Polarizability of Interacting Atoms: Relation to Collision-Induced Light Scattering and Dielectric Models

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The polarizability tensor of a pair of interacting He atoms has been calculated as a function of internuclear separation r using the fully self-consistent Hartree–Fock theory. It was found that the trace of the polarizability tensor, $\alpha(r)$, to which the second dielectric virial coefficient B_ϵ is directly proportional, decreases with decreasing r, giving a theoretical value of $B_\epsilon = -0.093$ a.u. at room temperature, compared with the experimental result $B_\epsilon = -0.06 \pm 0.04$ a.u., measured by Orcutt and Cole [J. Chem. Phys. **46**, 697 (1967)]. This is the first calculation that predicts the correct sign of B_ϵ. We conclude that for He the effects of overlap are of opposite sign from and of sufficient magnitude to overcome the contributions of the van der Waals interaction to $\alpha(r)$. Furthermore, the anisotropy of the pair polarizability $\beta(r)$ can be represented by a simple form: $\beta(r) = 6\alpha^2 r^{-3} - \lambda\, e^{-r/r_0}$, where $r_0 = 0.74$ a.u., and the collision-induced light-scattering spectrum predicted by this form has an essentially exponential line shape. These results are in qualitative agreement with recent work on collision-induced light-scattering spectra from rare gases.

I. INTRODUCTION

The interaction between charge displacements induced by an electric field causes the polarizability in colliding molecules or atoms to differ from the sum of the polarizability tensors of the isolated species. Several phenomena are either caused or significantly affected by this polarizability change, among them being the dielectric constant,[1-6] the Kerr effect,[7] collision-induced light scattering (CIS),[8-14] as well as various nonlinear optical effects, such as self-trapping and self-phase modulation of light.[15,16] Despite the wide range of phenomena involving the polarizability and the considerable body of both experimental and theoretical investigation, present-day knowledge of the dependence of the polarizability tensor on intermolecular coordinates cannot be considered to be adequate even for cases involving the interaction of just two molecules. Consider, for example, the simplest possible case, namely, the helium atom. All theoretical treatments to date, both classical and quantum mechanical, have been unable to predict the correct sign of the change of the average polarizability of a pair of He atoms with distance, let alone the functional form.

A sensible first step then in understanding the various density-dependent phenomena listed above is to investigate in detail the polarizability tensor of a pair of He atoms as a function of their separation and to examine the applicability of the results obtained to other, more general, atomic and molecular systems. This is the goal of the present

work. We first review the relation of the various phenomena to the polarizability tensor, then evaluate the tensor for a pair of He atoms using Hartree–Fock methods.

II. PHENOMENOLOGY

Before proceeding further, it is worthwhile to give a precise meaning of the polarizability tensor as used in the present investigation since some confusion exists in the recent literature because of essentially semantic problems, especially in the area of collision-induced light scattering. We define the polarizability tensor of a set of N atoms in a vacuum by the relation

$$\alpha_{ij}(\vec{r}_1, \ldots, \vec{r}_N) = \lim_{|\vec{E}^0| \to 0} \frac{\partial M_i(\vec{r}_1, \ldots, \vec{r}_N)}{\partial E_j^0}, \quad (1)$$

where i, j are indices for the laboratory coordinate frame and $M_i(\vec{r}_1, \ldots, \vec{r}_N)$ represents the ith component of the electric dipole moment of the N atoms when located at the positions $\vec{r}_1, \ldots, \vec{r}_N$. $\vec{E}^0$ is the electric field due to external charges and is to be distinguished from the local field $\vec{E}$. We assume the spatial variation of $\vec{E}^0$ to be small compared with the relevant intermolecular distances.

