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Density dependence of ^{129}Xe N.M.R. chemical shifts in O_2 and NO

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Previous work on ^{1}H, ^{19}F and ^{129}Xe N.M.R. chemical shifts in gaseous systems [1–3] shows that, within experimental error, the chemical shift is linearly dependent on density (except in the case of pure xenon in which the density dependence of the ^{129}Xe chemical shift shows a definite curvature [3]). That is, in the virial expansion of chemical shielding in powers of density, ρ:

$$\sigma = \sigma_0 + \sigma_1 \rho + \sigma_2 \rho^2 + \ \dots ,$$

only the linear density term need be included. σ_1 is measured as the slope of the plot of chemical shift versus density. For a mixture of xenon and a second gas A,

$$\sigma \simeq \sigma_0 + \sigma_1(\mathrm{Xe{-}Xe})\rho_{\mathrm{Xe}} + \sigma_1(\mathrm{Xe{-}A})\rho_A ,$$

where ρ_{Xe} and ρ_A are the densities of xenon and A. Since σ_1(Xe–Xe) has previously been determined with good precision, σ_1(Xe–A) is readily determined. Our previous work on the ^{129}Xe shifts in mixtures with other gases such as Ar, Kr, CO_2, HCl, CH_4, CF_4 and the fluoromethanes showed slopes, σ_1(Xe–A), of 3120 to 12 280 p.p.m./mole cm^{-3}.

Additional data have now been obtained for mixtures of Xe with O_2 and Xe with NO at room temperature. The results are shown in figure 1. The standard deviations given include only random errors. In the case of NO there may be a small (certainly no more than 10 per cent) systematic error resulting from reaction between NO and Hg in the few seconds that they are in contact while the remaining NO is being swept into the sample tube from the calibrated volume. This would lead to a slightly smaller σ_1. The ^{129}Xe shifts are downfield, as usual, and appear to be linear, within experimental error in the density of O_2 or NO. The slopes are much larger than any observed before in the gas phase. The susceptibility of the second gas, which was generally small and diamagnetic in the previous work, is now a sizeable fraction of the shift observed. If corrected for the susceptibility, the density dependence would be given by $\sigma_1(\mathrm{Xe{-}}A) - (2\pi/3)\chi_A$, where χ_A is the molar susceptibility of the second gas A. These are given in the table, where data on argon are included for comparison. The density dependence due to specific interactions between Xe and O_2 or NO molecules is thus found to be much larger than any values previously measured in gases.

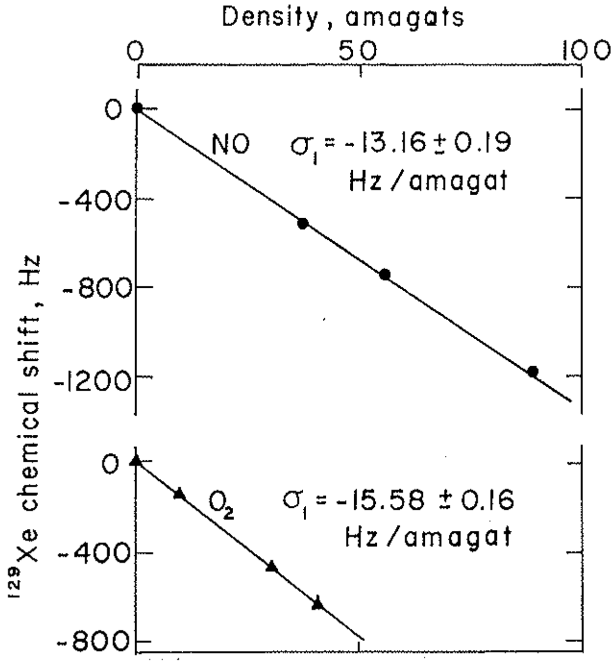

Figure 1. Density dependence of the ^{129}Xe chemical shift in mixtures of xenon and O_2, xenon and NO, at 25 °C, 16·60 MHz.

