Variation of chemical shielding with intermolecular interactions and rovibrational motion. II. ^{15}N and ^{13}C nuclei in NNO and CO_2

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In the gas phase, the chemical shielding of a nucleus in terms of temperature and density can be written in a virial expansion, $\sigma(T,\rho)=\sigma_0(T)+\sigma_1(T)\rho+\sigma_2(T)\rho^2+\cdots$. $\sigma_0(T)$ and $\sigma_1(T)$ functions have been determined for ^{13}C in CO_2 and both ^{15}N nuclei in NNO. As expected, the terminal ^{15}N has the largest chemical shift. The results are compared with data for other systems such as ^1H, ^{19}F, ^{31}P, and ^{129}Xe.

The chemical shielding of a nucleus in a molecule of a pure imperfect gas can be expressed by a virial expansion in the form of

$$\sigma(T,\ \rho)=\sigma_0(T)+\sigma_1(T)\rho+\sigma_2(T)\rho^2+\cdots\ ,$$

where $\sigma_0(T)$ is the temperature dependence of chemical shielding in the isolated molecule and $\sigma_1(T)$ and $\sigma_2(T)$ give the temperature dependence of the second and third virial coefficients of chemical shielding, respectively. $\sigma_0(T)$ is determined by the contributions due to anharmonic vibration and centrifugal distortion in the isolated molecule.[1] $\sigma_1(T)$ is determined by the contributions from bimolecular interactions and the density dependence of bulk susceptibility of the perturber gas.[2] For a spherically symmetric molecule, $\sigma_1(T)$ can be written as

$$\sigma_1(T)=4\pi\int_0^\infty \sigma(R)\,e^{-V(R)/kT}R^2\,dR\ ,$$

where R is the distance between the molecule and a perturbing molecule, and $\sigma(R)$ is the chemical shielding of the nucleus in the molecule as a function of its distance from the perturber. $\sigma_2(T)$ is due to termolecular and higher order interactions. In samples of sufficiently low density, the terms in ρ^2 or higher order will be negligible so that it is possible to get $\sigma_1(T)$ to a high degree of precision. At each temperature, σ_1 is the slope of the straight line obtained by plotting the observed resonance frequency vs density of gas while the information about σ_0 is in the intercept of this same plot.

Theoretically, the thermal average of chemical shielding may be expressed in terms of the thermal average of powers of the dimensionless normal coordinates.[1] For this theoretical calculation, we need the harmonic frequencies, rotational constants, and cubic force constants in dimensionless normal coordinates. These constants are completely known only for diatomics and for triatomic molecules such as CO_2, CS_2, HCN, OCS, and NNO.[3] They are less completely known for ClCN, HCP, O_3, OF_2, SO_2, SeO_2, GeF_2, SiF_2, H_2O, H_2S, and H_2Se by use of somewhat simplified force fields. For this and other reasons, we choose two typical triatomic molecules, CO_2 and NNO, for the experimental measurements which may later be compared with theoretical calculations. Of the triatomic molecules listed above, the ones which are suitable for the determination of $\sigma_0(T)$ are those which satisfy all of the following conditions: (a) the molecules must contain magnetic nuclei which have fairly reasonable sensitivity in terms of the isotopic abundance of spin $\frac{1}{2}$ nuclei and magnitude of the magnetic moment (we avoid the complication of quadrupolar nuclei); (b) these magnetic nuclei should have shifts with respect to temperature which are expected to be relatively large (e.g., ^{13}C, ^{15}N, ^{19}F, rather than ^1H) so they can be measured with small relative error; and (c) the compound should remain gaseous over a relatively wide range of densities and experimentally accessible temperatures, in order that the functional dependence of both σ_0 and σ_1 on temperature can be obtained.

The experimental $\sigma_0(T)$ and $\sigma_1(T)$ of ^{13}C in CO_2 and ^{15}N nuclei in NNO are reported here. This is the first observation of these quantities for ^{15}N.

RESULTS

Pulsed Fourier transform NMR spectra were observed with a Bruker spectrometer operating at a field strength of 21 kG equipped with a variable temperature controller and a Nicolet 1080 data acquisition system.[4] The samples of nitrous oxide were 99% ^{15}N doubly labeled and the samples of CO_2 were prepared from 90% ^{13}C-enriched $BaCO_3$. Sealed samples of pure gas with measured densities ranging from 9 to 47 amagat were placed in a 5 mm NMR tube containing the liquid lock substance. Sample preparation has been described previously.[4] In mixtures of NNO with Xe, SiF_4, or CF_4, the NNO densities were kept close to 10 amagat and the densities of the perturber gas were varied from 18 to 34 amagat.

