

Ab initio calculation of the dipole moment of He-Ar and the collision-induced absorption spectra

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For the study of induced dipole moments, the collisional He-Ar complex is treated as a molecule in self-consistent-field (SCF) and size-consistent coupled-electron-pair approximation (CEPA) calculations. The basis superposition error is effectively avoided by using nonorthogonal local orbital sets. The results suggest that the SCF plus approximate dispersion dipoles commonly considered may be at best in accidental agreement with experiment because of fortuitous cancellation: for He-Ar, the hitherto neglected intra-atomic correlation increases the exchange dipole by as much as 30% while the dispersion dipole (which has the opposite polarity of the exchange dipole) is almost 3 times larger than a perturbation estimate of the leading term has indicated. Collision-induced absorption spectra are computed on the basis of the *ab initio* dipole-moment function, and compared with Bosomworth and Gush's celebrated measurement. We observe close agreement at frequencies where the absorption is strong. Only at the high and low ends of the measured frequency range does the measurement fall below theory by up to 20%, possibly because of the greater experimental uncertainties associated with weak absorption. Other measurements at relatively high densities have resulted in integrated two-body absorption intensities in reasonable agreement with our binary theory.

INTRODUCTION

Collision-induced absorption (CIA) spectra of helium-argon and similar rare-gas mixtures typically show rather broad line shapes,¹⁻³ due to the short lifetime of collisional complexes. The intensity and line shape depend sensitively on the induced dipole moment and interaction potential over a relatively small region around the collision diameter.⁴⁻⁷ While there are numerous sources of information on potentials, such as spectroscopic data, molecular-beam experiments, or bulk properties,^{8,9} the induced dipole functions have been empirically defined mainly by an inversion of CIA spectra, and theoretically form perturbation or self-consistent-field- (SCF-) type computations.

The processes which generate the induced dipole moments are well known.^{10,11} They are related to the interaction terms known from van der Waals potentials. At long range, dispersion forces lead to an induced dipole whose expansion, in terms of inverse powers of separation, has the leading term D_7R^{-7} . At short range, exchange effects generate an "overlap" dipole which falls off exponentially with increasing separation. For dissimilar noble-gas atomic pairs, at separations comparable to the collision diameter, the overlap contribution dominates and the dispersion dipole tends to reduce its strength, somewhat.

The computation of induced dipole moments poses problems similar to those familiar from the calculations of van der Waals potentials. First, the dipole moments are rather small and arise from very minor distortions of the charge distributions. For example, for He-Ar, the di-

pole moment of 0.0075 a.u. at separations equal to the collision diameter, $\sigma=5.65$ bohrs, corresponds to a shift of the Ar outer-shell charge center by only 0.001 bohr, a very small fraction of its "radius" of $(\langle r^2 \rangle / 8)^{1/2} \sim 1.45$ bohrs. A perturbational treatment seems natural for such small effects but the notorious problems of accounting for the exchange effects at short range have not yet been overcome. On the other hand, standard quantum-chemical methods, i.e., variational SCF and configuration-interaction (CI) calculations, suffer from the very slow convergence of the dispersion attraction with size of the basis set, and from basis-set superposition errors, which may lead to spurious attractive contributions from unphysical changes of intra-atomic correlation. Due to the inability to account for high-angular-momentum interatomic correlation, van der Waals potentials that closely model the region of the well have been obtained only for light systems like He-He (Ref. 12) and He-H₂ (Ref. 13), while such potentials are not available for systems like Ne-Ne or He-Ar. The computation of collision-induced dipole moments is, in principle, equally demanding and only a few calculations are known. However, since collision-induced absorption probes the dipole moment mainly in a region where exchange or induction terms strongly dominate the dispersion contributions, there is a good chance that *ab initio* calculations can provide useful data on dipole-moment functions.

