An empirical chemical shielding function for interacting atoms from direct inversion of NMR data

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For two spherically symmetric molecules it is possible to directly determine the chemical shielding function $\sigma(R)$ from the experimental values of the second virial coefficient of chemical shielding $\sigma_1(T)$ by inversion of the integral equation $\sigma_1(T) = 4\pi \int_0^\infty \sigma(R)\exp[-V(R)/kT]R^2\,dR$. Various inversion methods are considered and applied to the xenon system yielding a chemical shielding function which, when integrated over all configurations, yields satisfactory agreement with experimental values of $\sigma_1(T)$.

Previous ^{1}H, ^{19}F, and ^{129}Xe NMR studies in gaseous systems show that the chemical shift has an essentially linear dependence on density at sufficiently low densities, but precise measurements on ^{129}Xe show that higher order terms in the virial expansion of chemical shielding are important[1]:

$$\sigma(\rho, T) = \sigma_0 + \sigma_1(T)\rho + \sigma_2(T)\rho^2 + \sigma_3(T)\rho^3 + \ldots,$$

where, ρ is the density, and at room temperature:

$$\sigma_1 = -0.548 \pm 0.004 \text{ ppm/amagat},$$

$$\sigma_2 = (-0.169 \pm 0.02) \times 10^{-3} \text{ ppm/amagat},^2$$

$$\sigma_3 = (0.163 \pm 0.01) \times 10^{-5} \text{ ppm/amagat}.^3$$

Precise measurement of $\sigma_1(T)$ in the temperature range 220 to 440 K have been carried out for ^{129}Xe in xenon gas.[2] More precise Fourier transform NMR experiments were carried out for xenon samples of much lower densities (3 to 28 amagats) giving a more accurate set of values for $\sigma_1(T)$ for xenon.[3]

The new experimental values of $\sigma_1(T)$ have been fitted to a 5th degree polynomial:

$$\sigma_1(T) = -0.553 + 0.1114\times10^{-2}\tau - 0.765\times10^{-5}\tau^2 + 0.436\times10^{-7}\tau^3 - 0.132\times10^{-9}\tau^4 - 0.545\times10^{-12}\tau^5 \text{ ppm amagat}^{-1},$$

where $\tau = (T - 300)$ K.

Theoretically, it is possible to obtain the functional form of the chemical shielding, σ, of two interacting molecules from very accurate measurements of the temperature dependence of σ_1. For spherically symmetric molecules such as Xe, the integration over all configurations is a simple one:

$$\sigma_1(T) = 4\pi \int_0^\infty \sigma(R)\exp\left(\frac{-V(R)}{kT}\right) R^2\,dR,$$

so that the chemical shielding of two interacting spherically symmetric molecules is in terms of only one independent variable, R, the internuclear distance. Previous interpretation of $\sigma(R)$ in terms of a sum of contributions due to neighbor-molecule magnetic anisotropy, polar contributions, van der Waals and repulsive interactions, has been modestly successful in the case of ^{1}H and ^{19}F, and less so in the case of ^{129}Xe.[1,4] Part of the difficulty may have been the lack of good potential functions for a pair of molecules under consideration. The rest may be due to the semi-quantitative, albeit intuitive models used for the different contributions. In order to have a check on the applicability of these models, it is necessary to have a directly determined functional form for $\sigma(R)$. This is possible if $\sigma_1(T)$ can be determined reasonably precisely over a wide range of temperatures for a gas whose intermolecular potential is likewise precisely determined. The intermolecular potential for Xe–Xe has been obtained recently by fitting differential cross-section data, second virial coefficients, and other data.[5] One then only needs a suitable inversion procedure in order to carry out a numerical solution for $\sigma(R)$ using precise data points for $\sigma_1(T)$. Different inversion methods applicable to this type of integral equation are discussed and applied to $\sigma_1(T)$ to obtain a chemical shielding function for xenon.