The NMR spectra of NNO were taken at 9.1 MHz

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over a temperature range of 260–380 K for six samples of known density ranging from 11 to 47 amagat. For CO_2, spectra were taken at 22.6 MHz at somewhat lower temperatures, 220–380 K in four samples with densities of 9–40 amagat. The ^{15}N spectra required 64–512 transients depending on the density of the sample. Only 16–128 transients were necessary for ^{13}C spectra. ^{13}C in CO_2 had a linewidth of about 2 Hz and ^{15}N in NNO peaks were about 1.2 Hz wide. The ^1H resonance signal of the methyl group in liquid toluene was used as the external reference to stabilize the magnetic field.

In both NNO and CO_2 molecules, σ_1 of ^{15}N and ^{13}C becomes smaller with increasing temperature, leading to an upfield shift with temperature for a given sample, while σ_0 leads to a downfield shift with increasing temperature. Due to the dominance of the temperature dependence of σ_0 over that of σ_1, the net result is that the ^{15}N and ^{13}C signals move downfield with increasing temperature. This behavior is similar to that of ^{19}F in BF_3, CF_4, SiF_4, and SF_6. However, the shifts are much smaller here.[5] The ^{13}C signal in CO_2 shifted a total of 5.7 Hz and the central ^{15}N a total of 4.7 Hz in the range of temperatures and densities used here. On the other hand, the terminal ^{15}N shifted 13.1 Hz under the same conditions.

The $^{15}N^{15}NO$ NMR spectrum shows a typical AX spectrum with a coupling constant of 8.9 Hz. This is in agreement with the value obtained by Bhattacharyya and Dailey for NNO in CCl_4 solution and in the isotropic phase of the liquid crystal EBBA, -9.16 ± 0.30 Hz.[6] The temperature and density dependence of this coupling constant was less than 0.1 Hz, within our experimental precision. This limit is a statistical one since the spectrum in the frequency domain is a set of discrete points 0.25 Hz apart under the conditions in which the spectra were taken. We assign the lower field doublet to the central ^{15}N and the higher field doublet to the terminal ^{15}N. The resonance frequency is taken to be the average of the two components of the doublet. The assignment of the ^{15}N signals is in agreement with that of Bhattacharyya and Dailey for $^{15}N_2O$ dissolved in a nematic phase liquid crystal.[6] They estimate that the absolute values of the central and terminal ^{15}N shielding constants are about 20 and 104 ppm, respectively.

TABLE I. Frequency shifts in the limit of zero density, $\Delta\nu_0$, for ^{15}N in $^{15}N_2O$ at 9.12 MHz and for ^{13}C in CO_2 at 22.63 MHz, relative to 300 K (in Hz).

	Terminal ^{15}N		Central ^{15}N		^{13}C in CO_2	
T	$\Delta\nu_0$	S.D.[a]	$\Delta\nu_0$	S.D.[a]	$\Delta\nu_0$	S.D.[a]
230					−0.85	0.62
240					−0.73	0.56
250					−0.61	0.55
260	−2.91	0.28	−1.36	0.11	−0.49	0.53
270	−2.26	0.17	−1.01	0.07	−0.36	0.51
280	−1.55	0.09	−0.67	0.04	−0.24	0.48
290	−0.79	0.03	−0.33	0.03	−0.12	0.46
300	0	0.03	0	0.02	0	0.45
310	0.82	0.05	0.32	0.03	0.12	0.46
320	1.66	0.06	0.64	0.04	0.24	0.49
330	2.50	0.07	0.94	0.04	0.36	0.52
340	3.34	0.07	1.24	0.05	0.49	0.54
350	4.16	0.07	1.52	0.04	0.61	0.54
360	4.96	0.07	1.79	0.03	0.73	0.51
370	5.72	0.08	2.05	0.02	0.85	0.46
380	6.43	0.12	2.29	0.04	0.97	0.42

[a] The average error is 0.98% of the total shift observed in the terminal ^{15}N, 1.2% of that in the central ^{15}N, and 28% of that in ^{13}C.

