Contact interaction between ^{129}Xe and nitric oxide

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The chemical shift of ^{129}Xe in nitric oxide gas has been observed as a function of temperature and density of NO. The derivative of the frequency with respect to density gives the second virial coefficient of chemical shielding of ^{129}Xe in nitric oxide, σ_1(Xe—NO)$=-0.6840+1.5516\times10^{-3}\tau-1.3142\times10^{-5}\tau^2+7.2769\times10^{-8}\tau^3$ ppm amagat^{-1}, in which $\tau=T-300$, and T goes from 220 to 380 K. The results are compared with the Xe in oxygen gas and the contact contribution to σ_1(Xe—NO) is determined. By using Ar as the diamagnetic counterpart of an NO or O_2 molecule, empirical values of the integral $\int\rho_{\text{spin}}e^{-V/kT}dx^3$ are obtained for the Xe—NO and the Xe—O_2 interaction. The empirical values of this integral are greater for the Xe—NO pair than the Xe—O_2 pair. Both exhibit a slight temperature dependence.

We have observed chemical shifts of ^{129}Xe in various diamagnetic gases and also in oxygen gas.[1] In a mixture of gases, the chemical shielding of a nucleus in a probe molecule A may be expressed in a virial expansion as follows,[2]

$$\sigma(\rho_A,\ \rho_B,\ T)=\sigma_0+\sigma_1(\text{A}-\text{B})\,\rho_B+\sigma_1(\text{A}-\text{A})\,\rho_A+\cdots \qquad (1)$$

σ_0 is an intrinsic property of the probe molecule, and is in general a function of temperature due to vibrational and rotational degrees of freedom of the probe molecule. σ_1(A–B) and σ_1(A–A) are the second virial coefficients of chemical shielding, also functions of temperature, characteristic of the binary interaction between probe and perturber molecule, and between two probe molecules, respectively. In diamagnetic gases, the magnitude and the temperature dependence of σ_1(A–B) and of σ_1(A–A) are found to be related to the characteristics of the intermolecular potential: the position of the minimum and the well depth.[3,4] The observed magnitudes and temperature dependence of σ_1 for the paramagnetic gases fall well outside the values for diamagnetic gases of the same molecular size and number of electrons. In the case of ^{129}Xe probe in oxygen gas, the observation of a $1/T$ dependence of that residual portion of σ_1, which is due to something other than interaction with diamagnetic molecules, established the nature of this other interaction as a contact mechanism.[5] On the NMR time scale, a given Xe atom collides with so many O_2 molecules that the net effect is given by the nonzero average, $\langle S_z\rangle$, over the O_2 electronic spin states. The scalar coupling between this and the ^{129}Xe nuclear spin leads to the contact chemical shift. The dominant temperature dependence, which in the case of O_2 follows the Curie law, is that of the temperature dependence of the populations of the spin states. Superimposed on this, of course, is the less dominant temperature dependence due to the unpaired electron spin density at the ^{129}Xe nucleus varying with the Xe–O_2 configuration, averaged over the ensemble of such configurations. The theoretical calculations of Buckingham and Kollman established that a theoretical estimate of the contact shift does provide an interaction of sufficiently large magnitude so that there is no need to invoke any valence type interactions or an unusual potential function for Xe, interacting with paramagnetic molecules.[6] In fact, they used a Lennard-Jones type of potential with a well depth which is about the same as that for Xe–Ar. They also established that the anisotropy of the potential had very little effect on the calculated σ_1. Therefore, the observed σ_1(Xe–O_2) is drastically different from the observed σ_1(Xe–Ar) for reasons other than the anisotropy of the Xe–O_2 potential.

Nitric oxide is another paramagnetic molecule which we have used as a perturber of ^{129}Xe. Our previous report on it was at room temperature only.[1] This paper describes our results on the temperature dependence of σ_1(Xe–NO) over the temperature range 220–380 K. We interpret these results on the same basis as the σ_1(Xe–O_2) temperature dependence, taking into consideration the fact that the nitric oxide molecule has a doublet ground electronic state and therefore a temperature dependent average magnetic moment.