METHODS FOR INVERSION OF $\sigma_1(T)$ DATA

The integral equation which has to be solved is:

$$4\pi \int^\infty \sigma(R) e^{-V(R)/kT} R^2\,dR = \sigma_1(T)$$

in which the kernel is $K(R, T) = 4\pi e^{-V(R)/kT}R^2$, and $\sigma(R)$ is the unknown function of R, the variation of chemical shielding with intermolecular distance for two spherically symmetric molecules, and the $\sigma_1(T)$ are the measured second virial coefficients for chemical shielding in the range of temperatures 240 to 440 K. This integral equation is of the type

$$\int_a^b K(x, y) f(y) dy = g(x) \tag{1}$$

which is a Fredholm integral equation of the first kind. The success in solving Eq. (1) by any method depends to a large extent on the accuracy of $g(x)$ and the shape of $K(x, y)$.[6]

Solution of Eq. (1) may be possible by analytical means using known transforms which exist for certain forms of $K(x, y)$. However, even if one could find a known transform for the specific form of $K(x, y)$ such transforms invariably involve integration over the full range of x values ($-\infty$ to $+\infty$ or 0 to ∞). In those cases where $g(x)$ are experimentally measured quantities, consisting of a finite number of experimental data points of limited accuracy over a small portion of the full range of x values, such integrals have to be performed over intervals of the x axis for which no experimental data are

available and extrapolation is doubtful.

Solution of Eq. (1) by the well-known quadrature (so-called "algebraic") methods[7] generally yield linear systems of equations which can be solved if the form of $g(x)$ is known with very high accuracy. The definite integral on the left-hand side of the equation may be replaced by a summation of n terms of the form:

$$\int_a^b K(x,y)f(y)dy = \sum_{j=1}^{n} H_j\, K(y_j, x)f(y_j) + \epsilon_n,$$

where the abscissae y_j as well as the corresponding weight coefficients H_j have been chosen to attain the desired degree of accuracy with a given number of terms, and to suppress the magnitude of the error term ϵ_n below a pre-assigned limit. For n preselected discrete values of T this integral equation can be written as:

$$\sum_{j=1}^{n} H_j\, K(y_j, x_i)f(y_j) = g(x_i) \quad i = 1, 2 \ldots n \ .$$

With the values of $H_jK(y_j, x_i)$ as well as $g(x_i)$ regarded as known, the above represents nothing else but a simultaneous system of n algebraic equations for the determination of n unknown values of $f(y_j)$. Theoretically, this system can be solved uniquely for the $f(y_j)$'s and a polynomial of $(n-1)$st degree passing through these n ordinates will then represent the corresponding approximation to the solution of the integral equation, since the errors ϵ_n can presumably be made as small as we please by adopting a sufficiently large value of n. This method is useful provided $g(x)$ is known for all values of x with unlimited accuracy. Otherwise it often fails because the linear system of equations is usually too ill-conditioned ot tolerate any errors in the $g(x)$.

One can resort to the approximation of $f(y)$ by a finite series of functions and the evaluation of their coefficients by a least-squares method. If we let $f(y) = \sum_{k=1}^{n} c_k F(y)$, where $F(y)$ are the series of functions (reducing functions) used, our integral equation reduces to:

$$\begin{aligned} g(x_1) &= \sum_{k=1}^{n} c_k \int_a^b K(x_1, y)F(y)dy \\ &\ \ \vdots \qquad\qquad \vdots \\ g(x_m) &= \sum_{k=1}^{n} c_k \int_a^b K(x_m, y)F(y)dy \ . \end{aligned}$$

The parameters c_k are obtained by a least squares analysis of this set of linear equations. While this method is more stable to errors in $g(x)$, it has the obvious disadvantage of forcing the solution to take a fixed functional form, especially serious since the number of arbitrary coefficients must be considerably smaller than the number of data points $g(x)$ to ensure that the resulting linear system will be sufficiently overdetermined to give a reliable solution.

Several methods for solving integral equations of this type numerically have been proposed[8] for certain kernels $K(x, y)$. No method has been very successful for arbitrary kernels when the function $g(x)$ is known with only modest accuracy and only over a modest range of x values. We may think of this equation as a linear operator on $f(y)$ to produce $g(x)$. This operator does not have a bounded inverse, as has been shown by Phillips.[8] We will assume here that it does have an inverse.