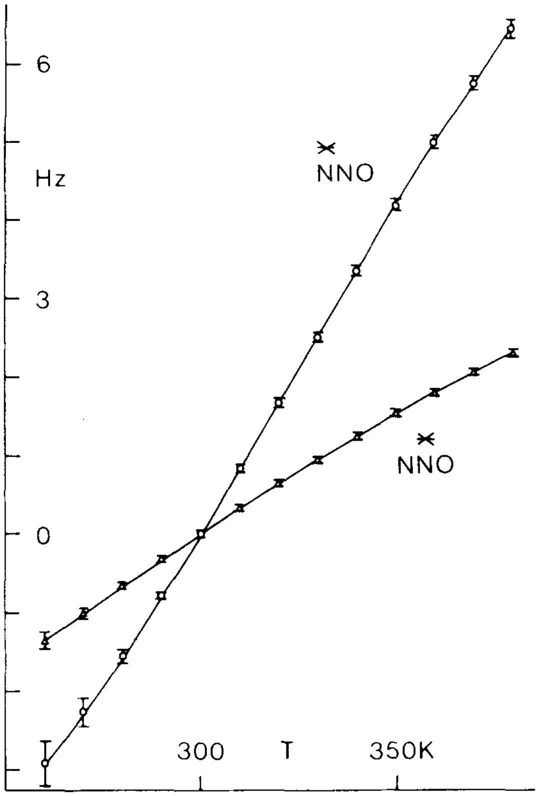

FIG. 1. Frequency shifts due to rovibrational motion measured at 9.12 MHz for ^{15}N in an isolated NNO molecule.

The resonance frequencies observed over a wide temperature range for each sample are fitted to a polynomial of degree 2 or 3 in terms of $(T-300)$ K. The precisely known temperature dependence of the reference substance is subtracted out and from the known densities of the samples, the σ_1 is determined as the slope of frequency vs density plots for each temperature.[5,7] When the effect of the density dependence of the gas is removed from each sample, the remaining temperature dependence is a measure of $\sigma_0(T)$. The results from all samples are combined to yield a statistical average and standard deviation for each temperature. Frequency shifts due to rovibrational motion which were obtained in this fashion are shown in Table I and Fig. 1 for ^{15}N nuclei in NNO.

In the case of CO_2, the temperature dependence of σ_1 is smaller than the errors accompanying the measurement and that of σ_0 is only about the same order of magnitude as the temperature dependence of the reference substance. Thus, the data analysis was carried out in a different manner. An average σ_1 was obtained. The product of this average σ_1 and the sample density

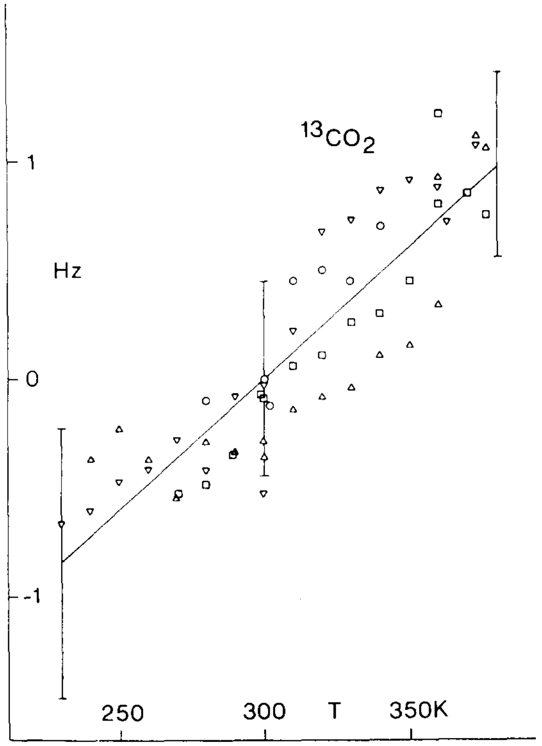

FIG. 2. Frequency shifts due to rovibrational motion measured at 22.6 MHz for ^{13}C in an isolated CO_2 molecule.

was subtracted from each data point in order to remove intermolecular effects. The reference substance temperature dependence was fitted to a linear equation and subtracted from each data point. The results are shown in Fig. 2. The error bars shown in Fig. 2 reflect a combination of the original errors in the temperature dependence of the reference, the standard deviation of the fit to a linear equation for the reference, and the standard deviation of the fit of the points shown in the figure of a linear $\sigma_0(T)$. Even when a quadratic fit is used rather than a linear fit, the curvature observed in $\sigma_0(T)$ is entirely within the combined experimental errors.

TABLE II. $\sigma_1(T)$ in Hz/amagat for ^{15}N in N_2O at 9.12 MHz.

