Variation of chemical shielding with intermolecular interactions and rovibrational motion. IV. ^{11}B and ^{13}C nuclei in BF_3 and CH_4

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The temperature dependence of chemical shielding of ^{11}B and ^{13}C in an isolated BF_3 or CH_4 molecule is found to be negligibly small. It mat be generally true that the chemical shielding of a nucleus located at the center of symmetry of a molecule changes very little with vibration and rotation. The second virial coefficients σ_1 are reported for these systems, as well as the dependence of the ^{11}B–^{19}F coupling constant on temperature and density.

The NMR shift of a nucleus in a gas can be described in terms of a virial expansion of the chemical shielding parameter

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

The effects of binary intermolecular interactions are quantitatively represented by the $\sigma_1(T)$ function which is obtained experimentally from the density dependence of the NMR shift in the gas phase. The changes in chemical shielding due to anharmonic vibration and centrifugal distortion in the isolated molecule are represented by the $\sigma_0(T)$ function. By observing the NMR spectrum of several samples of known density over a range of temperatures, both $\sigma_1(T)$ and $[\sigma_0(T)-\sigma_0(300)]$ functions can be measured experimentally.

Previous studies of the temperature and density dependence of the NMR signal of a nucleus in a gaseous system have involved the peripheral nuclei in a molecule. Most of the effort has been centered around ^{19}F and ^{1}H,[1–4] but other nuclei such as ^{13}C in CO,[4] ^{15}N in ^{15}NNO,[5] and ^{31}P in PH_3[6] have been studied as well. The difference between a peripheral nucleus and one at a more central location in the molecule has been noted in the NNO molecule.[5] Here one had the opportunity to observe the temperature and density dependence of both nuclei at the same time. It was found that the end ^{15}N nucleus had a more pronounced temperature dependence in both σ_0 and σ_1, and also a larger magnitude of σ_1. The σ_1 difference is easily explained in terms of the noncentral nature of the intermolecular potential between an NNO molecule and any other molecule; the so-called "site effect" leads to a larger σ_1 for peripheral atoms compared to central ones. The smaller temperature dependence of the central ^{15}N in NNO compared to that of the end ^{15}N was noted also. However, there was not enough data on nuclei of centrally located atoms in molecules to determine whether it is generally true that nuclei of centrally located atoms have less pronounced temperature dependence compared to peripheral atoms. In this study we consider two nuclei, ^{13}C in CH_4 and ^{11}B in BF_3, as examples to test the general applicability of this observation.

EXPERIMENTAL RESULTS

Fourier transform NMR spectroscopy for ^{11}B and ^{13}C was carried out in ^{13}C-enriched CH_4 and natural BF_3. Details pertaining to temperature regulation and sample preparation,[7] sources of error,[8] line fitting procedures,[4] and analysis of data[3] have been given elsewhere. The ^{11}B spectrum consists of the 1 : 3 : 3 : 1 multiplet resulting from coupling with the fluorine. Determination of the temperature dependence of the parameters of this spectrum required matching of the observed spectrum with a calculated one. A theoretical spectrum made up of four Lorentzian functions using a given linewidth parameter, a coupling constant parameter, and the theoretical intensity ratio was generated with the Nicolet software inside the Fourier transform package. This theoretical spectrum is subtracted from the observed spectrum and the residual is stored. Visual comparison of the residuals on the scope was used in this iterative procedure. The final comparison in the last step of the iteration was done on the recorded residual spectra. This process allowed the determination of the center of the multiplet, the coupling constant and the linewidth to within one or two cursor positions. Under the conditions of the data acquisition one cursor position is equivalent to 0.25 Hz. Figure 1 demonstrates the goodness of the fit with variation in J. The ^{13}C in CH_4 spectra had sufficiently narrow lines and a statistically constant J_{CH} which allowed the determination of the temperature dependence of the ^{13}C frequency without the line fitting procedures which were necessary for ^{11}B in BF_3. Here all the components of the multiplet were used in the determination of the temperature dependence except in instances where the outer peaks could not be located with the same precision as the inner ones. Examples of the observed temperature dependence for ^{11}B in BF_3 and ^{13}C in CH_4 are shown in Figs. 2 and 3 for one of the samples.