The use of statistical-mechanical cluster-expansion techniques enables one to describe the dielectric properties of a macroscopic assembly of atoms (molecules) up to terms involving ρ^n by considering $\alpha_{ij}(\vec{r}_1, \ldots, \vec{r}_n)$ only. $\underline{\alpha}(\vec{r}_1, \ldots, \vec{r}_n)$ can in turn be written as a sum of terms (irreducible cluster functions) involving only $n-1$ atoms, $n-2$ atoms, etc., together with a remaining strictly n-

body term. Let us consider first the dielectric constant ϵ for a moderately dense gas of spherical molecules. It can be shown[1-4] that one may expand the Clausius–Mossotti function, $(\epsilon-1)/(\epsilon+2)$, in terms of the number density ρ,

$$(\epsilon-1)/(\epsilon+2)= \tfrac{4}{3}\pi\alpha\rho + B_\epsilon\rho^2 + C_\epsilon\rho^3 + \cdots, \quad (2)$$

where α is the polarizability of the isolated molecule and B_ϵ, C_ϵ, ..., are the second, third, ..., dielectric virial coefficients. Furthermore, the explicit form for B_ϵ is

$$B_\epsilon = \tfrac{8}{3}\pi^2 \int_0^\infty dr\, r^2 \alpha(r)\, e^{-V(r)/kT}$$
$$= \tfrac{2}{3}\pi\langle\alpha(r)\rangle, \quad (3)$$

where $\alpha(r)$ is the change in the trace of the pair polarizability tensor, given in the principal axis frame by

$$\alpha(r) \equiv \tfrac{1}{3}[\alpha_{\parallel}(r)+2\alpha_{\perp}(r)] - 2\alpha. \quad (4)$$

Here $\alpha_{\parallel}(r)$ and $\alpha_{\perp}(r)$ are the longitudinal and transverse components of the pair polarizability tensor at an intermolecular separation r, respectively, and $\langle\ \rangle$ indicates an ensemble average over all pairs in the field $\vec{E}^0 = 0$. Likewise, the density dependence of the refractive index n is obtained by substituting n^2 for ϵ and using the polarizability at the frequency of the light wave. [For the rare gases, where the first absorption is in the far ultraviolet, the polarizability at visible-light frequencies is only slightly (a few percent) higher than the static value.] Thus, the density dependence of the dielectric constant reflects the average change in the polarizability of a pair of interacting particles. Not only does the average polarizability of a pair of interacting atoms change, but during the collision the pair becomes anisotropic, so that the induced dipole moment in general points along an axis other than that of the incident electric vector. This effect is characterized by the induced anisotropy in the polarizability $\beta(r) = \alpha_{\parallel}(r) - \alpha_{\perp}(r)$, a quantity reflected in both the CIS spectrum and the Kerr effect.

There are two distinct types of information contained in the CIS spectrum: dynamical information on the motion of the pair, and the form of both the induced polarizability $\alpha(r)$ and its anisotropy $\beta(r)$. We are here concerned mainly with the form of the pair polarizability tensor. Collision-induced spectra are also a useful dynamical probe, especially for 3-, 4-, etc., body collisions that are inaccessible to molecular-beam studies and have already yielded qualitatively significant information about simple liquids. To avoid dealing with collision trajectories, we will consider here only the moments of the two-body spectrum[13,17,18]:

$$I^{(n)} = \int_{-\infty}^{\infty} d\omega\, \omega^n I(\omega), \quad (5)$$

which involve ensemble averages at a single time only. The explicit relationship of $I(\omega)$ to the incremental polarizability is discussed in Sec. V.

The second Kerr virial coefficient has been shown to be directly proportional to $\langle\beta^2(r)\rangle$[7]:

$$B_K = \frac{8\pi^2 N_0^2}{405kT}\langle\beta^2(r)\rangle. \quad (6)$$

The nonlinear optical effects involve ensemble averages of $\beta(r)$ in a nonzero electric field.[15,16] To lowest order in E^2 they are closely related to the Kerr effect.