In order to solve Eq. (1) numerically we make a matrix approximation to it:

$$\sum_{i=0}^{n} w_i k_{ji} f_i = g_j \quad \text{or} \quad \mathbf{Af} = \mathbf{g}$$

where $A_{ji} = w_i k_{ji}$, $k_{ji} = K(x_j, y_i)$, $g_j = g(x_j)$, and $f_i = f(y_i)$, and the w_i are weight factors whose values depend on the quadrature formula used. It is found that as the mesh width decreases, the solutions first become more accurate, but eventually begin to get worse. How soon the solutions begin to get worse depends on the accuracy of $g(x)$. Larger errors in g cause the solutions to get worse sooner. Also, the error in each of the approximate solutions tends to be an oscillatory function of x. See for example, Ref. 8. Improvements to reduce the oscillations in the desired function $f(y)$ have been suggested. Since the function $g(x)$ is not known accurately, we should state the problem as

$$\int_a^b K(x, y)f(y)dy = g(x) + \epsilon(x),$$

where $\epsilon(x)$ is an arbitrary function except for some condition on the size of $\epsilon(x)$. In matrix form:

$$\mathbf{Af} = \mathbf{g} + \boldsymbol{\epsilon}. \tag{2}$$

In Eq. (2) Phillips described a method whereby a controlled smoothing could be induced in the solution obtained, by the inversion of the quadrature approximation to the integral equation.[8] The smoothest acceptable solution is defined in the sense of minimizing the second-difference expression: $\sum_i (f_{i-1} - 2f_i + f_{i+1}^2)$ with the auxiliary conditions: $\mathbf{Af} = \mathbf{g} + \boldsymbol{\epsilon}$ and $\sum_i \epsilon_i^2 = \text{constant}$. The quantity to be minimized is then

$$\sum_i (f_{i-1} - 2f_i + f_{i+1})^2 + \gamma^{-1} \sum_i \epsilon_i^2 \ ,$$

γ being an undetermined multiplier. The solution obtained was $f = (A + \gamma B)^{-1} g$, B being a matrix related to A^{-1} matrix elements by

$$B_{jk} = A^{-1}_{k-2,j} - 4A^{-1}_{k-1,j} + 6A^{-1}_{k,j} - 4A^{-1}_{k+1,j} + A^{-1}_{k+2,j} \ .$$

Both the sums of the squares of the errors $\sum_i \epsilon_i^2$ and the smoothness of the solution depend on γ and it is on these grounds that γ is selected—solutions are found for several values of γ. The largest value for γ is selected which still gives a value of $\sum_i \epsilon_i^2$ consistent with the experimental errors in g.

A modification of Phillips' method and extension to nonsquare A matrices was suggested by Twomey[9] and it is this method which is used here. The expression to be minimized is differentiated with respect to the f_i rather than the ϵ_i, resulting in

$$0 = \gamma^{-1} \sum_j \epsilon_j A_{ji} + (f_{i-2} - 4f_{i-1} + 6f_i - 4f_{i+1} + f_{i+2}).$$

Elimination of ϵ between Eq. (2) and the above equation gives the solution of the form: $f = (A^T A + \gamma B)^{-1} A^T g$ where A^T = transpose of A, and B is the matrix

$$\begin{bmatrix} 1 & -2 & 1 & & & 0 \\ -2 & 5 & -4 & 1 & & \\ 1 & -4 & 6 & -4 & 1 & \\ 0 & 1 & -4 & 6 & -4 & 1 \\ & 0 & & & & \end{bmatrix} .$$

This method works when A is *not* a square matrix, that is, when the number of points in the quadrature used is not equal to the number of experimental data points in $g(x)$.

To calculate the matrix A, we have to choose a quadrature method for the integral.[7] If $f(x)$ were a function which can be suitably approximated by a polynomial in ascending powers of x, our integral would clearly diverge if one of its limits equals infinity, as it is in our case. If $f(x)$ is such a function, it must therefore be pre-multiplied, before integration, by a suitable weight function $w(x)$ which remains positive throughout the interval of integration and approaches zero faster than $f(x)$ tends to infinity at the singular limit, so that the integral of $w(x)\,f(x)$ converges. We adopt $w(x) = e^{-x}$ out of many other functions which could have served the same purpose. Since one of our limits of integration is infinite, we pre-multiply the function by e^{-x} in order to ensure that the integral will actually remain convergent for the limits 0 to ∞. We can then use the Gauss–Laguerre quadrature formula