	Terminal ^{15}N		Central ^{15}N	
T	σ_1	S.D.[a]	σ_1	S.D.[a]
220				
230				
240				
250				
260	0.1024	0.0127	0.0366	0.0034
270	0.0969	0.0076	0.0317	0.0024
280	0.0920	0.0038	0.0281	0.0026
290	0.0879	0.0019	0.0257	0.0031
300	0.0845	0.0026	0.0243	0.0034
310	0.0818	0.0040	0.0238	0.0036
320	0.0798	0.0050	0.0240	0.0038
330	0.0786	0.0057	0.0247	0.0040
340	0.0782	0.0061	0.0257	0.0040
350	0.0786	0.0061	0.0270	0.0037
360	0.0798	0.0060	0.0283	0.0031
370	0.0818	0.0058	0.0294	0.0023
380	0.0846	0.0065	0.0303	0.0031

[a] Most of the error is due to density errors.

TABLE III. $\sigma_1(T)$ for end ^{15}N in N_2O mixtures with Xe, SiF_4, and CF_4 at 9.120 MHz, in Hz/amagat.

	Xe		SiF_4		CF_4	
T	σ_1	S.D.	σ_1	S.D.	σ_1	S.D.
260	0.227	0.0304	0.158	0.0218	0.117	0.0161
270	0.215	0.0188	0.146	0.0120	0.107	0.0114
280	0.204	0.0114	0.135	0.0060	0.098	0.0086
290	0.194	0.0079	0.125	0.0061	0.090	0.0066
300	0.184	0.0085	0.116	0.0087	0.083	0.0053
310	0.176	0.0113	0.107	0.0106	0.076	0.0053
320	0.169	0.0148	0.100	0.0116	0.071	0.0067
330	0.162	0.0179	0.094	0.0117	0.065	0.0088
340	0.158	0.0203	0.088	0.0113	0.061	0.0109
350	0.155	0.0217	0.084	0.0107	0.057	0.0125
360	0.154	0.0228	0.081	0.0102	0.053	0.0139
370	0.155	0.0260	0.079	0.0103	0.050	0.0158
380	0.158	0.0349	0.078	0.0114	0.047	0.0197

In Tables II–IV and Figs. 3 and 4 are shown the second virial coefficients of chemical shielding, $\sigma_1(T)$, for both ^{15}N nuclei in NNO interacting with NNO, Xe, SiF_4, and CF_4. The temperature dependence of σ_1 for both ^{15}N nuclei in NNO interacting with NNO is not much larger than the absolute error at each temperature. Thus, the $\sigma_1(T)$ functions for these systems are not as reliable as the others. The curvature of these functions are quite unlike other $\sigma_1(T)$ functions previously reported by us and other workers for various nuclei.[4,5,8–10] However, the precision of the results do not warrant any special significance which might be attributed to such unusual behavior. A monotonically decreasing curve could easily fit the same results within the error bars. The magnitude of σ_1 is larger by a factor of about 4 for the terminal ^{15}N compared to the central ^{15}N in NNO. The temperature dependence of the terminal ^{15}N is also more pronounced than that of the central atom. This is in agreement with our previous observations in

TABLE IV. $\sigma_1(T)$ for central ^{15}N in N_2O mixtures with Xe, SiF_4, and CF_4 at 9.121 MHz, in Hz/amagat.

	Xe		SiF_4		CF_4	
T	σ_1	S.D.	σ_1	S.D.	σ_1	S.D.
260	0.0900	0.0252	0.0533	0.0092	0.0520	0.0176
270	0.0825	0.0199	0.0451	0.0076	0.0451	0.0095
280	0.0757	0.0157	0.0392	0.0082	0.0390	0.0055
290	0.0694	0.0125	0.0350	0.0074	0.0336	0.0054
300	0.0639	0.0101	0.0323	0.0052	0.0290	0.0060
310	0.0591	0.0086	0.0308	0.0032	0.0251	0.0060
320	0.0552	0.0083	0.0300	0.0051	0.0219	0.0056
330	0.0522	0.0087	0.0296	0.0088	0.0194	0.0056
340	0.0501	0.0093	0.0293	0.0118	0.0175	0.0064
350	0.0490	0.0099	0.0286	0.0133	0.0163	0.0079
360	0.0490	0.0106	0.0273	0.0124	0.0157	0.0095
370	0.0501	0.0124	0.0250	0.0088	0.0157	0.0107
380	0.0525	0.0166	0.0213	0.0059	0.0162	0.0111