PREVIOUS CALCULATIONS

Calculations of induced dipole moments have recently been reviewed by Meyer.¹⁴ Here we briefly discuss previ-

ous work relevant to the He-Ar system. The exchange dipole has first been investigated by Matcha and Nesbet¹⁵ in SCF calculations with double- ζ -plus-polarization basis sets, optimized at the very short distance of 2 bohrs. Since severe numerical problems occurred at distances around the collision diameter, the results had to be extrapolated on the basis of their apparent exponential dependence on the separation R . The comparison with a spectroscopic measurement by means of a classical line-shape calculation¹⁶ indicated that the theoretical dipoles were somewhat too small. This prompted Levine¹⁷ to estimate the leading dispersion coefficient D_7 with a semiclassical treatment based on the Drude model. Byers Brown and Whisnant¹⁸ recast the perturbational expression for D_7 in terms of frequency-dependent atomic properties; another reformulation has been given later.¹⁹ These properties involve dipole and quadrupole transition moments between excited states which have not been measured. A theoretical determination of these moments is difficult and accurate results are available only for H and He from a variation perturbation treatment.¹⁸ However, Whisnant and Byers Brown¹⁸ were able to relate the dominant term D_7 to the van der Waals coefficient C_6 and a ratio of atomic quantities which can be obtained by procedures used for calculating atomic polarizabilities. They determined D_7 values for several rare-gas-atom pairs which are now commonly used. The approximation involved was shown to be in error by only about 10% for H-He, but for heavier systems, such as He-Ar, the accuracy is difficult to assess. Significant contributions from higher-order terms D_9 , D_{11} , etc. are expected. The values of D_9 , D_{11} , etc. have, however, never been estimated and the effect of damping of the dispersion contributions at near range is also presently unknown.

The negative dispersion dipoles, when combined with the SCF dipoles,¹⁵ increased the discrepancy with experiment.¹⁸ Lacey and Byers Brown,²⁰ therefore, reconsidered the exchange dipole based on the assumption of pure exchange between otherwise undistorted Hartree-Fock wave functions of the colliding atoms. This assumption avoids the source of the superposition errors. For Ne-Ar, their results are in good agreement with the previous SCF results,¹⁵ but for He-Ne, the opposite sign was observed, and for He-Ar a difference by a factor of 2.

Empirical induced dipoles have been obtained by Birnbaum *et al.*⁴ from collision-induced absorption spectra for mixtures of argon with helium, neon, and krypton, based on an exponential-plus-dispersion functional form of the induced dipole and using the most recent semiempirical interaction potentials. While the measured profiles for Ar-Ne and Ar-Kr could be reproduced closely, for He-Ar, there remained a small but significant average deviation of +4%. Because certain empirical dipole moments differed by up to 40% from the theoretical dipole moments of Lacey and Byers Brown, Birnbaum, Krauss, and Frommhold⁵ recalculated the overlap dipole from Hartree-Fock wave functions. The Slater-type orbital (STO) basis set was again essentially of double- ζ quality, but augmented by single diffuse s and d functions optimized for dipole polarizability. Saturation of the basis set was indicated by small effects from orbital exponent vari-

ation. Agreement with experiment was significantly improved in the case of Ne-Ar for which the theoretical dipole moment appears to be correct to within 5%. For Ar-Kr, however, the moment is now too large by about 20%. The differences between the pure exchange²⁰ and the SCF dipole results are surprisingly large. They are probably related to some approximations made in the actual calculations of Lacey and Byers Brown. We mention, furthermore, two treatments of the exchange and dispersion dipole based on the electron-gas and Drude-model shell displacements^{21,22} which, however, cannot be used for quantitative, reliable computations.

Considering the accuracy of the experimental intensities which we estimate to be in the order of 10%, and the sensitivity of the theoretical intensities to the potential—a 1% variation in the collision diameter causes a change in the intensities in excess of 10%—the overall agreement between experiment and a theory based on the Hartree-Fock (HF) plus dispersion dipole seems satisfactory. We point out, however, that to a certain extent, the agreement is fortuitous. As briefly mentioned above, electron correlation is included only in form of the leading D_7 dispersion term.¹⁸ No estimate exists for either the higher-order terms or the effect of damping, which are likely to be significant. On the other hand, the inclusion of intra-atomic correlation increases the “size” of the noble-gas atoms as the correlated $\langle r^2 \rangle$ expectation values indicate, which are larger than the corresponding HF values by 0.6% for He and Ar, and by a surprising 3% for Ne.²³ Therefore, the exchange-interaction and overlap dipole may be expected to increase. Indeed, intra-atomic correlation enhances the exchange repulsion for He-He (Ref. 24) and He-H₂ (Ref. 13) by about +10%, but for Ne-Ne (Ref. 25) by as much as 25%. A corresponding increase in the exchange dipole is quite likely, and it may be expected to cancel, to some extent, the neglected higher-order dispersion terms. The delicate balance between these two effects is probably responsible for the Hartree-Fock plus D_7 dipole being deficient in the case of He-Ar and excessive for Ne-Kr.

