Second virial coefficient of ^{129}Xe chemical shielding in mixtures of Xe with spherical top molecules CH_4, CF_4, and SiF_4

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^{129}Xe chemical shifts in mixtures of Xe with CH_4, CF_4, and SiF_4 as a function of temperature and density have been obtained by pulsed Fourier transform NMR spectroscopy. The low densities of gases used and the previously determined ^{129}Xe shifts in pure xenon enable the determination of the chemical shielding contribution which is linear in density for Xe–CH_4, Xe–CF_4, and Xe–SiF_4 molecular pairs, with a high degree of precision. An approximate reduced second virial coefficient of chemical shielding for ^{129}Xe in Xe interacting with other molecules can be defined, which leads to superposition of Xe–Xe and Xe–Kr curves over a large part of the reduced temperature range for which data is available. Estimates of well depths for Xe–Ar, Xe–CH_4, Xe–CF_4, Xe–SiF_4, and Xe–HCl have been obtained by this method.

Information on intermolecular forces comes from very diverse sources.[1] Information about these forces can be extracted by analysis of measurements of an observable quantity which has some functional dependence on the intermolecular potential. The degree of success depends on the accuracy of the measurements, on the completeness of the theory connecting the potential to the molecular properties measured, and on the sensitivity of this connection. In some cases, there may not be a one-to-one mapping of the potential onto the measured property so that even if one were able to obtain extremely accurate data a unique potential may not be obtainable. In each measurable property from which intermolecular forces have been "extracted," the intermolecular potential is involved in a way which is somewhat different from other measurable properties. Thus, if one had several very accurate observables each of which involve the intermolecular potential in some theoretically established way, it would be feasible to obtain the intermolecular potential with some degree of confidence.

An approach to intermolecular forces from the point of view of NMR gas phase measurements has the advantage that one sees only A–B and A–A interactions when using the nucleus in molecule A as a probe, experimental NMR measurements are capable of extremely high resolution and precision, and that in NMR a great deal of redundancy in information can be obtained so that strong restrictions can be placed on any theoretical interpretation. One can use different nuclei of a colliding pair of molecules as probes, therby obtaining more information. For example, in studying the collisions between Xe and SiF_4 molecules, the ^{129}Xe, ^{29}Si, and ^{19}F resonances can each be observed. The temperature dependence of each of the measurables would have to be satisfied by any theoretical interpretation.

With the simplest molecules, the rare gases, we hope to be able to test the NMR observables against the best available potential functions. Xenon is an ideal probe molecule. Its advantages are many: The molecule has no structure or electrical moments. Being a monatomic molecule, any change in the electronic distribution is transmitted directly to the Xe nucleus. The ^{129}Xe isotope being studied is abundant (26.24%) and has no electric quadrupole moment. The shifts are large, and unlike ^{1}H and ^{19}F shifts they are not dominated by bulk susceptibilities. Xe has no rotational or vibrational degrees of freedom, so that there are no complications from the temperature dependence of the shielding in the isolated molecule.

While there is the available precision and redundancy of information, there is also the NMR connection, that is, the theory connecting the intermolecular potential to the molecular property measured. It is not so much the connection between the intermolecular potential and the observable which needs to be determined, as it is the molecular property itself, in this case, the chemical shielding as a function of the distance between the probe molecule and the molecule with which it is interacting, $\sigma(R)$, which needs to be determined.

In the NMR studies which we are conducting, the observables are resonance frequencies of nuclei as a function of temperature and density.[2] We can express the observed density dependence of chemical shielding σ, as

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

where the $\sigma_1(T)\rho$ term is due to binary interactions, and $\sigma_1(T)$ may be referred to as the second virial coefficient of chemical shielding.