The typical density dependence of ^{11}B in BF_3 and ^{13}C in CH_4 are shown in Figs. 4 and 5 for a given temperature. The slope of the straight line is the value of σ_1 at that temperature. σ_1 was found to be essentially temperature independent for ^{11}B in BF_3, within our ex-

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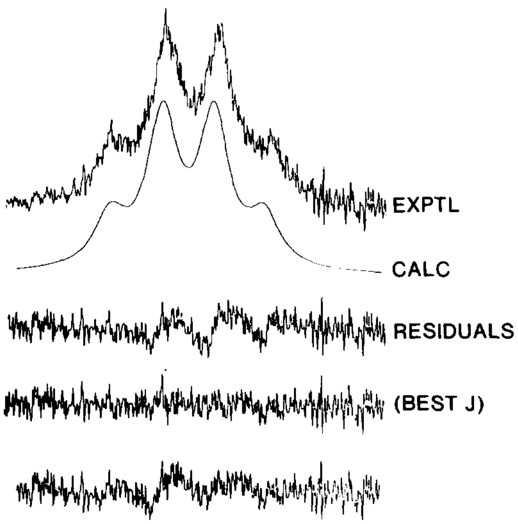

FIG. 1. Demonstration of the goodness of fit of ^{11}B NMR spectrum in BF_3 with the variation in J value. The three residuals shown, from the top, are for $J=17.75$, 18.25, and 18.75 Hz, respectively.

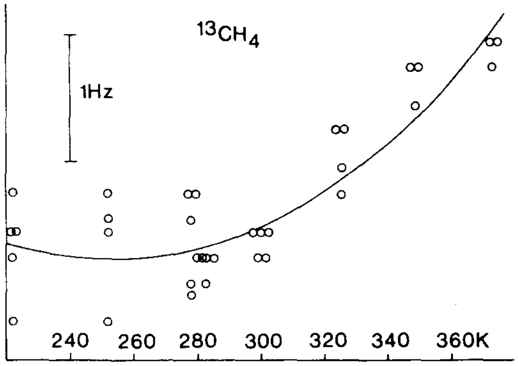

FIG. 3. Raw data for ^{13}C in 36.59 amagat sample of CH_4 gas.

perimental precision. The temperature dependence of σ_1 for ^{13}C in CH_4 could be determined. It is shown in Fig. 6 and is tabulated in Table I. The change of σ_1 with temperature is found to be in the usual direction, more downfield with decreasing temperature. Although Jackowski and Raynes report a temperature dependence for ^{13}C in CH_4 in the opposite direction, their experimental precision did not allow this to be established.[9]

When the intermolecular effects are removed from the raw data by subtracting out $\sigma_1(T)\rho$ from the observed frequencies, the remainder will be the temperature dependence of the reference (in this case, the ^1H in the CH_4 group of toluene) and the $\sigma_0(T)$ which is desired. In both cases the remainder showed no temperature dependence beyond that of the reference. That is, the $\sigma_0(T)$ is so slightly varying with temperature that any temperature dependence is smaller than our random errors. This is demonstrated by the ^{13}C in CH_4 samples shown in Fig. 7. The straight line represents the temperature dependence of the reference. It is obvious that there is no temperature dependence left to be attributed to $\sigma_0(T)$. The ^{11}B in BF_3 gives the same result. We are unable to observe $\sigma_0(T)$ in both ^{13}C in CH_4 and ^{11}B in BF_3. At best we can give an upper limit to the total change in σ_0 over the entire temperature range used here. This is less than 0.5 Hz in both cases.