NEW COMPUTATIONS OF THE DIPOLE MOMENT

An investigation of these correlation effects by CI calculations of the molecular complex He-Ar is desirable. As mentioned above, a considerable problem is the extremely slow convergence of the dispersion effects with the expansion of the basis set. If the basis set is tailored to account especially well for dispersion terms—i.e., by adding mainly diffuse functions—there is an artificial enhancement of the effect of the intra-atomic correlation because electron charge moves into the outer fringes of the wave function. A way out may be to calculate the two correlation effects separately, using different basis sets, but there is a non-negligible coupling which is well known from work concerning the dispersion potential.^{13,26}

In view of these difficulties, we have undertaken correlated dipole calculations for He-Ar, the smallest system for which accurate measurements are available, using the following procedures.

(1) The Hartree-Fock wave function is transformed to localized orbitals in order to identify intra-atomic and in-

TABLE I. Exponents of the GTO basis set.

Ar	14s:	0.085, 0.190 16, 0.472 85, 1.175 78 (Ref. 23); + 10 largest exponents from the 12s set of Huzinaga ^a 5 innermost functions contracted
	10p:	0.092 31, 0.223 94, 0.537 45, 1.289 87 (Ref. 23); + 6 largest exponents from the 9p set of Huzinaga ^a 4 innermost functions contracted
	3d:	0.16, 0.55, 1.65
	2f:	0.3, 0.9
He	10s:	10s set of Huzinaga ^b 5 innermost functions contracted
	3p:	0.23, 0.7, 2.8
	2f:	0.45, 1.40

^aS. Huzinaga, Division of Theoretical Chemistry, University of Alberta, Technical Report, 1970 (unpublished).

^bS. Huzinaga, J. Chem. Phys. **42**, 1293 (1964).

teratomic (dispersion) correlation terms.

(2) The Hartree-Fock basis set of Gaussian-type orbitals (GTO's) (14s,10p for Ar, as adapted to polarizability calculations by Reinsch and Meyer,²³ 10s for He) is first augmented by 2d,1f sets for Ar and 2p,1d sets for He, which are carefully optimized for intra-atomic correlation. Single diffuse d and f sets for Ar, and p and d sets for He, are then added and optimized to account for dipole and quadrupole atom polarizabilities as well as the corresponding terms of the dispersion attraction. Various further extensions of the basis set yielded changes of the dipole moment of less than 2% at 5.5 bohrs. The exponents of the GTO's are given in Table I.

(3) Superposition errors are avoided at the CI level by restricting the intra-atomic correlation to different molecular-orbital subspaces which are spanned by the atoms' "own" basis functions only, after projecting out the occupied Hartree-Fock orbitals. This is readily implemented in the self-consistent electron-pair (SCEP) technique,^{27,28} which allows the use of different orbital sets for different electron pairs, or even of nonorthogonal external orbitals. This method of avoiding superposition errors is also inherent in the local CI method recently proposed by Pulay.²⁹

(4) The size-consistent coupled-electron-pair approximation^{30,31} (CEPA-1) is used to account approximately for higher-order substitutions, since otherwise intra-atomic correlation reduces the dispersion terms unduly.

The effect of triple substitutions has been discussed in detail by Meyer *et al.*¹³ for He-H₂. It is particularly large for systems containing helium because of the great energy gain (~0.07 hartree) connected with the 1s relaxation in the perturbed 1s2p He configuration. This effect is only partly accounted for by the CEPA, but no attempt has been made here to include triple substitutions explicitly. The CEPA-1 method has been used widely and successfully for calculating dipole moments and polarizabilities of small molecules and their ions.³² The comparison with measured dipole moments, polarizabilities, as well as in-

frared intensities, shows that absolute values, as well as derivatives with respect to internuclear separation, are usually predicted with a small percent of uncertainty. With the basis set used here, the CEPA-1 atomic polarizabilities amount to 10.87 and 1.382 a.u. for argon and helium, respectively, as compared to the accepted values of 11.1 and 1.385 a.u.³³ This again indicates an uncertainty of ~3%.

