^{19}F nuclear magnetic shielding scale from gas phase studies

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By using results of density and temperature studies, ^{19}F nuclear magnetic resonance frequencies measured in 20 gases of known densities are reduced to the zero-density limit at 300 K. From these we obtain differences in shielding between rovibrationally averaged isolated molecules at this temperature. The magnitudes of the corrections linking the shielding in the liquid phase to the isolated molecule at its equilibrium configuration are discussed. These corrections are not necessarily small and are required in deriving an accurate absolute shielding of any molecule from the known absolute shielding of another molecule by observing the NMR chemical shift between the two.

I. INTRODUCTION

High-resolution NMR in nonoriented fluids is able to measure only the difference between the mean shielding of the nucleus of interest in one chemical environment and the mean shielding in some reference environment:

$$\Delta\sigma = \sigma - \sigma_{ref} \ .$$

We may write this more explicitly in terms of the specific chemical environments, e.g.,

$$\Delta\sigma = \sigma^{A}(\text{solution},\ T,\ x_A,\ x_i) - \sigma^{B}(\text{pure liquid},\ T) \ .$$

What is observed is $\Delta\sigma$ itself, which can normally be measured with great accuracy (sometimes better than 0.001 ppm). In principle, shielding differences from diverse laboratories can be brought together into one scale in which all the numbers are finally expressed relative to a single reference substance. However, the difficulty lies not so much in the errors associated with each reported $\Delta\sigma$ in the literature (these are usually small), but more so in the poor specification of the conditions which determine the total chemical environment of the nucleus, e.g., those shown in parentheses in the above example. In the past, specifying such conditions was not considered particularly important. Thus, scales were constructed from data obtained under a wide variety of conditions. The main use of such scales were for identification purposes and therefore it was completely sufficient to know more or less where the NMR signal would be relative to some commonly used liquid reference such as TMS. They served and continue to serve this purpose extremely well.[1]

With the increasing sophistication of NMR instrumentation and the increasing availability of single molecule (molecular beam) observations of shielding components, coupled with higher accuracy of theoretical shielding calculations, better shielding scales have become feasible and also desirable. The establishment of an absolute shielding scale for a chosen nuclear species is an attempt to obtain the value of σ for one suitable compound and then to obtain with this the values of σ for that nucleus in other chemical environments by using very accurately measured differences $\Delta\sigma$ between chemical environments that are carefully specified and duplicated. Early attempts at this have been entirely consistent with the accuracy with which the absolute σ for one or more suitable compounds could be measured.[2] For example, mixing up $\Delta\sigma$ from molecules in solution or neat liquids with gas phase or with isolated molecule (molecular beam) results is not incorrect, if (as in the case of early ^{14}N and ^{13}C absolute shielding scales) the values could only be ascertained to ± 10 ppm.

In this paper, we point out the magnitudes of errors which arise from the poor specification of conditions which define the chemical environment of the molecules being compared. Variables such as temperature, density or concentration and concentrations of other components affect σ to some greater or lesser degree, depending on the molecular species. The purpose of this work is to attempt to provide a new set of measured differences $\Delta\sigma$ for ^{19}F between chemical environments which are (1) carefully specified and duplicated, and (2) as close to the isolated molecule as possible. By providing this set of measured differences, we hope to supply a means of obtaining in the future a reasonably accurate absolute shielding scale, limited primarily by the accuracy with which the absolute shielding of any one of the molecules can be obtained.

MAGNITUDES OF THE CORRECTIONS LINKING THE SHIELDING IN THE LIQUID PHASE TO THE ISOLATED MOLECULE AT ITS EQUILIBRIUM CONFIGURATION

An empirical absolute shielding constant is usually obtained by

$$\sigma_{emp} = \sigma_0^{p} + \sigma_e^{d} \ ,$$

where σ_0^{p} are values related to spin-rotation constants measured for a given vibrational state of a molecule.[3-5]

