of necessity rather high ion concentrations. (For comparison, the conductances are comparable to those of 0.1 molar salt solutions in water.) It is of interest that the observed values of ϵ^* indicate the existence of higher frequency relaxations of relatively small amplitude. This is qualitatively in agreement with the theoretical prediction of a series of relaxation times from τ_D to the longitudinal relaxation time $\tau_L = (\epsilon_\infty/\epsilon_S)\tau_D$, but detailed comparisons must await further analysis of the data and theoretical calculations.

We believe that these and other results, to be published later, are a striking confirmation of the theoretical predictions and of little recognized but important ion–solvent interaction effects in electrolyte solutions. Studies of the effects in other solvents for smaller ion concentrations and without hydrogen bonding or proton transfer are in progress.

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NOTES

Second virial coefficient of ^{129}Xe chemical shielding in Xe interacting with CO and N_2 molecules

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The density and temperature dependence of ^{129}Xe chemical shifts have been observed in mixtures of xenon with various gases.[1,2] In all these systems it has been found that it is possible to make NMR measurements in gases at sufficiently low density such that only binary intermolecular interactions are observed. Then the chemical shielding of ^{129}Xe may be written as

$$\sigma_{^{129}\text{Xe}} = \sigma_0 + \sigma_1(^{129}\text{Xe}, \text{Xe})\rho_{\text{Xe}} + \sigma_1(^{129}\text{Xe}, \text{A})\rho_{\text{A}} .$$

Since the second virial coefficient of chemical shielding of ^{129}Xe has been measured in pure xenon, then the effects due to the second term in the above equation are known. By using samples of low density in xenon, the effects due to $\sigma_1(^{129}\text{Xe}, \text{A})$ can be made dominant and can be measured with a high degree of precision. The temperature dependence of $\sigma_1(^{129}\text{Xe}, \text{A})$ has been determined for various molecules (Xe, Kr, Ar, CF_4, CH_4, SiF_4, SF_6, C_2H_2, C_2H_4, C_2H_6, HCl, HBr, NNO, CO_2, and BF_3). The values of σ_1 for ^{129}Xe interacting with these molecules range from 4–13.7 Hz/amagat at room temperature. In general the temperature dependence of σ_1 has been found to be related to the magnitude of σ_1. The systems with the larger values of σ_1 were also found to exhibit the greatest temperature dependence. Although a partial analysis of this behavior has been possible for xenon interacting with spherical tops, the successful quantiative treatment of this behavior has lagged considerably behind the precision of the experimental measurements of the $\sigma_1(T)$ function.

All the $\sigma_1(T)$ functions previously reported for ^{129}Xe as well as for other nuclei (e.g., ^{19}F and ^{13}C)[3-5] have been found to have negative temperature coefficients: The magnitude of σ_1 decreased with increasing tempera-

TABLE I. ^{129}Xe $\sigma_1(T)$ function for Xe interacting with CO and N_2 in ppm/amagat. $\tau = T - 300$ K.

	σ_1				average s.d.
CO	-0.25244	$-2.639\times10^{-4}\tau$	$+3.304\times10^{-7}\tau^2$	$+5.328\times10^{-9}\tau^3$	0.0276
N_2	-0.20947	$-1.447\times10^{-4}\tau$	$-6.818\times10^{-7}\tau^2$	$+1.179\times10^{-8}\tau^3$	0.0203

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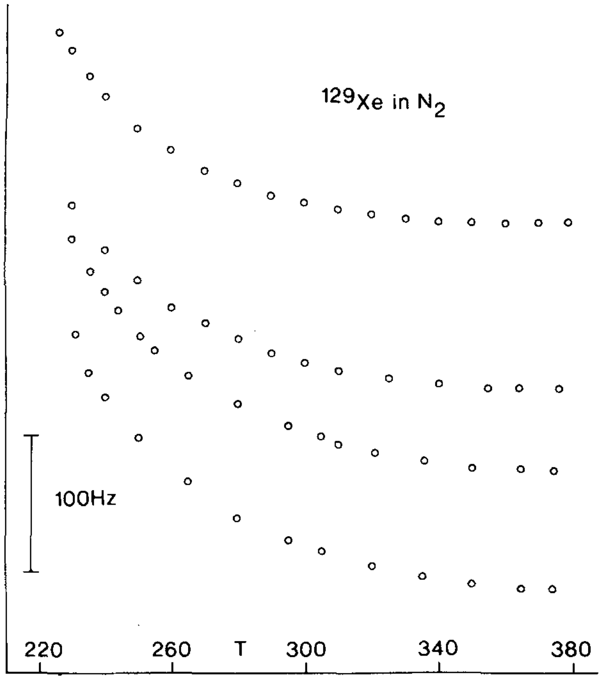