$$\int_0^\infty e^{-x} f(x)dx = \sum_j^n h_j f(a_j)$$

where

$$h_j = \frac{(n!)^2}{a_j[L_n^I(a_j)]^2} \quad ,$$

where L_n = Laguerre polynomial of degree n, and a_j = roots of the Laguerre polynomial. The weighting coefficients h_j and the abscissae a_j for the Gauss–Laguerre quadrature for various n have been evaluated in the past by different authors.[10] We can therefore express our integral of interest as

$$\int_0^\infty K(R, T)\sigma(R)dR = \sum_{j=1}^n H_j K(R_j, T)\sigma(R_j),$$

where the weighting factors are $H_j = h_j/e^{-a}j$ in terms of the known weighting factors and roots of the Gauss–Laguerre quadratures and the kernel is $K(R_j, T_i) = 4\pi a_j^2 e^{-V(a_j)/kT_i}$. In matrix form, our Fredholm integral equation,

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

can be cast into $\mathbf{A}\sigma = \sigma_1$ where σ = values of the chemical shielding function $\sigma(R)$, $\sigma_1 = \sigma_1(T)$, experimental values of the second virial coefficient for chemical shielding, and

$$(A)_{ij} = \frac{h_j 4\pi a_j^2 e^{-V(a_j)/kT_i}}{e^{-a}j}$$

in which T_i are the chosen temperature increments in the range 240 to 440 °K. We then can find the solution σ by solving

$$\sigma = (\mathbf{A}^T\mathbf{A} + \gamma\mathbf{B})^{-1}\mathbf{A}^T\sigma_1,$$

where **A** and **B** (previously defined) are known, σ_1, are experimental points, and γ is an undetermined multipler whose value is chosen such as to be that value which gives the smoothest function and still falls within the magnitude of experimental error in σ_1.

An iterative procedure is set up in which γ is chosen (between zero and $\sum_i \epsilon_i^2$), σ is calculated and plotted out to check for smoothness. As a final check, we insert the obtained values of σ back into the integral, evaluate the integral numerically for each T_i, and compare with experimental points $\sigma_1(T_i)$.

RESULTS

The Xe potential function used here is that of Barker, Watts, Lee, Schafer, and Lee.[5] The Xe–Xe potential of Barker *et al.* was determined by fitting molecular beam scattering data, the first eleven vibrational levels of Xe dimer which have been observed, gas viscosities, second virial coefficients, and the cohesive energy of crystalline xenon at 0 K, all within experimental error. It is undoubtedly the best available Xe–Xe potential. The results of the inversion using this potential function are discussed below.

Using Twomey's method[9]: We initially chose a Laguerre polynomial of degree 15, thus there are 15 quadrature points. There are 21 points in $\sigma_1(T)$ if intervals of 10 °K are taken. Taking smaller intervals in σ_1 did not lead to significant improvement. Thus a matrix of dimension 21×15 was set up. A computer program which accepted the a_i (roots of the Laguerre polynomial and the abscissas for the Gauss–Laguerre quadrature), the h_j (weighting coefficients), both taken from Salzer and Zucker,[10] T_i (absolute temperature), and $\sigma_1(T_i)$ (the experimental values of the second virial coefficient of chemical shielding at each temperature) was written. The program sets up the matrix A and B. For any input of the smoothing parameter γ, the vector $(A^TA + \gamma B)^{-1}A^T\sigma_1$, which is the result of the inversion process, is σ, the calculated value of the function at the various quadrature abscissae. It was found that abscissae points $r < 0.75r_e$ or $r > 1.5r_e$ (r_e for Xe = 4.36 Å) did not contribute significantly to the solution but considerably extended the time used for matrix manipulation. Likewise, it was found that taking smaller temperature increments did not significantly improve the solution. Gamma values up to 0.01 were tried. Since γ has to be within the experimental error in $\sigma_1(T)$, which we estimate to be less than 0.005 ppm amagat^{-1}, use of $\gamma > 0.005$ leads to over-damping. The results for $\gamma = 5 \times 10^{-4}$ are shown in Fig. 1 and in Table I.

Since the raw data are collected for each sample of given density as a function of temperature, the experimental results on σ_1 could just as well have been reported in terms of $d\sigma_1/dT$.

