Effect of interactions with nonspherical molecules on ^{129}Xe magnetic shielding

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Second virial coefficients of chemical shielding are reported for Xe interacting with HBr, HCl, CO_2, N_2O, C_2H_2, C_2H_4, C_2H_6, and BF_3 from 230 to 440 K. Values range from 0.15 to 0.52 ppm amagat^{-1}. There is some evidence for the anisotropy of the potential function for Xe and these molecules.

The anisotropy of the intermolecular potential has attracted some interest in recent years. However, there is still very little quantitative information available even for atom–diatomic molecule pairs. The asymptotic form of the anisotropic long range potential has been derived by Buckingham,[1] and for simple systems estimates have been made of the parameters of the anisotropic part. While spectroscopic measurements on a number of van der Waals molecules have been made, the data for the hydrogen complexes with rare gases are the only ones at present capable of yielding realistic multidimensional potential energy surfaces. Such functions have been obtained by LeRoy and Kranendonk from nonlinear least-squares fits of model spectra calculated from trial potential energy functions to the observed precise measurements of the fine structure which accompanies collision-induced infrared absorption spectra of molecular hydrogen at low temperatures and densities.[2] The very precise measurement of these spectra by McKellar and Welsh yields the fine structure which is due to transitions between rotational levels of the van der Waals complexes formed between hydrogen molecules and Ne, Ar, Kr, and Xe atoms.[3]

It has been shown by Neilsen and Gordon that significant information about the anisotropic intermolecular potential is contained in experimental data related to rotationally inelastic collisions such as spin and rotational relaxation times and line shapes of infrared or Raman lines.[4] Anisotropic intermolecular potentials for H_2–He have been obtained by Riehl *et al.* from an analysis of spin–lattice relaxation times, and by Shafer and Gordon from an analysis of rotational relaxation times, spin–lattice relaxation times, and Raman line shapes.[5] Neilsen and Gordon have found the potential parameters which give the best agreement between selected experimental data and the values obtained by semiclassical calculations on the rotationally inelastic collisions between HCl and argon.[6] The temperature dependence of the sound absorption is found to be very sensitive to the anisotropy of the potential whereas the temperature dependence of the spin relaxation times are not. They find that combining the results of different experiments (for example, linewidths and line shifts of far infrared dipole absorption lines, and proton spin relaxation times) permits more information about the anisotropy of the potential to be extracted since different experiments provide different pieces of information about the potential. The limitations on the accuracy of the potential parameters are nearly entirely those of the uncertainty of the experimental data. As more experiments are done and data of greater accuracy are obtained, the degree to which the parameters are forced to compensate for the restricted potential form can be lessened by the adoption of a more flexible function. There is a clear need for more experimental data which are capable of being obtained with high precision and which are sensitive to the anisotropy of the potential function.

The nuclear magnetic shielding of ^{129}Xe is a very good probe for intermolecular interactions. Since an isolated xenon atom has no rotational, vibrational, or low-lying electronic states, it should have an NMR signal which is independent of temperature. Any temperature dependence of the ^{129}Xe signal which is observed in a sample containing xenon and other molecules must therefore be due to the dependence of the intermolecular interactions on temperature. By observing ^{129}Xe in samples containing a very low density of xenon and varying densities of another gas, we are able to determine the change in frequency with respect to density at various temperatures. This, the second virial coefficient of ^{129}Xe chemical shielding, σ_1, is always found to decrease in magnitude as the temperature is increased. We have previously measured σ_1 for Xe interacting with Xe, Kr, and Ar, and with spherical top molecules such as CH_4, CF_4, and SiF_4.[14] In this paper, we report second virial coefficients of ^{129}Xe chemical shielding for Xe interacting with nonspherical molecules. We hope to find some evidence of the anisotropy of the potential between Xe and solvent molecules which are rod shaped and disk shaped, as opposed to spherical ones.