EXPERIMENTAL

^{129}Xe spectra were observed in natural abundance using the pulse Fourier transform NMR method, in samples containing 10–13 amagat of Xe and 10–18 amagat of nitric oxide. The magnetic field was stabilized using the resonance signal of the methyl protons of toluene. The field strength was adjusted so that this signal could be observed at exactly 90.010471 MHz. The resonance frequency at various temperatures and densities occurred over a 400 Hz range and line widths were of the order of 5 to 10 Hz. Sample preparation and temperature regulation were carried out as described in previous work.[3] The samples were prepared in tubes with a smaller diameter than the standard tubes previously used, and the densities of nitric oxide were kept below 20 amagat in order to avoid problems with spinning sidebands such as those previously observed in samples having high densities of oxygen.[5] Even at these low densities of NO, the Xe–NO contribu-

TABLE I. Absolute temperatue dependence of the methyl protons in toluene[a] at 24.896 MHz.

T	Hz	Std. dev.
220	+2.86	0.72
230	+2.36	0.53
240	+1.91	0.44
250	+1.50	0.42
260	+1.12	0.39
270	+0.79	0.36
280	+0.49	0.31
290	+0.23	0.26
300	0.00	0.24
310	−0.20	0.26
320	−0.37	0.32
330	−0.51	0.38
340	−0.62	0.41
350	−0.71	0.41
360	−0.78	0.36
370	−0.83	0.26
380	−0.86	0.15

[a] These data are adequately represented by $\nu = \nu_{300} - 2.138\times10^{-2}(T-300) + 1.564\times10^{-4}(T-300)^2 - 2.903\times10^{-7}(T-300)^3$ Hz. In terms of field shifts, $\Delta H/H = \sigma_{300} + 8.587\times10^{-4}(T-300) - 6.282\times10^{-6}(T-300)^2 + 1.166\times10^{-8}(T-300)^3$.

tion to the shift dominates over that due to Xe–Xe interactions.

Since these experiments were conducted using a single new lock substance (the methyl protons of toluene), the calibration of the lock substance against our standard pure Xe samples was carried out. Six xenon samples with densities ranging from 3 to 28 amagat were observed between the freezing and boiling temperatures of the lock substance. The temperature dependence of the lock substance was obtained in the usual manner.[7] The methyl protons of pure liquid toluene have a temperature dependence shown in Table I.

RESULTS

The values of σ_1(Xe–Xe) obtained using toluene as a reference substance are superimposable over the values previously reported using other reference substances and need not be repeated here.[3] Since the range of temperatures was much wider than ever before covered with a single reference substance, we found that the observed frequencies can not be adequately described as a quadratic function of temperature. Thus, all our data were fitted to a third degree polynomial and all subsequent analyses of the data were carried out using a cubic equation. Since σ_1(Xe–Xe) in pure xenon samples has been determined with a high degree of precision using this new lock substance, we are able to determine σ_1(Xe–NO) in mixtures of Xe and NO. The second virial coefficient of chemical shielding of ^{129}Xe in nitric oxide gas, σ_1(Xe–NO) is shown in Fig. 1. The following equation adequately describes its temperature dependence,

$$\sigma_1\,(\text{Xe–NO}) = -0.6840 + 1.5516\times10^{-3}\,\tau - 1.3142\times10^{-5}\tau^2 + 7.2769\times10^{-8}\,\tau^3 \text{ ppm amagat}^{-1}\,, \qquad (1)$$

where $\tau = T - 300$ K. The absolute error in the value of σ_1 is 0.017 ppm amagat^{-1} (a relative error of about 2.5%). The error in the temperature dependence of σ_1 is much smaller, $d\sigma_1/dT$ is known to within $\pm 1.25\times10^{-5}$ ppm amagat^{-1} deg^{-1}, about 0.8%.

DISCUSSION

The observed σ_1 (Xe–NO) is made up of several contributions. First, there is the σ_1 due to the bulk susceptibility of NO itself which can be calculated from its molar paramagnetic susceptibility in a cylindrical sample as follows[8]:

$$\sigma_{1_{\text{bulk}}} = (2\pi/3)\,\chi_{\text{mol}}\ . \qquad (2)$$

Secondly, we assume that there is a contribution which is of the same nature as that which exists in the interaction of Xe with diamagnetic molecules. This we expect to be identical to that of σ_1 (Xe–Y) where Y is a diamagnetic molecule which has an intermolecular potential with xenon which has the identical shape as the potential for xenon with NO. Since the potential parameters of Xe–NO are not known, the best we can do at the present time is to use combining rules. The most accurate well depth for Xe is 282 K,[9] the value for NO is old and probably too shallow.[10] Using the usual geometric combining rule for well depths, $\epsilon_{AB} = (\epsilon_A \times \epsilon_B)^{1/2}$, and the arithmetic combining rule for collision diameter, $r_{0_{AB}} = (r_{0_A} + r_{0_B})/2$, we get $\epsilon_{\text{Xe–NO}} \simeq 192$ K, $\epsilon_{\text{Xe–O}_2} \simeq 185$ K, $r_{0_{\text{Xe–NO}}} \simeq 3.53$ Å, and $r_{0_{\text{Xe–O}_2}} \simeq 3.68$ Å. For Xe–Ar the most recent values are 186 K and 3.6 Å.[11] The parameters for this potential are sufficiently close to those of Xe–NO and Xe–O_2 so that we may use the Xe–Ar σ_1 as a model for the Xe–NO and Xe–O_2 interaction, if NO and O_2 had been diamagnetic.