III. PREVIOUS INVESTIGATIONS

The first, and simplest, approaches to the influence of interatomic forces on the pair polarizability tensor were classical in nature and date back some fifty years.[19] They characterized the atoms by a constant polarizability. As two such particles approach each other in the presence of an external field, the induced dipole moments modify their local fields, resulting in a change in the total induced moment of the pair. This point-dipole approximation gives the following results for the change in the pair polarizability:

$$\alpha(r) = \frac{4\alpha^3}{r^6}\left(1 - \frac{\alpha}{r^3} - \frac{2\alpha^2}{r^6}\right)^{-1}, \quad (7a)$$

$$\beta(r) = \frac{6\alpha^2}{r^3}\left(1 - \frac{\alpha}{r^3} - \frac{2\alpha^2}{r^6}\right)^{-1}. \quad (7b)$$

The leading terms

$$\alpha(r) = 4\alpha^2 r^{-6} \quad \text{and} \quad \beta(r) = 6\alpha^2 r^{-3} \quad (8)$$

are the dominant contributions for thermally accessible values of r. Other terms in the series typically lead to corrections of order 2–3% for the rare gases. However, it has been shown quantum mechanically[2] that these classical equations are correct only up to order r^{-3}, so while the classical result is asymptotically correct for $\beta(r)$ this is not true for $\alpha(r)$. In most calculations investigators have only used the leading terms of the classical expressions. Experiments on rare gases show that $\langle\alpha(r)\rangle$[5] and $\langle\beta(r)\rangle$[7,10,13] are significantly smaller than the values predicted from the point-dipole approximation. In addition, $\langle\alpha(r)\rangle$ is negative for the light rare gases He and Ne, a result in qualitative disagreement with Eq. (8). Ely and McQuarrie[6] have shown that quantum contributions to the ensemble-averaging process in $\langle\alpha(r)\rangle$ affect the results of the classical calculation by less than 2%. They concluded that the observed discrepancies must then be due to inadequacy of the point-dipole model.

Recently, Certain and Fortune[20] applied variational techniques to carry out accurate calculations

of the coefficients of the r^{-6} term for He. They find that, to terms of order r^{-6},

$$\alpha(r) = 14.86\alpha^3 r^{-6} \qquad (9a)$$

and

$$\beta(r) = 6\alpha^2 r^{-3} + 12.07\alpha^3 r^{-6}, \qquad (9b)$$

compared with the classical-point-dipole values of

$$\alpha(r) = 4\alpha^3 r^{-6} \qquad (10a)$$

and

$$\beta(r) = 6\alpha^2 r^{-3} + 6\alpha^3 r^{-6}. \qquad (10b)$$

Hence, this correction leads to an even greater discrepancy with experiment. There remains the strong possibility that the long-range induced dipole expansion used above breaks down at distances where overlap effects become appreciable.

The first attempt to calculate the short-range effect was made by de Boer et al.,[21] who simulated the influence of the repulsive interactions by considering the change in polarizability of a hydrogen atom squeezed into a small spherical box. This resulted in a decrease in the polarizability. Later Du Pré and McTague,[22] using the $^3\Sigma$ state of H_2 as a model for colliding pairs of rare-gas atoms, showed that the incremental polarizability $\alpha(r)$ can indeed become negative at intermediate distances, showing theoretically for the first time that B_ϵ can be a negative quantity.

Lim, Linder, and Kromhout[23] have examined the short-range contributions by computing the polarizability of two He atoms of various separations using Hartree–Fock perturbative theory. They concluded that the effects of overlap and exchange did not produce the negative value of $\langle\alpha(r)\rangle$ measured by Orcutt and Cole.[5] However, their calculations give a value of the polarizability of the separated He atoms 25% off from experiment and hence one should not expect a high degree of reliability in these results.

It thus seemed necessary to reexamine the Hartree–Fock technique to see if it could yield reliable results for the effects of intermolecular interactions on the polarizability tensor of atoms not connected by chemical bonds. *Note added in proof.* We have recently learned that A. D. Buckingham and R. S. Watts (personal communication) have also made a similar investigation utilizing a considerably smaller basis set.

IV. METHODS AND RESULTS

To obtain the components of the polarizability tensor for two interacting helium atoms we carried out three separate Hartree–Fock calculations at each internuclear distance. We first determined

the Hartree–Fock energy of the He_2 system in the absence of an external field. To determine the induced moment we did another fully self-consistent field calculation for the He_2 system in an external field of specified strength. This method then involves the full solution of the Hartree–Fock equations in the presence of a finite electric field.[24] The field chosen is small enough such that in terms of a perturbation expansion we can assume that for each orbital $\phi_i \approx \phi_i^{(0)} + \phi_i^{(1)}$ and $W \approx W^{(0)} + E^2 W^{(2)}$ and higher orders are negligible. From the solution of these equations one obtains wave functions that can be used to calculate the induced dipole moment $\mu(E)$ for a particular field. The ratio of the dipole moment to the field is the polarizability $\alpha(E)$. In the limit that the applied field goes to zero this method of calculation is clearly equivalent to the perturbation Hartree–Fock scheme.