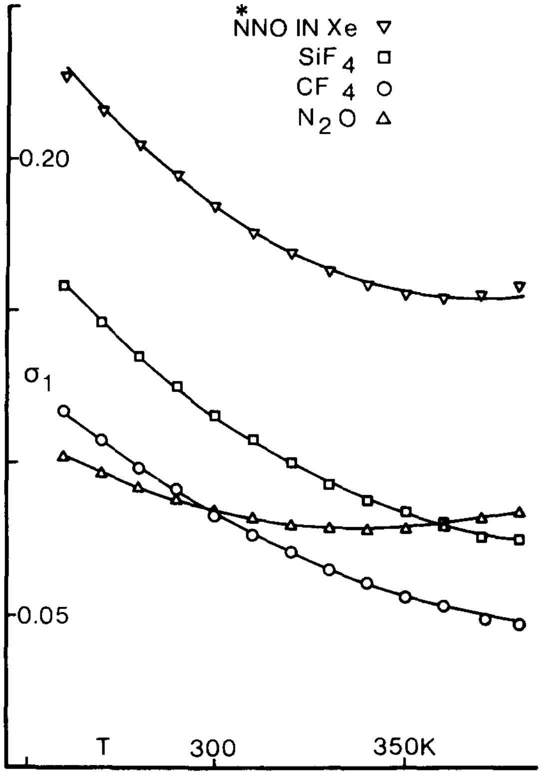

FIG. 3. The second virial coefficient of ^{15}N chemical shielding for the end ^{15}N in NNO interacting with NNO, CF_4, SiF_4, and Xe, in Hz/amagat at 9.12 MHz.

^{129}Xe and ^{19}F that the $\sigma_1(T)$ function has a greater temperature dependence for those systems with larger magnitudes of σ_1.[4,5,9,10] The temperature dependence of σ_1 for the ^{13}C nucleus in CO_2 was within the experimental error. Thus only an average value is reported.

Table V shows a summary of the $\sigma_0(T)$ and $\sigma_1(T)$ functions obtained in this work. $\sigma_0(T)$ is given in terms of $(\langle\sigma\rangle^T - \langle\sigma\rangle^{300})$ functions for ^{13}C and ^{15}N nuclei in these molecules. These are not the absolute magnitudes of the isotropic shielding but only the differences between the average shielding for the isolated molecule at some temperature T, $\langle\sigma\rangle^T$, and that at the chosen standard temperature which is 300 K, $\langle\sigma\rangle^{300}$.

By observing the ^{15}N spectra in a 1 : 1 mixture of $^{15}N^{15}NO$ and $^{15}N^{14}NO$, we can obtain the isotope shift of the end ^{15}N. These mixtures ranged from 20 to 40 amagat in density. The triplet due to ^{15}N in $^{15}N^{14}NO$ partly overlapped one of the two doublets from ^{15}N in $^{15}N^{15}NO$. The value of $\sigma(^{15}N \text{ in } ^{15}N^{15}NO) - \sigma(^{15}N \text{ in } ^{15}N^{14}NO)$ was found to be $+0.12$ ppm (measured as 1.03 Hz at 9.12 MHz), with a temperature and a density dependence of less than about 0.01 ppm. The isotope shift for the central ^{15}N, $\sigma(^{15}N \text{ in } ^{15}N^{15}NO) - \sigma(^{15}N \text{ in } ^{14}N^{15}NO)$, was not measured, but it is expected to be much smaller due to the generally smaller shifts we have found for the central N nucleus in NNO.

TABLE V. Temperature dependence of ^{15}N and ^{13}C shielding in ppm, expressed as field shifts in the form of a function $a_0 + a_1\tau + a_2\tau^2 + a_3\tau^3$ in which $\tau = T - 300$; $[\sigma(T,\rho) = \sigma_0(T) + \sigma_1(T)\rho]$.

	$\langle\sigma_0\rangle^T - \langle\sigma_0\rangle^{300}$, ppm		
Molecule	$10^3\, a_1$	$10^5\, a_2$	$10^7\, a_3$
CO_2	−0.5369		
N_2O (central)	−3.5881	+0.4102	+0.2009
N_2O (end)	−8.8816	−1.4682	+1.9513
	$\sigma_1(T)$, ppm/amagat		
Molecular pair	$10^3\, a_0$	$10^5\, a_1$	$10^7\, a_2$
^{13}C (CO_2, CO_2)	−2.0988		
Central ^{15}N (N_2O, N_2O)	−2.9956	1.3668	−2.9581
(N_2O, Xe)	−6.6254	5.1801	−4.9585
(N_2O, CF_4)	−3.5207	5.0964	−3.6901
(N_2O, SiF_4)	−3.7200	3.4457	−2.8666
End ^{15}N (N_2O, N_2O)	−9.8900	3.8364	−4.1778
(N_2O, Xe)	−22.0309	10.5648	−7.0529
(N_2O, CF_4)	−9.7594	8.0196	−3.5812
(N_2O, SiF_4)	−14.4045	10.0618	−5.4367