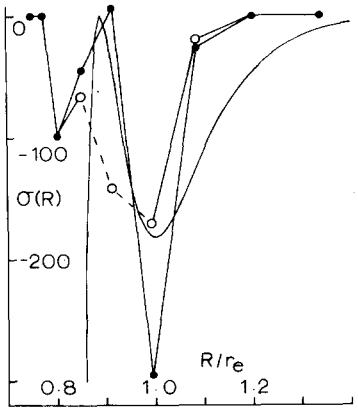

FIG. 1. The chemical shielding function vs intermolecular distance resulting from direct inversion of $\sigma_1(T)$, with $\gamma = 5 \times 10^{-4}$ (●). The $\sigma(R)$ obtained by inversion of $d\sigma_1(T)/dT$ (○) is also shown but the derivative gives no information in the region where V is close to zero, thus the point at $0.9148 r_e$ is connected to others by dashed lines. The solid curve is the best analytic function found: $f(V^2) = -1.8126 \times 10^{-4} \mid V(R)/V(r_e) \mid^2$.

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

Inversion of the experimental first derivative with respect to temperature can be carried out by the same method as for the experimental $\sigma_1(T)$. Here, the resulting $\sigma(R)$ is expected to be much more sensitive to the form of the Xe–Xe potential. The results are shown in Fig. 1 and in Table I for $\gamma = 5 \times 10^{-6}$.

The results of the inversion are sensitive to the depth of the potential. A well depth (ϵ) which is too small, such as 221 K, an old value for the well-depth for the Xe potential, gives rise to oscillations in the empirical $\sigma(R)$, as the method tries to fit experimental points with a poor $V(R)$ and fails. The functional form of the potential is not too critical. A Lennard-Jones 6-12 function with the same ϵ and r_0 parameters as Barker *et al*'s potential function, gives an empirical $\sigma(R)$ which is very close to that obtained using the potential function of Barker *et al*. The root mean square deviation of one from the other is 1.42 ppm, which is small compared with the value of $\sigma(R)$ at $0.994 r_e$ which is −291 ppm.

The empirical $\sigma(R)$ function resulting from direct inversion of the $\sigma_1(T)$ data or the first derivative appears as a function with a minimum appearing at $R = r_e$ and an apparent node at $R = r_0$, where $V(R)$ vanishes. The points at $R < 0.8 r_e$ are probably less reliable than the rest. The contribution to the σ_1 integral from this region is very small owing to the very small values of $\exp[-V(R)/kT]$ within the temperature range explored by the experiment. With the available data, the $\sigma(R)$ obtained is probably good within $1.1 r_e > R > 0.80 r_e$. More information on $\sigma(R)$ could be obtained in the region $R < 0.80 r_e$ if higher temperature data were available. However the temperature range that would have to be covered experimentally is presently inacessible since $\exp[-V(R)/kT]$ falls off very rapidly as R becomes small. In order to obtain information on $\sigma(R = 0.75 r_e)$ which is comparable to the present information on $\sigma(R = 0.80 r_e)$, σ_1 has to be measured up to $T = 1126$ K, since it is at this temperature that $\exp[-V(R)/kT]$ at $R = 0.80 r_e$, $T = 440$ K is equal to that $R = 0.75 r_e$.

This empirical chemical shielding function, $\sigma(R)$, represents the difference between the chemical shielding of a Xe nucleus in an interacting pair and that of a Xe nucleus in an isolated Xe atom. Thus, $\sigma(R)$ should theoretically approach zero as R goes to infinity. The empirical chemical shielding function found here does seem to have that limiting behavior.

