Temperature and density dependence of ^{129}Xe chemical shift in rare gas mixtures

Cynthia J. Jameson

Department of Chemistry, University of Illinois at Chicago Circle, Chicago, Illinois 60680

A. Keith Jameson

Department of Chemistry, Loyola University, Chicago, Illinois 60626

Sheila M. Cohen

Department of Chemistry, University of Illinois at Chicago Circle, Chicago, Illinois 60680

(Received 20 November 1974)

Pulsed Fourier transform NMR spectroscopy was used to obtain ^{129}Xe chemical shifts in gases with densities of xenon much lower than ever before observed. At densities of 3–28 amagat, the contamination of the desired linear term in chemical shielding by contributions due to three-body or higher order interactions is completely eliminated. This allows the determination of very precise values of $\sigma_1(T)$ for ^{129}Xe in xenon, krypton, and argon gas.

In our previous work on ^{129}Xe NMR chemical shifts, we found that as we proceeded to higher densities, the effect of three-body or higher order interactions is to give the apparent second virial coefficient of chemical shielding a greater curvature with temperature than it should have.[1] Under the cw mode of running the NMR spectrometer, even with signal averaging of the cw spectra to improve the signal to noise ratio, there were practical limitations on the lower limit of Xe density which could be observed. Thus, no samples with densities below 20 amagats could be observed previously. However, in order to obtain values of the second virial coefficient uncontaminated with 3-body or higher order interactions, it is necessary to observe samples with much lower densities of Xe. Using the pulsed Fourier transform mode of operation it is possible to routinely observe ^{129}Xe resonance in samples containing as little as 3 amagats of Xe. The results reported here are the second virial coefficients of ^{129}Xe chemical shielding in pure xenon, ^{129}Xe in krypton, and ^{129}Xe in argon gas. The new data in pure xenon should be nearly entirely due to binary interactions and give more accurate values of $\sigma_1(T)$. Such values are shown in Table I.

EXPERIMENTAL

Natural abundance ^{129}Xe NMR spectra were obtained at 24.89 MHz on a Bruker HFX-90 variable frequency spectrometer. The pulsed Fourier transform (FT) mode was utilized consistently in this work. A Bruker B-KF 322s pulsed NMR spectrometer provided gated rf power amplification, and a NIC-293 controller served as a pulse programmer. A Nicolet 1080 data system was used to accumulate the free-induction decays. Because of the simplicity of the ^{129}Xe spectra, acquisition of 2K data points on each free-induction decay provided adequate definition. Depending on the density of xenon in the sample, a satisfactory signal-to-noise ratio was achieved by collecting 32 to 512 such transients. In most cases the apparent sensitivity was improved further by exponential weighting of the free-induction decays prior to transformation on the data-system computer. The transformed, phase-corrected real spectra provided chemical shift accuracy of better than 0.4 Hz per channel.

In the pure gas, the ^{129}Xe relaxation time is extremely long.[2] Thus, trace amounts of oxygen (~ 0.2 amagats) were added to each sample to shorten T_1 sufficiently that realistic pulse recycle times could be used. With this modification, a recycle time of 2.67 sec was typical; a 90°/4 rf pulse had a duration of about 4 μsec. The correction of the xenon chemical shift for the effect of the measured amount of trace oxygen is a straightforward calculation. With particular reference to samples of low density in xenon, the increased precision and signal enhancement obtainable with this technique over those possible using cw-mode operation are impressive and more than compensate for the minor inconvenience of the oxygen correction. Whereas heretofore the lowest sample density practical was ~ 20 amagats in xenon, we now routinely take spectra of acceptable S/N ratio of samples that are of ultra-low density in xenon (~ 5 amagats) by collecting only 256 to 512 transient responses.

Achievement of the optimum signal under cw operation necessitated observation of the first audio sideband of the ^{129}Xe resonance frequency. The FT results, however, correspond to the ^{129}Xe resonance frequency centerband. The magnetic field strength was identical in each case and the two experiments are brought into agreement by adding the modulation frequency (3.9 kHz) to each cw-mode resonance frequency.