The $^{11}B-^{19}F$ coupling constant was found to be temperature dependent in BF_3 gas. This coupling constant had previously been observed in liquid BF_3 by Bacon *et al.*[10] The values of the $^{11}B-^{19}F$ coupling constant which they observed appeared to have a nonlinear dependence on temperature below 190 K. We compare their values from 193 to 301 K in the liquid with the values we observed in the gas in Fig. 8. The $^{11}B-^{19}F$ coupling constant may be written in terms of a virial expression in the same way as the chemical shielding:

$$J(T,\rho)=J_0(T)+J_1(T)\rho+\cdots .$$

If we let $J_0(T)$ be a linear function

$$J_0(T)=J_e+aT,\ \text{Hz},$$

where J_e is the value of the coupling constant at the equilibrium configuration of the BF_3 molecule and aT reflects the temperature dependence of J due to anharmonic vibration and centrifugal distortion.[11] $J_1(T)$ is the analog of $\sigma_1(T)$ and is a measure of the inter-

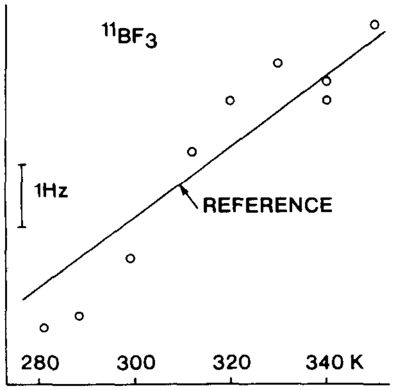

FIG. 2. Raw data for ^{11}B in 37.13 amagat sample of BF_3 gas. The frequencies are observed at 28.878 MHz using ^{19}F of C_6F_6 signal to stabilize the field. All of the temperature dependence can be attributed to the shift of the C_6F_6.

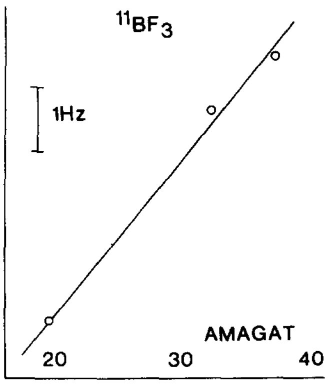

FIG. 4 Density dependence of ^{11}B in BF_3 at 300 K. The slope of the line is the value of σ_1. All other plots at various temperatures have essentially the same slope, within experimental error.

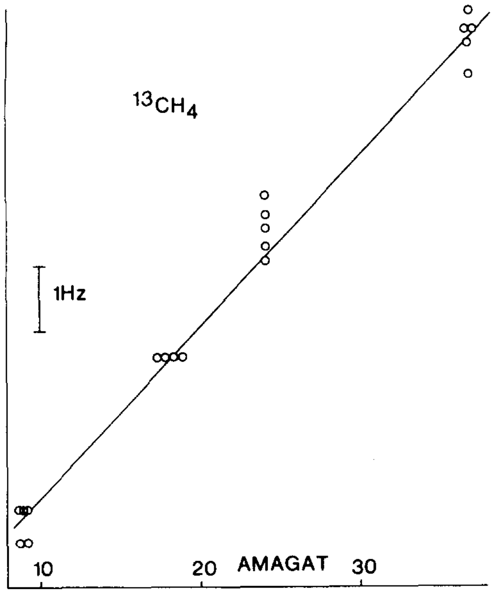

FIG. 5. Density dependence of ^{13}C in CH_4 at 220 K. The slope of the line is the value of σ_1 at 220 K.

TABLE I. Second virial coefficient of chemical shielding for ^{13}C in CH_4 interacting with another CH_4 in Hz/amagat at 22.63 MHz.

T	σ_1	S. D.
220	0.2699	0.060
230	0.2593	0.040
240	0.2507	0.032
250	0.2437	0.027
260	0.2382	0.022
270	0.2338	0.018
280	0.2306	0.015
290	0.2282	0.011
300	0.2265	0.008
310	0.2252	0.004
320	0.2241	0.005
330	0.2231	0.012
340	0.2219	0.022
350	0.2203	0.034
360	0.2182	0.049
370	0.2153	0.067
380	0.2114	0.090

molecular effects on the coupling constant. Let $J_1(T)$ be a linear function:

$$J_1(T) = b + cT, \text{ Hz/amagat.}$$

The density of liquid BF_3 is given by Landolt-Bornstein as $2.6999-0.00642T$ g cm^{-3} between 145 and 374 K.[13] From the experimental values of J in the gas, least squares fitted to a straight line and the experimental values of J in liquid, the parameters J_e, a, b, and c can all be obtained. The resulting $J_0(T)$ and $J_1(T)$ are shown in Table II. This appears to be one of the few cases in which the temperature and density dependence of the coupling constant can be observed in the gas phase.[14] The results are totally consistent with the liquid data of Bacon *et al.* The $J_0(T)$ and $J_1(T)$ are given in Table II as linear functions because the precision of the data is not sufficient to warrant the use of a higher degree polynomial.

The linewidths of ^{11}B are obtained incidentally. They are a measure of T_2 and since the correlation times are sufficiently short in gases of such low densities as our samples, they also are a measure of T_1. The log of (1/linewidth) is plotted vs log$T$ in Fig. 9 for the 37 amagat sample. The slope of the straight line shown is -1.24 ± 0.2. This is surprising because earlier work by Hinshaw and Hubbard[15] on T_1 of ^{11}B in BF_3 gas was reported to be consistent with a -0.5 slope, that is, a $T^{-1/2}$ dependence of T_1 rather than a $T^{-3/2}$ dependence which our slope of -1.24 appears to be consistent with. The difference may lie in the density measurements. Our density is determined by measuring the pressure of

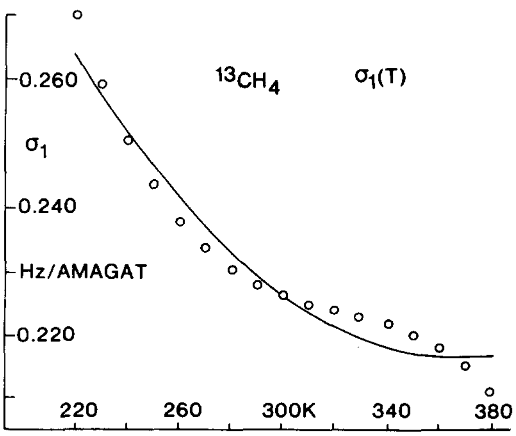

FIG. 6. The $\sigma_1(T)$ function for ^{13}C in CH_4 in Hz/amagat at 22.63 MHz.

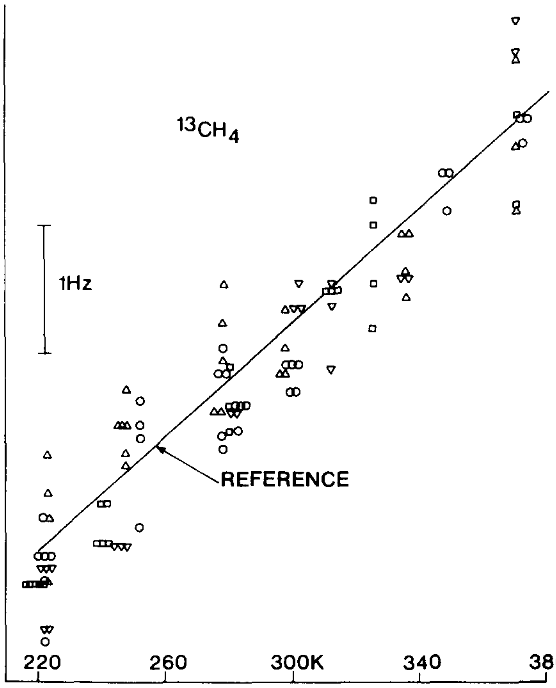

FIG. 7. The remainder frequencies after subtraction of $\sigma_1 \rho$ for each sample. The line gives the temperature shift due to the reference [^1H (CH_3) of toluene].