A	σ_1	$(2\pi/3)\chi_A$	$\sigma_1-(2\pi/3)\chi_A$
O_2	-21037 ± 216	$+6978$	-28015
NO	-17769 ± 256	$+2967$	-20736
Ar†	-3119	-39	-3080

† Argon is included for comparison, it has roughly the same polarizability.

Values of σ_1(Xe–A) at 25 °C in p.p.m./mole cm^{-3}.

The xenon absorption signal is considerably broader in the mixtures of Xe and O_2 and Xe and NO than in mixtures of Xe and diamagnetic gases. However, in the dispersion mode, in which all measurements were done, the shorter relaxation times of Xe in O_2 and NO led to a better signal (one which did not saturate as easily as the Xe signal in diamagnetic gases).

It was found earlier that the density dependence due to specific interactions between Xe and other gas molecules appeared to be dependent to some extent on the polarizability of the foreign gas, as shown in figure 2. However, O_2 and NO appear anomalously high on this plot. One hypothesis to explain the unusually large shifts is that the mechanism is the Knight or contact shift. There are several possible contributions here: the finite density of the nitric oxide or oxygen unpaired electrons at the xenon nucleus even in the absence of any interactions between their electrons, the overlap contribution, the spin polarization of the closed shells of xenon and even a pseudo-contact contribution due to the anisotropy of the *g* tensor. Another hypothesis is that valence interactions between xenon and oxygen result in a deeper potential well than the mean of the xenon–xenon and oxygen–oxygen potential wells, thereby giving rise to a large

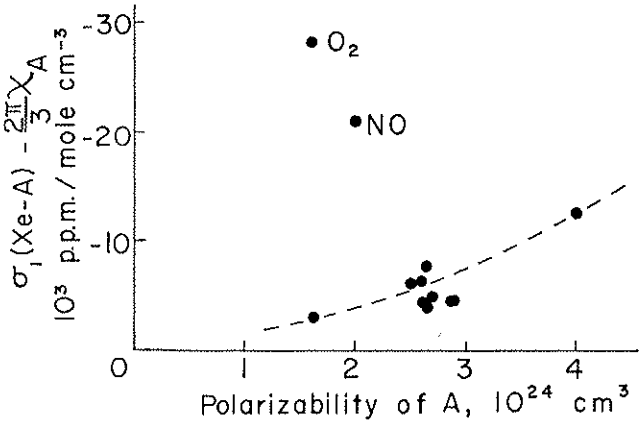

Figure 2. Variation of density dependence of ^{129}Xe chemical shift (corrected for bulk susceptibility) with the polarizability of solvent gas *A*. The unlabelled points correspond to Ar, Kr, CO_2, HCl, CH_4, CF_4, CH_3F, CH_2F_2, CHF_3 and Xe itself.

downfield shift. It is likely that the results can be explained by a combination of the above mechanisms.

If the first is the dominant mechanism, then we are seeing contact shifts of this type for the first time. Contact shifts are normally observed when the unpaired electron is on the same molecule as the nucleus under observation. In this case, however, the ^{129}Xe nucleus in the xenon molecule and the unpaired electron in the oxygen molecule meet only during a collision and the average over such transient meetings is observed. If the second is the dominant mechanism then we might well be able to determine the xenon–oxygen potential curve experimentally, which in this case would be vastly different from the mean of the xenon–xenon and oxygen–oxygen potential curves. This would not be entirely surprising in the light of known compounds like XeO_3.

The temperature dependence of these shifts is presently being studied. This may allow us to distinguish between the possibilities considered above.

It should be noted that in the ^{1}H and ^{19}F N.M.R. of gases such as CH_4 or CF_4 mixed with O_2, σ_1 is so small as to be overwhelmed by the bulk susceptibility density dependence, leading to net *upfield* shifts [4].

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