6808	SF_6, SF_6	−1.9752	+2.1311	+4.6054
SiF_4	−0.3809	+0.1345	SiF_4, SiF_4	−1.9374	+4.6594	−2.641
			SiF_4, CH_4	−1.6052	+1.4579	−1.0572
			SiF_4, PF_5	−2.4278	+8.0268	−4.3928

for much of the discrepancy between the results of Mohanty and Bernstein and our own. It should be pointed out that at room temperature where their large systematic error is not present, there is complete agreement (within the combined standard deviations) between their data and ours. Table V summarizes the second virial coefficients of ^{19}F chemical shielding, $\sigma_1(T)$, for these molecules. The temperature dependence of $\sigma_1(CF_4)$ is so slight that we are unable to measure it with sufficient precision. The value of σ_1 at room temperature obtained from eleven samples is 0.9732 Hz/amagat.

The opposite curvature of σ_1 for SF_6 compared to the other molecules shown in Fig. 3 does not have significance. Table III indicates that the magnitude of the error at each temperature is such as to be just as consistent with curvature in the same direction as the SiF_4 and BF_3 samples.

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