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^{129}Xe contact shift in oxygen gas

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We have determined the temperature dependence of σ_1 of ^{129}Xe in oxygen gas. These results were obtained by measurement of the resonance frequency of ^{129}Xe in gas samples of known densities in Xe and O_2. The shift of the resonance frequency due to Xe–Xe interactions has been measured in pure Xe gas samples with improved precision. This allows the determination of σ_1(Xe–O_2) by subtracting out the known effect of Xe–Xe interactions in mixed Xe–O_2 samples. σ_1(Xe–O_2) values are reported here for the temperature range 220 to 440 K. The values of σ_1(Xe–O_2) are adequately described by the polynomial function in p.p.m. amagat^{-1} $\sigma_1(\mathrm{Xe{-}O_2}) = -1{\cdot}061 + 3{\cdot}64\times10^{-3}\tau - 2{\cdot}19\times10^{-5}\tau^2 + 9{\cdot}58\times10^{-8}\tau^3 - 2{\cdot}08\times10^{-10}\tau^4$, where $\tau = (T - 300\ \mathrm{K})$. It is found that the temperature dependence of σ_1(Xe–O_2) can be interpreted in terms of a contact interaction between Xe and the paramagnetic O_2 molecule.

1. INTRODUCTION

^{129}Xe N.M.R. studies in the gas phase show that the ^{129}Xe chemical shift has an essentially linear dependence on density at densities well below 100 amagats† [1]. The virial expansion of chemical shielding of a nucleus in a probe molecule A in a system consisting of a mixture of A and B gases is

$$\sigma(\rho_A, \rho_B, T) = \sigma_0 + \sigma_1(\mathrm{A{-}B})(T)\rho_B + \sigma_1(\mathrm{A{-}A})(T)\rho_A + \dots ,$$

where, σ_1(A–A)(T) is the second virial coefficient of chemical shielding for the probe molecule and σ_1(A–B)(T) is the second virial coefficient of chemical shielding for the probe molecule interacting with B, the perturber molecule. In order to obtain σ_1(A–B) accurately as a function of temperature, it is necessary to have previously determined σ_1(A–A) as a function of temperature with a high degree of accuracy. The latter has been carried out for ^{129}Xe [2].

Previous work on the ^{129}Xe N.M.R. chemical shifts in paramagnetic gases O_2 and NO at room temperature showed a linear dependence of the ^{129}Xe shift with density of O_2 (or NO) and unusually large slopes [3]:

$$\sigma_1(\mathrm{Xe{-}O_2}) = -1{\cdot}25\ \text{p.p.m./amagat}$$

and

$$\sigma_1(\mathrm{Xe{-}NO}) = -0{\cdot}924\ \text{p.p.m./amagat}.$$

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† The amagat is a unit of molar density; 1 amagat is the density of the real gas under consideration at 1 atm = 101 325 Pa and 0°C = 273·15 K.

These values were much greater than the value of σ_1 at room temperature for a perturber of comparable polarizability, such as Ar (σ_1(Xe–Ar) = $-0{\cdot}137$ p.p.m./amagat).

These results were attributed by the authors to the contact mechanism and possibly an unusually deep Xe–O_2 or Xe–NO potential function. The results were interpreted by Buckingham and Kollman [4] in terms of the overlap of the Xe(5s) with the O_2 ($\pi_g{}^*$) or NO (π^*) orbitals, leading to a net spin density at the nucleus. The calculated shift was found to be sensitive to the wave functions used for Xe and O_2 and to the intermolecular potential. Due to this and to the lack of data on the temperature dependence of σ_1 it was difficult to conclude whether the overlap mechanism suggested by Buckingham was dominant or even whether the observed shifts were primarily due to the Fermi contact interaction. With precisely determined σ_1(Xe–Xe) as a function of temperature [2], it has been possible to determine the temperature dependence of σ_1 of ^{129}Xe in O_2 gas, and to determine from this the primary mechanism for the large downfield shifts which have been observed.