The chemical shielding function $\sigma(R)$ for two interact-

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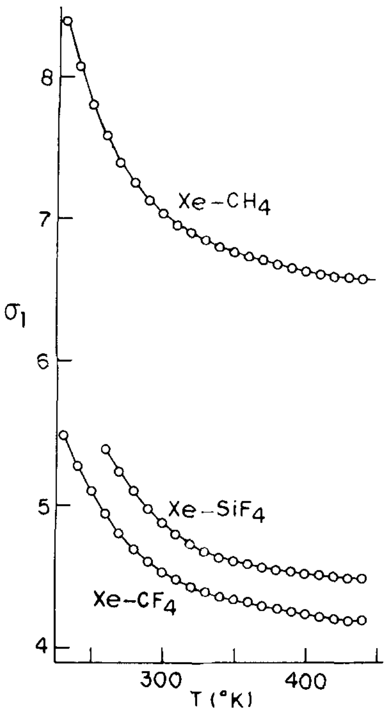

FIG. 1. Temperature dependence of the second virial coefficient of chemical shielding, $\sigma_1(T)$ in Hz amagat^{-1}, for ^{129}Xe in mixtures of Xe with the spherical top molecules, CH_4, CF_4, and SiF_4.

ing Xe atoms as a function of their intermolecular distance has been empirically obtained by mathematical inversion of σ_1 data for xenon,[3] from the integral equation

$$\sigma_1(T) = 4\pi \int_0^\infty \sigma(R)\, e^{-V(R)/kT} R^2 dR, \tag{1}$$

using the most accurate Xe–Xe potential available, that of Barker *et al.*[4] The empirical $\sigma(R)$ which was obtained appears to have a shape not unlike that of the incremental polarizability of interacting atoms, $\alpha(R)$, except for the sign. $\sigma(R)$ for a pair of interacting rare gas atoms is positive at small R, has a node in the vicinity of r_0, a minimum in the vicinity of r_e and approaches zero as R goes to infinity. It was found that a fair fit to the experimental $\sigma_1(T)$ is obtained from a $\sigma(R)$ function of the form $V^2(R)$, which mimics the behavior of the empirical shielding function in the intermolecular distances which are most significant in determining $\sigma_1(T)$.[3]

In this study, we observe ^{129}Xe in mixtures of Xe with CH_4, CF_4, and SiF_4. The intermolecular potential for Xe interacting with one of these spherical tops is probably more nearly spherically symmetric than it is for Xe interacting with other molecules of lower symmetry. Thus, we expect to be able to use Eq. (1) for these molecular pairs as well as for the rare gas pairs. We attempt to find a suitable reduced form of the second virial coefficient of chemical shielding, and thereby develop a method for estimating well depths from the NMR observable.

EXPERIMENTAL RESULTS

For a mixture of Xe and a perturber gas A, the ^{129}Xe shielding is given by:

$$\sigma = \sigma_0 + \sigma_1(\text{Xe–Xe})\rho_{\text{Xe}} + \sigma_1(\text{Xe–A})\rho_{\text{A}} + \cdots .$$

There are contributions due to Xe–A interactions and Xe–Xe interactions. The contribution which is linear with respect to density of Xe, $\sigma_1(\text{Xe–Xe})\rho_{\text{Xe}}$, is already known from our previous studies of pure xenon.[2] The contribution which is linear with respect to density of the perturber gas, $\sigma_1(\text{Xe–A})\rho_{\text{A}}$, is the desired second virial coefficient for the Xe-perturber gas molecular pair. Natural abundance ^{129}Xe NMR spectra were observed using pulsed Fourier transform mode, in samples containing 8–9 amagat of Xe and 20–40 amagat of perturber gas. The densities of Xe are kept this low in order to minimize the $\sigma_1(\text{Xe–Xe})\rho_{\text{Xe}}$ contribution and especially, to minimize contamination of the σ_1 values by three-body or higher order interactions. We had previously obtained very accurate results of temperature and density dependence for pure xenon so that $d\sigma_1(T)/dT$ is known to within 0.5%.[2] With this, the contribution to the frequency shifts due to the Xe–Xe interactions is readily separable, thus allowing shifts due to Xe–perturber interactions to be determined with a high degree of precision.