Unlike experimental data related to rotationally inelastic collisions, chemical shifts are not so simply related to the intermolecular potential. The general form of the relationship between the observed quantity $\sigma_1(T)$ and the potential $V(R, \theta)$ is well known:

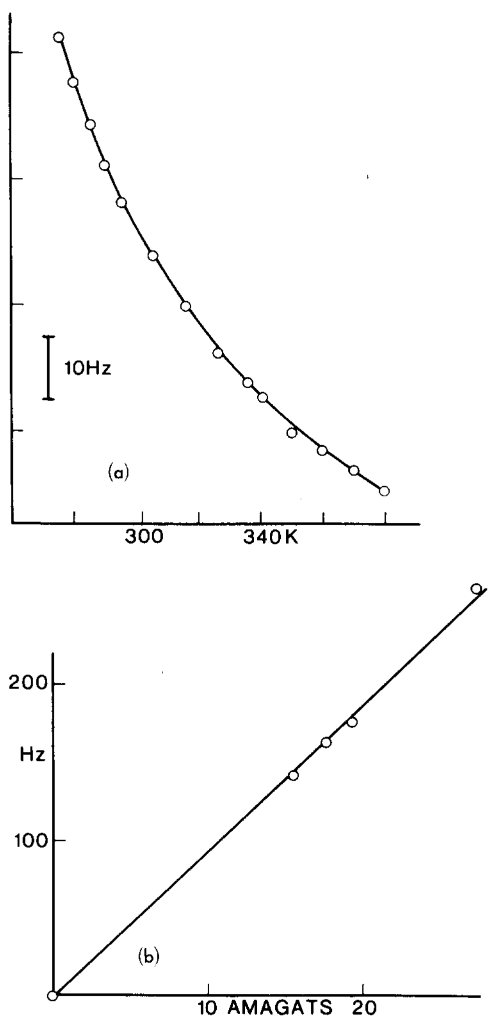

FIG. 1. Typical results showing (a) raw data, (b) linear dependence of frequency on density at a given temperature. The slope is the value of σ_1 at that temperature.

$$\sigma_1(T)=2\pi\int_{r=0}^{\infty}\int_{\theta=0}^{\pi}\sigma(R,\theta)\,e^{-V(R,\theta)/kT}R^2dR\sin\theta d\theta.$$

However, $\sigma(R, \theta)$ is itself not known either in general form or for a specific system. Previous attempts to describe it in terms of separate contributions had only limited success.[7,8] While the data we report here are not at present amenable to extraction of anisotropic potential parameters, they are sufficiently precise as to be ultimately useful when the formalism for $\sigma(R, \theta)$ is developed. From the comparison of these data with data for spherical or nearly spherical molecules we conclude that the temperature dependence of σ_1 as well as its magnitude is very sensitive to the anisotropy of the potential.

EXPERIMENTAL

^{129}Xe NMR spectra were observed using the pulsed Fourier transform mode at 24.89 MHz. The samples contained typically 8 amagat of Xe, which is 24% ^{129}Xe in natural abundance. A satisfactory signal to noise ratio was achieved routinely by collecting 256 free-induction decays using a $\pi/4$ pulse. Measured trace amounts of oxygen, about 0.2 amagat, were added to shorten T_1 so that pulse repetition rates of about 2.67 sec could be used. The details of sample preparation, sources of error, and instrumentation can be found in an earlier paper.[9] The perturber gases used were HBr, HCl, CO_2, N_2O, C_2H_2, C_2H_4, C_2H_6, and BF_3 at densities of 10–40 amagat, (1 amagat$=2.68\times10^{19}$ molecule cm^{-3}). The shifts observed for each sample were over several hundred hertz. The ^{129}Xe signals of all samples appeared over a spread of 1200 Hz.

RESULTS

The data analysis is as described in earlier work.[9] For each sample the observed frequency vs temperature data is fitted to a polynomial of degree 2 or 3. The temperature dependence of the lock substance and the effect of Xe–Xe and Xe–O_2 interactions are subtracted out, using the results from previous measurements in pure xenon and in mixtures of xenon and O_2.[10] The remaining frequencies give linear plots with respect to density of the perturber gas, as shown in Fig. 1. This linear behavior indicates that interactions of higher order than binary need not be considered at these densities. Earlier data on room temperature values of σ_1 for Xe in CO_2 and HCl compare favorably with those obtained here.[11] The values of σ_1 are given in Table I and plotted in Fig. 2.

