Gas-to-liquid shifts in NMR and the validity of the second virial coefficient of chemical shielding

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The density dependence of NMR chemical shifts is a measure of intermolecular interactions.[1] For a dilute gas σ can be expanded as $\sigma(T,\rho)=\sigma_0(T)+\sigma_1(T)\rho+\sigma_2(T)\rho^2+\cdots$. The density dependence of the nuclear magnetic resonance frequency for ^{129}Xe in xenon gas has been found to be nonlinear over several hundred amagats.[2] At room temperature and a density of 200 amagat the $\sigma_1\rho$ contribution to the shift was -110 ppm whereas the higher order contributions were $+6$ ppm. The density dependence of NMR chemical shifts have also been observed for ^{1}H, ^{11}B, ^{13}C, ^{15}N, ^{19}F, and ^{31}P nuclei in various gases.[3-5] In all these cases, we observed no deviation from linearity of shifts with density using sample densities less than 40 amagat, and we reported σ_1 as $(\partial\nu/\partial\rho)_T$.

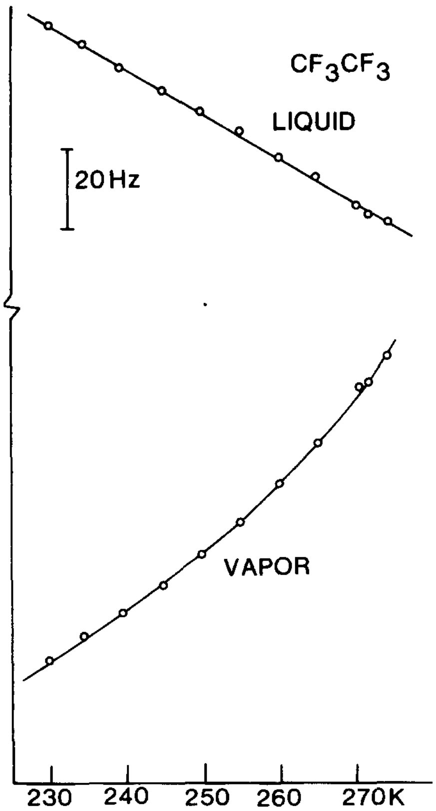

FIG. 1. ^{19}F NMR frequencies of liquid CF$_3$CF$_3$ in equilibrium with saturated vapor.

To test the validity of the σ_1 values which we reported for these nuclei, we would have to extend the range of observation of chemical shifts in gases to substantially higher densities, as we did for xenon. There are experimental difficulties associated with this. Fortunately we can obtain equivalent information from gas-to-liquid shifts measured by observing the NMR signal for both vapor and liquid samples containing liquid in equilibrium with vapor. Since the density of liquid and saturated vapor are known as functions of temperature for many substances, a comparison can be made between the apparent σ_1 measured for the liquid and that obtained for low density gases. Comparison of $(\partial\nu/\partial\rho)_{\text{gas}}(\rho_{\text{liq}}-\rho_{\text{vap}})$ with the gas-to-liquid shift, $\nu_{\text{liq}}(T,\rho_{\text{liq}})-\nu_{\text{vap}}(T,\rho_{\text{vap}})$, will show the importance of the higher order terms. Alternatively we can compare $A=(\partial\nu/\partial\rho)_{\text{gas}}$ with $B=(\nu_{\text{liq}}(T,\rho_{\text{liq}})-\nu_{\text{vap}}(T,\rho_{\text{vap}}))/(\rho_{\text{liq}}-\rho_{\text{vap}})$. In xenon, $B-A$ is opposite in sign to σ_1. Although we have not measured the gas-to-liquid shifts in xenon, our gas phase data overlaps in temperature with data for the liquid.[6] At 244 K the observed shift of liquid relative to the isolated xenon atom is -161 ppm, whereas $\sigma_1\rho_{\text{liq}}=-318$ ppm. Thus, for liquid xenon the higher order terms are $+157$ ppm, close to 50% of the linear term. In this note we report NMR measurements in low density gas samples

TABLE I. Values of $\sigma_1(T)$ for ^{19}F in various gases, in Hz/amagat at 84.68 MHz.