The Hartree–Fock equations are solved using the full Hamiltonian, i.e., the field-free Hamiltonian plus the electron-field interaction. One then assumes that the wave function is an antisymmetrized product of doubly occupied orbitals that, in turn, are given as an expansion of atomic basis functions. In these calculations we use Gaussian-type orbitals (GTO) centered on the two helium atoms. For convenience we use one large basis for all three calculations, i.e., the field-free case and those for the field parallel to and perpendicular to the He-He axis. If we denote a zero-order basis as $\{\chi^0\}$ and the polarization functions with the field in the k direction by $\{\chi^{(1)}\}_k$, our procedure is then to carry out all calculations in the basis $\{\chi^{(0)}\} + \{\chi^{(1)}\}_x + \{\chi^{(1)}\}_z$.

From previous calculations[25] on various atoms and molecules we selected the following basis that should adequately describe all important shifts in orbital amplitudes due to the applied field. On each center we use a basis of five s-, four p_z-, four p_x-, one d_{zz}-, and one d_{xz}-like orbitals. The orbital exponents for the s basis are 70.0, 22.0, 7.0, 2.2, 0.7, 0.22, and 0.07. The first three s-basis functions are contracted to a single function with contraction coefficients of 0.0089826, 0.0203747, and 0.0928285, respectively. For the calculation on the isolated He atom we did not contract the s basis but the isolated atom coefficients were used to determine the contraction coefficients. This makes very little difference in the total energies and induced moments. The exponents of the p_z- and p_x-like basis functions are 2.2, 0.7, 0.22, and 0.07, and that of the d-like functions is 0.22.

Calculations were done at the following internuclear distances: 3.5, 4.0, 4.5, 5.0, 5.5, 6.0, 7.0, 8.0, 10.0 a.u., and also for the isolated helium atoms. From the Hartree–Fock energy of the He atom we obtain − 2.85999 a.u. and a polariza-

TABLE I. Hartree–Fock potential curve for He$_2$.

r (a.u.)	Present work[a]	Gilbert and Wahl[b]	Kestner[c]
3.5	0.004345	0.004434	...
4.0	0.001344	0.001379	0.001365
4.5	0.000398	...	...
5.0	0.000107	0.000125	...
5.5	0.000021	0.000037	0.000037
6.0	0.00000	0.000011	0.000011

[a] In atomic units, relative to an energy of -2.85999 a.u. for the He atom.

[b] T. L. Gilbert and A. C. Wahl, J. Chem. Phys. **47**, 3425 (1967).

[c] N. Kestner, J. Chem. Phys. **48**, 252 (1968).

TABLE II. Polarizabilities of He$_2$ for various nuclear separations (r). All polarizabilities are in a.u. The polarizability of an isolated He atom was computed in this work to be 1.325.

r (a.u.)	$\alpha_\perp$	$\alpha_\parallel$	$\alpha_\perp - 2\alpha_{He}$	$\alpha_\parallel - 2\alpha_{He}$
10.0	2.65	2.65	0.0	0.0
8.0	2.647	2.654	-0.003	0.004
7.0	2.642	2.664	-0.008	0.014
6.0	2.635	2.675	-0.015	0.025
5.5	2.630	2.681	-0.020	0.031
5.0	2.621	2.686	-0.029	0.036
4.5	2.610	2.688	-0.040	0.038
4.0	2.582	2.678	-0.068	0.028
3.5	2.540	2.653	-0.110	0.003

bility of 1.325 a. u. This value of the polarizability agrees well with the fully self-consistent field value of 1.32 a.u. by Cohen[26] and with the experimental value of 1.384 a.u.[27] This lends some confidence to the calculations of the pair properties. From the field-free calculations we derive the potential-energy curve for the interaction of two helium atoms. In Table I we list the potential energy at several internuclear distances. These energies are relative to a total energy of -5.71998 a.u. for He$_2$ at infinite separation.