The ^{15}N–^{14}N coupling constant was 6.35 Hz and had a temperature and density dependence which was of the order of or less than 0.1 Hz, within the precision of the measurements. The isotope shift in the coupling constant is obtained as the difference $J_{^{15}N^{14}N} - J_{^{15}N^{15}N}\,\mu_{^{14}N}/\mu_{^{15}N}$. Using the magnetic moments by Baker, Anderson, and Ramsey for ^{14}N and ^{15}N (0.403562 nm for ^{14}N and -0.283049 nm for ^{15}N),[11] this difference is found to be $6.35 - 6.24 = 0.11$ Hz, just within our experimental precision. Therefore, neither the temperature/density dependence nor the isotopic shift of the coupling constant could be measured.

The 40 amagat sample of CO_2 was cooled to tempera-

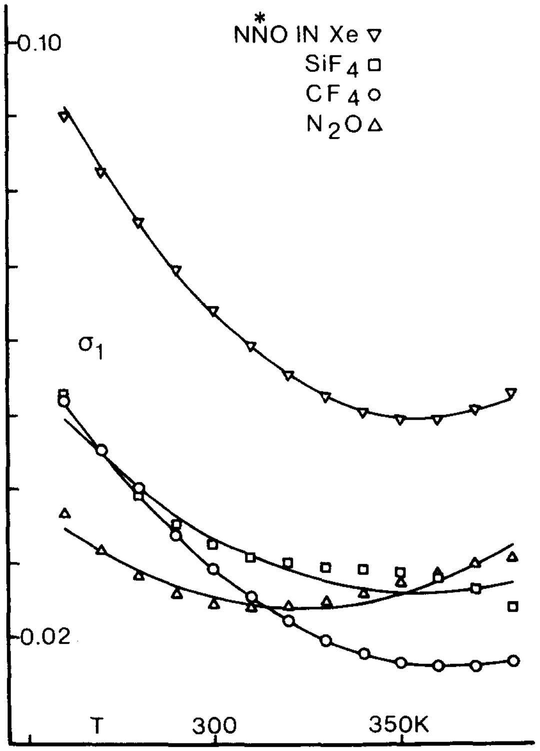

FIG. 4. The second virial coefficient of ^{15}N chemical shielding for the central ^{15}N in NNO interacting with NNO, CF_4, SiF_4, and Xe, in Hz/amagat at 9.12 MHz.

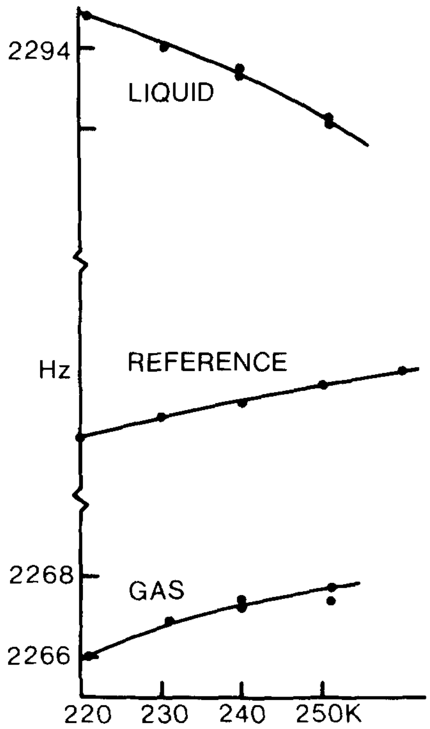

FIG. 5. The ^{13}C resonance frequencies at 22.63 MHz for CO_2 gas and liquid in equilibrium at various temperatures, showing the gas to liquid shifts at constant volume.

tures past the liquefaction point so that resonance signals from both liquid and gas were observed. The results are shown in Fig. 5.