The results of the direct inversion method came as a surprise, since a monotonically decreasing $\sigma(R)$ such as in Adrian's model[11] for $\sigma(R)$ was initially expected. Examination of the numerical $\sigma(R)$ leads one to suspect that $\sigma(R)$ may be related to some power of the absolute value of $V(R)$. Various functional forms of $\sigma(R)$, including the family of functions $\mid V(R) \mid^n$ were assumed for $\sigma(R)$, to see how well $\sigma_1(T)$ can be fitted by such trial shielding functions. A computer program was written which accepts the functional form, normalizes it such as to lead to a σ_1 (at $T = 270$) in agreement with experiment, and carries out the integration to yield σ_1 at various temperatures. The functional forms which were tried were

$$\exp(-\alpha R^n),\ \exp[-\alpha(R-\beta)^n],\ \mid V(R) \mid^n,\ n = 1, 2, \ldots$$

as well as linear combinations of these. None of the first two functions gave a satisfactory fit to the experimental $\sigma_1(T)$ although the ones which came closest in these families of functions was $\exp(-0.5 R^4)$. Most difficult to reproduce was the curvature of the experimental $\sigma_1(T)$. Functions which gave steep slopes [high values of $d\sigma_1(T)/dT$] at the lower temperatures ($T < 300$ K) could not reproduce the low values of $d\sigma_1(T)/dT$ at higher temperatures ($T > 300$ K). A fair fit to the experimental $\sigma_1(T)$ was obtained with $\mid V(R) \mid^2$. This function, normalized to the experimental value at 270 K, is

TABLE I. Numerical chemical shielding function, in ppm, obtained by direct inversion of experimental σ_1 and its first derivative, using Twomey's method.

R/r_e	from σ_1	from $d\sigma_1/dT$
0.754	+0.07	+0.04
0.772	+0.54	−1.69
0.805	−98.39	−93.93
0.852	−45.27	−64.84
0.915	+6.04	−144.26
0.994	−291.51	−169.70
1.090	−27.24	−20.35
1.205	−0.11	−1.02
1.340	+0.08	−0.03
1.498	+0.005	−0.0006

$$f(V^2) = -1.8126\times10^{-4}\,|V(R)/V(r_e)|^2.$$

A monotomic function such as an exponential (or a linear combination of exponentials) gives poor agreement with experiment. As a typical example of an exponential function for $\sigma(R)$, we take Adrian's theoretical function. The $\sigma(R)$ he calculated gave a change of σ_1 over the temperature range 231 to 347 K of only 4.13×10^{-4} ppm amagat$^{-1}\cdot$ deg^{-1},[11] which is a much smaller temperature dependence than the observed 14.8×10^{-4} ppm amagat$^{-1}\cdot$deg^{-1} over the same temperature range. A modified theoretical $\sigma(R)$ reported later by Adrian, of the form $A\exp[9.801(R-r_0)/r_0]$, where $r_0 = 3.91$ Å, likewise gives poor agreement with experiment. If the value of A is allowed to be an empirical factor, such as to have perfect agreement with experiment at 270 K, a more favorable comparison is possible. Even so, an exponential function such as Adrian's cannot give a satisfactory fit to the experimental data. The $\sigma_1(T)$ calculated using this function and Barker *et al*'s potential, falls well outside experimental precision. In particular, it is found that functions of simple exponential form or a linear combination of exponentials, have no possibility of giving rise to a range in σ_1 [that is, $\sigma_1(T=230) - \sigma_1(T=440)$] as large as that observed experimentally. Functions of the form $\exp(-\alpha R^n)$ and $\exp[-\alpha(R-\beta)^2]$, on the other hand, can be parametrized such as to give a large enough difference in σ_1 between 230 and 440 K, but the $\sigma_1(T)$ curves calculated from them suffer from a lack of curvature which is at odds with the experimental data. Figures 2–4 show curves of σ_1, $d\sigma_1/dT$, and $d^2\sigma_1/dT^2$ calculated using an exponential function. These are to be compared with the respective curves for the experiment as well as the best analytic function found so far, $f(V^2)$. The agreement between experimental $\sigma_1(T)$ and its derivatives and the curves calculated using $f(V^2)$ is only marginally acceptable. The precision and accuracy of the data is somewhat better than the discrepancy between experiment and the $f(V^2)$ results. The discrepancy between the experiment and the exponential function is well outside the experimental accuracy. As noted earlier, the curvature of σ_1 as a function of T is very poorly reproduced by an exponential. $f(V^2)$ gives a closer approximation but is only marginally adequate. The inadequacy of an exponential form is most apparent in the plots of $d\sigma_1/dT$ and $d^2\sigma_1/dT^2$.