The components of the polarizability tensor for He$_2$ at several internuclear distances are listed in Table II. The calculated values are probably accurate to within 5%. At large separations the anisotropy in the polarizability tensor must be positive, i.e., $\beta(r) = 6\alpha_0^3/r^3$. At distances as large as 8 a.u., the calculated components of the polarizability, $\alpha_\parallel(r)$ and $\alpha_\perp(r)$, are very nearly equal and one would require a very accurate calculation of $\alpha_\parallel(r)$ and $\alpha_\perp(r)$ to obtain $\beta(r)$ to one or two significant figures. For these large separations we simply sent $\beta(r)$ smoothly to zero for r greater than 10 a.u. This has no significant effect on calculation of the collision-induced properties since the dominant contribution to the effects comes around $r = \sigma$, where σ is the Lennard-Jones diameter.

Figure 1 shows plots of the incremental polarizabilities. We can conclude the following: (i) the perpendicular incremental polarizability $\alpha_\perp(r) - 2\alpha_{He}$ is always negative and decreases with decreasing r, and (ii) the parallel incremental polarizability $\alpha_\parallel(r) - 2\alpha_{He}$ is positive over the range of r studied and initially increases and then decreases with decreasing r. The opposite signs of the incremental polarizabilities agree with the assertion by McTague and Birnbaum[9,12] as being necessary to explain the discrepancies between the calculated (from the point-dipole model) value of the second dielectric and Kerr virial coefficients and the experimental values. Furthermore, these functions $\alpha_\parallel(r) - 2\alpha_{He}$ and $\alpha_\perp(r) - 2\alpha_{He}$ duplicate in form the incremental polarizabilities computed by Du Pré

and McTague[22] for interacting hydrogen atoms in the repulsive triplet state.

The calculated isotropic polarizability $\alpha(r)$ in Eq. (4) is shown in curve a of Fig. 2; curve b shows $\alpha(r)$ given by the point-dipole model, Eq. (9a). The second virial coefficient B_ϵ derived from the calculated incremental isotropic polarizability $\alpha(r)$, Fig. 2, agrees well with experiment not only in magnitude but moreover it has the right sign. For $T = 300$ °K we obtained the value -0.093 a.u.; the experimental value is -0.06 ± 0.04 a.u. This is the first calculation in this area that obtains the correct sign. For computing $g(r)$ we used the Lennard-Jones (6–12) potential function for He ($\sigma = 4.83$ a.u., $\epsilon/k = 10.22$ °K). It would make very little difference if we used our calculated $V(r)$ at these high reduced temperature. From this we conclude that $\alpha(r)$ predominantly depends on the overlap forces and that the point-dipole-model expression for $\alpha(r)$, Eq. (9a), is inadequate for the range of r, where overlap forces are important.

In Fig. 2, curve c shows our calculated values of $\beta(r)$, the anisotropic polarizability,

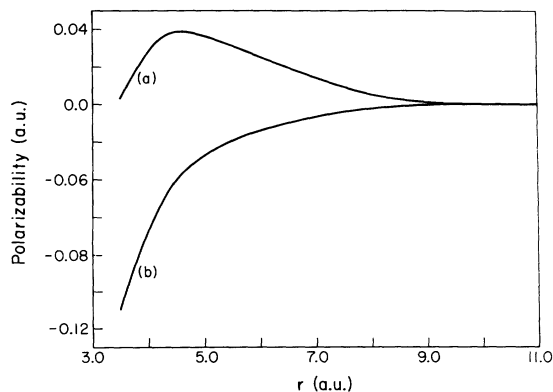$$\beta(r) = \alpha_\parallel(r) - \alpha_\perp(r). \tag{11}$$

FIG. 1. Incremental polarizabilities of He$_2$ as a function of the internuclear distance r: (a) $\alpha_\parallel(r) - 2\alpha_{He}$; (b) $\alpha_\perp(r) - 2\alpha_{He}$.