The experiment remains as previously reported[1] in all other significant details, such as sample preparation, temperature regulation, internal field/frequency lock system (either ^{19}F or ^{1}H depending upon temperature range), use of a frequency synthesizer to generate the mixing frequency, and use of three lock substances, viz., 1,4-dibromotetrafluorobenzene, hexafluorobenzene, and TMS, to cover the temperature range from 440 °K down to the point of liquefaction of the sample.

Control samples of pure xenon of approximately the

TABLE I. $\sigma_1(\text{Xe}-A)$, the second virial coefficient of xenon with various rare gases, in Hz amagat^{-1} at 24.897 MHz.[a] $\sigma_1(\tau)=a_0+a_1\tau+a_2\tau^2+a_3\tau^3+\cdots$, where $\tau=T-300$ K.

A	a_0	a_1 $\times 10^3$	a_2 $\times 10^5$	a_3 $\times 10^7$	a_4 $\times 10^9$	a_5 $\times 10^{11}$
Xe[b]	13.763	−28.525	20.424	−9.015	2.173	−0.262
Kr	7.267	−8.780	9.864	−10.450	6.852	−1.781
Ar	4.688	−2.902	3.089	−5.757	5.383	−1.671

[a] The numberical data above may be expressed in terms of $\Delta H/H$ and in units of ppm amagat^{-1} by reversing all signs and dividing by 24.897.

[b] This was obtained in samples of densities 3 to 28 amagats and supercedes the earlier reported $\sigma_1(T)$ function for Xe.

same density as the Xe density in the mixtures were prepared at the same time and their spectra taken along with the mixtures, as a check for possible systematic experimental errors. The densities of the buffer gas were kept to 40 amagats or less in order to minimize the contributions of σ_2 and higher order terms in the virial expansion of the chemical shielding.

There are several sources of error in our measurements:

1. Temperature control: The automatic temperature regulator is accurate to at least 1 °C, with a precision of about ± 0.2 °C. A xenon sample is used as a secondary thermometer as a control to assure accuracy of the regulator from month to month.

2. Peak measurement: In the Fourier transform mode the spectrum, transformed to the frequency domain, is composed of discrete points. Under our conditions these are separated by 0.4 Hz so the peak position is measured to ± 0.2 Hz (maximum deviation).

3. Sample volume: Each sample tube is calibrated with Hg. The major error comes in sealing the sample tube. Careful tests place this error at $<\pm 0.001$ ml. Under our conditions this would lead to an expected error in density of $\sim\pm 0.5\%$ and hence an error in frequency of <0.3 Hz at 5 amagats of Xe. This agrees well with our observed standard deviation of ~ 0.2 Hz for pure Xe data. Errors because of (a) inaccuracies in the density of Hg due to temperature variation during calibration, (b) temperature coefficient of expansion of borosilicate tubing, and (c) compressibility of borosilicate tubing have been estimated. Even though (b) and (c) cause systematic errors they are all so small as to have negligible contributions when compared to our observed random errors.

4. Gas measurement: The gases are measured with a precision of ± 0.3 torr, ± 0.1 °C by noting the pressure of the gas trapped in a calibrated volume (27.18 ml) at room temperature at 50–300 torr. The ideal gas law at 300 °K and < 300 torr is used to calculate the moles of trapped gas. The gas defect under these conditions for the rare gases is totally negligible. The trapped gas is then swept into and frozen in a previously calibrated sample tube. Incomplete freezing of the gas, due to its finite vapor pressure at 77 °K, results in an error of no more than 0.2 amagats.

5. Higher-order interactions: The observed chemical shielding σ can be expressed as

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

where the $\sigma_1\rho$ term is due to binary interactions, the $\sigma_2\rho^2$ term is due to three-body interactions, etc. Interactions more complex than binary have been demonstrated to occur in pure xenon.[3] Binary interactions are the primary interest in this work. Hence, in order to obtain σ_1 unambiguously, measurements have to be carried out in a density regime low enough to insure that effects of higher order interactions are really negligible in comparison with our demonstrated experimental errors. In the case of pure xenon, $\sigma_2(T)$ has been obtained between 250 and 300 K.[1] From this the error made at various temperatures by neglecting terms beyond those which are linear in density can be estimated. At 250 K this error is no larger than 2 Hz for a sample containing 8 amagats of xenon. Thus, the small many-body contribution of Xe_n $(n>2)$ can be neglected at all accessible temperatures for a xenon density of about 8 amagats.