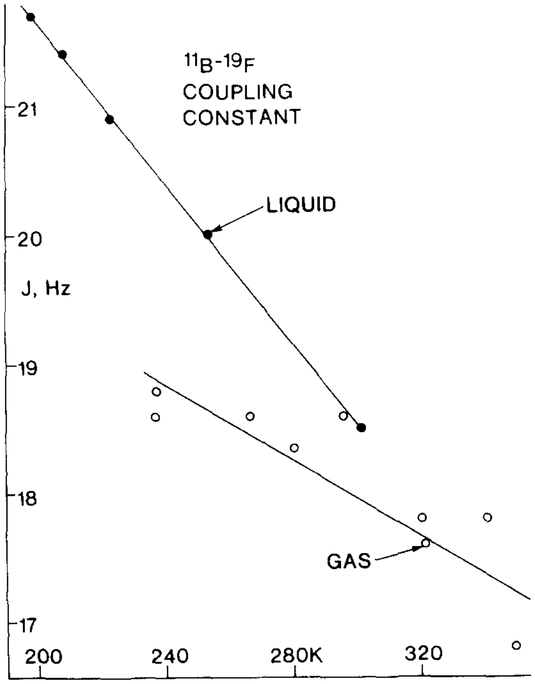

FIG. 8. Temperature dependence of the $^{11}B-^{19}F$ coupling constant in liquid BF_3 (solid circles) from Ref. 9 and in gaseous BF_3 (open circles) this work. The straight lines are best least squares fit to the data.

BF_3 gas in a section of vacuum line which is a large calibrated volume at room temperature. This gas is swept with mercury into a calibrated sample tube, then frozen and sealed. The pressure in the large calibrated volume is subatmospheric, thus deviations from ideality do not give rise to large errors. On the other hand, Hinshaw and Hubbard did not measure densities but rather pressures up to 1700 psi. The densities were presumably obtained from available PVT data. Because of the possible errors in PVT data and because only three temperatures were used by Hinshaw and Hubbard, their best fit to $T_1/\rho = aT^{-n}$ with $n = 0.5$ may not be inconsistent with our best fit to $T^{-1.24}$. Furthermore, the nearly $T^{-3/2}$ dependence suggests the possibility that quadrupolar relaxation may not be the dominant mechanism but that spin-rotation relaxation may be important.

CONCLUSION

We have been able to obtain the $\sigma_1(T)$ function for ^{13}C in CH_4 and ^{11}B in BF_3. The latter is essentially constant within experimental error. The $\sigma_0(T)$ functions for ^{13}C in CH_4 and ^{11}B in BF_3 are so slowly varying with temperature that we are unable to specify them except in terms of an upper limit to the change in σ_0 over the entire temperature range studied. We estimate this to be less than 0.02 ppm over 100° for both ^{11}B in BF_3 and ^{13}C in CH_4. Thus, it appears that nuclei of atoms which are centrally located in the molecule have much smaller temperature dependence of chemical shielding in the isolated molecule than do nuclei in peripheral atoms. The change in chemical shielding with temperature in the isolated molecule is due to anharmonic vibration and centrifugal distortion.[12,16] The theoretical interpretation of this effect is in terms of a Taylor series expansion of σ:

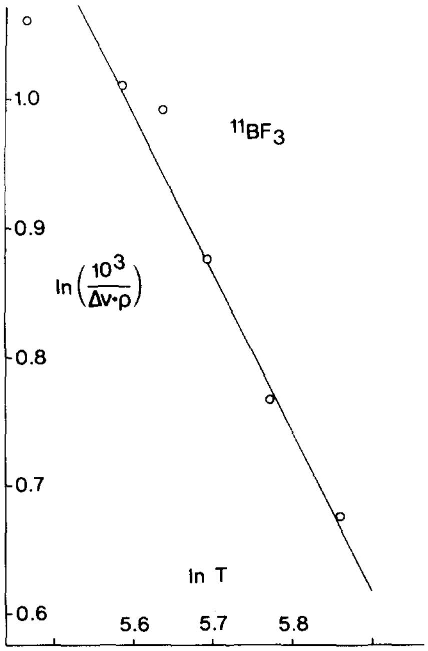

FIG. 9. Temperature dependence of (1/linewidth) of ^{11}B in BF_3 gas. The slope of the line is -1.24 ± 0.2.