FIG. 1. Xenon-129 NMR frequencies observed as a function of temperature in samples with the following densities (top to bottom): 39.26 Xe and 145.18 N_2, 39.15 Xe and 127.54 N_2, 40.10 Xe and 103.80 N_2, 40.00 Xe and 90.83 N_2, all in amagats.

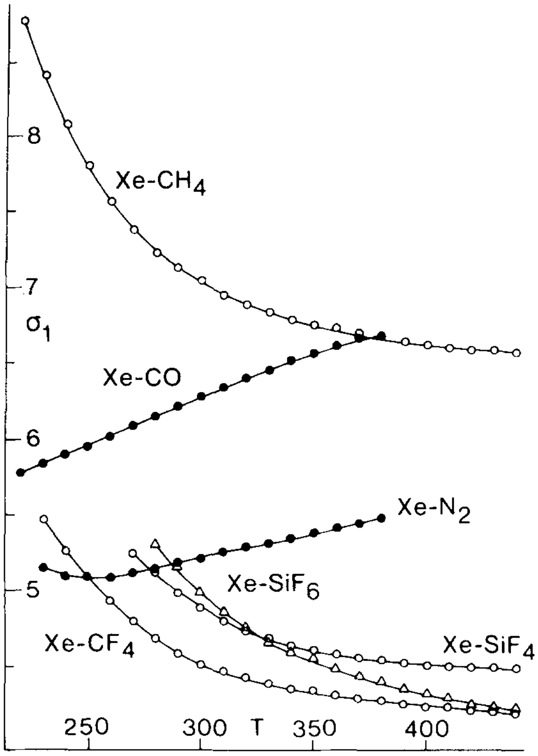

FIG. 2. σ_1 in Hz/amagat at 24.89 MHz for ^{129}Xe in CO and N_2, compared with other systems previously reported (Ref. 2).

ture. There is no *a priori* reason why this should be uniformly true for all systems. However, no counter-examples have ever been previously observed. In this work we report for the first time $\sigma_1(T)$ functions with a positive temperature coefficient, which we observed in ^{129}Xe interacting with N_2 and CO.

The experimental details, sources of error and method of data analysis have been described in previous papers.[2] Xenon-129 FT NMR spectra were observed at 24.89 MHz in samples containing 40 amagat of xenon and 30–145 amagat of N_2 or CO. The typical results are shown in Fig. 1. The frequency separation between a high density sample and a low density sample is seen to increase as the temperature increases. Thus, the raw data indicate that the magnitude of σ_1 increases with increasing temperature for ^{129}Xe in Xe interacting with either a CO or an N_2 molecule. Figure 2 shows the $\sigma_1(T)$ function for both these systems, compared with Xe in CH_4, CF_4, SiF_4, and SF_6. The values are given in Table I with the standard deviations. The magnitudes of σ_1 are known only to within 10% relative error, primarily due to errors in the density of the samples. However, the precision of the temperature dependence for each sample is sufficiently high to give a relative error in $d\sigma_1/dT$ of only 0.75% for ^{129}Xe in CO and 2% for ^{129}Xe in N_2.

Although these $\sigma_1(T)$ functions behave unlike all others previously reported, it is not necessary to invoke any new model to account for this behavior. Consider a $\sigma(R)$ function such as the one resulting from the direct inversion of $\sigma_1(T)$ in pure xenon.[6] So long as the magnitude of the $\sigma(R)$ function is large at $R \simeq r_e$ then the integral

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

results in a $\sigma_1(T)$ function whose magnitude is decreasing with T, such as the Xe in CH_4, SiF_4, SF_6, or CF_4 systems shown in Fig. 2. If however, the magnitude of $\sigma(R)$ is small at $R \simeq r_e$ and large elsewhere, e.g., inside r_0, then the integral results in a $\sigma_1(T)$ function whose magnitude increases with increasing temperature, such as the one observed here for ^{129}Xe interacting with CO or N_2.

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