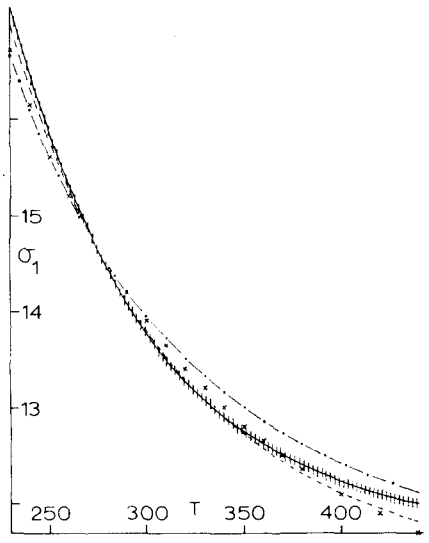

FIG. 2. Values of $\sigma_1(T)$ calculated using trial $\sigma(R)$ functions of the following forms: $x = \exp(-0.5R^4)$, - - - $f(V^2)$ and —·— Adrian's $A\exp[-9.801(R-R_0)/R_0]$ all normalized to reproduce $\sigma_1(T=270\text{ K})$. The experimental $\sigma_1(T)$ is drawn in as a solid curve for comparison, in units of Hz amagat^{-1}, shaded to indicate the precision of the data.

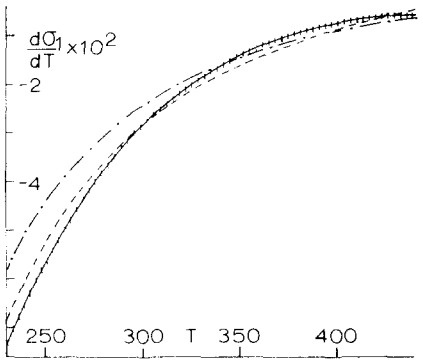

FIG. 3. Values of $d\sigma_1(T)/dT$ calculated using trial $\sigma(R)$ functions: - - - $f(V^2)$, —·— the exponential. The experimental $d\sigma_1(T)/dT$ is drawn in as a solid curve for comparison, in units of Hz amagat$^{-1}\cdot$ deg^{-1}, shaded to indicate the precision of the data.

DISCUSSION

Even though the temperature range over which we have determined $\sigma_1(T)$ is rather large (200 K) by experimental standards, it is still a relatively small range by theoretical standards, since theoretically T goes from 0 to ∞. The experimental temperature range covered explores all portions of the R domain, but some regions less effectively than others. We find that higher temperatures sample more effectively the smaller values of R (in the predominantly repulsive region)

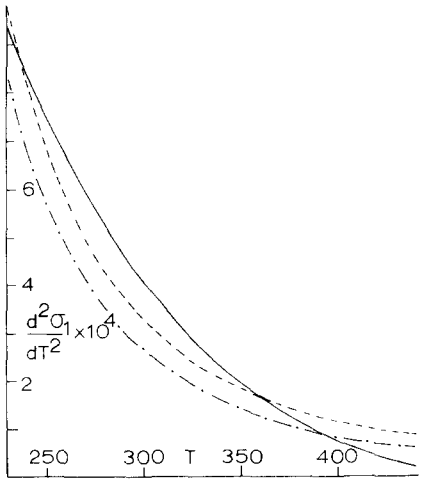

FIG. 4. Values of $d^2\sigma_1(T)/dT^2$ calculated using trial $\sigma(R)$ functions: - - - $f(V^2)$, —·— the exponential, compared with the experimental $d^2\sigma_1(T)/dT^2$.

whereas much lower temperatures sample the well region more effectively. We find that with the experimental temperature range of 220 to 440 K, we can obtain almost no information about $\sigma(R)$ for $R < 0.75 r_e$ or $R > 1.5 r_e$.

The nonmonotonic dependence of $\sigma(R)$ on internuclear distance was surprising at first. However, upon comparison with other systems it appears to be quite reasonable. For example, for two interacting F atoms, the chemical shielding relative to the bare F nucleus, σ_0,

isolated F atom[12]: $\sigma_0 = +470.71 \times 10^{-6}$

F_2 molecule[13] ($R = 1.418$ Å): $\sigma_0 = -232.6 \times 10^{-6}$

united atom (Ar)[12]: $\sigma_0 = +1237.64 \times 10^{-6}$.