$$\sigma_B = \sigma_e + 3(\partial\sigma_B/\partial\Delta r)_{eq}\langle \Delta r\rangle^T + \cdots,$$

and

$$\sigma_C = \sigma_e + 4(\partial\sigma_C/\partial\Delta r)_{eq}\langle \Delta r\rangle^T + \cdots .$$

The thermal average of the B–F bond stretch has been calculated.[17] The thermal average of the C–H bond stretch can be calculated by the same method using the cubic force constants and other molecular constants given by Kuchitsu and Bartell.[18] Both $\langle \Delta r_{CH}\rangle^T$ and

TABLE II. Temperature dependence of the $^{11}B-^{19}F$ coupling constant in the isolated BF_3 molecule $J_0(T)$, the second virial coefficient of the coupling constant $J_1(T)$, and of chemical shielding $\sigma_1(T)$.

	^{11}B, BF_3	^{13}C, CH_4
$J_0(T)$, Hz	$22.176-0.014705T$	
$J_1(T)$, Hz/amagat	$6.3706\times10^{-3}-3.214\times10^{-6}T$	
$\sigma_1(T)$, ppm/amagat	-0.00848 ± 0.0009	$-0.010007+1.3\times10^{-5}(T-300)$ $-9.8\times10^{-8}(T-300)^2$

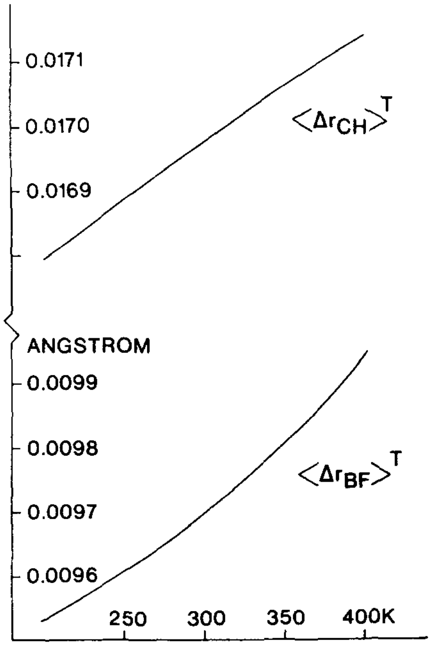

FIG. 10. The thermal average of the B–F and C–H bond stretch in BF_3 and CH_4 molecules calculated according to Ref. 13.

$\langle \Delta r_{BF} \rangle^T$ functions are shown in Fig. 10. Since $\langle \Delta r_{BF} \rangle^T$ changes by 0.200×10^{-3} Å from 250 to 350 K and the total change in σ over the same temperature range is less than 0.02 ppm, then $|(\partial\sigma_B/\partial\Delta r_{BF})_{eq}|$ is less than 33 ppm/Å. Similarly, $\langle \Delta r_{CH} \rangle^T$ changes by 0.178×10^{-3} Å from 250 to 350 K, which leads to an upper limit for $|(\partial\sigma_C/\partial\Delta r_{CH})_{eq}|$ of 28 ppm/Å. These values are small compared to $(\partial\sigma/\partial\Delta r)$ values previously reported for peripheral nuclei.[1,2,17,18] It is not surprising that the ^{11}B and ^{13}C chemical shielding do not vary greatly with symmetrical bond extensions. The paramagnetic contribution is likely to be the dominant contribution to the shielding in a peripheral atom due to the asymmetry of the electronic environment. As the bond stretches, the paramagnetic contribution changes because the asymmetry of the electronic environment is changed. For a nucleus located at the center of symmetry of the molecule, the paramagnetic contribution is smaller than that of a peripheral nucleus due to the high symmetry of the electronic environment, and since the symmetry is preserved with symmetrical bond extensions the $(\partial\sigma/\partial\Delta r)$ is expected to be small. This is borne out by our results for ^{11}B in BF_3 and ^{13}C in CH_4.

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