The experimental details are the same as those previously reported for pure xenon gas [2]. The Xe in O_2 gas samples ranged in Xe densities from 28·4 amagats to 68·2 amagats and in O_2 densities from 8·09 to 15·14 amagats. Many other samples with much higher densities of O_2 were prepared but the severity of the spinning side-band problem increased with increasing density of the paramagnetic gas and precluded N.M.R. measurements of samples of higher density of O_2. In any case, the downfield shifts observed with O_2 are so large that there was no necessity to use higher densities of O_2. At these low densities the assumption of binary interactions between Xe and O_2 should be very good.

There are several possible sources of error in our measurements. The densities are accurate to within about 1 per cent, the temperature is known accurately to within 1°C with a stability of ±0·2°C. Errors in frequency measurements, incomplete freezing of the gas during sample preparation, errors in pressure measurements, and compressibility and thermal expansion of the glass ampules are smaller than the errors in density or temperature. A more complete discussion of errors may be found in reference [2]. The resulting error in σ_1(Xe–O_2) is expected to be on the order of ±1 per cent. The observed scatter in our data is compatible with these expected sources of error.

2. Results

The shifts in the ^{129}Xe resonance signal with temperature in samples of varying densities in Xe and O_2 are due to (*a*) the temperature dependence of the lock solvent itself [5], (*b*) the temperature dependence of the second virial coefficient of chemical shielding, σ_1, due to Xe–Xe interactions, (*c*) the temperature dependence of the second virial coefficient of shielding due to Xe–O_2 interactions and (*d*) the temperature dependence of higher-order virial coefficients of shielding due to interactions between three or more molecules. Any temperature dependence due to higher-order interactions such as one Xe atom and two or more oxygen molecules are negligible at the low densities of O_2 which are used here.

The temperature dependence due to higher-order interactions involving only Xe atoms, as well as (*a*) and (*b*) are also observed in the pure Xe experiment with the same lock solvents [2]. Thus, the parameters obtained in the pure xenon experiment can be used in the analysis of the Xe in O_2 data, so that the remaining temperature dependence is that of $\sigma_1(\mathrm{Xe{-}O_2})$ itself.

The raw data (^{129}Xe resonance frequency as a function of temperature) for each sample is fitted in a least-squares sense to a polynomial of degree 2.

$$\nu = a_0(\rho_{\mathrm{Xe}}, \rho_{\mathrm{O_2}}) + a_1(\rho_{\mathrm{Xe}}, \rho_{\mathrm{O_2}})(T - t_0) + a_2(\rho_{\mathrm{Xe}}, \rho_{\mathrm{O_2}})(T - t_0)^2,$$

where we have chosen t_0 for the various lock solvents as: $t_0 = 300$ K for the TMS and C_6F_6 ranges and $t_0 = 350$ K for the dibromotetrafluorobenzene range.

For each lock substance temperature range, the pure xenon contribution (including the temperature dependence of the lock substance) is subtracted out, using the results of reference [2]. The remaining frequency versus temperature functions for each sample are then used in a linear least squares fit of frequency versus density of O_2 at each temperature. A computer programme was written to carry out these analyses in a routine manner. The slopes obtained by this process are plotted against temperature in figure 1. A least squares fit to a 4th-order polynomial in temperature adequately describes the temperature dependence. In terms of $\Delta H/H$ in p.p.m. amagat^{-1}:

$$\sigma_1(\mathrm{Xe{-}O_2}) = -1\cdot0610 + 3\cdot64 \times 10^{-3}\,\tau - 2\cdot187 \times 10^{-5}\,\tau^2 + 9\cdot583 \times 10^{-8}\,\tau^3 - 2\cdot075 \times 10^{-10}\,\tau^4,$$

where $\tau = T - 300$ K.