The experimental details and method of analysis have been previously described.[2] The results are shown in Fig. 1 and Table 1. These values include the bulk susceptibility contribution to σ_1, which is equal to $2\pi\chi/3$ for a cylindrical sample, where χ is the molar susceptibility of the medium (CH_4, SiF_4, CF_4), approximately independent of pressure and temperature for diamagnetic materials. At 24.897 MHz, the bulk susceptibility contribution is 0.040, 0.144, and 0.072 Hz amagat^{-1} for CH_4, SiF_4, and CF_4, respectively. These constitute only a minor fraction of the observed σ_1 (0.6%, 2.9%, and 1.6% of the value of σ_1 at room temperature, respectively).

A REDUCED FORM OF σ_1 FOR RARE GASES

For spherically symmetric molecules such as the rare gases, the second virial coefficient of chemical shielding, σ_1, can be written in reduced form as

$$\sigma_1(\theta) = 4\pi r_e^3 \int_0^\infty \sigma(x) \exp^{-V^*(x)/\theta} x^2 dx,$$

TABLE I. σ_1(Xe–A), the second virial coefficient of ^{129}Xe chemical shielding in xenon with various gases, in Hz amagat^{-1} at 24.897 MHz.

$\sigma_1(\tau) = a_0 + a_1\tau + a_2\tau^2 + a_3\tau^3 + \cdots$, where $\tau = T - 300$ K.

A	a_0	a_1 $\times 10^3$	a_2 $\times 10^5$	a_3 $\times 10^7$	a_4 $\times 10^9$	a_5 $\times 10^{11}$
CH_4	7.036	−8.517	9.296	−7.158	2.51	−0.151
SiF_4	4.89	−9.062	9.180	−2.167	−3.25	1.735
CF_4	4.536	−6.317	7.293	−4.557	−0.079	0.746

where ϵ is the depth of the potential well,

$$\theta = kT/\epsilon, \quad x = R/r_e, \quad V^*(x) = V(x)/\epsilon.$$

$V^*(x)$ for rare gases is approximately independent of the rare gas pair. For this reason, the reduced second virial coefficient, $B^*(\theta) = B/Nr_0^3$, is approximately the same for many molecular pairs. In the same spirit as $B^*(\theta)$, $\sigma_1(\theta)/r_e^3$ would be expected to be the same for the rare gas pairs if $\sigma(x)$ were identical for Xe–Xe, Xe–Kr, and Xe–Ar. Calculations show that $\sigma_1(\theta)/r_e^3$ for Xe–Kr and Xe–Ar differ from $\sigma_1(\theta)/r_e^3$ for Xe–Xe roughly by a factor of $\frac{2}{3}$ and $\frac{1}{2}$, respectively. This shows, that the second virial coefficient for chemical shielding is more complicated than $B^*(\theta)$, that $\sigma(x)$ is not independent of the molecular pair. In principle this increased complexity means that correspondingly more information is available in $\sigma_1(\theta)$ than in $B^*(\theta)$.

It has been noted that the reduced second derivatives and reduced third derivatives at the minimum of the most accurate rare gas potentials are remarkably similar.[4] This similarity of shape of $V(R)$ is much closer than one would have any reason to expect on the basis of the empirical success of the law 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 Xe–Xe system it was found that a fair agreement with the experimental $\sigma_1(T)$ for Xe_2 could be obtained by using a function of the form $V^2(R)$. If $aV^2(R)$ mimics $\sigma(R)$ over the range of values of R which is of major importance to $\sigma_1(T)$, then

$$\sigma(x) \simeq \text{constant} \mid V^*(x) \mid^2,$$

where the constant will not be dependent on the system if there is a universal form for the chemical shielding function. Then,

$$\sigma_1(\theta) = 4\pi r_e^3 \text{ constant } \epsilon^2 \int_0^\infty \mid V^*(x) \mid^2 e^{-V^*(x)/\theta} x^2 dx.$$

