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

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The absolute ^{19}F nuclear magnetic shielding at 300 K is reported for 13 molecules containing 21 chemically different ^{19}F nuclei.

The experimentalist's ability to measure resonance frequencies precisely has provided a continuing challenge to theoreticians who calculate molecular electronic properties such as nuclear magnetic shielding. Earlier difficulties in reproducing chemical shifts are beginning to be overcome for small molecules. The increasing availability of improved theoretical calculations of nuclear magnetic shielding[1–7] necessitates direct comparisons with absolute shielding rather than differences in shielding between molecules, and individual elements of the shielding tensor rather than their isotropic average. The challenge to the experimentalist is therefore twofold. One is to provide components of the shielding tensor relative to the isotropic average; these are now becoming more widely available for a variety of nuclei. The other is to provide an absolute isotropic shielding which is free of intermolecular effects, and if possible, a rovibrational correction for the difference between the shielding in an isolated molecule at a given temperature, $\sigma_0(T)$, and a rigid molecule at its equilibrium configuration. The latter, σ_e, and perhaps some of its derivatives, are theoretically calculated. What is usually observed are differences σ(liq. ref.) $-$ σ(neat liq. A). Therefore, there is a need for absolute shielding values which are as close as is experimentally possible to the calculated σ_e. We provide these by making measurements of differences in nuclear shielding in gases at the zero-pressure limit, under conditions such that the values relative to one another are known to high precision. In addition, it is necessary to know the absolute shielding of one of these molecules, in order to convert all values obtained at the zero-pressure limit to absolute shielding. For ^{19}F the HF molecule was used as this primary reference.

Hindermann and Cornwell used the observed ^{19}F spin-rotation constant to calculate the absolute σ_0 for HF, the theoretically most tractable case.[8] By measuring the chemical shift between HF and SiF_4 at the zero-density limit, they found the absolute σ_0 for the secondary reference molecule, SiF_4, an experimentally practical reference. The absolute σ_0 for other molecules are then determined from measured chemical shifts between the molecule and SiF_4 at the zero-density limit.

We have made measurements of ^{19}F resonance frequencies in several fluorine-containing pure gases of known density under identical conditions. Using the results of previous measurements which allow us to characterize each gas with respect to the density and temperature dependence of the ^{19}F shielding, we are able to reduce the measured resonance frequencies to the zero-density limit at 300 K. These provide differences in ^{19}F shielding between rovibrationally averaged independent molecules at this temperature. In a previous paper, (paper I)[9] we reported the details of the experimental procedures, the method of analysis, and the results for several molecules. In this paper, we report measurements on additional molecules, obtained with the procedures described in paper I. Several molecules from paper I have been included in the measurements in order to serve as a check for internal consistency. Results are in Table I for the additions. The absolute shielding of a thermally averaged SiF_4 molecule was taken from Hindermann and Cornwell. Thus, all differences $\sigma_0(A) - \sigma_0(SiF_4)$ at 300 K can be converted to thermal average absolute shielding, as shown in Table I.

There exist independent absolute shielding information for two of the molecules reported here. The ^{19}F spin-rotation constants have been measured in CF_2H_2 and in $CF_2{=}CH_2$ molecules.[10,11] Using theoretical values of the diamagnetic shielding at the equilibrium configuration and the paramagnetic shielding calculated from the observed thermal average ^{19}F spin-rotation constant, the absolute shielding is obtained. The theoretical diamagnetic part could be in error by about 1–2 ppm and the spin-rotation constant is reported with an experimental precision which leads to an expected error of ± 20 ppm in the paramagnetic shielding. For CF_2H_2 our value of σ_0 is 339 ppm, whereas that calculated from the spin-rotation constant is 337 ppm.[10] For $CF_2{=}CH_2$ our value of σ_0 is 279, whereas that from the spin-rotation constant is 272 ppm.[11] The agreement is surprisingly good, leading us to believe that the accuracy of the spin-rotation constants is better than indicated by Kukolich *et al.*[10,11] The reverse of this process is unfortunately not possible in general. The sum $\Sigma_\alpha M_{\alpha\alpha}/G_{\alpha\alpha}^{(e)}$ can be determined from an isotropic shielding value, where $G_{\alpha\alpha}$ are rotational constants and $M_{\alpha\alpha}$ are the spin-rotation constants in the principal axis system of the inertia tensor. Therefore, from the rovibrationally averaged absolute shielding in the gas phase it is possible to obtain the average spin-rotation constant only for linear molecules and spherical tops. Only the full shielding tensors obtained from oriented molecules (such as those measured by Ripmeester *et al.*[12] for some of the molecules in Table I) can provide spin-rotation constants in molecules of lower symmetry.