T, K	CF$_3$Br	CF$_3$CF$_3$	CF$_3$H
240			0.918 ± 0.117
250		1.602 ± 0.134	0.909 ± 0.094
260		1.560 ± 0.128	0.896 ± 0.076
270	2.475 ± 0.129	1.523 ± 0.127	0.878 ± 0.065
280	2.440 ± 0.089	1.490 ± 0.128	0.855 ± 0.058
290	2.391 ± 0.064	1.461 ± 0.130	0.828 ± 0.055
300	2.327 ± 0.052[a]	1.435 ± 0.133	0.796 ± 0.057
310	2.248 ± 0.052	1.414 ± 0.137	0.760 ± 0.064
320	2.155 ± 0.061	1.396 ± 0.144	0.719 ± 0.077
330	2.048 ± 0.079	1.383 ± 0.157	0.674 ± 0.096
340	1.926 ± 0.104	1.373 ± 0.177	0.624 ± 0.121
350	1.790 ± 0.142	1.367 ± 0.207	0.570 ± 0.151
360	1.639 ± 0.195	1.365 ± 0.245	0.511 ± 0.187
370	1.474 ± 0.269	1.367 ± 0.291	0.448 ± 0.230
380	1.295 ± 0.369	1.373 ± 0.347	0.380 ± 0.279

[a] 2.17 ± 0.12 was obtained from a separate set of samples at 300 K.

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TABLE II. Comparison of gas-to-liquid shifts with σ_1 obtained from low density gas phase NMR.[a]

System	T K	ρ_{liq} amagat	ρ_{vap} amagat	$\nu_L - \nu_v$ Hz	B Hz/amagat	B–A Hz/amagat	$(B/A) - 1$
CF_3H	240	380.69	15.22	301.8	0.826	−0.092 ± 0.117	
	250	361.06	21.48	280.8	0.827	−0.082 ± 0.094	< 10%
	260	339.69	29.49	257.05	0.829	−0.067 ± 0.076	
	270	316.33	39.48	227.	0.820	−0.058 ± 0.065	
CF_3CF_3	230	231.14	5.80	359.4	1.595		
	240	222.30	8.00	336.0	1.568		
	250	212.93	10.75	308.6	1.526	−0.076 ± 0.134	
	260	202.96	14.10	280.3	1.484	−0.076 ± 0.128	< 8%
	270	192.34	18.10	241.7	1.387	−0.136 ± 0.127	
CH_3F	242.05	493.88	9.134	732.	1.510		
	252.13	476.87	12.238	694.	1.494		
	261.78	459.97	15.825	651.	1.466		
	268.80	447.26	18.849	612.	1.428		
	274.38	436.87	21.537	582.	1.401		
	280.04	426.09	24.504	551.7	1.374	−0.006 ± 0.15	< 11%
CF_3Cl	248	273.31	13.34	417	1.60		
	258	261.33	18.26	382	1.57		
	268	247.75	24.72	348	1.56		
	278	232.45	33.42	313	1.57	−0.186 ± 0.16	(10.6 ± 9)%
CF_3Br	260.5	226.95	6.96	449.0	1.73		
	270.5	258.55	9.39	426.0	1.71		
	280.5	249.47	12.48	399.0	1.68		
	290.5	239.62	16.43	369.0	1.65		
	300.5	228.63	21.53	332.0	1.60	−0.57 ± 0.12	(26.2 ± 6)%

[a] Values of A from Table I (except for CH_3F, Ref. 10); densities from Ref. 9.

as well as gas-to-liquid shifts for ^{19}F nuclei in several systems, and obtain values of B–A as a measure of higher order terms.

NMR spectra were observed with a FT Bruker spectrometer at 21.1 kgauss. At a given temperature the observed frequencies in the gas phase are linear with density, with the slopes (values of σ_1) varying with temperature, given in Table I. Upon condensation the NMR signal observed at higher temperatures split into two signals, the liquid signal downfield from the saturated vapor. For example, see Fig. 1. (This had been observed for ^{13}C in CO_2 and ^{31}P in P_4 as well.)[7,8] By observing the frequency difference between liquid and vapor at a given temperature, the large frequency shifts due to $\sigma_0(T)$ are eliminated. For most of the systems studied, experimental B and A values are identical, within estimated errors in A. The experimental errors associated with the difficult low density gas studies do not allow us to elicit a quantitative measure of higher order terms in these ^{19}F systems except for CF_3Br. We can only report an upper limit as a fraction of the expected shift for a given liquid density in the last column of Table II. Although the B–A values found here are small compared with xenon (in which the higher order terms varied from 6% to 50% of the linear term at comparable densities), like xenon they are all opposite in sign to σ_1. The small higher order terms in these systems indicate that the method of obtaining σ_1 by a linear fit in gas samples with densities under 40 amagat is valid.

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