Curve d is the result of the point-dipole model, Eq. (8).

In order to show the nature of the deviation from the long-range asymptotic form, Fig. 3 is a semi-log plot of

$$\beta_{ov}(r) \equiv - [\beta(r) - 6\alpha^2 r^{-3}] . \tag{12}$$

This additional effect, which we label for convenience β_{ov}, is seen from the plot to be exponential and of the form

$$\beta_{ov}(r) \sim - e^{-1.35r(a.u.)} , \quad \text{or equivalently} - e^{-6.60(r/\sigma)} . \tag{13}$$

This is compatible with intuitive notions of the functional form of overlap-type processes. It also agrees with a moment analysis of the CIS spectrum of Ar. [13] It is not surprising that the effective polarizability can be represented by a simple sum over a reasonable range of r and, in fact, the longest-range terms (to order r^{-6}) can be rigorously written as a sum. Such expressions are common in the treatment of intermolecular forces. Likewise Fig. 4 shows that $\alpha(r)$ is essentially exponential in the region $r \approx \sigma$.

V. CHARACTERISTICS OF THE COLLISION-INDUCED LIGHT SCATTERING SPECTRUM

Ben-Reuven and Gershon, [28] among others, [12,13,17] have obtained expressions that relate the light-

scattering spectrum $I(\omega)$ to appropriate correlation functions $J(t)$:

$$I(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} J(t) e^{-i\omega t} dt . \tag{14}$$

Here $J(t) = (CV\rho^2/2\epsilon^2)F(t)$ is the correlation function for light scattered by pairs of the same species. In the above V is the scattering volume, ρ is the number of molecules per cm^3, ϵ is the permittivity of the fluid, and

$$C = Vk_i^4 I_i (4\pi R_0)^{-2} . \tag{15}$$

In Eq. (15), $\vec{k}_i$ and I_i are, respectively, the propagation vector and the intensity of the incident beam, and R_0 is the distance from the detector to an arbitrary point in the sample. (R_0 is assumed much greater than the sample dimensions.) The function $F(t)$ is[12]

$$F(t) = \langle \alpha(0)\alpha(t) \rangle (\vec{n}_i \cdot \vec{n}_f)^2$$

$$+ \langle \beta(0)\beta(t)P_2(X) \rangle \{45^{-1}[3 + (\vec{n}_i \cdot \vec{n}_f)^2]\} , \tag{16}$$

where $\vec{n}_i$ and $\vec{n}_f$ are the unit polarization vectors of the incident and scattered beams, respectively. The function $P_2(X)$, where $X = \cos\theta(t)$, is the second Legendre polynomial

$$P_2(X) = \frac{1}{2}[3\cos^2\theta(t) - 1] , \tag{17}$$

and $\theta(t)$ is the angle between the internuclear vector at time $t = 0$ relative to that of time t. For colliding atoms $\alpha(t)$ and $\beta(t)$ are defined as
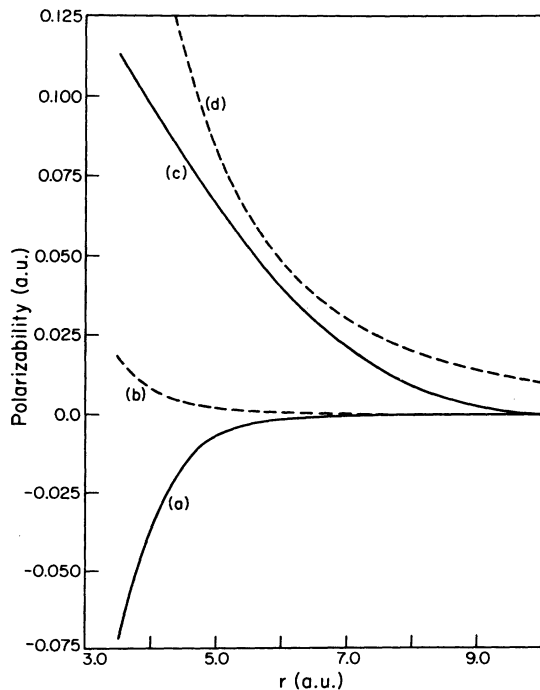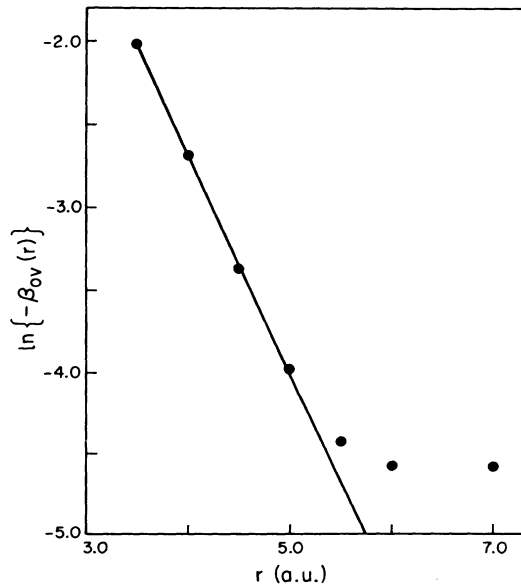