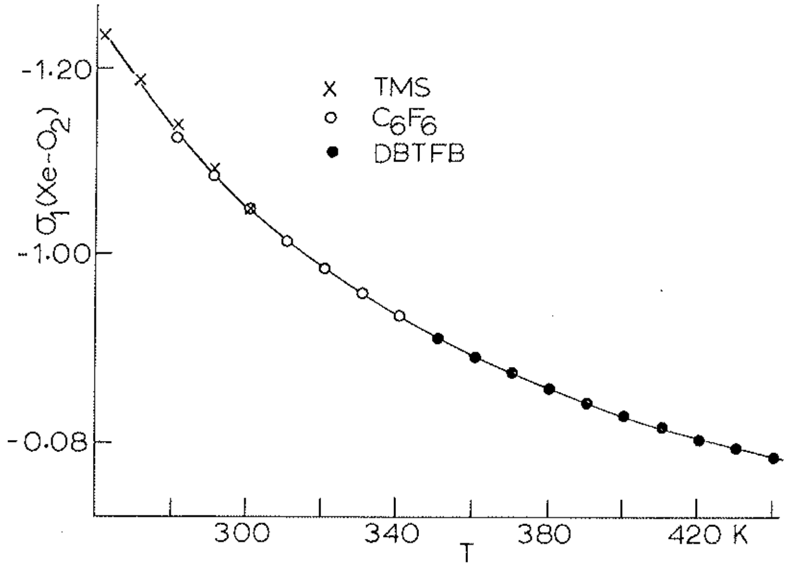

Figure 1. Temperature dependence of the second virial coefficient of chemical shielding, $\sigma_1(\mathrm{Xe{-}O_2})$ in p.p.m. amagat^{-1}, for ^{129}Xe in oxygen gas.

3. DISCUSSION

In our earlier work [3] it was apparent that for O_2 as the buffer gas, σ_1 was unusually large, on the order of 5 to 10 times as great as would be expected for buffer gases with approximately the same polarizability. The most plausible hypothesis to explain this anomaly is that the paramagnetic nature of O_2 gives rise to an intermolecular contact interaction which is quite large [4]. This was supported by the similarities of $\sigma_1(\mathrm{Xe{-}O_2})$ and $\sigma_1(\mathrm{Xe{-}NO})$ values measured at room temperature. The contact interaction could be explained as follows. On the N.M.R. time-scale a Xe atom undergoes many collisions with O_2 molecules, so that a given Xe atom collides with O_2 in all electronic spin states, the *net* spin populations giving rise to a non-zero $\langle S_z \rangle$. The scalar coupling between this and the ^{129}Xe nuclear spin leads to the contact chemical shift.

A test of the above hypothesis regarding $\sigma_1(\text{Xe–O}_2)$ being due primarily to a contact interaction should be provided by the temperature dependent data shown in figure 1. The contact mechanism should follow a Curie law dependence. Suppose we write the observed $\sigma_1(\text{Xe–O}_2)$ as due to two contributions : the proposed contact interaction and the usual intermolecular interaction found in diamagnetic systems.

Assumption 1. Assuming that the Xe–O_2 interaction can be approximated as being between two spherically symmetric species, we can write

$$\sigma_1(\text{Xe–O}_2) = 4\pi \int_0^\infty \left\{ \frac{\sigma_c(R)}{T/300\text{ K}} + \sigma_d(R) \right\} \exp(-V/kT) R^2 \, dR,$$

where

$\sigma_c(R)$ = contribution to shielding due to the contact interaction as a function of internuclear separation,

$\sigma_d(R)$ = shielding function for the usual non-contact interaction observed for diamagnetic gases.

300 K is arbitrarily chosen as a normalization factor for T. Without knowing $\sigma_c(R)$ or $\sigma_d(R)$, an absolute test of our hypothesis cannot be carried out. However, by making some more or less crude assumptions a reasonable test may be made. $\sigma_1(\text{Xe–O}_2)$ may be rewritten as

$$\sigma_1(\text{Xe–O}_2) = C + D,$$

where

$$C = 4\pi \int_0^\infty (300\text{ K}\ \sigma_c(R)/T) \exp(-V/kT) R^2 \, dR,$$

$$D = 4\pi \int_0^\infty \sigma_d(R) \exp(-V/kT) R^2 \, dR.$$

At temperatures for which $D/C \ll 1$, we may be able to get away with a rough approximation for D.