For comparison, literature values for condensed phase data in solution and neat liquids have been converted to absolute shielding by using the value for neat liquid $CFCl_3$ at 300 K in a cylindrical sample perpendicular to the field, $\sigma = 188.7$ ppm.[8] These are shown in Table I. We have previously discussed in paper I the various contributions to the nuclear magnetic shielding in condensed phases, and the typical magnitudes of the differences between chemical shifts measured in condensed phases and the chemical shifts between thermal-average independent molecules.[9] In many cases, a large part of the difference between the last two col-

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TABLE I. ^{19}F nuclear magnetic shielding in the zero-density limit relative to an isolated SiF_4 molecule. The absolute shielding, σ_0 based on HF as primary reference are compared with shielding calculated from literature values of condensed phase chemical shifts.

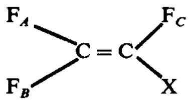
A	$[\sigma_0^A(300\ K) - \sigma_0^{SiF_4}(300\ K)]$	$\sigma_0^A(300\ K)^a$	σ(liquid phase)^b
SiF_4	0.0	363.2	348.3–352.2
SO_2F_2	-198.53 ± 0.02	164.7	152.2–156.8
$CFCl_3$	-167.55 ± 0.02	195.7	188.7
CF_3I	-163.58 ± 0.01	199.6	181.1–194.0
CF_3CN	-111.14 ± 0.02	252.1	
$CFHCl_2$	-86.94 ± 0.02	276.3	269.6
CF_2H_2	-24.07 ± 0.01	339.1	331.8–336.7
CH_3F^c	$+107.71 \pm 0.05$	471.0	460.6–465.0
CF_3H^c	-89.06 ± 0.01	274.1	265.2–272.7
$CF_4{}^c$	-104.21 ± 0.02	259.0	247.8–257.7
CF_2HCH_3	-56.83 ± 0.01	306.4	297.9–298.7
$CF_2{=}CF_2$	-32.46 ± 0.01	330.7	323.7
$CF_2{=}CH_2$	-84.09 ± 0.04	279.0	270
$CF_2{=}CFH$, A^d	-65.73 ± 0.02	297.5	290.3–291.7
B	-37.89 ± 0.02	325.3	315.7–318.1
C	$+41.00 \pm 0.02$	404.2	373.7 (?)^e
$CF_2{=}CFCl$,A	-63.05 ± 0.02	300.1	293.7
B	-46.54 ± 0.02	316.7	309.7
C	-22.62 ± 0.02	340.6	333.7
$CF_2{=}CFBr$,A	-67.34 ± 0.04	295.4	285.1–286.7
B	-48.99 ± 0.04	314.2	305.5–306.7
C	-21.77 ± 0.03	341.4	333.7
$CF_2{=}CFI$,A	-76.39 ± 0.02	286.8	275.5–282.7
B	-52.69 ± 0.03	310.5	300.7–304.7
C	-16.86 ± 0.02	346.3	337–344.7

[a] Based on Hindermann and Cornwell's HF value of 410 ± 6 ppm (Ref. 8).

[b] Converted from chemical shifts tabulated in J. W. Emsley and L. Phillips, Prog. NMR Spectrosc. 7, 1–526 (1971); C. H. Dungan and J. R. Van Wazer, *Compilation of Reported* ^{19}*F NMR Chemical Shifts* (Wiley, New York, 1970); V. Wray, Annu. Rep. NMR Spectrosc. B 10, 1–508 (1980), using $CFCl_3$ (liquid) absolute shielding of 188.7 ppm.

[c] From Ref. 9, repeated here to complete the CH_nF_{4-n} sequence.

[d] The three fluorine nuclei are labeled as follows:



[e] This particular F chemical shift was quoted in several papers but all have the same original source: P. M. Borodin, F. I. Skripov, Izvest. Vysshikh Vcheb. Zavedenii Radiofiz. 1, 69 (1958). We have no explanation for the large discrepancy between our value and this one.

umns in Table I can be accounted for with gas-to-liquid shifts of the order of 3–9 ppm which have been measured in this laboratory. The remaining differences may be due to any number of the following: bulk susceptibility effects in the use of external referencing, solvent effects on the internal $CFCl_3$ reference, solvent effects on the molecule of interest, errors in conversion to $CFCl_3$ from other reference liquids, and unregulated temperatures.

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