DISCUSSION

We see in Figs. 1 and 2 that the shift due to rovibrational motion of the end ^{15}N is -0.00853 ppm/deg, that of central ^{15}N is -0.00334 ppm/deg, and the ^{13}C is about -0.00054 ppm/deg. The difference between the central ^{15}N and ^{13}C may be due in part to the differences in the rovibrational constants of the two systems. The most important contribution to the temperature dependence comes from the interaction of the nontotally symmetric vibration with the totally symmetric vibration, with the temperature dependence being determined primarily by the harmonic frequency of the nontotally symmetric vibration which appears in the term $\coth(hc\omega_2/2kT)$.[1] The harmonic frequencies in NNO are all smaller than the corresponding harmonic frequencies in CO_2. Of the three modes of vibration, the lowest frequency one contributes the largest temperature dependence.[1] In particular, ω_2 in $^{15}N^{15}NO$ is 579.17 cm^{-1} while in $^{13}C^{16}O_2$ ω_2 is 655.65 cm^{-1}.[12,13] The smaller ω_2 leads to a larger temperature dependence in $\coth(hc\omega_2/2kT)$.[1] Thus, the thermal average of the totally symmetric normal coordinate, $\langle q_1\rangle^T$, will have a larger temperature dependence in NNO than in CO_2. Of course, the temperature shifts are also dependent on the magnitude of $(\partial\sigma/\partial R)_{eq}$ which will be somewhat different for ^{13}C than for ^{15}N, particularly due to the differences in electronic environment around the central atom of CO_2 and NNO.

Comparing the shifts due to rovibrational motion in the two ^{15}N nuclei of the same molecule, we find that the therminal ^{15}N has a larger shift with temperature than the central ^{15}N in NNO (See Fig. 1). This difference is due entirely to the differences in $(\partial\sigma_{N\,(\mathrm{terminal})}/\partial R)_{eq}$ and $(\partial\sigma_{N\,(\mathrm{central})}/\partial R)_{eq}$ in NNO. Since both nuclei are in the same molecule the molecular constants in the rovibrational terms are strictly identical. For the end ^{15}N nucleus $(\partial\sigma/\partial R_{NN})_{eq}$ is expected to be larger than $(\partial\sigma/\partial R_{NO})_{eq}$, whereas for the central ^{15}N nucleus $(\partial\sigma/\partial R_{NN})_{eq}$ and $(\partial\sigma/\partial R_{NO})_{eq}$ are probably comparable. The larger shifts of the terminal ^{15}N (about 2.6 times as large as that of the central ^{15}N) may indicate that $(\partial\sigma/\partial R_{NN})_{eq}$ is that much greater for the end ^{15}N than for the central ^{15}N.

The measured $\sigma_1(T)$ includes the density dependence in bulk susceptibility, which can be calculated from the molar susceptibilities of the perturber molecule.[14] Table VI gives σ_{1_b}, the values of the bulk susceptibility contribution to σ_1, and the σ_1 values observed at room temperature. For the central ^{15}N in NNO and that ^{13}C in CO_2 the observed σ_1 is nearly entirely due to the bulk susceptibility of the perturber. The remainder is seen to be smaller than or about the same size as the standard deviation of the observed σ_1. For the terminal ^{15}N in NNO, $(\sigma_1-\sigma_{1_b})$ increases in the following order of the perturber: $CF_4 < NNO < SiF_4 < Xe$. This order is not unlike that observed for other nuclei in the presence of these perturber molecules. NNO is the only one out of place in its effectiveness as a perturber. For ^{129}Xe NNO has been found to be less effective than CF_4.[10] The difference may be due in part to the slightly polar nature

TABLE VI. The bulk susceptibility and other contributions to σ_1 of N_2O and CO_2 in Hz/amagat at 300 K observed at 9.12 MHz for ^{15}N and at 22.63 MHz for ^{13}C.

		Central ^{13}C and ^{15}N				Terminal ^{15}N		
Obs Nucleus	Perturber	σ_{1_b}	σ_1 obs	$\sigma_1-\sigma_{1_b}$	S.D. in σ_1 obs	σ_1 obs	$\sigma_1-\sigma_{1_b}$	S.D. in σ_1 obs
^{13}C	CO_2	0.0438	0.0475	0.0037	0.0100			
^{15}N	NNO	0.0161	0.0243	0.0087	0.0034	0.0845	0.0684	0.0026
^{15}N	CF_4	0.0264	0.0290	0.0026	0.0060	0.0829	0.0565	0.0053
^{15}N	SiF_4	0.0330	0.0323	-0.0007	0.0052	0.1158	0.0828	0.0087
^{15}N	Xe	0.0386	0.0639	0.0253	0.0101	0.1844	0.1458	0.0085

TABLE VII. Comparison of magnitudes of σ_1 for various nuclei, in ppm/amagat.