DISCUSSION

It has been pointed out by Buckingham, Schaefer, and Schneider that chemical shifts arise in liquid solutions

TABLE I. σ_1(Xe–A), the second virial coefficient of xenon chemical shielding due to interaction with molecule A in Hz/amagat at 24.89 MHz.[a] $\sigma_1(\tau)=a_0+a_1\tau+a_2\tau^2+\cdots$, where $\tau=T-300$ K.

A	T(K)	a_0	10^3a_1	10^5a_2	10^7a_3	10^9a_4	$10^{11}a_5$
HBr	280–340	12.11	−37.08	30.72	0.3082	−0.8077	
C_2H_2	270–380	11.2124	−20.810	18.8147	−8.9587		
C_2H_4	275–385	10.659	−25.61	15.289	0.0266		
C_2H_6	275–385	10.230	−35.674	25.884	0.0119		
HCl	250–440	8.353	−19.56	19.72	−11.38	1.070	0.9926
CO_2	270–440	4.779	−12.28	12.40	−5.894	−0.746	1.038
N_2O	260–440	4.121	−10.472	10.295	1.537	−8.353	3.374
BF_3	230–380	4.0513	−5.6305	5.76025	−3.26592		

[a] Field shifts, $\sigma_1(T)$, in units of ppm/amagat can be obtained by multiplying the above coefficients by $-1/24.89$.

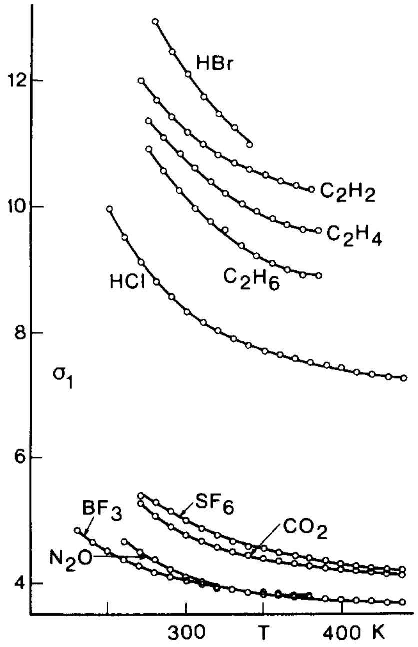

FIG. 2. Second virial coefficient of chemical shielding, σ_1, for ^{129}Xe nucleus, for various molecular pairs Xe and A, where A is shown as the label of the curve.

due to the anisotropy in the susceptibility of solvent molecules.[12] Buckingham *et al.* find the contribution to the chemical shielding due to the anisotropy of the susceptibility of axially symmetric molecules to be

$$\sigma_a = -(\chi_\parallel - \chi_\perp)(3\cos^2\theta - 1)/3R^3,$$

where θ is the angle between R and the axis of the solvent molecule. This is the asymptotic form of the anisotropic long range contribution. For a model of a liquid made up of hard sphere solute and hard cylinder solvent molecules,

$$\sigma_a \simeq (\chi_\parallel - \chi_\perp)/3R^3$$

since the mean value of $(3\cos^2\theta - 1)$ is around -1. On the other hand, the effect of a disk-shaped solvent molecule such as BF_3 on the chemical shielding of a spherical molecule such as Xe would be

$$\sigma_a = -2(\chi_\parallel - \chi_\perp)/3R^3$$

since in this case the mean value of $(3\cos^2\theta - 1)$ is around 2. For liquid solutions σ_a is of the order of 0.5–1 ppm.

In gases, however, the asymptotic form of the anisotropy contribution is found to be negligibly small (unless both probe and perturber molecules have dipole moments) for a spherically symmetric potential function $V(R)$, to which has been added dipole–dipole and other polar interactions.[7] There should be a nonzero contribution of this type to σ_1 for an anisotropic potential function $V(R, \theta)$.