To the extent that $V^*(x)$, the reduced potential, has been found to be independent of the rare gas pair, the integral

$$\int_0^\infty |V^*(x)|^2 e^{-V^*/\theta} x^2 dx$$

will be independent of the rare gas pair, and we can define a reduced σ_1,

$$\sigma_1^*(\theta) = \sigma_1(\theta)/r_e^3\epsilon^2. \tag{2}$$

To the extent that a $\mid V^*(x) \mid^2$ mimics the shape of $\sigma(x)$, for those values of x which contribute primarily to $\sigma_1(T)$ in the temperature range studied, the reduced function Eq. (2) will be approximately the same for all rare gas pairs, with no adjustable or normalization factors.

We can check this empirically if accurate values of r_e and ϵ for Xe–Xe, Xe–Kr, and Xe–Ar are available. For Xe–Xe, the best available potential is that of Barker *et al.* and for Xe–Kr that of Lee *et al.*[4,5] These potentials were derived using a wide range of experimental evidence including, second virial coefficients, gas transport properties, solid state data, measurements of differential scattering cross sections, and spectroscopic information on dimers. As yet, there is no Xe–Ar potential which is of comparable accuracy, although $r_e = 4.06336$ Å appears to be the best value, and values of ϵ between 181 and 186 K appear to fit differential cross sections reasonably well, especially in the rainbow region,[6] though not as well as in the Xe–Xe and Xe–Kr cases.

Using our experimental data on $\sigma_1(T)$ for Xe–Kr and Xe–Xe, we have calculated the reduced function $\sigma_1^*(\theta)$.[2] The results are shown in Fig. 2. Our results show that the reduced $\sigma_1^*(\theta)$ for Xe–Xe and Xe–Kr are nearly superimposable over a wide range of θ with no adjustable or normalization parameters. For Xe–Ar, potential parameters are not available with the same accuracy. An estimate of well depth for the potential function of Xe–Ar can be obtained, by finding a best value for ϵ which would superimpose the reduced σ_1 for the Xe–Ar pair on the reduced σ_1 for Xe–Xe and Xe–Kr. For Xe–Ar, independent studies give a best value for $r_e = 4.06335$ Å,[6] which results in a superposition of the Xe–Ar reduced σ_1 curve with the Xe–Xe and Xe–Kr curves for an ϵ of 196 K.

This method of estimating well depths is dependent on several assumptions. The most severe one is the assumption of a universal functional form of the isotropic shielding function $\sigma(R)$ that is proportional to $V^2(R)$ in those regions of R contributing the most to the integral which is $\sigma_1(T)$. This assumption was based on the inversion of $\sigma_1(T)$ data for Xe–Xe. The resulting function, $\sigma(R)$, was found to be similar in shape to $V^2(R)$. Assuming a monotonically decreasing functional form for $\sigma(R)$ such as the theoretical function given by

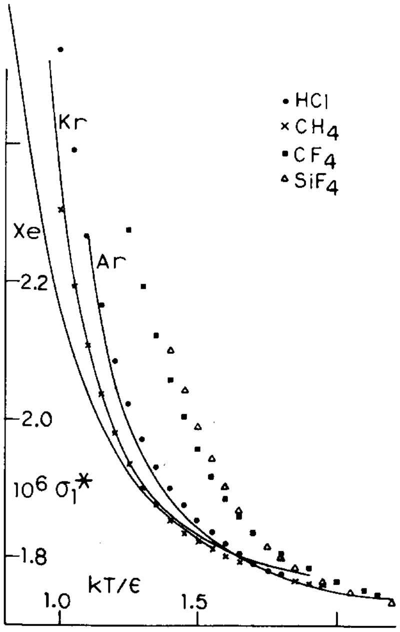

FIG. 2. Comparison of the reduced function $\sigma_1^* = \sigma_1(kT/\epsilon)/(r_e^3\epsilon^2)$ for various molecular pairs Xe–Y, where Y is the molecule indicated as the label of each curve.