Assumption 2. Assume D to be identical to σ_1 of some diamagnetic molecule with roughly the same molecular parameters as O_2. A likely candidate for this is Ar. Thus, if we were to fit

$$\{\sigma_1(\text{Xe–O}_2) - \sigma_1(\text{Xe–Ar})\} T/300\text{ K}$$

to a polynomial in T we would be able to determine whether or not there is an overwhelming $1/T$ dependence of the above function. Using our measured values for $\sigma_1(\text{Xe–Ar})$ as a function of temperature [6], we find

$$\{\sigma_1(\text{Xe–O}_2) - \sigma_1(\text{Xe–Ar})\} = (300\text{ K}/T)\{a_0 + a_1(T - 300\text{ K}) + a_2(T - 300\text{ K})^2 + a_3(T - 300\text{ K})^3 \text{ p.p.m. amagat}^{-1},$$

where

$$a_0 = -0{\cdot}871\,057, \quad a_1 = 4{\cdot}54 \times 10^{-4}\text{ K}^{-1}, \quad a_2 = -8{\cdot}15 \times 10^{-6}\text{ K}^{-2}, \quad a_3 = 2{\cdot}05 \times 10^{-8}\text{ K}^{-3}.$$

The overwhelming a_0 term does show that the temperature dependence of $\sigma_1(\text{Xe–O}_2)-\sigma_1(\text{Xe–Ar})$ is primarily of the form $1/T$.

The term labelled C, which we have been considering as the contribution due to the contact interaction, actually includes in it the O_2 bulk susceptibility contribution to $\sigma_1(\text{Xe–O}_2)$. The O_2 bulk susceptibility contribution to $\sigma_1(\text{Xe–O}_2)$ is not negligible and is $(2\pi/3)\chi$, where χ is the molar paramagnetic susceptibility of O_2 gas. Using Van Vleck's value for the molar susceptibility of O_2 [7], we find the bulk susceptibility contribution to be opposite in sign to the density-dependent chemical shielding and equal to (300 K/T)(0·3093) p.p.m. amagat^{-1}. Thus, the contact contribution to $\sigma_1(\text{Xe–O}_2)$ in p.p.m. amagat^{-1} is

$$\begin{aligned}\sigma_1(\text{Xe–O}_2,\ \text{contact}) &\cong \sigma_1(\text{Xe–O}_2)-\sigma_{\text{bulk}}-\sigma_1(\text{Xe–Ar})\\ &=(300\ \text{K}/T)\{-1{\cdot}18034+4{\cdot}54\times10^{-4}[(T/\text{K})-300]\\ &\quad -8{\cdot}15\times10^{-6}[(T/\text{K})-300]^2+2{\cdot}05\times10^{-8}[(T/\text{K})-300]^3\}.\end{aligned}$$

Further, if we make the unsupported assumption that

Assumption 3. $\sigma_c(R)\approx b\sigma_d(R)$, where b is a constant, and again take Ar as a system which interacts with Xe as a hypothetically diamagnetic O_2 would interact, then

$$\sigma_1(\text{Xe–O}_2)=[(300\ \text{K}/T)b+1]\sigma_1(\text{Xe–Ar}),$$

where $\sigma_1(\text{Xe–Ar})$ is the experimentally determined density-dependent chemical shielding for Xe in the presence of Ar. Then, a plot of

$$\log\left\{\frac{\sigma_1(\text{Xe–O}_2)}{\sigma_1(\text{Xe–Ar})}-1\right\}\ \text{versus}\ \log(1/T)$$

should give a linear plot with a slope of unity. Such a plot is shown in figure 2. We see that below 350 K the plot is indeed linear with a slope very nearly equal to 1·0. This lends further credence to the hypothesis that the unusually large value of σ_1 for Xe–O_2 is the result of an intermolecular contact interaction. It is interesting to note that extrapolation of the straight line in figure 2 gives an