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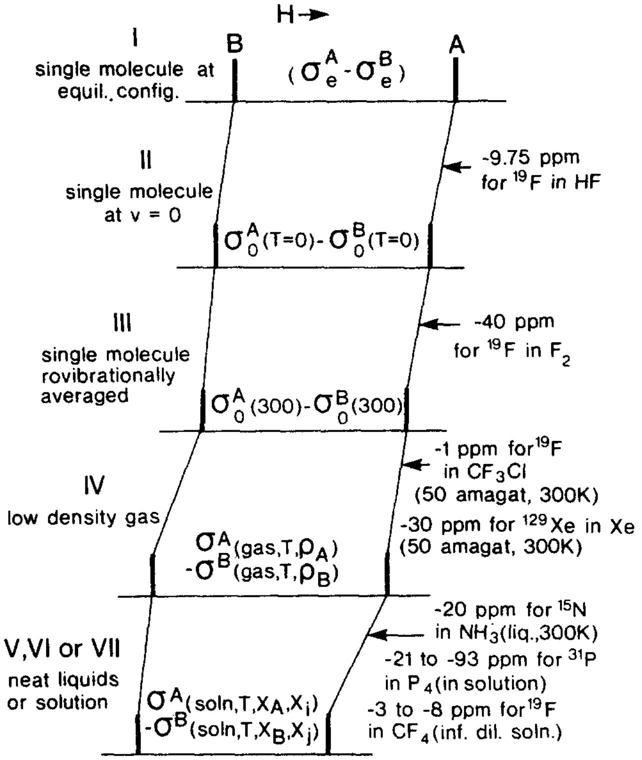

FIG. 1. Changes in the nuclear magnetic shielding with chemical environment. Some typical magnitudes for these changes are shown to indicate how large the errors can be if they are neglected. Data (from top to bottom) are from Refs. 8, 11, 12, 13, 14, 15, and 16, respectively.

σ_e^d are theoretical values calculated at the experimental equilibrium configuration. Comparisons with theoretically calculated $(\sigma_e^p + \sigma_e^d)$ are valid if rovibrational corrections on spin-rotation constants are small or can be calculated.[6–8]

In order to estimate σ_{emp} or σ_e in molecules for which σ_0^p have not been measured, chemical shifts between molecules in solution or neat liquids are used to relate to known σ_{emp} values, thus providing an approximate absolute shielding scale. The only exception is the ^{13}F shielding $[\sigma_0(303\ \text{K})]$ scale given by Hindermann and Cornwell, in which gases at the zero-pressure limit were used.[8] The questions that arise then are as follows: (a) How large are the shielding differences between various environment types? (b) How different are they for different molecules? Presumably, $\sigma_{emp}^A \simeq \sigma_{emp}^B + [\sigma^A(\text{soln}) - \sigma^B(\text{neat liq})]$, where the quantity in brackets is a measured chemical shift, is not too bad an approximation if $[\sigma^A(\text{soln}) - \sigma_e^A]$ and $[\sigma^B(\text{neat liq}) - \sigma_e^B]$ are both sufficiently small or if not small are very close to being equal.

TABLE I. The vibrational correction to the isolated molecule in its ground state.

Nucleus	$[\sigma_0(T=0\ \text{K}) - \sigma_e]$ (ppm)	Reference
^{13}C in CO	−2.13	17
^{17}O in CO	−2.48	17
^{1}H in HF	−0.34	18
^{19}F in HF	−9.3	18
^{14}N in N_2	−3.39	19

TABLE II. The rotational–vibrational correction for the isolated molecule, from the measured temperature dependence around 300 K, and the rotational and anharmonic constants for the molecule.

Nucleus	$[\sigma_0(300\ \text{K}) - \sigma_e]$ (ppm)	Reference
^{1}H in H_2	−0.38	20
HF	−0.38	8
HCl	−1.34	21
HBr	−7.11	22
^{19}F in HF	−9.75	8
ClF	−13.	11
F_2	−40.	11
SiF_4	−5.73	23
CF_4	−7.24	23
BF_3	−10.82	23
SF_6	−13.	24

In NMR studies of gas-to-solution shifts by several workers,[9,10] and in NMR studies in the gas phase (through to the liquid phase in some cases) in our laboratory, some shielding differences which connect solutions or liquid phase shielding to σ_e have been measured. The types of environments in which nuclear magnetic shielding have been studied may be characterized as follows:

I: isolated molecule at equilibrium nuclear configuration $\sigma_e = \sigma_e^p + \sigma_e^d$ (from theoretical calculations);