6. Isolation of the Xe–buffer interaction: By keeping the Xe density about 8 amagats, for reasons discussed above, our data can be reliably interpreted as due to contributions from three types of interactions:

$$\sigma=\sigma_0+T_{\text{Xe}}+T_{\text{O}_2}+T_A ,$$

where

$$T_{\text{Xe}}=\sigma_1(\text{Xe}-\text{Xe})\rho_{\text{Xe}} ,$$

$$T_{\text{O}_2}=\sigma_1(\text{Xe}-\text{O}_2)\rho_{\text{O}_2} ,$$

$$T_A=\sigma_1(\text{Xe}-A)\rho_A+\sigma_2(\text{Xe}-A)\rho_A^2+\cdots .$$

At low densities of buffer gas the term linear in buffer gas density (ρ_A) completely dominates. Typical values of the three terms are

$$T_{\text{Xe}}\sim 100\text{–}150\ \text{Hz} ,$$

$$T_{\text{O}_2}\sim 6\text{–}12\ \text{Hz} ,$$

$$T_A\sim 150\text{–}400\ \text{Hz} .$$

Hence, 50–70% of the chemical shift relative to the isolated xenon atom is due to the binary buffer gas–xenon interaction.

RESULTS

For each lock substance temperature range the frequency versus temperature data is adequately fitted in a least squares sense to a polynomial of degree 2:

$$\nu=a_0(\rho_A,\rho_{\text{O}_2},\rho_{\text{Xe}})+a_1(\rho_A,\rho_{\text{O}_2},\rho_{\text{Xe}})(T-t_0)+a_2(\rho_A,\rho_{\text{O}_2},\rho_{\text{Xe}})(T-t_0)^2 ,$$

where $t_0=300$ °K for the TMS and C_6F_6 ranges and $t_0=350$ °K for the DBTFB range. No significant improvement in standard deviation was obtained with higher degree polynomials.

For each sample and for each lock substance temperature range, the parameters $a_i(\rho_A,\rho_{\text{O}_2},\rho_{\text{Xe}})$, $i=0$, 1, 2 were obtained by the polynomial fitting procedure. The $a_i(\rho_{\text{Xe}})$ were calculated from previous pure xenon measurements and subtracted from the measured $a_i(\rho_A$

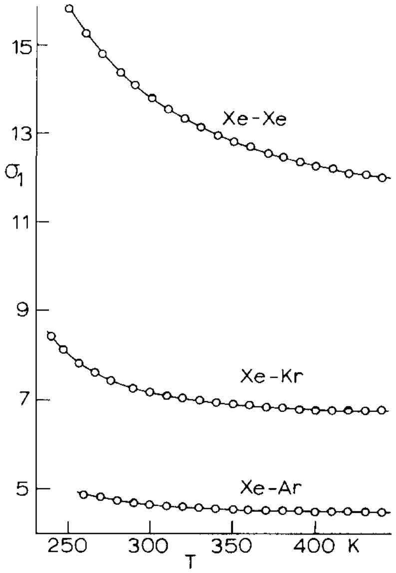

FIG. 1. Temperature dependence of the second virial coefficient of chemical shielding, $\sigma_1(T)$ in Hz amagat^{-1}, for ^{129}Xe in Xe, in Xe–Kr and Xe–Ar mixtures.

ρ_{O_2}, ρ_{Xe}) values. This has the effect of subtracting out all the lock solvent temperature dependence and the effect of Xe–Xe interactions, leaving only Xe–other gas interactions. To the precision that the polynomial describes the experimental frequency versus temperature data, this procedure leaves frequencies corrected to zero density in Xe in terms of $a_i(\rho_A, \rho_{O_2})$. In the same manner, the effect of Xe–O_2 interactions are subtracted out using the $a_i(\rho_{O_2})$ from previous xenon in oxygen gas measurements reported elsewhere,[4] leaving frequencies as a function of temperature in terms of $a_i(\rho_A)$. This procedure is valid only if no interactions of higher order than binary interactions are important. Plots of these ^{129}Xe frequencies vs density of the buffer gas are linear within experimental error.