Nucleus	Range of σ_1 values
^{1}H	-0.008 or less[a]
^{13}C	-0.0022 to -0.0105[a]
^{11}B	-0.0123[b]
^{15}N	-0.0026 to -0.02
^{19}F	-0.006 to -0.07[a,c]
^{31}P	-0.265[d]
^{129}Xe	-0.166 to -0.75[e]

[a] A. K. Jameson, K. Schuett, C. J. Jameson, H. Parker, and S. M. Cohen, J. Chem. Phys. **67**, 2821 (1977).

[b] C. J. Jameson, A. K. Jameson, and J. Moyer (unpublished results).

[c] Reference 5.

[d] Calculated by Rummens (Ref. 16) from G. Heckmann and E. Fluck, Mol. Phys. 23, 175 (1972).

[e] References 4, 7, 9, 10.

of NNO which gives rise to electrical contributions to σ_1 for the NNO–NNO pair.

The much larger $(\sigma_1 - \sigma_{1_b})$ for the terminal ^{15}N compared to the central ^{15}N may be due to the fact that the former is more exposed than the latter and is more easily affected by collisions. This idea was placed into quantitative form by Rummens and Bernstein for ^{1}H shifts.[15] They considered an effectively spherical solute molecule with the observed nucleus on a spherical shell around the center of mass. According to their model, the $(\sigma_1 - \sigma_{1_b})$ for more exposed nuclei should be greater than that for less exposed nuclei in the same molecule. This was found to be qualitatively correct; however, quantitative agreement could not be obtained. A review of the "site effect" and examples of such calculations are given by Rummens.[16]

The ^{13}C shifts of CO_2 gas in equilibrium with liquid CO_2 are shown in Fig. 5. We note that the frequency shift of the gas is nearly entirely due to the shift of the reference, whereas the shift of the liquid signal with temperature is much more pronounced. The positive sign of $d\sigma/dT$ observed for the liquid CO_2 is consistent with other liquid systems such as ^{1}H in liquid C_6H_{12} and other molecules studied by Rummens, Raynes, and Bernstein,[17] ^{1}H and ^{19}F in liquid reference substances,[18] and the ^{129}Xe shift in liquid xenon.[19] This positive sign is the result of a sum of a negative term $(d\sigma_0/dT)$ and positive terms ($\rho\, d\sigma_1/dT$, $\sigma_1\, d\rho/dT$, etc.) with the positive contributions dominating. For the gas, on the other hand, the negative terms ($d\sigma_0/dT$ and $\sigma_1\, d\rho/dT$) and the positive term ($\rho\, d\sigma_1/dT$) very nearly cancel out each other. We note that the "gas-to-liquid shift" is not the unique number implied by the single value reported for many systems. In Fig. 5 we see that it depends on temperature. As the temperature increases we expect the gas-to-liquid shift to become zero at the critical temperature. For ^{13}C in CO_2 this tendency is already apparent over the 30 degree range in which it has been observed. An estimate of the higher order terms, σ_2, etc., can be obtained from the gas-to-liquid shifts observed. The density of liquid CO_2 varies from 553 to 515 amagat between 220 and 250 K.[20] Since the gas to liquid shift varies from 29 to 24.4 Hz in the same temperature range, σ_1 (apparent) is 0.0534 to 0.0496 Hz/amagat for the liquid. The difference between these numbers and the observed σ_1 for the gas, about 0.047 Hz/amagat, is due to the higher order terms, which appear to be negligible in this case.

Having measured values for a variety of nuclei, there are some generalizations we can make regarding $\sigma_1(T)$: (a) The sign of σ_1 is negative, i.e., there is always a downfield shift with increasing density, (b) the systems with large values of σ_1 also have a large change in σ_1 with temperature, and (c) the usual temperature dependence of σ_1 is that its magnitude decreases with increasing temperature. With the ^{13}C and ^{15}N data given here, we can compare the magnitudes of σ_1 for various nuclei. These are shown in Table VII. We see that although there is a spread of magnitudes of σ_1 for each nucleus, the size of σ_1 roughly increases with the number of electrons of the atom. It is not surprising that the magnitude of σ_1 depends on atomic number in the same way as the range of chemical shifts does.[21] There is a range of σ_1 values for each nucleus due to differences in intermolecular potential functions; however, the average size of σ_1 for different nuclei is primarily dependent on $\sigma(R, \theta)$ in the vicinity of the potential minimum, the order of magnitude of which is expected to change with atomic number.

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