II: isolated molecule with vibrational correction for $v = 0\ \sigma_0(T = 0\ \text{K})$;

III: isolated molecule with rovibrational averaging at $T\ \sigma_0(T)$ (from resonance frequencies at the zero-pressure limit);

IV: molecule in low-density gas, density $= \rho$, temperature $= T$, $\sigma(T,\rho) = \sigma_0(T) + \sigma_1(T)\rho + \cdots$;

V: neat liquid $\sigma(\text{liq}, T) = \sigma_0(T) + \sigma'(T)\rho_{\text{liq}}(T) + \cdots$, where $\sigma'(T)$ is not the same as $\sigma_1(T)$ in the gas phase;

VI: solution in infinite dilution $\sigma(T, x_A \to 0, x_i) = \sigma_0(T) + \sigma_i'(T)x_i + \cdots$;

VII: solution $\sigma(T, x_A, x_i) = \sigma_0(T) + \sigma_A'(T)x_A + \sigma_i'(T)x_i + \cdots$, in which $\sigma_i(T)$, $\sigma_A'(T)$, and $\sigma_i'(T)$ include bulk susceptibility contributions depending on sample shape.

Shifts of the nuclear resonance signal as the molecule undergoes various environment changes are schematically shown in Fig. 1. Examples from the literature of the magnitudes of the differences in shielding between these various environments are shown in Tables I to V. It should be noted that these differences are neither very small nor are they uniform. However, most of them are smaller than 10 ppm and most of them are only a few tenths of a percent of the chemical shift range for the nucleus in question.

TABLE III. Vibrational–rotational corrections for an isolated molecule and the density dependence of σ in a gas.

	$[\sigma_0(350\ \mathrm{K}) - \sigma_0(300\ \mathrm{K})]$ (ppm)	$[\sigma(300\ \mathrm{K},\ \rho=50) - \sigma(300\ \mathrm{K},\ \rho=0)]$[a] (ppm)	Reference
^{19}F in BF_3	−0.12	−0.94	25
CF_4	−0.26	−0.58	25
SF_6	−0.66	−0.99	25
SiF_4	−0.18	−0.97	25
F_2	−1.9	−0.19[b]	26
ClF	−0.9	−2.40[b]	26
CF_3H	−0.36	−0.47	27, 12
CF_3CF_3	−0.66	−0.85	27, 12
CF_3Br	−0.58	−1.3	27, 12
CH_3F	−0.10	−0.78	28
CF_3Cl	−0.40	−1.00	27, 12
NF_3	−1.1	−0.34	29
PF_3	−0.44	−0.58	29
POF_3	−0.36	−1.14	29
PF_5 (ave.)		−0.95	29
SF_4 (ave.)	−0.80	−0.42	30
COF_2	−0.31	−0.99	30
CF_3CH_3	−0.74	−1.32	31
$C\underline{F_2}ClCF_3$	−0.89	−1.35	31
$C\underline{F_3}CF_2Cl$	−0.75	−1.45	31
CF_2Cl_2	−0.55	−1.21	32
CF_2HCl	−0.37	−0.86	32
^{13}C in CO	−0.016	−0.22	26, 33
CO_2	−0.025	−0.10	34
CH_4	nil	−0.50	35
^{1}H in HCl	−0.01	−0.37	21, 26
HBr	−0.10	−0.43	22, 26
NH_3	−0.02	−0.16	14
^{15}N in NH_3	+0.35	−2.5	14
$\underline{N}NO$	−0.45	−0.46	34
$N\underline{N}O$	−0.18	−0.13	34
N_2	−0.055	−0.21	33
^{31}P in PH_3	+0.23	−4.2	36
PF_3	−0.09	−0.32	29
POF_3	−0.07	−0.62	29
PF_5		−0.11	29
^{129}Xe in Xe	0	−30.	13

[a] Density ρ is in amagat, temperature in K. For comparison of magnitudes, these were calculated from observed shifts of samples of various densities. Samples at 50 amagat were not necessarily used.