It is possible to estimate the anisotropy of the potential function for Xe interacting with nonspherical molecules, such as in Xe–HCl from the anisotropy of the Ar–HCl potential function which has been examined by Neilsen and Gordon.[4] They report an optimized potential for Ar–HCl which gives the best agreement with the results of various experiments including linewidths of four far infrared dipole absorption lines and proton relaxation times at five temperatures. This potential function is

$$\begin{aligned} V(R\theta) = {} & V_{0a}(R)[1 + (0.32 \pm 0.05)\, P_1(\cos\theta)\,(r_m/R) \\ & + (0.24 \pm 0.10)\, P_2(\cos\theta)] \\ & + V_{0r}(R)[1 + (0.51 \pm 0.05)\, P_1(\cos\theta) \\ & + (0.78 \pm 0.10)\, P_2(\cos\theta)], \end{aligned}$$

where the isotropic part of the potential is taken to be

$$\begin{aligned} & V_{0a}(R) + V_{0r}(R) \\ & \quad = \epsilon\, \frac{6/\alpha}{1 - 6/\alpha} \exp\left[\alpha\left(1 - \frac{R}{r_m}\right)\right] - \frac{\epsilon}{1 - 6/\alpha}\left(\frac{r_m}{R}\right)^6, \end{aligned}$$

in which the constants are $\epsilon/k = 202$ K, $r_m = 3.805$ Å, $\alpha = 13.5$ for HCl–Ar. The average value of $(3\cos^2\theta - 1)/R^3$ for the HCl–Ar system is shown in Table II for various temperatures. Using -3×10^{-29} cm^3 for $(\chi_\parallel - \chi_\perp)$ for the HCl molecule, we find $\sigma_a \simeq -7.2$ ppm/(mole cm^{-3}) at 200 K. The contribution to σ_1 of Ar in HCl solvent is thus -0.0003 ppm amagat^{-1}. If the HCl–Xe potential has a value of $\langle(3\cos^2\theta - 1)/R^3\rangle$, which is comparable to that of Neilsen and Gordon's Ar–HCl potential, then the long-range limit of the anisotropic contribution to the ^{129}Xe shift in HCl is small indeed. The foregoing gives only a very crude estimate of the effect on σ_1 of the anisotropy of the potential function. A complete analysis should consider the integral

$$2\pi \int_{R=0}^{\infty} \int_{\theta=0}^{\pi} \sigma(R, \theta)\, e^{-V(R,\theta)/kT} R^2 dR \sin\theta d\theta.$$

Using the approximation of Buckingham *et al.*[12] is equivalent to assuming that in the long-range limit,

$$\sigma(R, \theta) \simeq \sigma_{iso}(R) - (\chi_\parallel - \chi_\perp)\left(\frac{3\cos^2\theta - 1}{3R^3}\right),$$

where $\sigma_{iso}(R)$ is an isotropic part of the chemical shielding similar to that found for xenon.[13] There is no evidence that $\sigma(R, \theta)$ is separable in this way for distances not large compared to molecular dimensions. In fact, this form of $\sigma_1(R, \theta)$ gives a positive second derivative $(\partial^2/\partial\theta^2)_{eq}$ at the equilibrium configuration of the van der Waals molecule. Other data indicate that $(\partial^2\sigma/\partial\theta^2)_{eq}$ is negative for linear triatomic molecules.[19] Thus, the long-range limit does not provide us with a quantitative estimate of the anisotropic contribution to σ_1.

TABLE II. Average value of $(3\cos^2\theta - 1)/R^3$ for the HCl–Ar system calculated using the Neilsen and Gordon potential function.[a]

$$\left\langle\frac{3\cos^2\theta - 1}{R^3}\right\rangle = \iint 2\pi\, \frac{(3\cos^2\theta - 1)}{R^3}\, e^{-V/kt} R^2 dR \sin\theta d\theta$$

T(K)	$\langle(3\cos^2\theta - 1)/R^3\rangle$
100	-3.729
200	-1.194
300	-0.828
400	-0.691
500	-0.620

[a] Reference 4.