TABLE II. Equilibrium intermolecular distances for rare gas atoms interacting with diatomic molecules.[a]

Molecular pair	Experimental values isotropic r_e(Å)	R_0(Å)	Ref.	Rule of thumb values isotropic r_e(Å)
Ar–HF	3.504	3.586	8	
Ar–$H^{35}Cl$	3.805, 3.974	4.04	9, 10	
Ar–^{35}ClF	3.86	3.90	11	
Ar–H_2		3.94	12	3.864
Kr–H_2		4.07	12	4.01
Xe–H_2		4.25	12	4.21
Ar–N_2		3.09 ± 0.2	13	3.54

[a] Distances are equilibrium distances (r_e) between the atom and the center of mass of the diatomic molecule. The corresponding average distances are R_0.

Adrian[7] gives only fair agreement with experimental data and leads to $\sigma_1(T)$ functions which are not as sensitive to the depth of the potential well. The rather good agreement of the reduced σ_1 for Xe–Kr and Xe–Ar with that of Xe–Xe is encouraging. Complete coincidence of the $\sigma_1(\theta)/(r_e^3\epsilon^2)$ is not to be expected for several reasons: (a) The integral $\sigma_1(T)$ is sensitive to differing portions of the R domain depending on the temperature, owing to the form of the kernel ($e^{-V(R)/kT}$), and (b) the function $\sigma(R)$ is not adequately represented by $f(V^2)$, as has been observed in the case of Xe–Xe interaction (Fig. 2 of Ref. 3).

The deviations of the curves in Fig. 2 from complete superimposition over the entire reduced temperature range are a measure of the inadequacy of the functional form $V^2(R)$ in reproducing the experimental $\sigma_1(T)$.[3] The greatest deviations found between the experimental $\sigma_1(T)$ and the value of the integral,

$$4\pi\int_0^\infty f[V^2(R)]\exp^{-V(R)/kT}R^2dR,$$

do occur in the range of reduced temperatures $T^* < 1.0$ for Xe–Xe.

Nevertheless, it appears that if the value of r_e is known to within 0.01 Å, then the value of ϵ can be estimated to within a few percent by this method, if the results for Xe–Xe, Xe–Kr, and Xe–Ar are typical.

APPLICATIONS

In proposing a form of a reduced second virial coefficient of chemical shielding, we limited the above discussion to the rare gases, for which accurate potentials as well as precise $\sigma_1(T)$ data are available. In addition, the intermolecular potentials involved are truly spherically symmetric since they involve interactions of monatomic molecules. The spherical top molecules are not spherically symmetric, so that the intermolecular potential for the Xe–spherical top interaction is expected to be anisotropic. However, for Xe interacting with molecules with structure, the least anisotropic potentials are expected to be those involving spherical tops. Thus, our initial application of this method for the estimation of ϵ from $\sigma_1(T)$ data is for Xe–CH_4, Xe–CF_4, and Xe–SiF_4. In order to apply this method to these molecular pairs, we need to have values of r_e for these pairs of molecules.

TABLE III. Estimated r_e values using a modified Bernstein's rule of thumb.

Molecular pair	r_e(Å)
Xe–CH_4	4.21
Xe–CF_4	4.21
Xe–SiF_4	4.29

TABLE IV. Estimated ϵ values using superposition of reduced σ_1.

Molecular pair	ϵ, K
Xe–Ar	196
Xe–HCl	240
Xe–CH_4	224
Xe–CF_4	181
Xe–SiF_4	182

Since the experimental r_e values for the pairs of molecules studied here are not known presently, some method of estimating r_e has to be devised which is consistent with experimental r_e values for other systems. A modified rule of thumb is used here (see Appendix and Table II) and the r_e values are given in Table III.