The various contributions to the dipole moment of He-Ar are shown in Table II for the internuclear separation of 5.5 bohrs, which is slightly less than the collision diameter. The SCF (exchange plus distortion) dipole is fairly close to the best previous value,⁵ but the deviation of 4% is not insignificant for the comparison with experiment. STO functions as used in Ref. 5 have a certain advantage in describing the tail region of the wave function, but our 9p GTO set is more flexible than the 4p STO set. Intra-atomic correlation is seen to increase the overlap dipole by a surprising 30%. Interatomic correlation adds a dispersion dipole which is about 3 times as large as the D₇ dispersion term of Whisnant and Byers Brown.¹⁸ It lowers the total dipole back to a value which is only slightly smaller than the pure SCF value. It deviates by only +3% from the empirical dipole.⁴ This is a rather gratifying agreement, probably somewhat fortuitous since, again, we do not expect our intra-atomic and interatomic correlation contributions to have individually converged to this margin. From a counterpoise calculation,³⁴ we find the residual basis superposition error to amount to only 0.5% at both levels, SCF and CI, well below the 5% accuracy we may claim for the final dipole moment. The dispersion dipole multiplied by R⁷ shows a maximum at about 5.2 bohrs, indicating the range where short-range damping effects begin to effectively reduce the dispersion terms. Because the damping functions are unknown, it is difficult to separate the individual dispersion terms from the total dispersion dipole.

Figure 1 displays the He-Ar dipole functions from various sources for comparison. None of the theoretical

TABLE II. Interaction energies and dipole moments for He-Ar at $R = 5.5$ bohrs, in 10^{-6} a.u.

	E	μ	
SCF	826	7618	
SCF + intra-CI	1159	10090	
SCF + inter-CI	-57	5132	
SCF + intra- and inter-CI	391	7455	
Experiment	240 ^b	7240 ^a	
	201 ^c		
Other calculations			
Matcha and Nesbet (Ref. 15):	SCF	900	4050
Whisnant and Byers Brown (Ref. 18):	D_7		-821
Lacey and Byers Brown (Ref. 20):	exchange		7560
	exchange + D_7		6740
Birnbaum <i>et al.</i> (Ref. 5):	SCF	810	7300
	SCF + D_7		6480
Ahlrichs <i>et al.</i> (Ref. 36):	SCF	819	

^aEmpirical model (Ref. 4).^bHFD potential (Ref. 36).^cSPFD-2 potential (Ref. 8).

curves show a curvature comparable to that of the empirical dipole function.⁴ It is difficult to see which effect could cause this curvature. The empirical function is known to have an unreasonably large D_7 term, and the fit of the experimental intensities is not really a good one.

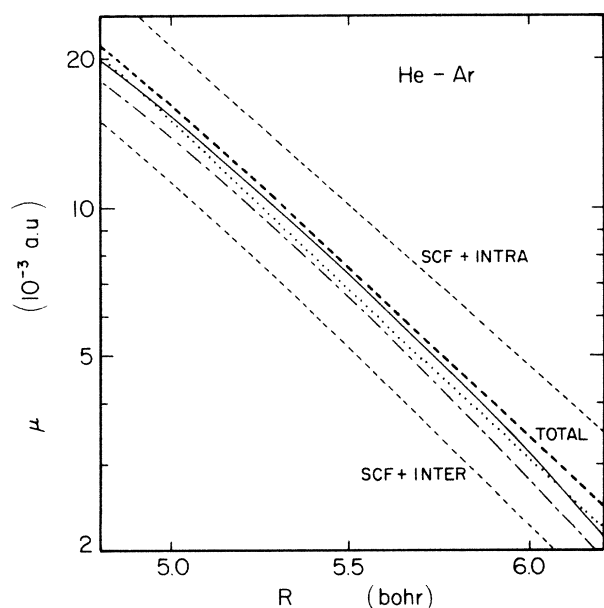


FIG. 1. Collision-induced dipole moment for He-Ar. Dashed lines: this work, SCF and CEPA calculations. Solid line: empirical dipole of Birnbaum *et al.* (Ref. 4). Dashed-dotted line: exchange + D_7 dipole of Lacey and Byers Brown (Ref. 20). Dotted line: SCF + D_7 dipole of Krauss *et al.* (Ref. 5).