[b] The published values of σ_1 for F_2 and ClF (Ref. 26) are in error by a constant factor due to an erroneous calibration of a section of the all-metal vacuum line used for these gases only. The correct σ_1 are

$$\sigma_1^{F_2} = (-0.372 \pm 0.052) \times 10^{-2}\ \mathrm{ppm/amagat},$$

$$\sigma_1^{ClF} = (-4.79 \pm 0.31) \times 10^{-2} + 1.245 \times 10^{-4}\,(T - 300\ \mathrm{K}) + 2.186 \times 10^{-6}\,(T - 300\ \mathrm{K})^2\ \mathrm{ppm/amagat}.$$

EXISTING SHIELDING SCALES

Absolute shielding scales have been compiled for several nuclear species: ^{1}H,[47-49] ^{19}F,[8,50,51] ^{14}N,[2,50] ^{13}C,[50,49] and ^{31}P.[50] These are based on a limited number of measured spin-rotation constants. For example, the ^{13}C shielding scale is based on the CO molecule as the primary reference.[52] The ^{19}F scale is based on HF,[2] the ^{14}N scale on N_2,[2] the ^{31}P scale on PH_3,[53] and the ^{1}H scale on the ratio of the magnetic moment in atomic hydrogen to that in H_2O.[48]

Presently, the only shielding scale which has been compiled in an internally consistent way is the one for ^{19}F in a small set of molecules whose chemical shifts were measured by Hindermann and Cornwell in the limit of zero pressure at room temperature.[8] These authors corrected the observed spin-rotation constant in HF to the equilibrium configuration, from which they obtained σ_e^p. The latter combined with the theoretical value of σ_e^d gave σ_e for HF. This σ_e was then converted to σ_0 at room temperature by making the rovibrational correction. Once the absolute σ_0 for HF was known, they could then find the absolute σ_0 for their secondary reference molecule (SiF_4) by measuring the chemical shift between

TABLE IV. Gas to liquid shifts.

Nucleus	T (K)	[σ(liq, T) − σ(equil. vapor, T)] (ppm)	Reference
^1H in H_2O	298.2	−4.368	37
^{13}C in CO_2	220	−1.28	34
^{15}N in NH_3	300	−19.5	14
NH_3	195.5	−22.6	38
CH_3NH_2	179.7	−9.4	38
$(CH_3)_2NH$	177	−3.2	38
$(CH_3)_3N$	156	−6.9	38
CH_3CN	227.5	+11.3	38
^{17}O in H_2O	488	−36 ± 1	39
^{19}F in ClF	220	−25.6	40
COF_2	230	−9.0	30
CF_3Br	260	−5.3	12
CF_3H	260	−3.2	12
CF_3Cl	260	−4.5	12
CH_3F	260	−7.7	12
CF_3CF_3	260	−3.3	12
^{31}P in P_4	526	−77.	41
^{129}Xe in Xe	244	−200.	42, 43

HF and SiF_4 at the zero-pressure limit. The absolute σ_0 for the other molecules on their scale were then determined from measured chemical shifts from SiF_4. Since all the measured chemical shifts correspond to the zero-pressure limit, Hindermann and Cornwell's scale is a list of absolute σ_0 (i.e., for the isolated molecule) at room temperature. In addition, they found the absolute shielding σ(liq, T, cyl) of $CFCl_9$. With this connection, other measurements of shifts relative to liquid $CFCl_3$ can be converted to absolute σ(liq or soln, T, cyl) by other workers.