While HCl is not a spherical top, the Xe–HCl pair is included in this discussion because its counterpart, Ar–HCl, is relatively well studied. From the Ar–HCl isotropic r_e value of 3.805 Å, we can obtain a value of r_e for Xe–HCl by using the difference in orbital radii of Ar and Xe.[9] Thus, we use an r_e value for Xe–HCl of (3.805 Å $-r_{Ar}+r_{Xe}$) or 4.155 Å. The second virial coefficient of ^{129}Xe in Xe–HCl has been measured experimentally as a function of temperature over the range 250–440 K and is reported elsewhere with other linear molecules.[14]

With these values of r_e for Xe–CH_4, Xe–CF_4, Xe–SiF_4 and Xe–HCl, we can apply the previously described method of estimating ϵ. We compare the "reduced second virial coefficients," $\sigma_1^*(\theta)$, for these molecular pairs with those of the rare-gas pairs and find a value of ϵ which brings their rediced σ_1 into coincidence with those of the rare-gas pairs. The results are shown in Fig. 2. The values of ϵ estimated for these molecular pairs are shown in Table IV.

The Xe–CF_4 and Xe–SiF_4 reduced σ_1 curves are noticeably deviant from the other molecular pairs. They can be brought into coincidence with the others by an unrealistically small value of $r_e = 3.8$, in which case their estimated well depths would be 209.5 and 216.5 K, respectively.

This method of estimating well depths leads to unreliable results if

(a) the functional form of $\sigma(R)$ is not a universal one but is substantially different for different molecular pairs. For example, the minimum in $\sigma(R)$ may occur at $R \neq r_e$. For interacting open shell atoms we can find out if this is the case by analyzing the experimental intrinsic temperature dependence of chemical shifts in the isolated diatomic molecule. From the latter we can derive $(d\sigma/dR)_{R=r_e}$. If we find different signs and magnitudes of this quantity for different diatomic molecules, then we know that $\sigma(R)$ does not have a universal form for interacting open shell atoms.[14] However, this does not allow us to infer anything concrete about $\sigma(R)$ for interacting closed shells. If the functional form of $\sigma(R)$ is not universal, then deviations between different $\sigma_1(\theta)$ curves would be worse at lower reduced temperatures, because at these temperatures the integral $\sigma_1(T)$ is most sensitive to the well region.

(b) Even if there were a universal functional form for $\sigma(R)$ it is not quite $f(V^2)$. We have seen that in the Xe–Xe case at least, $f(V^2)$ does not give a perfect fit to the experimental $\sigma_1(T)$.[3] Thus, the form of the reduced σ_1 is probably not quite $\sigma_1(kT/\epsilon)/(r_e^3 \epsilon^2)$.

(c) The reduced potential $V^*(R)$ itself is not quite a universal function as shown by the very accurate potentials for mixed rare gases, especially for mixed pairs of atoms in which one of the atoms is He.[15,16]

Thus, we know that this method cannot lead to unequivocal values of ϵ. However, the estimates of ϵ values are probably not too bad. There are no accurate potential parameters available for Xe–CH_4 and other pairs, with which to compare our values. Combining rules for estimating ϵ might be used if accurate $(CH_4)_2$, $(SiF_4)_2$, and $(CF_4)_2$ potentials were available. Typical values of ϵ for these molecules are 148 K for CH_4 and SiF_4, and 152 K for CF_4. These data are of the same quality as the old value of 221 K for Xe_2, so they are probably smaller than the correct well depths. Combined with 282 K for Xe_2, these would give geometric mean ϵ values of about 204 for Xe–CH_4 and Xe–SiF_4 and 207 for Xe–CF. For pairs of rare gases, differential scattering cross sections, transport properties, and spectroscopic data have yielded detailed and accurate potential functions. However, for molecular pairs in which one or both of the pair is a molecule with structure, the differential cross section yields ambiguous results. The ordinarily used interpretation of molecular beam scattering observations assumes only single-channel elastic scattering and does not take cognizance of other channels corresponding to concurrent inelastic processes. Molecules with structure have rotational and vibrational degrees of freedom which can provide substantial contributions to the differential cross section from channels involving translational–rotational energy transfer and other internal inelastic processes. Until time-of-flight measurements become routine, the quantitative analysis of such data is intractable.