Thus, relative to the isolated F atoms, the shielding function $\sigma(R)$ has the following values:

$\sigma(R = \infty) = 0$, $\sigma(R = 1.48\ \text{Å}) = -703 \times 10^{-6}$,

$\sigma(R = 0) = +766.93 \times 10^{-6}$.

Thus, for two interacting F atoms, the shielding function is nonmonotonic and has at least one node between $R = 1.418$ Å and $R = 0$. It is therefore not surprising that the empirical $\sigma(R)$ which we have obtained for two interacting Xe atoms appears to have a nonmonotonic dependence on internuclear distance.

For the united atom formed from two Xe atoms, $Z = 108$, $\sigma_0 = 14688.7 \times 10^{-6}$.[14] This was found by fitting the calculated shielding values for $Z = 1$ to 36 and $Z = 42$, 54, and 86 to a three-parameter formula and extrapolating to higher Z. With the calculated $\sigma_0 = 5638.5$ ppm for Xe atom,[14] the value of $\sigma(R = 0)$ for two interacting Xe atoms should be:

$$\sigma(R = 0) = \sigma_0(\text{united atom}) - \sigma_0(\text{isolated Xe atom})$$
$$= +9050.2 \text{ ppm}.$$

Since the empirical value of $\sigma(R = 4.3623$ Å) is around -200 ppm, this implies that $\sigma(R)$ for two interacting Xe atoms does have at least one node between $R = r_e$ and $R = 0$. The shape of $\sigma(R)$ for Xe_2 may not be unlike that of the incremental polarizability of interacting atoms, $\alpha(R)$, except for the sign. $\alpha(R)$ for a pair of interacting rare gas atoms is negative at small R, has a node in the vicinity of r_0, a maximum in the vicinity of r_e, and approaches zero as R goes to infinity.[15]

The fair fit to the experimental $\sigma_1(T)$ which is obtained from a function of the form $|V(R)|^2$ is probably not significant. There is no *a priori* reason why the shielding function for two interacting molecules should be proportional to the square of the intermolecular potential. Nevertheless, in the case of xenon, $f(V^2)$ does appear to have the right shape to give fair agreement with the results of direct inversion of $\sigma_1(T)$ data. The $\sigma(R)$ function found by inversion is more peaked at $R \sim r_e$ than $f(V^2)$ can be if it is to reproduce the $\sigma_1(T)$ at the higher temperatures, and $f(V^2)$ does not have the same behavior between $R = 0.8\ r_e$ and $R = 0$ as the $\sigma(R)$ found by inversion. Nevertheless the fair agreement shown in Fig. 2–4 suggests interesting possibilities.

It was noted by Barker *et al.* that the reduced second derivatives and reduced third derivatives at the minimum of the best rare gas potentials are remarkably similar.[5] This similarity of shape of $V(R)$ is much closer than one had any reason to expect except on the basis of the empirical success of corresponding states. Thus, *if* $\sigma(R)$ can be represented by some power of $V(R)$ then the reduced second virial coefficients of chemical shielding for Xe–Xe, Xe–Kr, Xe–Ar, etc., should likewise be similar. In the reduced form, $X = R/r_e$, $V^*(X) = V(X)/\epsilon$, and $T^* = kT/\epsilon$. This leads to

$$\sigma_1(T^*) = 4\pi r_e^3 \,\text{const}\,\epsilon^n \int_0^\infty |V^*(X)|^n \exp\left(\frac{-V^*(X)}{kT^*}\right) X^2\, dx.$$

The integral is a constant, independent of the pair of atoms (Xe–Xe or Xe–Kr or Xe–Ar) if the law of corresponding states holds. Thus, if $\sigma(R)$ is at all representable by a power of $V(R)$, then we expect to find nearly equal values of $(\sigma_1(T)/r_e^3\epsilon^n)$ at the same reduced temperature, $T^* = kT/\epsilon$ for Xe–Xe, Xe–Kr, and Xe–Ar. We have found this to be approximately correct for $n = 2$, using combining values for ϵ and r_0 for unlike atom pairs.[3] The critical test awaits good values of ϵ from the laboratory of Y. T. Lee in which the Xe–Kr and Xe–Ar potentials are currently being refined.[16]

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