Finally, there is the contact interaction due to the paramagnetic nature of NO and O_2. The local magnetic field experienced by a nucleus due to a net $\langle S_z\rangle \neq 0$, is given by

$$\Delta H = \frac{A\langle S_z\rangle}{g_N\,\beta_N}\ . \qquad (3)$$

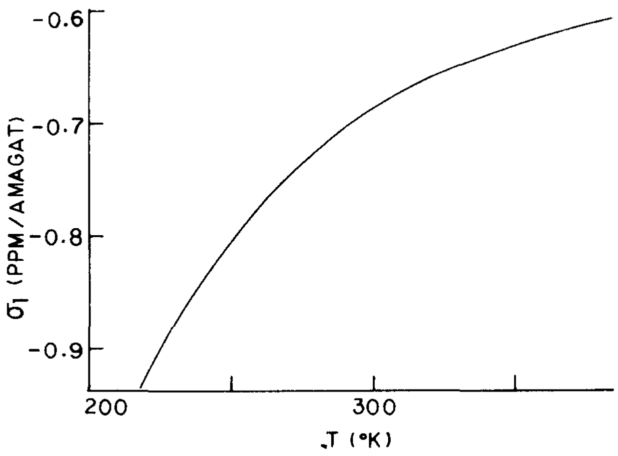

FIG. 1. The temperature dependence of the second virial coefficient of ^{129}Xe chemical shielding in nitric oxide gas.

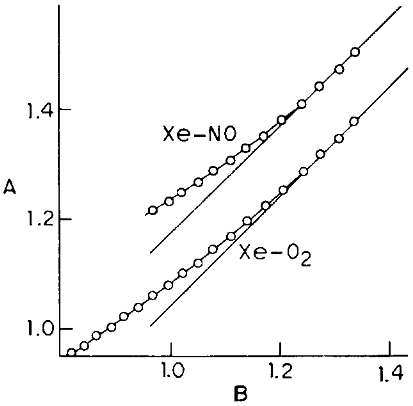

FIG. 2. A plot showing a limiting slope of 1.0 at the low temperature end of the scale for both the Xe–O_2 and Xe-NO data, illustrating the dominance of the $1/T$ dependence, a property of the contact mechanism. The quantities plotted are

$$\mathrm{A}=\ln\left[\frac{\sigma_{1\mathrm{obs}}(\mathrm{Xe{-}NO})-\sigma_1(\mathrm{Xe{-}Ar})}{\mu^2_{\mathrm{eff}}\,\sigma_1(\mathrm{Xe{-}Ar})}\right],$$

$$\mathrm{B}=\ln(1000/T).$$

$\langle S_z\rangle$ is proportional to the applied field,

$$S_z=\frac{-\chi_{\mathrm{mol}}H}{N_A g_e \beta_e}\ , \tag{4}$$

and the electron–nuclear spin interaction constant is

$$A=\frac{4\pi}{3}\, g_e\,\beta_e g_N\,\beta_N\,\rho_{\mathrm{spin}}\ . \tag{5}$$

Here, ρ_{spin} is the unpaired spin density at the nucleus in question and usually has a magnitude between 0 and 1 for a single unpaired electron. χ_{mol} is the molar paramagnetic susceptibility, which is

$$\chi_{\mathrm{mol}}=\frac{N_A\,\overline{\mu^2_{\mathrm{eff}}}}{3kT}\ . \tag{6}$$

All the other symbols have their standard meanings. Thus, the contact shift is

$$\frac{\Delta H}{H}=\frac{-4\pi\,\overline{\mu^2_{\mathrm{eff}}}}{9kT}\,\rho_{\mathrm{spin}}\ . \tag{7}$$

The average over all possible configurations of the Xe–NO or Xe–O_2 pair gives a contact contribution to σ_1 of

$$\sigma_1(\mathrm{contact})=\frac{-4\pi\,\overline{\mu^2_{\mathrm{eff}}}}{9kT}\int\rho_{\mathrm{spin}}\,e^{-V/kT}\,dx^3\ , \tag{8}$$

in which dx^3 is the general volume element for integration, and V is the intermolecular potential function.

