Variation of chemical shielding with intermolecular interactions and rovibrational motion. VI. ^{19}F in SF_4 and COF_2

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The ^{19}F nuclear resonance frequency in SF_4 and COF_2 molecules were measured as a function of density ρ and temperature T in the gas phase. In the virial expansion $\sigma(T,\rho)=\sigma_0(T)+\sigma_1(T)\rho+\cdots$, the effect of intermolecular interactions on nuclear magnetic shielding is given by $\sigma_1(T)$ for low densities, and the average of the shielding over vibration and rotation is observed as $\sigma_0(T)-\sigma_0(300\ K)$. For SF_4, the measurements are made in the fast-exchange limit, so that the average over the Berry-pseudorotation type exchange is observed. The average shielding terms are as follows: $[\sigma_{0av}(T)-\sigma_{0av}(300\ K)]=-4.332\times10^{-3}(T-300)-1.3465\times10^{-5}(T-300)^2+1.623\times10^{-8}(T-300)^3$ ppm for COF_2 and $-1.297\times10^{-2}(T-300)-7.047\times10^{-6}\times(T-300)^2$ ppm for SF_4. $\sigma_1(T)=-(1.987\pm0.14)\times10^{-2}+8.907\times10^{-5}(T-300)-7.983\times10^{-7}\times(T-300)^2$ ppm/amagat for COF_2 and $-(8.35\pm1.5)\times10^{-3}$ ppm/amagat for SF_4. These functions are defined over the temperature range 230–380 K for COF_2 and 300–380 K for SF_4.

INTRODUCTION

The temperature dependence of the ^{19}F NMR spectrum of liquid SF_4 at low temperatures has been extensively examined.[1–6] The line shapes observed for carefully purified liquid SF_4[1] are in good agreement with those calculated assuming the intramolecular fluorine exchange characteristic of Berry pseudorotation[7] and do not closely resemble those calculated on the basis of intermolecular permutation of fluorines. That the exchange is an intramolecular one is further supported by the observations that in the absence of impurities, the exchange reaction is (a) independent of the concentration of SF_4,[1] (b) unaffected by a change in medium from pure SF_4 to butene–SF_4,[1] and (c) has the same activation energy of exchange in the liquid, solution, or gas phase.[8] The exchange rate is substantially increased by impurities and the spectrum becomes consistent with several plausible intermolecular mechanisms.[1,6] Medium effects on coupling constants and chemical shifts have also been interpreted as indicating intermolecular association in liquid SF_4.[9] In the absence of impurities the fast exchange limit (exchange lifetime $\tau\sim0.0001$ s) in liquid SF_4 is reached at temperatures well below room temperature, with broadening becoming apparent below 220 K for NMR spectra taken at 9.2 MHz.[1]

In the gas phase, intramolecular Berry-type exchange processes have been invoked in the interpretation of observations on the SF_4 molecule by infrared spectroscopy,[10,11] electron diffraction,[12,13] Raman spectroscopy,[14] and NMR.[8] In this study we measure the temperature and density dependence of the ^{19}F NMR spectrum of SF_4 in the gas phase from 300 to 380 K. The intramolecular exchange rate at room temperature in the gas phase corresponds to the fast exchange limit in ^{19}F NMR spectra taken at 84.6 MHz. Thus, only a narrow single peak is observed in all our experiments. We obtain the intermolecular effects on the *average* ^{19}F nuclear shielding as σ_1 and the temperature dependence of ^{19}F shielding in the isolated molecule undergoing Berry pseudorotation as $\sigma_0(T)$ in

$$\sigma_{av}(\rho,T)=\sigma_{0_{av}}(T)+\sigma_{1_{av}}(T)\rho+\cdots .$$

We compare the results for SF_4 with those for the SF_6 molecule, whose $\sigma_0(T)$ appears to be reasonably understood.[15]

COF_2 is another small molecule for which the ^{19}F NMR spectrum has previously been studied only in the liquid phase.[16] In this study we measure both σ_1 and σ_0 as a function of temperature and compare COF_2 with the isoelectronic BF_3 molecule, whose $\sigma_0(T)$ also appears to be well understood.[17]