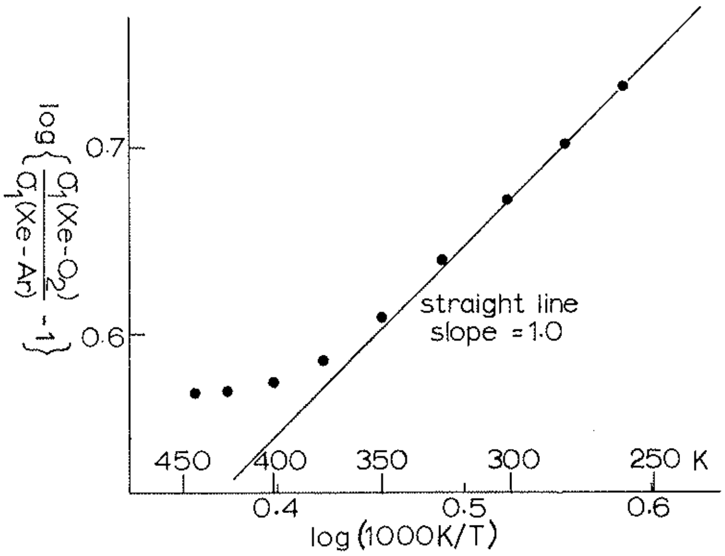

Figure 2. Demonstration of the limiting $1/T$ dependence of the contact contribution to $\sigma_1(\text{Xe–O}_2)$.

intercept which results in a value of b which is very close to 3. This indicates that the shielding function for Xe interacting with a paramagnetic O_2 is of the same order of magnitude as the shielding function for Xe interacting with a diamagnetic Ar.

The deviation above 350 K in figure 2 might be explained in a variety of ways. The higher the temperature the smaller the term labelled C will be. When term C is no longer much greater than term D, the effects of our crude assumption 2 will be more obvious. Assumption 3, $\sigma_c(R) \approx b\sigma_d(R)$, might be approximately realistic if the range of R sampled by the ensemble average is small. Both are due to correlation effects, with $\sigma_d(R)$ due to Coulomb correlation and $\sigma_c(R)$ due to spin correlation. However, as T increases, a larger range of R becomes important and it is unrealistic to assume that $\sigma_c(R) \approx b\sigma_d(R)$ holds over a wide range of R values. This could easily account for the wide discrepancy at elevated temperatures in figure 2.

The interpretation of the shielding function $\sigma_c(R)$ in terms of the spin density at the Xe nucleus as it is affected by the O_2 molecule still remains to be done. There are several mechanisms for **I . S** interaction which might be responsible. Watson and Freeman [8] suggest overlap, covalency, and exchange polarization effects as possible mechanisms for the induced hyperfine field at the nucleus of a normally non-magnetic ion or atom by neighbouring magnetic ions. All of these mechanisms lead to a shielding function

$$\sigma_c(R) = -\tfrac{2}{3}\beta_N g_e^2 \left(\frac{\beta_e^2}{3kT}\right) S(S+1)\ |\psi \text{ (at Xe nucleus)}|^2,$$

where $|\psi \text{ (at Xe nucleus)}|^2$ is the net electron spin density at the Xe nucleus.

Neglecting exchange polarization, the spin ↑ density at the Xe nucleus at a distance R from the oxygen molecule is

$$\begin{aligned}|\psi \text{ (at Xe nucleus)}|^2 = (S+\gamma)^2|\chi(0)|^2 + (S^2-\gamma^2)|\phi(R)|^2 \\ -(S+\gamma)\{\phi^*(R)\chi(0)+\phi(R)\chi^*(0)\},\end{aligned}$$

where χ and ϕ are the Xe 5s and the O_2 molecular orbitals evaluated at the Xe nucleus, respectively, S is the overlap integral between the Xe 5s and the O_2 molecular orbital and γ is the covalency mixing coefficient.

In particular, the overlap contribution has been discussed by Buckingham and Kollman [4] as the major contribution to the net electron spin density at the Xe nucleus. Their calculations do show that the overlap contribution alone is sufficient to account for the size of σ_1 at room temperature. However, there is also the exchange polarization contribution which may not be completely neglected. Let us examine the size of this contribution.