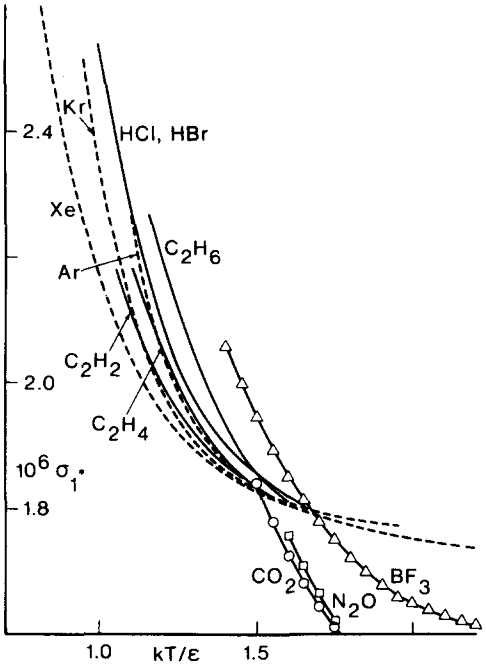

FIG. 3. Reduced σ_1 plotted against reduced temperature for assumed values of well depths.

If the anisotropy effects are indeed as small as that calculated for Ar–HCl with the Buckingham model, then the interpretation of the σ_1 for Xe interacting with nonspherical molecules should not be quantitatively different from the interpretation of the σ_1 for Xe interacting with spherical molecules.[14] The reduced σ_1 values plotted vs reduced temperature should then fall roughly within the family of reduced curves for Xe with spherical tops.[14] Let us see if this is the case. In Fig. 3 are plots of the reduced curves calculated using approximate $r_{\min}$ values from various sources. The parameters for the potential functions are given in Table III. We note that the Xe–HCl and Xe–HBr curves behave like those of Xe–Kr and Xe–Ar. It is seen in Table III that there is difficulty in casting the Xe–CO_2, Xe–N_2O, and Xe–BF_3 in the same form as the other molecular pairs. This might be an indication that the anisotropic effects are not small in these cases.

TABLE III. Parameters for Xe–A potential functions.

A	$r_{\min}$(Å)	Apparent ε(K)
C_2H_2	4.481[a]	250
C_2H_4	4.455[a]	245
C_2H_6	4.531[b]	231
HCl	4.155[b]	240
HBr	4.4[a]	258
CH_4	4.21[b]	224
SiF_4	4.29[b]	182
CF_4	4.21[b]	181
CO_2	4.455[a]	Poor fit
	4.0[c]	195
N_2O	4.72[a]	Poor fit
	4.0[c]	184
BF_3	4.54[a]	Poor fit
	4.0[c]	185

[a] Calculated using Lennard-Jones r_0 from Ref. 15 and arithmetic combining rule.
[b] Calculated using modified rule of thumb in Ref. 14.
[c] Combining rule using Lennard-Jones r_0 from Ref. 15 gives values which result in a poor fit. A value of 4.0 Å was assumed.

TABLE IV. Anisotropy of the optical polarizability and the coefficient of the $P_2(\cos\theta)$ term in the potential.[a]

A	$\alpha_{\parallel}-\alpha_{\perp}$(Å^3)	P2A for Xe–A / P2A for Xe–HCl
HCl	0.311	1.0
CO_2	2.10	6.76
N_2O	2.96	9.64
Ethane	0.771	2.48
Ethylene	~1.81	~5.83
Acetylene	1.86	5.99

[a] From Ref. 16.

Let us consider the related molecules C_2H_2, C_2H_4, and C_2H_6. Their polarizabilities are, in increasing order, 3.49, 4.22, and 4.47 Å^3 for acetylene, ethylene, and ethane, respectively. Since the magnitude of σ_1 of ^{129}Xe usually increases in the same order as the polarizabilities of the molecules with which it is interacting, we expect the magnitudes of $\sigma_1(\text{Xe}-C_2H_2)$, $\sigma_1(\text{Xe}-C_2H_4)$, and $\sigma_1(\text{Xe}-C_2H_6)$ to be in increasing order. The observed order is just the reverse of this. C_2H_2 has a large induced magnetic moment when the internuclear axis is aligned with the magnetic field. In C_2H_4 and C_2H_6, the presence of the additional hydrogens would tend to diminish the circulation of electrons about the C–C axis somewhat. We observed that $\sigma_1(\text{Xe}-C_2H_2)$ is greater than $\sigma_1(\text{Xe}-C_2H_4)$ which is greater than $\sigma_1(\text{Xe}-C_2H_6)$, the spread of σ_1 values being 0.04 ppm/amagat at room temperature. The direction of this trend is indeed as expected on the basis of the diminishing anisotropy of susceptibility in the asymptotic form of the anisotropy contribution in going from C_2H_2 to C_2H_6.