If we can use the observed σ_1 (Xe–Ar) in place of the diamagnetic portion of $\sigma_{1_{\mathrm{obs}}}$(Xe–NO) and $\sigma_{1_{\mathrm{obs}}}$(Xe–$O_2$), and suppose that the integral $\int\rho_{\mathrm{spin}}\,e^{-V/kT}dx^3$ has almost the same temperature dependence as the diamagnetic portion, that is, that this integral is approximately proportional to σ_1(Xe–Ar) also, then *at low temperatures*, where the latter assumption does not skew the results too badly, the plot of

$$\log\left\{\frac{\sigma_{1\mathrm{obs}}(\mathrm{Xe{-}NO})-\sigma_1(\mathrm{Xe{-}Ar})}{\mu^2_{\mathrm{eff}}\,\sigma_1(\mathrm{Xe{-}Ar})}\right\}\ \mathrm{vs}\ \log\frac{1}{T}$$

should give a straight line with slope equal to unity. The limiting slope of 1 exhibits the dominant $1/T$ dependence of both the contact contribution and the bulk susceptibility contribution. Figure 2 shows the plots for Xe–NO and the analogous one for Xe–O_2, except that in the case of O_2, $\overline{\mu^2_{\mathrm{eff}}}=4S(S+1)=8\ \mu_B$. Indeed, the limiting slopes equal 1.0. When extended, these straight lines have an intercept for the Xe–NO curve which is greater than that for the Xe–O_2 curve, implying that $\int\rho_{\mathrm{spin}}\,e^{-V/kT}\,dx^3$ is greater for Xe–NO by a factor of 1.24 than for Xe–O_2. We will examine this matter in more detail below.

The $\overline{\mu^2_{\mathrm{eff}}}$ for NO is itself temperature dependent.[12] The normal state of the nitric oxide molecule is known spectroscopically to be a regular $^2\pi$ doublet of width $h\Delta\nu=120.9\ \mathrm{cm}^{-1}$, with the lower doublet component having $\Lambda=1$, $\Sigma=-1/2$. Since $\Lambda=1$, $S=1/2$, the high temperature limit of μ^2 is $4S(S+1)+\Lambda^2$ or $4\ \mu_B$.[2] For O_2 the high temperature limit of $8\ \mu_B$ holds over a wide range of temperatures. However, in NO, $h\Delta\nu$ is of the order of kT at room temperature so that the more complicated intermediate case derived by Van Vleck obtains rather than the high temperature limit.[12] Van Vleck has shown that the average value of μ^2_{eff} for NO is

$$\overline{\mu^2_{\mathrm{eff}}}=\frac{1-e^{-x}+xe^{-x}}{x+xe^{-x}}\times 4\ , \tag{9}$$

where $x=h\Delta\nu/kT=173/T$. This expression reproduced the available experimental data to within experimental error for temperatures above the normal boiling point of NO.[12] Therefore, we use it here.

When we use the σ_1(Xe–Ar) for the diamagnetic portion of the observed σ_1(Xe–NO) and σ_1(Xe–O_2), we get an empirical contact contribution equal to

$$\sigma_{1_{\mathrm{obs}}}-\sigma_1(\mathrm{Xe{-}Ar})-\sigma_{\mathrm{bulk}}(\mathrm{NO})\ .$$

Since $\overline{\mu^2_{\mathrm{eff}}}$ is known for NO, the value of σ_{bulk}(NO) is known. Thus, we have empirical values of the contact portion of σ_1(Xe–NO). From this, and from Eq. (8) we calculate empirical values for $\int\rho_{\mathrm{spin}}\,e^{-V/kT}\,dx^3$. These values are shown in Table II for both the Xe–NO and the Xe–O_2 pairs. It is probably not valid to use the same potential function for both of the quasidegenerate ($^2\Pi_{1/2}$ and $^2\Pi_{3/2}$) states of NO. These states of NO can lead to differing admixture of the unpaired electron into the Xe 5s orbital. The use of the Xe–Ar potential parameters in place of both Xe–NO($^2\Pi_{1/2}$) and Xe–NO($^2\Pi_{3/2}$) potentials is probably a poor approximation. The empirical values of the integral given in Table II include both the $^2\Pi_{1/2}$ and the $^2\Pi_{3/2}$ states of NO, however different their respective contributions may be. (We thank a referee for calling this point to our attention.)