EXPERIMENTAL

COF_2 and SF_4 obtained from Matheson were degased and vacuum distilled to eliminate any high-boiling impurities. Handling of these fluorinating agents in a glass vacuum system was done quickly to minimize reaction. Any decomposition could be monitored by observing the small amount of SiF_4 in our samples. We estimate the SiF_4 present as less than 2% in all cases. With SF_4 a small amount (substantially less than 1 mg) of solid NaF was placed in the bottom of each sample tube to act as getter for any HF formed. Spectra were taken at 300 K and in 10 K increments up to 380 K; finally, a repeat spectrum was taken at 300 K to insure that no decomposition occurred which might have systematically affected our $\sigma(T)$ data. Pulsed Fourier transform ^{19}F spectra were taken at 84.7 MHz (21.1 kG) using a Bruker

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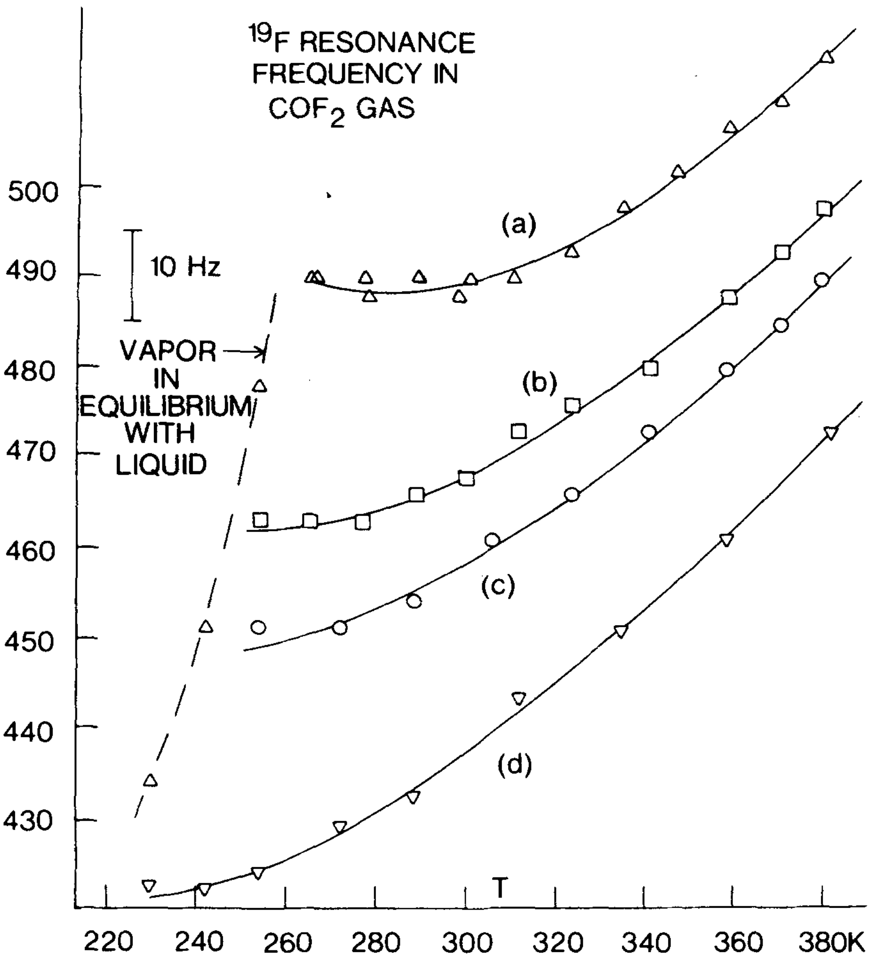

FIG. 1. The temperature dependence of the ^{19}F resonance frequency in pure COF_2 gas samples of the following densities: (a) 39.7, (b) 25.4, (c) 18.0, and (d) 9.0 amagat. When liquefaction occurs the density of the vapor in equilibrium with the liquid changes with temperature. These curves clearly show a temperature dependent σ_1 for COF_2. Data were taken at 84.683 MHz.

HFX-90 variable frequency spectrometer, Bruker B-KF 322s pulse system, Nicolet NIC-293 pulse programmer, and 1080 data acquisition system. A pulse width of 6 μs with a repetition rate of 0.5–2 s was employed depending on density and temperature. Data were acquired in 1 or 2 K of memory and zero filled to 8 K. 32–512 transients were accumulated depending on the density of gas in these tubes with low filling factor. Temperatures were varied from 230–380 K for COF_2 and 300–380 K for SF_4. This is the fast exchange limit for SF_4, so that only a single peak is observed. No attempt was made to obtain separate $\sigma_0(T)$ and $\sigma_1(T)$ data for the two types of F in SF_4. Observation of the individual ^{19}F nuclei in SF_4 in the slow exchange limit would have necessitated going to temperatures below 250 K. Our experience is that low vapor pressure and short T_2 would combine to yield information of poor precision (broad peaks and low intensity) in the vapor phase at these temperatures.