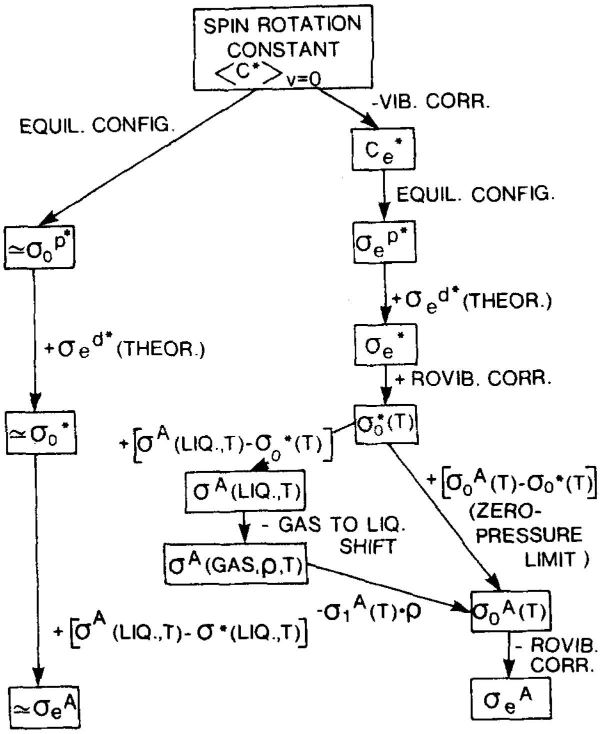

FIG. 2. Building up an absolute shielding scale from the absolute shielding of one primary reference whose spin–rotation constant is accurately known. The usual approach in the absence of complete data is shown on the left. The corrections which have been left out by so doing are shown on the right. The following notations are used: * denotes the primary reference molecule, A any other compound, subscript 0 the isolated molecule, and subscript e the equilibrium configuration.

The approach by Hindermann and Cornwell is obviously the way to proceed for the other nuclei. Unfortunately, other shielding scales suffer from a variety of problems, the major one being poorly specified chemical environments to which the absolute shielding values apply. There is a tendency for users of such scales to interpret the individual entries as σ_e, which they are not. Figure 2 illustrates the missing corrections, the typical magnitudes of which have already been shown in Tables I to V. Without these corrections, chemical shifts between liquids at various temperatures will not correspond to differences between a set of σ_{emp} values (e.g., NH_3, N_2, HCN, ClCN).[54]

In some cases, the limiting error is that associated with the measured spin–rotation constant of the primary reference molecule. Then the quoted error in the absolute shielding values is usually larger than such corrections, so there is little necessity for making them. Recently, however, more accurate values have become available for the shielding or spin–rotation constants of possible primary reference molecules such as H_2O,[55] CO,[56] NH_2,[57] and NNO.[58] At the same time, chemical shifts in the zero-pressure limit are beginning to become available with density dependent NMR studies in the gas phase.[59] In this paper, we make use of temperature and density dependent NMR studies in the gas phase to find ^{19}F chemical shifts between isolated molecules at a given temperature (300 K). Included are nearly all of the molecules in Hindermann and Cornwell's scale as well as 14 others.

EXPERIMENTAL PROCEDURE

We have previously observed the density and temperature dependence of the ^{19}F resonance frequency of some

TABLE V. Temperature dependence of shielding in the liquid phase.

Nucleus	T(K)	[σ(liq, T+50) − σ(liq, T)] (ppm)	Reference
^1H in H_2O	273.2	+0.549	37
p-xylene (CH_3)	300	+0.055	44
toluene (CH_3)	300	+0.029	45
TMS	240	+0.16	44, 46
acetone	300	+0.09	46
^{13}C in CO_2	220	+0.20	34
TMS	250	+0.63	40
^{15}N in NH_3	300	+3.875	14
NH_3	220	+2.15	38
CH_3NH_2	220	+0.8	38
$(CH_3)_2NH$	220	+0.25	38
$(CH_3)_3N$	220	+1.0	38
CH_3CN	220	−1.05	38
^{17}O in H_2O	300	+5.3	39
^{19}F in ClF	200	+8.26	40
COF_2	230	+2.46	40
CF_3Br	240	+0.74	40
CF_3H	240	+0.96	40
CF_3Cl	240	+1.28	40
CF_3CF_3	230	+0.69	40
CH_3F	240	+1.92	40
$CFCl_3$	240	+0.24	44
C_6F_6	290	+0.104	44
^{31}P in P_4	526	+3.5	41

TABLE VI. ^{19}F nuclear magnetic shielding in the isolated molecule relative to an isolated SiF_4 molecule (ppm).