Buckingham and Kollman calculated the overlap contribution to these integrals using a variety of isotropic and anisotropic potentials, either a Slater type or a numerical 5s function for Xe atom, and single zeta orbitals for NO and O_2, as well as a double zeta function for O_2. Since no double zeta functions are available for NO, only the results for single zeta functions for both

TABLE II. Empirical values of $\int \rho_{\text{spin}} e^{-V/kT} dx^3$ for Xe–NO and Xe–O_2 pairs. [a]

T, K	Xe–NO	Xe–O_2	Ratio (Xe–NO)/(Xe–O_2)
260	2.4479	1.9607	1.2485
270	2.4224	1.9423	1.2472
280	2.403	1.9263	1.2475
290	2.3901	1.9127	1.2496
300	2.3836	1.9017	1.2534
310	2.3832	1.8931	1.2589
320	2.3885	1.8871	1.2657
330	2.3985	1.8834	1.2735
340	2.4121	1.8821	1.2816
350	2.4278	1.8829	1.2894
360	2.4439	1.8857	1.296
370	2.4583	1.8904	1.3004
380	2.4687	1.8967	1.3016
390		1.9042	
400		1.9128	
410		1.9221	
420		1.9317	
430		1.9413	
440		1.9504	

[a] Although σ_1(Xe–NO) was observed from 220 to 380 K, σ_1(Xe–Ar) was only availalable from 260 K and up.

may be compared. The anisotropy of the potentials did not affect their calculated integrals very much. For the single zeta wavefunctions and a numerical 5*s* function for Xe, the overlap contributions to $\int \rho_{\text{spin}} e^{-V/kT} dx^3$, calculated by Buckingham and Kollman, are 6.4 for Xe–O_2 and 7.7 for Xe–NO, for potential parameters of 3.78 Å, 180 K for Xe–O_2, 3.635 Å, 190 K for Xe–NO. These values do not include contributions from inner *s* orbitals of Xe or for polarization of Xe *s* orbitals by the unpaired electron.

The calculation of $\int \rho_{\text{spin}} e^{-V/kT} dx^3$ is very sensitive to the wavefunctions used, as shown by Buckingham and Kollman in their Table III. It is also sensitive to the r_0 or $r_{\min}$ of the potential function used. Depending on whether ρ_{spin} peaks inside r_0 near $r_{\min}$, or outside $r_{\min}$, the above integral could be monotonically increasing with increasing temperature, monotonically decreasing with increasing temperature or have an extremum at some intermediate temperature. Buckingham and Kollman's calculated integrals monotonically increase with increasing temperature, but the change is small, about a 14% change over a 67° change in temperature for both NO and O_2. Our empirical values for the integral show very little change over a wide range of temperatures for both Xe–O_2 and Xe–NO. Since the change in the empirical value of the integral is only 3% to 4% over the entire temperature range, the slight minimum observed is probably not real. This small change is well within the error in approximating a diamagnetic O_2 or NO by an argon atom.

Comparison of the Xe–NO with the Xe–O_2 integrals given in Table II shows that the NO integral is somewhat greater, with the ratio of (Xe–NO)/(Xe–O_2) being around 1.25 and slightly increasing with increasing temperature to a value of 1.30. This slight monotonic change may not be meaningful since the change is only 4% over the 120° change in temperature. As Buckingham and Kollman pointed out, the integral $\int \rho_{\text{spin}} e^{-V/kT} dx^3$ is expected to be larger for Xe–NO than for Xe–O_2 because of the smaller value of the collision diameter, r_0, for NO and because the π^* molecular orbital is more diffuse around the N atom in NO, compared to the π_g^* orbital around the O atoms in O_2, thus enhancing the overlap contributions to the integral. Their theoretical values of this integral have a ratio of 7.7/6.4 or 1.20, which is very close to our ratio of empirical values. This seems to indicate that the calculations of Buckingham and Kollman describe the differences between the Xe–NO and the Xe–O_2 encounters fairly well. The greatest problem they had in calculating ρ_{spin} was in assigning a value for the Xe 5*s* function at the Xe nucleus, a factor which is common to both the Xe–NO and the Xe–O_2 calculations. In the ratio of the two integrals this factor drops out and as we have seen, their calculations do show a ratio very close to the empirical one. This favorable agreement with experiment was not noted in their original paper due to some minor errors, such as an unnecessary factor of $\frac{1}{2}$ in the Xe–O_2 integral and an erroneous expression for the temperature dependent magnetic moment of NO. These corrections were made in the numerical values which we have quoted here and attributed to Buckingham and Kollman.

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