RESULTS AND DISCUSSION

The density and temperature dependence of the ^{19}F nuclear resonance in COF_2 gas is shown in Fig. 1. The nonlinear temperature dependence of σ_0 is quite obvious in this case, as is the temperature dependence of σ_1. In contrast, the average shielding data for SF_4 gas in the range 300–380 K appeared to be completely consistent with parallel linear functions for the ^{19}F frequency vs temperature in samples of various densities.

The effect of intermolecular interactions on ^{19}F shielding

The densities of the gas samples studied here are sufficiently low that all plots of frequencies vs density at a given temperature were found to be linear. The linear density dependence of nuclear shielding is measured by taking $(\partial\nu/\partial\rho)$ at various temperatures. These results are shown in Table I for SF_4 and COF_2, compared with SF_6 and BF_3, respectively. These quantities are significantly greater than the bulk susceptibility contributions to σ_1, which can be estimated from the known sample geometry and magnetizabilities.[18] Thus, a large part of the observed σ_1 is due to binary interactions of molecules. There are insufficient data (polarizabilities and ionization potentials, Lennard-Jones parameters) for SF_4 and COF_2 molecules for a comparison of σ_1 values on the basis of the theory by Raynes, Buckingham, and Bernstein.[18] It is also not possible at this time to observe the influence of the fluxional nature of SF_4 on the intermolecular effects on ^{19}F nuclear shielding.

The gas-liquid shift in COF_2

Another measure of the effect of intermolecular interactions on nuclear shielding is the chemical shift between the liquid and vapor signals measured in the liquid in equilibrium with vapor at a given temperature. Since intramolecular dynamic effects (anharmonic vibration, centrifugal distortion, etc.) can be assumed to be iden-

TABLE I. Effect of intermolecular interactions on ^{19}F shielding expressed as σ_1, measured by taking $(\partial\nu/\partial\rho)$. $\sigma_1(T)=a_0+a_1(T-300)+a_2(T-300)^2$ ppm/amagat.

	σ_1				
Gas	a_0	$10^5 a_1$	$10^7 a_2$	χ_m (10^6 cm^3/mol)	σ_{1b} (ppm/amagat)
SF_4	-0.00835 ± 0.0015			-34.3[b]	-0.0032
SF_6[a]	-0.019752 ± 0.0015	2.1311	4.6054	$-44.$[c]	-0.00411
COF_2	-0.01987 ± 0.0014	8.907	-7.983	-26.4[d]	-0.0025
BF_3[a]	-0.01872 ± 0.0018	2.375	-0.194	-26.9[e]	-0.0025

[a] Reference 20.
[b] Estimated from SF_6 value.
[c] P. W. Selwood, *Magnetochemistry* (Interscience, New York, 1964).
[d] R. P. Blickensderfer, J. H. S. Wang, and W. H. Flygare, J. Chem. Phys. 51, 3196 (1969).
[e] Estimated with Pascal's constants.

tical in both phases at a given temperature, this chemical shift, the gas–liquid shift, is a measure of the effect of intermolecular interactions on nuclear shielding. However, the presence of multiple-body interactions in the liquid phase as opposed to binary interactions in the dilute gas will give rise to an apparent σ_1 from gas–liquid shifts which is different from that obtained from low-density gas samples. Figure 2 shows the liquid and vapor data for ^{19}F in COF_2. Comparison of the apparent σ_1 obtained here for COF_2 with σ_1 from the gas phase measurements is given in Table II. It has been found in several systems that the apparent σ_1 from gas–liquid shifts is smaller in magnitude than σ_1, i.e., the higher-order terms $(\sigma_2\rho^2+\cdots)$ appear to be opposite in sign to $\sigma_1\rho$.[19] This does not appear to be the case in the ^{19}F shielding in COF_2. However, the difference is small enough that it may not be significant when the combined errors in the liquid density and in $\sigma_1(T)$ are considered.