Since the O_2 molecular orbital $\phi_\uparrow$ is occupied and the $\phi_\downarrow$ is not, the exchange interactions between $\phi_\uparrow$ and all other ↑ orbitals will result in a different spatial function for ↑ than for ↓ orbitals. In particular, the spatial part of $\chi_\uparrow$ will be different from that of $\chi_\downarrow$. Naively expressed, the exchange interaction pulls the spin ↑ electron into the spatial regions of high probability for the $\phi_\uparrow$ electron (away from the Xe nucleus), thus yielding a net spin ↓ at the χ nucleus. While this is an oversimplified picture, actual calculations of spin ↑ and spin ↓ functions by extended or projected Hartree–Fock methods on various systems do show this trend [8]. Since the relative magnitude of the spin-polarization term has been shown to be *dominant* in some cases [8], they cannot necessarily be neglected in the case of $\mathrm{Xe}+\mathrm{O}_2$. Unfortunately, the calculation of spin-polarization effects would require Hartree–Fock calculations on the $\mathrm{Xe}+\mathrm{O}_2$ multi-electron system, allowing different spatial functions for spin ↑ than for spin ↓ electrons.

A perturbation approach would involve calculations of integrals of the type shown below for polarization of Xe s-electrons by the O_2 unpaired electrons.

From the cross term in the 2nd-order perturbation energy :

$$a_{\mathrm{Xe}}{}^{(\text{due to core polarization})} = -2\sum_i \frac{\langle\psi_0|\mathscr{H}'|\psi_i\rangle\langle\psi_i|\dfrac{8\pi g_{\mathrm{N}}\beta_{\mathrm{N}}}{3\langle S_z\rangle}\sum_k \delta(r_{\mathrm{Xe}\,k})S_{zk}|\psi_0\rangle}{E_i-E_0},$$

where $\mathscr{H}'=$exchange interaction hamiltonian, as in sigma–pi interaction, $=\sum_{\sigma,\pi}(e^2/r_{\sigma\pi})P_{\sigma\pi}$, σ are electrons in Xe orbitals, π are unpaired electrons of O_2. $P_{\sigma\pi}$ is the permutation operator. This leads to terms of the type :

$$\frac{8\pi}{3}g_{\mathrm{N}}\beta_{\mathrm{N}}\frac{\langle 5\mathrm{s}_{\mathrm{Xe}}{}^{(1)}\mathrm{O}_2{}^{(2)}|\dfrac{1}{r_{12}}|\mathrm{O}_2{}^{(1)}6\mathrm{s}_{\mathrm{Xe}}{}^{(2)}\rangle\langle 5\mathrm{s}_{\mathrm{Xe}}|\delta(r_{\mathrm{Xe}})|6\mathrm{s}_{\mathrm{Xe}}\rangle}{(E_{6\mathrm{s}}-E_{5\mathrm{s}})}.$$

Because of the $\delta(r_{\mathrm{Xe}})$ operator, Xe p and d-orbitals need not be considered. We should have a sum over all s-orbitals instead of just the above term for the 5s. Excitations from 4s, 3s, 2s or 1s orbitals of Xe to the unoccupied ones require much more energy, however, they also have larger densities at the Xe nucleus, so they should be included :

$$a_{\mathrm{Xe}}{}^{(\text{due to core polarization})} = \frac{8\pi}{3}g_{\mathrm{N}}\beta_{\mathrm{N}}\sum_{n\mathrm{s}=1\mathrm{s}}^{5\mathrm{s}} \times\frac{\langle n\mathrm{s}_{\mathrm{Xe}}{}^{(1)}\mathrm{O}_2{}^{(2)}|\dfrac{1}{r_{12}}|\mathrm{O}_2{}^{(1)}6\mathrm{s}_{\mathrm{Xe}}{}^{(2)}\rangle}{(E_{6\mathrm{s}}-E_{n\mathrm{s}})}n\mathrm{s}_{\mathrm{Xe}}{}^{(0)}6\mathrm{s}_{\mathrm{Xe}}{}^{(0)}.$$