Gordon and Kim have proposed a method for generating interaction potentials between closed shell systems, which is less time consuming than Hartree–Fock and configuration interaction methods.[17] Gordon and Kim derive kinetic, exchange, and correlation energies from a statistical treatment of an infinite uniform electron gas. Because of their statistical basis, the application of their equations to a system involving Xe and a polyatomic molecule should give better results than applications to systems with a small number of electrons. It would be interesting to compare our results with theoretical potentials obtained by such methods. If such calculated potentials were sufficiently reliable, it would be possible to carry out an inversion of our $\sigma_1(T)$ data, to reveal the empirical $\sigma(R)$ functions for Xe–CH_4, Xe–SiF_4, and Xe–CF_4.

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APPENDIX: ESTIMATION OF r_e VALUES

Bernstein's rule of thumb (B) has been sucessful when applied to pairs of rare gas atoms[18]:

$$r_e = r_i + r_j + C,$$

where C is a constant parameter, 2.0 Å in the original version of this rule of thumb, r_i and r_j are the orbital radii of the pair of atoms for which r_e is being estimated.[19] The following potentials were used[15,16,20-22]: Farrar and Lee's potential for He_2, Farrar, Lee, Goldman, and Klein's potential for Ne_2; Barker, Fisher, and Watts' potential for Ar_2; Barker, Watts, Lee, Schafer, and Lee's potentials for Kr_2 and Xe_2. For the mixed pairs we used Chen, Siska, and Lee's potentials for rare gases with He; Ng, Lee, and Barker's potentials for rare gases with Ne; and Lee, Henderson, and Barker's potentials for Ar–Kr, Ar–Xe, and Kr–Xe. Using these r_e's and the orbital radii of Waber and Cromer, we find the best value for parameter C, which has an average value of 2.408 Å with a standard deviation of 0.0286 Å. The mixed pairs with He were not included because the calculated values of ϵ were unusually high.

The potentials for rare gas atoms interacting with structured molecules are not as readily available. There are some values of r_e available for diatomic molecules interacting with rare gas atoms. They are given in Table II. The values of r_e (equilibrium distances) and R_0 (average distances) are not expected to be identical. Since some of these potential functions are fairly anharmonic, r_e is probably less than R_0. Ar–N_2 has a T-shaped structure,[13] whereas the rare gas–H_2 van der Waals molecules have a nearly freely-rotating H_2.[12] A modification of Bernstein's rule of thumb (B), using the more recent value of C, may ap-

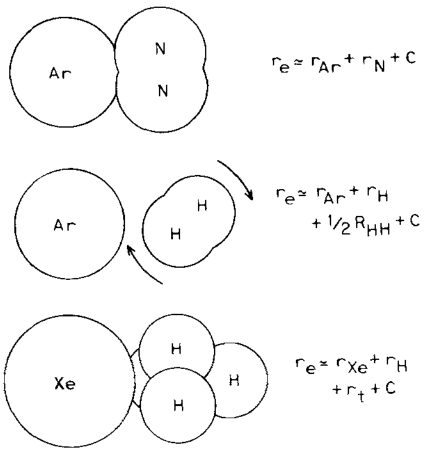

FIG. 3. Rule of thumb for determining r_e for some van der Waals molecules. r_{Ar}, r_N, r_H, and r_{Xe} are orbital radii, $C = 2.40$ Å and r_t is the perpendicular distance from the center of a face of the tetrahedron. The spheres have the respective van der Waals radii.