The average ^{19}F shielding in the zero-pressure limit

When the density dependent terms are removed, data for each of the samples (e.g., as shown in Fig. 1) yield information on the temperature dependence of the ^{19}F shielding in the zero-pressure limit, i.e., in the limit of the isolated molecule. These are shown in Figs. 2 and 3, and each is least-squares fitted to a polynomial function in powers of $(T-300)$, given in Table III. The temperature dependence of $\sigma_0(T)$ can be expressed in terms of linear combinations of $\coth(hc\omega_i/2kT)$ functions, where ω_i are the harmonic vibrational frequencies of the molecule.[17] The vibrational frequencies of SF_4

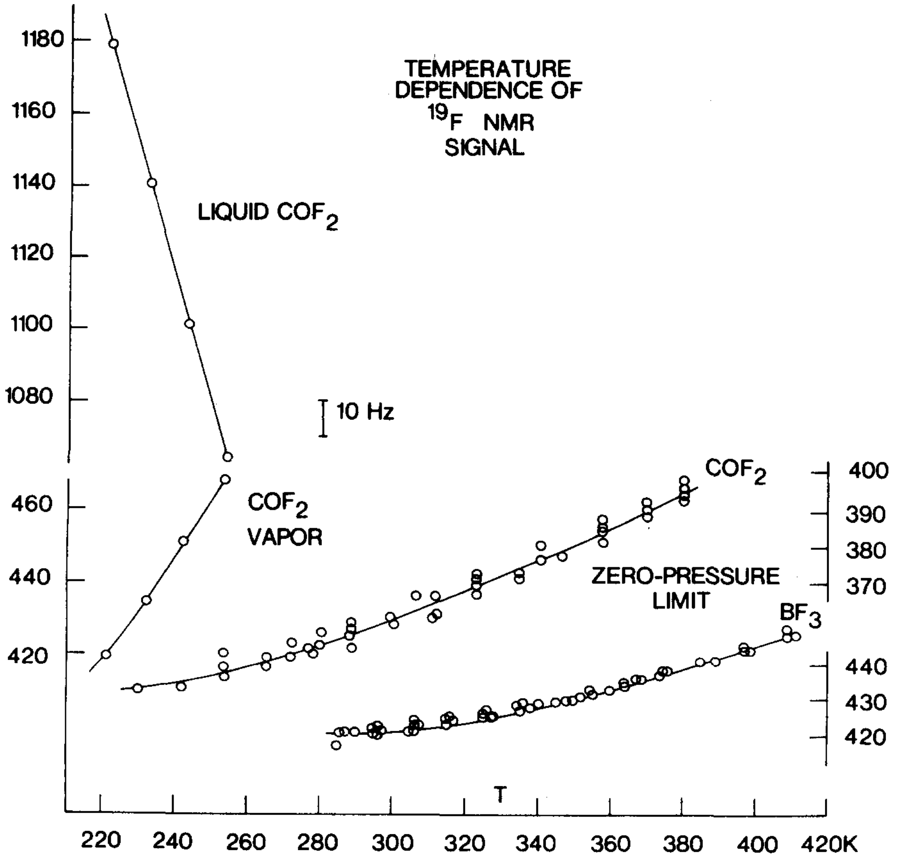

FIG. 2. The gas–liquid shift in COF_2, the chemical shift between the liquid and vapor in equilibrium with it, as a function of temperature is 596 $-5.9(T-260$ K) Hz at 84.683 MHz. Also shown is the temperature dependence of ^{19}F resonance in the COF_2 molecule compared with BF_3, both at the zero-pressure limit. See Ref. 26 for the measured ^{19}F chemical shift between the COF_2 and BF_3 molecules at 300 K.