FIG. 2. Incremental isotropic and anisotropic polarizabilities of He$_2$ as a function of the internuclear distance r: (a) our calculated values for $\alpha(r)$; (b) $\alpha(r) = 14.86$ $\alpha^3 r^{-6}$; (c) our calculated values for $\beta(r)$; (d) $\beta(r) = 6\alpha^2 r^{-3}$.

FIG. 3. Semilog plot of β_{ov}. Since $\beta(r) = \alpha_{\parallel}(r) - \alpha_{\perp}(r)$ is the difference of two polarizability components, the values of $\beta(r)$ at large r, where these components are almost equal, can contain large fractional errors. These errors are reflected in this plot at distances greater than $r = 5.5$ a.u.

$$\alpha(t) = \alpha(r(t)) = \tfrac{1}{3}[\alpha_{\shortparallel}(r(t)) + 2\alpha_{\perp}(r(t))] - 2\alpha_{He}, \quad (18a)$$

$$\beta(t) = \beta(r(t)) = \alpha_{\shortparallel}(r(t)) - \alpha_{\perp}(r(t)). \quad (18b)$$

For the case where the detector measures both the x- and z-polarized components of the scattered radiation in an experiment with the y axis parallel to k_i and the x axis parallel to the propagation vector k_f of the scattered radiation, we obtain from Eq. (16)

$$F_z(t) = \langle \alpha(0)\alpha(t) \rangle + \tfrac{7}{45} \langle \beta(0)\beta(t)P_2(X) \rangle, \quad (19a)$$

$$F_x(t) = \tfrac{3}{45} \langle \beta(0)\beta(t)P_2(X) \rangle, \quad (19b)$$

where x and z refer to the direction of polarization of the incident light. From Eqs. (19) and (14) we obtain the spectral distributions. Defining the Fourier transforms $A(\omega)$ and $B(\omega)$ as

$$A(\omega) = \int_{-\infty}^{\infty} \langle \alpha(0)\alpha(t) \rangle \, e^{-i\omega t} \, dt, \quad (20a)$$

$$B(\omega) = \int_{-\infty}^{\infty} \langle \beta(0)\beta(t)P_2(X) \rangle \, e^{-i\omega t} \, dt, \quad (20b)$$