The sign of the above contributions depends on the sign of the exchange integrals of the type

$$\langle 5\mathrm{s}_{\mathrm{Xe}}{}^{(1)}\mathrm{O}_2{}^{(2)}|(1/r_{12})|\mathrm{O}_2{}^{(1)}6\mathrm{s}_{\mathrm{Xe}}{}^{(2)}\rangle.$$

A good guess is that these integrals are most likely *negative*, leading to an upfield shift. This guess is based on observations of *negative* effective fields at nuclei in ferromagnetic metals which have successfully been interpreted in terms of polarization of inner s electrons by one or more unpaired 3d-electrons [8]. Also, the rule of thumb in M.O. calculations is that 2-centre exchange integrals are negative for overlapping orbitals which have the *same* sign in the regions of overlap. Care has to be exercised in applying this to s-orbitals because the s-functions change sign as many times as $(n-1)$. However, in this calculation, this need not be worrisome since, in collision, the O_2 molecular orbital has sizeable overlap only with the outermost portion of the Xe ns orbital.

The usual rough approximation of these exchange integrals is by an energy factor times the overlap integrals. The energy factor should be negative according to the above arguments and the usual approximation is to use the excitation energy ΔE itself :

$$\langle 5s_{Xe}{}^{(1)}O_2{}^{(2)}|\frac{1}{r_{12}}|O_2{}^{(1)}6s_{Xe}{}^{(2)}\rangle \simeq -\Delta E_{5s\to 6s}\langle 5s_{Xe}|O_2\rangle\langle 6s_{Xe}|O_2\rangle.$$

Thus,

$$a_{Xe}{}^{(\text{core polarization})} \cong -\frac{8\pi}{3} g_N\beta_N\langle 6s_{Xe}|O_2\rangle\chi_{6s}{}^{(0)} \cdot \sum_{ns=1s}^{5s} \langle ns_{Xe}|O_2\rangle\chi_{ns}{}^{(0)}.$$

This contribution leads to an upfield shift and cancels out part of the overlap and covalency effects. Looking at the above equation and comparing it with that which one would get from the positive spin density due to overlap and covalency effects, we note that the leading overlap term $(S^2{}_{5s-O_2}|\chi(0)|^2)$ would be of the same order of magnitude as the leading term

$$-S_{5s-O_2}S_{6s-O_2}\chi_{5s}(0)\chi_{6s}(0)$$

in the approximate perturbation approach to core polarization. Thus, the complete neglect of exchange polarization in this case is probably too drastic an approximation.

Buckingham and Kollman found that for the overlap mechanism the calculated σ_1 value is very sensitive to the functions used for the Xe 5s and the O_2 $\pi_g{}^*$ orbitals and also the intermolecular potential. A complete calculation of the temperature dependence of $\sigma_1(\text{Xe–O}_2)$ including the exchange polarization terms awaits the emergence of atomic and molecular functions and a potential function more accurate than those already used by Buckingham and Kollman.

4. CONCLUSIONS

The temperature dependence of $\sigma_1(\text{Xe–O}_2)$ reported here shows a dominant $1/T$ relationship. Thus, the experimental data can be interpreted adequately by a Fermi contact interaction which is expected to show this Curie-type behaviour. In the low-temperature region (below 350 K) where the contact term is expected to dominate over the normal Xe shifts expected from interaction with diamagnetic molecules, the experimental data behave entirely as would be expected, giving a linear plot with a slope of unity for

$$\log\left\{\frac{\sigma_1(\text{Xe–O}_2)}{\sigma_1(\text{Xe–O}_2{}^{d})}-1\right\} \text{ versus } \log(1/T),$$

where σ_1 for Xe and a diamagnetic O_2 ($O_2{}^d$) is taken to be closely approximated by $\sigma_1(\text{Xe–Ar})$. A theoretical calculation of $\sigma_c(R)$ requires more accurate wavefunctions for Xe and O_2. And since $\sigma_1(\text{Xe–O}_2)$ is an average over the Xe–O_2 encounters, a more accurate Xe–O_2 potential function is required for a complete theoretical calculation of the temperature dependence of $\sigma_1(\text{Xe–O}_2)$ reported here.

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