		$\sigma_0^A(T) - \sigma_0^A(300\text{ K}) = a_1(T-300\text{ K}) + a_2(T-300\text{ K})^2 + a_3(T-300\text{ K})^3$ [a]			
A	$[\sigma_0^A(300\text{ K}) - \sigma_0^{SiF_4}(300\text{ K})]$	T (K)	$10^2 a_1$	$10^5 a_2$	$10^7 a_3$
ClF	$+273.92 \pm 0.3$	280–350	-1.042	-18.785	$+8.462$
CH_3F	$+107.71 \pm 0.05$	280–370	-0.176		
SiF_4	0	270–390	-0.3809	$+0.1345$	
BF_3	-36.02 ± 0.06	290–410	-0.1335	-1.3990	
POF_3	-74.94 ± 0.03	290–370	-0.565	-2.97	$+0.829$
CF_3CF_3	-80.20 ± 0.03	250–380	-1.356	-1.676	$+1.429$
$C\underline{F}_3CF_2Cl$	-81.25 ± 0.01	240–370	-1.4485	-4.505	$+6.684$
CF_3H	-89.06 ± 0.01	240–380	-0.560	-2.854	$+0.2117$
$C\underline{F}_2ClCF_3$	-93.45 ± 0.01	240–370	-1.6789	-6.5886	$+8.4286$
CF_2ClH	-95.88 ± 0.01	300–370	-0.6831		
CF_4	-104.21 ± 0.02	270–410	-0.5007	-0.7722	
CF_3CH_3	-104.49 ± 0.05	220–370	-1.511	-0.9122	$+2.883$
PF_3	-134.83 ± 0.03	220–370	-0.673	-3.26	-1.195
CF_3Cl	-138.77 ± 0.01	220–380	-0.678	-2.180	$+0.2356$
COF_2	-141.50 ± 0.04	240–370	-0.5032	-1.8167	$+0.2544$
CF_3Br	-149.31 ± 0.02	270–380	-1.018	-5.190	$+3.898$
CF_2Cl_2	-160.53 ± 0.02	270–370	-1.100		
SF_6	-223.57 ± 0.04	280–390	-1.207	-2.6808	
SF_4	-244.44 ± 0.03	300–370	-1.507	-0.9507	
NF_3	-312.80 ± 0.06	220–370	-1.996	-5.23	$+0.587$
F_2	-595.96 ± 0.03	230–350	-3.400	-10.29	

[a] Consult Table III for references.

20 odd gases over a period of 4 years using a Bruker spectrometer operating at 21.1 kG in the Fourier transform mode. A tabulation of these frequencies would provide a shielding scale since we can use the observed density and temperature dependence to reduce the data to the zero density (and pressure) limit. The experimental procedure including sample preparation, temperature regulation, and line shape fitting have been described previously.[13,26,60] The following details the special precautions taken in obtaining the shifts between these gases in the zero-pressure limit.

Two sets of samples were used, both sets including 20 gases. Each set contained one of each gas chosen from the collection of sealed gas samples of various densities, each of which have been previously observed as a function of temperature (except ClF, F_2, COF_2, and SF_4 samples which were prepared and kept in liquid nitrogen until just before their spectra were taken; the old samples had shown evidence of decomposition after several months). The sample configuration was the same as we have used before: The sealed gas sample which is less than 5 cm long fits inside a standard thin-walled 5 mm o.d. NMR tube, with enough space in the annular region to hold about 0.03 ml of the lock solvent (toluene-d_8. The ^2D signal of the CD_3 group was used to stabilize the magnetic field. Temperature regulation of the spinning 5 mm sample assembly with dry nitrogen as the heat exchange gas was controlled by a Bruker BST-100/700 variable temperature system, as before. A sealed sample containing neat liquid C_6F_6 was prepared using the same type of sample tube as had been used for the gas samples. The spectrum of this sealed sample of neat liquid C_6F_6 was taken between spectra of gas samples to monitor any drifts in the lock frequency or other spectrometer instability.

Frequencies in the lock channel and the observe channel were both measured directly with a frequency counter with a 0.1 Hz resolution. This has been a standard procedure in our work since we noticed that the lock frequency drifts to some extent and the frequency synthesizer dials on the pulse spectrometer do not always read accurately. ^{19}F is such a sensitive nucleus that even for our gas samples with low filling factors, a free induction decay can be observed directly on the pulse spectrometer oscilloscope. It is possible to initially locate the resonance frequency to within 1–2 Hz by finding the frequency synthesizer setting which maximizes the period of oscillations in the FID. This allows us to directly preclude the possibility of "foldover" in the FT spectrum. The FT spectra of each set of samples were observed in one continuous run to minimize errors due to any changes in the spectrometer from one gas sample to the next. Three complete runs were carried out weeks apart to check for possible short-term spectrometer idiosyncracies which might lead to a systematic error. A sweep width of 1000 Hz was used in one and 2000 Hz was used in the others. 2 to 4 K data points were taken, zero filling to 8 K. Repetition rates were typically 0.3 s.