SPECTRAL PROFILES OF COLLISION-INDUCED ABSORPTION

Since it is convenient to work with analytical models, we have fitted the dipole strength, last column of Table III, as function of separation by least-mean-squares techniques and obtained the expression

$$\mu(R) = 0.0386 \exp[-1.371(R - 4.5) - 0.04832(R - 4.5)^2] - 290/R^7, \quad (1)$$

with μ and R in atomic units. The coefficient of -290 a.u. for the dispersion term has been determined by separately fitting the long-range dispersion contribution $\mu_{\text{tot}} - \mu_{\text{intra}}$ for separations from 6.5 to 7.5 bohrs. Although the functional form of the leading dispersion term is used, this coefficient models all dispersion contributions, including damping. Therefore, it is not directly comparable with $D_7 = -125$ a.u. of Ref. 18.

We have used expression (1), along with a most refined potential called the SPFD-2 model,⁸ to compute a spectral line shape. A rigorous quantum formalism described else-

TABLE III. Induced dipole moment (10^{-6} a.u.).

R (bohrs)	SCF	SCF + intra	SCF + inter	Total
4.5	30081	39510	22781	30434
5	15529	20918	11149	15891
5.5	7618	10090	5132	7455
6	3585	4721	2217	3369
6.5	1633	2127	892	1440
7	728	934	327	580
7.5	308	402	100	216

where has been used.^{4,7} In Fig. 2, we show the comparison of theory and measurement in the form of the spectral function $g(\omega)$, which is related to the absorption coefficient $\alpha(\omega)$ according to

$$\alpha(\omega) = \frac{4\pi^2}{3\hbar c} n_a n_b \omega [1 - \exp(-\hbar\omega/kT)] g(\omega). \quad (2)$$

In this expression, \hbar designates Planck's constant, c the speed of light, k the Boltzmann constant, and n_a and n_b the particle densities of helium and argon. We note that at the intermediate frequencies, from ~ 100 to beyond 400 cm^{-1} , the fundamental theory agrees with the measurement of Bosomworth and Gush;² deviations are well within the experimental uncertainties which we estimate to be at the 10% level (provided the measured absorption is not too small). We note that at the low frequencies, from 60 to 80 cm^{-1} , experimental difficulties made the measurement impossible. The substantial scatter of the data points from 50 to 60 cm^{-1} is probably related to the small values of the absorption coefficient $\alpha(\omega)$ which enhance the uncertainty of the measurement. Similarly, with increasing frequency ($> 400 \text{ cm}^{-1}$), the experimental points appear to be scattered more and more, indicating greater uncertainty as the absorption falls off to very small values.

Summarizing, we find the agreement of measurement² and theory satisfactory. As was noted above, we estimate that the accuracy of the induced dipole computations is better than 5% at separations around the collision diameter. Similar accuracies of induced-dipole computations have been confirmed for other systems^{14,35} (He-H₂, H₂-H₂, H₂-Ar) and may be considered a new standard for the type of *ab initio* computations described here. Additional uncertainties arise from the numerical precision of the

line-shape computations ($\approx 2\%$), and also from the remaining small uncertainties of the interaction potential. The latter are hard to estimate, but we mention that other refined potential models, the SPDF and Hartree-Fock plus damped dispersion (HFD-2) models,^{8,36} give spectral intensities 5–10% smaller than those obtained with the SPDF-2 model. The estimated overall uncertainty of the line-shape computations is thus in the range of 10%, and theory and measurement are in agreement within the combined error limits. We note that for frequencies above 85 cm^{-1} , in a semilogarithmic grid, theory suggests a slightly concave profile while the measurement exhibits a discernible convexity. However, as far as we can determine, no realistic variation of the input dipole moment and potential model will reproduce the observed convexity of the measurement, which we suspect may be an artifact, perhaps related to small absorption, $\alpha(\omega)$, at the low and high ends of the measured frequency range. New measurements, preferable at a variety of temperatures, are desirable to determine whether the slightly concave shape is indeed the correct one.