A computer program was written to fit the experimental points to a polynomial of degree 2, subtract out the Xe–Xe and lock solvent contributions, and subtract out the Xe–O_2 interactions. For each temperature a least squares fit of the resulting frequency versus density of the foreign gas is carried out by the program, and the slope, $\sigma_1(\text{Xe}-A)$ is determined at each temperature. These temperature dependent second virial coefficients of chemical shielding for the rare gases are shown in Fig. 1. The resulting $\sigma_1(\text{Xe}-A)$ vs T over all three temperature ranges can adequately be described in terms of a polynomial of degree 5 in $\tau = T - 300$ K. These functions are given in Table 1. Terms up to at least τ^3 are needed to obtain a reasonable fit. No minima are observed in the temperature ranges which have been covered. This does not preclude the possibility of a minimum at some higher temperature, however. Since the densities of the foreign gases were kept to 40 amagats or less, specifically to minimize the effect of the third virial coefficient and higher order terms in the virial expansion, no attempt was made to extract any value for σ_2 from the measurements.

Earlier data on σ_1 at room temperature[3] for Xe–Kr and Xe–Ar compare favorably with those obtained in this study. With the much lower densities used and the superior precision of the measurements, these present data give more accurate values for σ_1 than the earlier measurements.[1,3] In particular, the Xe in pure xenon data reported here gives more accurate second virial coefficients uncontaminated with 3-body or higher-order interactions, due to the ultra-low densities of samples used.

DISCUSSION

It is interesting to determine what the law of corresponding states implies regarding the relationship between the second virial coefficients of chemical shielding, σ_1, for Xe–Xe, Xe–Kr, and Xe–Ar pairs. For spherically symmetric molecules such as the rare gases, the integration of the chemical shielding function over all configurations is a simple one:

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

σ_1 can be written in "reduced" form as:

$$\sigma_1(\theta) = 4\pi r_e^3 \int_0^\infty \sigma(\rho) \exp\{-V'(\rho)/\theta\} \rho^2 d\rho$$

where $\theta = kT/\epsilon$, $\rho = r/r_e$, $V'(\rho) = V(\rho)/\epsilon$, with ϵ being the depth of the potential well. $V'(\rho)$ for rare gases is approximately independent of the rare gas pair. This is the reason that the reduced second virial coefficient, $B^*(\theta) = B/Nr_0^3$, is approximately the same for many molecular pairs. In the same spirit as $B^*(\theta)$, $\sigma_1(\theta)/r_e^3$ would be expected to be the same for the rare gas pairs if $\sigma(\rho)$ were identical for Xe–Xe, Xe–Kr, and Xe–Ar.

Calculations show that $\sigma_1(\theta)/r_e^3$ for Xe–Kr and Xe–Ar differ from $\sigma_1(\theta)/r_e^3$ for Xe–Xe roughly by a factor of 2/3 and 1/2, respectively. This shows that the second virial coefficient for chemical shielding is more complicated than $B^*(\theta)$, that $\sigma(\rho)$ is not independent of the molecular pair. In principle this increased complexity means that correspondingly more information is available in $\sigma_1(\theta)$ than in $B^*(\theta)$.

Finally, if $\sigma(R)$ were proportional to some power n of the intermolecular potential then $\sigma_1(\theta)/r_e^3\epsilon^n$ is expected to be approximately constant. The value of n is found to be clearly greater than 1, the best integral value being $n = 2$.

ACKNOWLEDGMENT

Acknowledgment is made to the National Science Foundation for the support of this research (GP-29717).

---

[1] C. J. Jameson, A. K. Jameson, and S. M. Cohen, J. Chem. Phys. 59, 4540 (1973).

[2] R. L. Streever and H. Y. Carr, Phys. Rev. 121, 20 (1961).

[3] A. K. Jameson, C. J. Jameson, and H. S. Gutowsky, J. Chem. Phys. 53, 2310 (1970); E. Kanegsberg, B. Pass, and H. Y. Carr, Phys. Rev. Lett. 23, 572 (1969).

[4] C. J. Jameson, A. K. Jameson, and S. M. Cohen, to be published.