Since the data are reduced to the zero-pressure limit, there will be no remaining bulk susceptibility correction for the gas samples. The differences in volume susceptibility of the glass sample tubes themselves were determined by breaking off the tips after all the measurements were completed and observing neat liquid C_6F_6 in each opened gas sample tube. These measurements for the glass correction were carried out in the same way, ob-

TABLE VII. ^{19}F chemical shielding of two neat liquid references relative to an isolated SiF_4 molecule, in cylindrical sample tubes with the axis perpendicular to the field.

	$[\sigma(\text{liq, 300 K, cyl}, \perp) - \sigma_0^{SiF_4}(300\text{ K})]$	$\sigma(\text{liq}, T) - \sigma(\text{liq, 300 K}) = a_1(T - 300\text{ K}) + a_2(T = 300\text{ K})^2$ [a]		
		T (K)	$10^3 a_1$	$10^5 a_2$
$CFCl_3$	-174.28 ± 0.02[b,c]	220–300	5.501	0.9274
C_6F_6	-7.72 ± 0.02[c]	280–340	2.589	1.645

[a] Reference 17. See this reference for the errors associated with these functions.

[b] This value is in agreement with Hindermann and Cornwell's value of -174.5 ± 0.5 ppm.

[c] These numbers only indicate reproducibility in our laboratory (a sealed sample tube containing the neat liquid, inside a standard 5 mm NMR sample tube with toluene-d_8 lock substance). Other sample arrangements may lead to values which differ from ours.

serving the sealed liquid C_6F_6 sample after each one. The same 5 mm NMR tube was used throughout.

Some peaks (ClF, NF_3, and F_2) were tens or hundreds of Hz wide and required fitting to a Lorentzian for more precise location of the center.

RESULTS AND DISCUSSION

Observed resonance frequencies were reduced to the zero density limit at 300 K using previously measured σ_1 values for each gas. The results corresponding to a rovibrationally averaged isolated molecule at 300 K are expressed relative to SiF_4 as a standard. Neat liquid C_6F_6 is included to provide a means by which shielding differences in the liquid phase may be related to this set of measurements. The results are shown in Table VI as $[\sigma_0^A(300\text{ K}) - \sigma_0^{SiF_4}(300\text{ K})]$ for each molecule A. These values were obtained by dividing the frequency differences at the zero-pressure limit by the resonance frequency of the bare nucleus (which we locate from a plot of absolute σ_0 values from Hindermann and Cornwell[8] vs our resonance frequencies). The values of $[\sigma_0(300\text{ K}) - \sigma_0^{SiF_4}(300\text{ K})]/[1 - \sigma_0^{SiF_4}(300\text{ K})]$ which are obtained by dividing frequency differences by the resonance frequency of SiF_4 are directly comparable with the values in Table II of Ref. 8: 274.0 (273.73 ± 0.10),[8] -36.03 (-36.11 ± 0.10) -89.10 ($-89.04 \pm$?), -104.25 (-104.19 ± 0.10), -223.65 (-223.69 ± 0.07) and -596.17 (-596.0 ± 0.2) ppm for ClF, BF_3, CF_3H, CF_4, SF_6, and F_2, respectively. We see that there is complete agreement within experimental error with Hindermann and Cornwell's values for the six molecules we have in common. Table VII shows a comparison of the two commonly used liquid references $CFCl_3$ (used by Hindermann and Cornwell) and C_6F_6 for the convenience of workers using either one.

In Table VIII we show the absolute σ_0 for these molecules calculated from the measured shielding differences,

TABLE VIII. Comparison of ^{19}F absolute shielding (σ_0) from spin–rotation constants with absolute σ_0 obtained from this study using $\sigma_0^{SiF_4} = 363.2$ ppm (based on HF as primary reference molecule).