Other measurements of CIA spectra in He-Ar are known^{37–40} but, unfortunately, only one other spectrum³⁷ is available in sufficient detail that warrants a comparison with theory. Although it is by no means clear from the information given that we have a *binary* spectrum before us, we reproduce it in Fig. 3, along with a binary computed profile based on the same input as in Fig. 2. We note that the low-temperature work^{37–39} was undertaken at much higher densities than, for example, the measurement of Bosomworth and Gush, so that two- and three-body spectra could be obtained and separated experimentally. Figure 3 indicates a reasonable shape consistency of

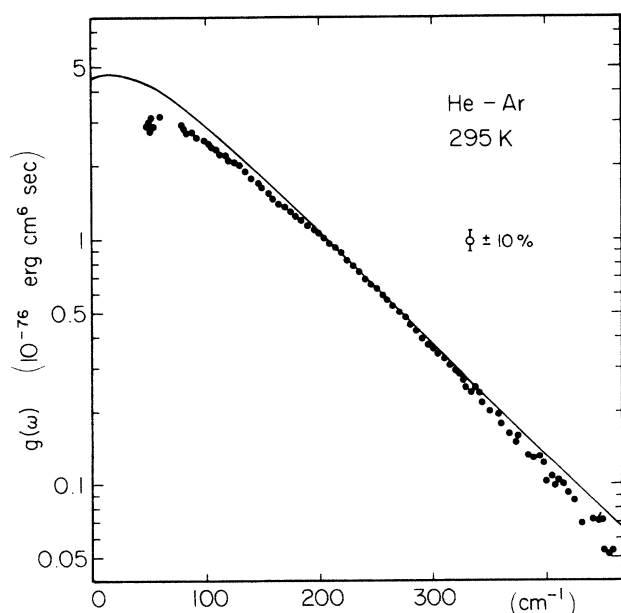


FIG. 2. Spectral function, $g(\omega)$, of He-Ar at 295 K as function of frequency. Comparison of theory (solid curve) and measurement (Ref. 2) (dots).

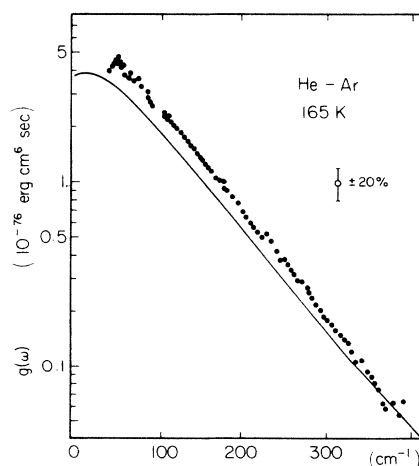


FIG. 3. Spectral function, $g(\omega)$, of He-Ar at 165 K as function of frequency. Comparison of theory (solid curve) and measurement (Ref. 37) (dots).

theory and measurement, but the measurement appears to be roughly 20% more intense everywhere. This is surprising because the comparison of the binary moments indicates that binary measured intensities are lower than our theory predicts. We will, therefore, discuss the spectral moments next and return to the discussion of the observed inconsistency below. Spectral moments are defined by

$$G_n = \int_0^\infty \omega^n [1 + (-1)^n \exp(-\hbar\omega/kT)] g(\omega) d\omega. \quad (3)$$

The zeroth moment ($n=0$) is a measure of the total intensity of the spectral function. The relationship of these moments with interaction potential and dipole function has been discussed by van Kranendonk.³ We use classical expressions with first-order quantum corrections given by Hartye *et al.*⁴¹ to obtain the values of zeroth and first moments ($n=0$ and 1) given in Table IV. For comparison with measured two-body integrated intensities, which are also given in the table, one should remember that the uncertainties of the experimental moments may be substantial. The first moment is proportional to the integral of the absorption coefficient, which is thus hardly more accurate than the measurement of $\alpha(\omega)$. Furthermore, the extrapolations to zero and infinite frequency introduce additional uncertainties which are often substantial. The main contributions to the zeroth moment, G_0 , come from the low frequencies at which absorption cannot be measured. The extrapolations which one is thus forced to resort to often amount to 30–50% of the total G_0 , which introduces substantial uncertainty of the experimental value. We note that the theoretical moments are all 10–30% greater than measurement, (Table IV). Since, in Fig. 2, the measurement lies consistently below theory, this is not surprising. However, in Fig. 3 we observe measured data fairly consistently above theory by an average of roughly 20%, and yet the theoretical moments quoted are greater than measured ones, by roughly the same amount. The explanation is not obvious to us but we note that the low-temperature measurements were taken at high densities of 156 amagat of argon, mixed with 66 amagat or more of helium. While the authors corrected the moments for three-body contributions, the spectral profile reproduced in Fig. 3 may be an uncorrected one; no specific details are given.³⁷

Work at the temperature of 480 K is also known.⁴⁰ However, for some time, it was recognized that the high-temperature measurement is inconsistent with all theoret-

cal estimates.^{4,5,38} For the sake of completeness, we quote the experimental values⁴⁰ of $G_0=0.35$ and $G_1=4.31$ (same units as in Table IV). For comparison, the theoretical values of the present work are $G_0=0.320$ and $G_1=2.17$.