The magnitude of the anisotropic effects may not be small in these cases. However, we lack the potential functions necessary for making a quantitative estimate at this time. The coefficient $P2A$ of the $P_2(\cos\theta)$ term in the attractive part of Neilsen and Gordon's potential determines to a large extent the average value of $(3\cos^2\theta-1)/R^3$. For HCl–argon this coefficient is fairly small. Although the potential parameters are not known for Xe–CO_2, Xe–N_2O, Xe–C_2H_6, Xe–C_2H_4, Xe–C_2H_2, and Xe–BF_3 we can estimate the average value of $(3\cos^2\theta-1)$ from the magnitude of the coefficient of the $P_2(\cos\theta)$ term in the potential. The dispersion part of this coefficient is the sole contribution when the molecule has no dipole moment, and is estimated by $(\alpha_{\parallel}-\alpha_{\perp})/3\alpha_{\text{Xe}}$. In Table IV are values of $\alpha_{\parallel}-\alpha_{\perp}$ which have been obtained through measurements of the depolarization of the light scattered by the gases.[16] We see that the $P2A$ coefficients for Xe–CO_2, etc, are 2.5–10 times as large as those for HCl. The values of $\chi_{\parallel}-\chi_{\perp}$ can be obtained by observing Zeeman molecular effects under high resolution. Flygare *et al.* have measured the anisotropy in diamagnetic susceptibility for several of these molecules. For most of these molecules $(\chi_{\perp} - \chi_{\parallel})$ is $(6-10)\times 10^{-6}$ cm^3 mole^{-1}.[17] Thus, it is quite possible for the anisotropic contribution to σ_1 for these molecular pairs to be much larger than -0.0003 ppm/amagat.

From Table II we note the temperature dependence of the long-range anisotropic term is different from that of the isotropic term. While the isotropic part of σ_1 has a limiting value at infinite temperature which is nonzero, the anisotropic term has a limiting value of zero. The anisotropic term becomes more important at low temperatures. Thus, we expect a more pronounced temperature dependence (a steeper curve at low temperatures) if the anisotropic part has the same sign as the isotropic, and a less pronounced temperature dependence if the anisotropic is opposite in sign to the isotropic. We see in Fig. 2 that while Xe–BF_3 and Xe–N_2O have nearly the same values at temperatures above 300 K, at lower temperatures they deviate from each other, the Xe–N_2O having a somewhat steeper curve than the Xe–BF_3. This is what would be expected from the anisotropy of the interaction with Xe of a rod-shaped molecule like N_2O as opposed to a disk-shaped molecule like BF_3.

It is of interest to note that some of these molecular pairs or their analogs have been detected as dimers in a molecular beam electric resonance spectrometer.[18] The beams are produced by expanding a gas mixture through a supersonic nozzle. XeHCl was found to be polar, indicating that there is net orientation of the HCl with respect to the Xe–Cl axis as opposed to having a freely rotating HCl. The analogs of $XeBF_3$ and XeNO, namely, $ArBF_3$, $KrBF_3$, and ArNO were also found to be polar. $ArBF_3$ showed a radio-frequency resonance whose variation with electric field indicated a symmetric top configuration, i.e., the argon is on the threefold axis of symmetry.

We have shown some evidence that the second virial coefficient of ^{129}Xe chemical shielding is sensitive to the anisotropy of the intermolecular potential between Xe and linear and disk-shaped molecules. While a lack of information about $\sigma(R, \theta)$ prevents us from extracting quantitative information about the anisotropy of the potential at this time, the experimental data are sufficiently precise to be useful for this purpose in the future.

The model used for the anisotropic part of σ_1 is the long-range limit. The short range limit is currently being characterized for linear triatomic molecules. From the temperature dependence of the chemical shielding of the isolated linear triatomic molecule, the derivatives $(\partial\sigma/\partial R_1)$, $(\partial\sigma/\partial R_2)$, and $(\partial^2\sigma/\partial\theta^2)$ at the equilibrium configuration can be obtained.[19] These derivatives provide some insight into the function $\sigma(R, \theta)$ at short range.

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