ply to the above molecular pairs as shown in Fig. 3. For example, for the T-shaped N_2Ar molecule

$$r_e \simeq r_{Ar} + r_N + 2.40\ \text{Å},$$

and for H_2X, where X = Ar, Kr, or Xe, and H_2 is nearly freely rotating,

$$r_e \simeq r_X + r_H + \tfrac{1}{2} R_{H-H} + 2.40\ \text{Å}.$$

The orbital radius of H is taken to be 0.444 which is appropriate for an effective Z in the H_2 molecule of 1.19. In the results shown in Table II, the rule of thumb appears to work successfully in the above cases, but in Ar–HCl, it seems to fail. If we use $r_e \simeq r_{Ar} + r_H + R_{H-Cl} + 2.40$ Å, we get 4.77 Å, which is 0.96 Å larger than the isotropic r_e which is reported for this molecule.[9]

In order to obtain reasonable estimates of r_e for Xe–CH_4, Xe–CF_4 and Xe–SiF_4, we adopt the modified rule of thumb. The expected geometry for these van der Waals molecules is that of closest approach, that is, with the Xe–C or Xe–Si internuclear axis perpendicular to the triangular faces of the tetrahedron (see Fig. 3). For this geometry, the modified rule of thumb would be:

$$r_e \simeq r_{Xe} + r_{H\ \text{or}\ F} + r_t + 2.40\ \text{Å},$$

where r_t, the distance between the center of the tetrahedron and the center of the triangular faces, is related to the bond length R of the tetrahedral molecule, $r_t = R/3$. Use of the modified rule of thumb gives the r_e values in Table III.

[1] "Intermolecular Forces," in *Advances in Chemical Physics*, edited by J. O. Hirschfelder (Wiley, New York, 1967), Vol. 12.
[2] C. J. Jameson, A. K. Jameson, and S. M. Cohen, J. Chem. Phys. **62**, 4224 (1975).
[3] C. J. Jameson, J. Chem. Phys. **63**, 5296 (1975).
[4] J. A. Barker, R. O. Watts, J. K. Lee, T. P. Schafer, and Y. T. Lee, J. Chem. Phys. **61**, 3081 (1974).
[5] J. K. Lee, D. Henderson, and J. A. Barker, Mol. Phys. **29**, 429 (1975).
[6] Y. T. Lee and T. P. Schafer (private communications).
[7] F. J. Adrian, Phys. Rev. Sec. A **136**, 980 (1964).
[8] S. J. Harris, S. E. Novick, and W. Klemperer, J. Chem. Phys. **60**, 3208 (1974).
[9] W. B. Neilsen and R. G. Gordon, J. Chem. Phys. **58**, 4149 (1973).
[10] S. E. Novick, P. Davies, S. J. Harris, and W. Klemperer, J. Chem. Phys. **59**, 2273 (1973).
[11] S. J. Harris, S. E. Novick, W. Klemperer, and W. Falconer, J. Chem. Phys. **61**, 193 (1974).
[12] A. R. W. McKellar and H. L. Welsh, J. Chem. Phys. **55**, 595 (1971).
[13] G. Henderson and G. E. Ewing, Mol. Phys. **27**, 903 (1974).
[14] C. J. Jameson, A. K. Jameson and S. M. Cohen (to be published).
[15] C. H. Chen, P. E. Siska, and Y. T. Lee, J. Chem. Phys. **59**, 601 (1973).
[16] C. Y. Ng, Y. T. Lee, and J. A. Barker, J. Chem. Phys. **61**, 1996 (1974).
[17] R. G. Gordon and Y. S. Kim, J. Chem. Phys. **56**, 3122 (1972).
[18] R. B. Berstein and J. T. Muckerman, Adv. Chem. Phys. **12**, 389 (1967).
[19] J. T. Waber and D. T. Cromer, J. Chem. Phys. **42**, 4116 (1965).
[20] J. M. Farrar and Y. T. Lee, J. Chem. Phys. **56**, 5801 (1972).
[21] J. M. Farrar, Y. T. Lee, V. V. Goldman, and M. L. Klein, Chem. Phys. Lett. **19**, 359 (1973).
[22] J. A. Barker, R. A. Fisher, and R. O. Watts, Mol. Phys. **21**, 657 (1970).