We note that the SPFD-2 potential model is consistent with the existence of bound dimer states, HeAr. We find one vibrational state ($v=0$) with five rotational levels ($l=0, \dots, 4$) at the energies of -7.05 , -6.47 , -5.30 , -3.59 , and -1.39 cm^{-1} , and some predissociating states ($l=5, \dots, 8$) of rough energies and widths as 1.18 ± 0.03 , 3.9 ± 0.4 , 7.2 ± 2 , and 11 ± 5 cm^{-1} . The dimer concentrations are given by the law of mass action, $n_2 = n_a n_b K(T)$, where n_a, n_b are monomer and dimer number densities and $K(T)$ is a constant equal to 0.54×10^{-24} cm^3 at 295 K, or 1.3×10^{-24} cm^3 at 165 K. In other words, the dimer concentrations are quite weak, in the order of one-tenth of 1% at densities of ~ 10 –50 amagat. These dimers have a spectrum at low frequencies which is superimposed on the collision-induced spectra displayed in Figs. 2 and 3. It has the same density dependence as the latter, with intensities proportional to $n_a n_b$. Selection rules are $\Delta l = \pm 1$. Computations indicate a rotational band consisting of four lines at ~ 0.6 , 1.2, 1.7, and 2.2 cm^{-1} in the microwave region (bound-bound transitions), one bound-free transition to a predissociating state at 2.6 ± 0.03 cm^{-1} , and another discernible structure at 2.8 ± 0.4 cm^{-1} due to a transition between the two longest-lived predissociating states; transitions between the other resonances, and the nonresonant bound-free transitions give rise to a rather unstructured continuum, which falls off to very small levels above 10 or 20 cm^{-1} . The total intensities of the bound-bound and bound-free contributions amount to 0.7 and 6.0 (10^{-65} erg cm^6), respectively, at 295 K, and 1.8 and 13.0 (10^{-65} erg cm^6) at 165 K. These are to be compared with the zeroth moments, Table IV, which are seen to be roughly 2 orders of magnitude larger. The dimer spectra are, therefore, relatively weak and can usually be ignored in microwave studies of collision-induced absorption of He-Ar mixtures unless temperatures and pressures are quite low. We note that microwave methods⁴² have indicated an upper experimental limit of the absorption, $\alpha(\nu)/n_a n_b \nu^2 < 1.5 \times 10^{-10}$ cm amagat^{-2} . For the temperature of 295 K, we compute the consistent value of 1.32×10^{-10} cm amagat^{-2} from the fundamental theory. Here, $\nu = \omega/2\pi c$ is the frequency in cm^{-1} .

TABLE IV. Comparison of experimental and theoretical spectral moments.

Temperature (K)	Reference	G_0 (10^{-61} ergs cm^6)		G_1 (10^{-49} ergs cm^6/s)	
		Meas.	Calc.	Meas.	Calc.
140	39	0.094	0.126	0.74	0.938
165	39	0.118	0.141	0.88	1.036
200	39	0.130	0.162	1.02	1.172
240	39	0.167	0.185	1.18	1.325
295	2	0.17	0.217	1.32	1.529

TABLE V. Interaction energies (10^{-6} hartree). The total energies at infinite separation are for Ar: SCF, -529.806752 ; CEPA-1, -530.939240 . For He: SCF, -2.861669 ; CEPA-1, -2.901278 .

R (bohrs)	SCF	SCF + intra	SCF + inter	Total	Empirical ^a
4.5	6321	8845	2255	5075	5434
5	2300	3247	455	1589	1220
5.5	826	1159	-57	391	201
6	293	412	-158	32	-51
6.5	103	144	-143	-57	-93
7	36	50	-108	-64	-81
7.5	12	19	-76	-49	-60

^aSPFD-2 model, Ref. 8.