Molecule	σ_0 (ppm)[a]	σ_0 from spin-rotation[b] (ppm)	Reference	σ (liquid phase) from Dungan and van Wazer[c] (ppm)
ClF	637.1	630.7 ± 0.3	(61,51)[d]	625.6
CH_3F	471.0	471 ± 9	(62,63)	460.6–465.0
SiF_4	363.2	371.1 ± 3.3, 370	(64,65), (66,51)	348.3–352.2
BF_3	327.2	327	(66,51)	314.0–321.7
POF_3	288.2			277.6–281.0
CF_3CF_3	283.0			277.8
$C\underline{F}_3CF_2Cl$	281.9			
CF_3H	274.1			265.2–272.7
$C\underline{F}_2ClCF_3$	269.7			
CF_2ClH	267.3			
CF_3	259.0	260.8 ± 10.8, 258	(64,65), (66,51)	247.8–257.7
CF_3CH_3	258.7			250.4–253.7
PF_3	228.3			221.8–229.7
CF_3Cl	224.4			214.4–221.7
COF_2	221.6	228.0 ± 10	(67)	211.2–212.1[e]
CF_3Br	213.8			209.3–209.7
CF_2Cl_2	202.6			190.8–197.1
SF_6	139.6	162 ± 60	(68,51)	130.5–138.7
SF_4 (ave)	118.7			94.2
NF_3	50.3			41.8–50.7
F_2	-232.8	-219, -216 ± 1.3	(2,63), (69,51)	-234.2

[a] These assigned values will be displaced by a constant amount if σ_0 (HF) on which they are based (410.0 ppm) is found to be in error.

[b] Quoted errors are only those associated with uncertainty in the value of the spin–rotation constant.

[c] Chemical shifts relative to $CFCl_3$ (Ref. 1) were translated to values using σ (neat liq, $CFCl_3$) = 188.7 ppm (Ref. 8).

[d] The first reference is to the original experimental spin–rotation data and the second is to the derived absolute shielding from that data.

[e] Reference 70.

by using Hindermann and Cornwell's $\sigma_0(SiF_4) = 363.2$ ppm, based on their detailed analysis of σ_e for HF. We compare these with σ_0 from spin–rotation constants which are known for several molecules. The agreement is satisfactory for each one of the eight molecules (aside from HF) for which the ^{19}F spin–rotation constants have been measured. To illustrate the magnitudes of the discrepancies between chemical shifts measured in the liquid phase and shielding differences between these isolated molecules, we compare our values with the values compiled by Dungan and van Wazer for neat liquids and solutions. For comparison we used the absolute σ for neat liquid $CFCl_3$ and converted the compiled chemical shifts with this. The values are shown in Table VIII. We see the liquid phase values are lower than our isolated molecule values, as they should be, and that there are no glaring 20–30 ppm discrepancies as have been found in nitrogen shielding.[54]

Ultimately, we would like to relate the single molecule shielding differences in Table VI to absolute σ_e values. In order to do this, we need to have (a) values of the derivatives $(\partial\sigma/\partial q_s)_e$ and $(\partial^2\sigma/\partial q_s^2)_e$ with which we can calculate the rovibrational correction:

$$\sigma_0(T) = \sigma_e + \sum_s (\partial\sigma/\partial q_s)_e \langle q_s\rangle^T + \sum_s (\partial^2\sigma/\partial q_s^2)_e \langle q_s^2\rangle^T + \cdots ,$$

and (b) an adequate anharmonic force field for each molecule to be able to evaluate $\langle q_s\rangle^T$ and $\langle q_s^2\rangle^T$. While these are not yet available for most of the molecules given here, the empirical functions $[\sigma_0(T) - \sigma_0(300\ \mathrm{K})]$ which depend on these same parameters are already available for these molecules. They are also given in Table VI for convenience. Because the rovibrational corrections are not negligible (Tables I and II), and since they are approximately known for only a very few of the molecules, we do not provide an absolute shielding σ_e scale for ^{19}F. However, since the combination of theoretical derivatives of σ and the molecular constants from the anharmonic force field of the molecule have to be able to reproduce the measured $[\sigma_0(T) - \sigma_0(300\ \mathrm{K})]$ functions, the latter will ultimately provide an absolute shielding σ_e scale in the future.

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