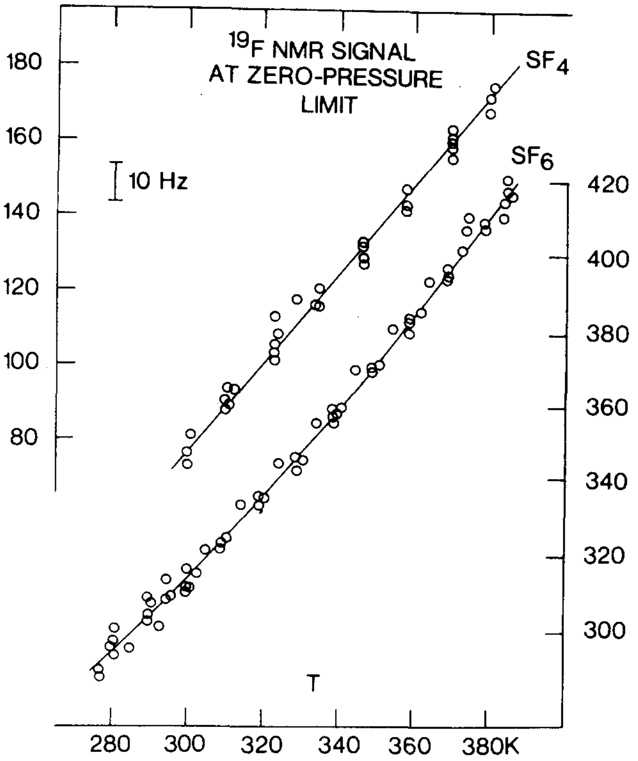

FIG. 3. The temperature dependence of ^{19}F resonance in the SF_4 molecule under fast exchange in the zero-pressure limit, compared with the SF_6 molecule at 84.69 MHz. See Ref. 26 for the measured ^{19}F chemical shift between the SF_4 and SF_6 molecules at 300 K.

and SF_6 are different, as are those of COF_2 compared to BF_3. It is remarkable that the SF_4 and SF_6 average shielding in the isolated molecule have very nearly the same temperature dependence in the range 300–380 K.[20] On the other hand, $\sigma_0(T)$ for COF_2 and BF_3 are quite different.

The interpretation of $\sigma_0(T)$ for nuclei in a molecule[17] depends on the availability of the anharmonic force constants as well as the eigenvectors of the quadratic force field. The quadratic force field of COF_2 has recently been computed theoretically,[21] and found to be in good agreement with the general harmonic force field determined from the vibrational spectra of all of the ^{13}C, ^{12}C and ^{16}O, ^{18}O isotopomers of the molecule.[22] The extent of anharmonicity is found to be small, with no clear distinction between stretching and bending modes.[22] The Urey–Bradley force field parameters for COF_2 have been determined and perhaps can be used to find approximate cubic force constants by an extension of the method of Kuchitsu and Bartell,[23,24] or by calculations such as are now beginning to emerge from programs by Overend and co-workers,[25] so that a quantitative interpretation of the $\sigma_0(T)$ function of ^{19}F in COF_2 may be carried out in the same manner as for BF_3.[17] However, due to the lower symmetry of the COF_2 compared to the BF_3 molecule, this procedure will not be a straightforward extension of the Kuchitsu–Bartell model. We hope to report on this in the future.

TABLE II. ^{19}F gas–liquid shift in COF_2 at 84.683 MHz.

T (K)	ρ_{liq}[a]	ρ_{vap}[a]	$\nu_{liq}-\nu_{vap}$ (Hz)	Apparent σ_1	σ_1 in gas
	(amagat)			(ppm/amagat)	
221.3	298.65	5.3	760	−0.306	
232.4	282.82	7.7	706	−0.0303	−0.0295
242.7	268.13	10.5	650	−0.0298	−0.0276
253.5	252.73	14.1	596	−0.0295	−0.0257

[a] O. Ruff and G. Miltschitzky, Z. Anorg. Allg. Chem. 221, 154 (1934).

TABLE III. Temperature dependence of ^{19}F nuclear shielding in some isolated molecules. $\sigma_0(T)-\sigma_0(300) = a_1(T-300)+a_2(T-300)^2+a_3(T-300)^3$ ppm.

Molecule	T (K)	a_1	$10^5 a_2$	$10^8 a_3$
SF_4	300–380	−0.01297	−0.7047	
SF_6[a]	280–390	−0.012073	−2.6808	
COF_2	230–380	−0.004332	−1.3465	1.623
BF_3[a]	290–410	−0.001335	−1.3990	

[a] Reference 20.

The nearly identical $d\sigma_0/dT$ at 300 K for SF_4 and SF_6 is probably fortuitous. The assignment of the fundamentals of the pseudotrigonal bipyramidal tetrafluorides is extremely difficult. The assignment of all nine fundamentals of the SF_4 molecule has been supported by calculations of the force field and mean amplitudes of vibration.[14] However, in spite of the availability of some ^{32}S–^{34}S isotopic data,[14] the quadratic force field of SF_4 is still underdetermined. Since the temperature dependence of σ_0 generally depends on cubic force constants as well as the eigenvectors of the quadratic force field, the interpretation of the $\sigma_0(T)$ function for the SF_4 molecule will have to wait. Only with a complete vibrational analysis of the SF_4 molecule (anharmonic force field) will it be possible to determine the effect of the Berry rearrangement on the temperature dependence of the average ^{19}F σ_0 in SF_4.

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