DISCUSSION OF THE INTERACTION POTENTIAL

Although our interest has focused on the dipole moments and the dispersion attraction is expected to show clear defects from the limited basis set used, it still appears worthwhile to discuss the interaction potential obtained. No better *ab initio* potential seems to be presently available. As described above, we have taken care to account quantitatively for the dipole polarizabilities of the interacting atoms. Therefore the C_6 contribution of the dispersion interaction should be well described. The C_8 contribution is also largely included by the f functions placed at the argon atom, and the d functions at helium. Due to missing g functions for argon, C_{10} is only partially accounted for, and higher terms are completely left out. The interaction energies calculated for various configuration spaces are given in Table V. Figure 4 compares our potential with the most recent semiempirical Hartree-Fock plus damped dispersion (HFD) model potential.³⁶ It also shows the decomposition of the two potentials into repulsive and attractive parts. Our Hartree-Fock repulsion energy is in complete agreement with earlier calculations^{5,36} but intra-atomic correlation increases this repulsion significantly. On the other hand, our dispersion attraction is considerably larger than that implied by the long-range coefficients C_6-C_{10} and the HFD model⁸ damping. The total potential shows a well depth of 22 K at 6.75 bohrs as compared to 29.5 K at 6.58 bohrs from the most recent semiempirical potential.⁸ Due to the defects in dispersion attraction, it seems unlikely that our potential should drop anywhere below the true interaction potential. Thus our result for $R=4.5$ bohr suggests that the SPFD-2 potential rises somewhat too steeply at short separations.

Since intra-atomic correlation has often been neglected in calculations of van der Waals potentials, we point out that in our case, this approximation leads to well depths as great as 45 K. We further note that our attraction is not consistent with the semiempirical damped dispersion model proposed by Tang and Toennies.⁴³ In addition to pure dispersion-type effects, we obviously include significant contributions from ionic structures. To some extent, this may be the consequence of starting from orthogonal localized orbitals on which the separation of correlation

energy into intra-atomic and interatomic contributions rests. A further discussion of this point will be taken up elsewhere.

We note that for the line-shape calculations, Fig. 2, it is important to use an accurate representation of the interaction potential near the root σ , defined by $V(\sigma)=0$. For that reason, the semiempirical advanced model was chosen in preference to a purely theoretical model which cannot represent this region of the interaction nearly as accurately.

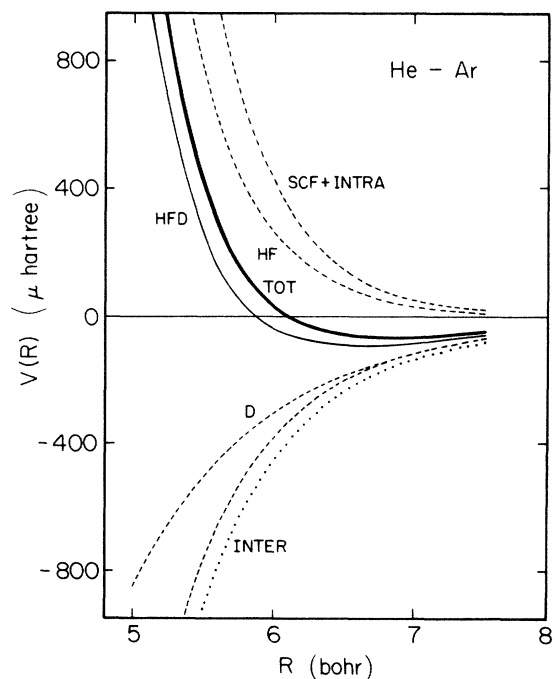


FIG. 4. Interaction potentials of the He-Ar system. Solid curves: total potentials; dashed curves: exchange-repulsion and dispersion-attraction contributions. Semiempirical potential (Ref. 8). HFD (thin solid line type), HF (dashed), D (dashed). Calculated potential: total (heavy solid line type), SCF + intra-atomic (dashed), intercorrelation (dashed). Dotted curve: dispersion-attraction required to yield semiempirical potential from calculated repulsion.

CONCLUSION

The He-Ar calculations presented here demonstrate that exchange effects due to intra-atomic correlation and higher-order dispersion terms contribute significantly to the induced dipole. However, these exchange and dispersion contributions may mutually nearly cancel as is the case for the He-Ar system considered here. Their combined contribution may well account for the differences between theory and experiment remaining to this day for other rare-gas systems.

For He-Ar, our correlated dipole moment function appears to be very reliable. It yields a spectral profile in

close agreement with the best measurement presently available.

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