the depolarization ratio $D(\omega) = I_x(\omega)/I_z(\omega)$ is then

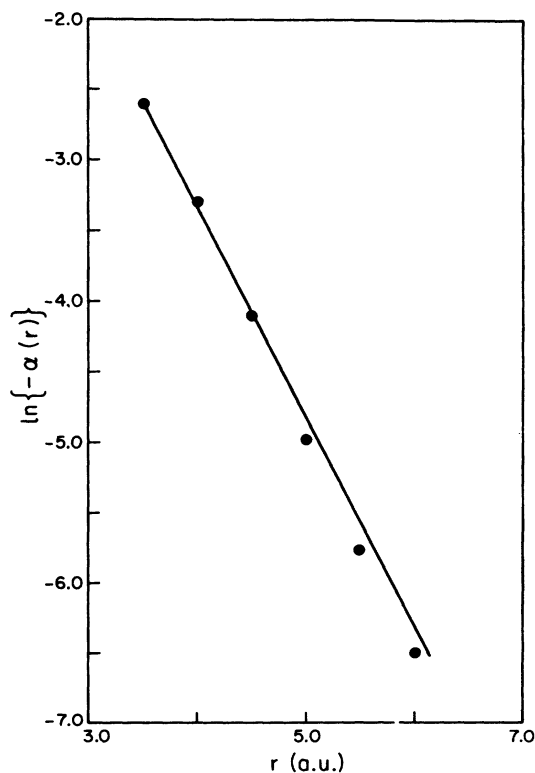$$D(\omega) = \frac{\tfrac{3}{45} B(\omega)}{A(\omega) + \tfrac{7}{45} B(\omega)}. \quad (21)$$

FIG. 4. Semilog plot of $-\alpha(r)$. The first three points are the most accurate and have been used to obtain the linear fit. The discrepancies between the linear curve and the remaining points are within the range of error in the calculated values of $\alpha(r)$.

TABLE III. Moment data for He_2 at 300 °K.

Second Kerr virial coefficient	3.1×10^{-15} esu
Half-width $\Delta\nu_{1/2} = (M_x^{(2)})^{1/2}$	31 cm^{-1}
$M_x^{(4)}/(M_x^{(2)})^2$	5.7

The light-scattering spectrum of gaseous He has been measured by Pike and Vaughan,[29] who find it to be highly depolarized with $D = 0.9 \pm 0.1$ at the single value of 25 cm^{-1}. These measurements were made at a temperature $T = 4.2$ °K and a pressure 0.96 atm and hence are not purely two body in nature. Our calculated integrated intensities give a value $D = 0.72$ at $T = 300$ °K. The calculations indicate that the predicted D values increase as T decreases, but our classical averaging procedures are inadequate for the low temperatures of the experiment.

We have also calculated the zeroth (integrated intensity), second, and fourth frequency moments[18] of the depolarized light-scattering spectrum at room temperature. These are summarized in Table III. Rather than list $M_x^{(0)}$, the integrated intensity, the second Kerr virial coefficient, to which it is proportional, is given. This quantity is three orders of magnitude smaller than that for argon.[7] This small magnitude probably explains the failure of a recent attempt to measure it.[7] The calculated spectral half-width is consistent with the trend observed in Ar, Kr, and Xe.[12]

The ratio

$$M_x^{(4)}/(M_x^{(2)})^2$$

characterizes the shape of the spectrum (ratio = 3 is a Gaussian spectrum, 6 an exponential spectrum, and infinity a Lorentzian spectrum). From Table III it is seen that the calculated moments strongly suggest an essentially exponential lineshape as has been observed in all the rare gases.[9-13]

VI. DISCUSSION

We have used a simple Hartree–Fock model to compute the components of the polarizability tensor of a pair of interacting helium atoms. This model gives a good result for the polarizability of an isolated He atom. Furthermore, the components of the polarizability tensor of the pair lead to values of various physical quantities that compare well with experiment. In particular, both the magnitude and the *sign* of the second dielectric constant are correctly given for the first time. The main features of the calculated $\alpha(r)$ and $\beta(r)$ can be summarized as follows. In the physically significant range of r, $\alpha(r)$ is negative in sign and is approximately exponential in shape. The anisotropy $\beta(r)$ can be represented by a simple sum of the classical

long-range point-dipole term and an exponential "overlap" term. This latter contribution is also of relatively long-range nature, corresponding to approximately r^{-6} at $r = \sigma$, and to the extent that one can extrapolate from helium to the other rare gases, is not consistent with the hypothesis of Bucaro and Litovitz[30] that the overlap contribution is of short range (r^{-9} or shorter).

We have found no simple scaling procedure that would allow the He data to be extended to the other rare-gas systems. We are therefore considering

similar calculations for other pairs of rare-gas atoms in an attempt to derive physically useful trends and to quantitatively explain the observed spectra. Such calculations will be more time consuming but still practical due to the simplicity and speed of the present procedure.

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