Van der Waals Forces for the Inert Gases

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Theoretical and experimental values of electric-dipole oscillator strengths for inert-gas atoms are analyzed to yield a set of oscillator strengths, which satisfy the Thomas-Kuhn sum rule, and which reproduce the experimental refractive indices and Verdet constants. These oscillator strengths are then used to calculate the long-range van der Waals interaction between all pairs of atoms selected from helium, neon, argon, krypton, and xenon. The derived interaction constants are probably in error by less than 10%. They disagree with the currently accepted values of the interaction constants.

INTRODUCTION

THE magnitudes of the long-range interactions between pairs of atoms are required in such diverse fields as low-energy elastic scattering, transport phenomena, crystal structure, and collision broadening of spectral lines.[1] In general, the quantum-mechanical calculation of this long range interaction is difficult and very few accurate theoretical calculations have been carried out. However, since the leading term in the series representation of the long-range force between two atoms can be expressed in terms of the electric-dipole oscillator strengths of the atoms,[2] we can determine the magnitude of the long-range interaction between atoms for which we have reliable oscillator strengths. Previous theoretical calculations have determined the long-range interaction between two hydrogen atoms,[3] between two helium atoms,[4,5] between helium and its two metastable states,[6] between the two metastable states of helium,[6] between the alkali atoms and hydrogen,[7] between the alkali atoms and the inert gas atoms,[7] between the alkali atoms and the alkali atoms,[7] and also between all pairs selected from H, He, Ne, and A.[5] Using recently measured experimental values of the photoionization cross sections for neon,[8] argon,[9,10] krypton,[11,12] and xenon[9,13] and theoretical values of the oscillator strengths of helium,[14] we obtain the long-range interaction between all the inert gases.

THEORY

For a pair of atoms A and B, which are in states of zero orbital angular momentum, the leading term in the series representation of the long-range interaction energy has the form $-C_{ab}/R^6$, where R is the distance between the atoms. If $\epsilon_m{}^a$ denotes the binding energy of atom A in the mth excited state and $\epsilon_n{}^b$ the binding energy of atom B in the nth excited state, measured in atomic units, the coefficient C_{ab} appropriate to A and B in the ground states may be written

$$C_{ab} = \tfrac{3}{2} \mathbf{S}_m{}' \mathbf{S}_n{}' \frac{f_m{}^a f_n{}^b}{(\epsilon_0{}^a - \epsilon_m{}^a)(\epsilon_0{}^b - \epsilon_n{}^b)(\epsilon_0{}^a + \epsilon_0{}^b - \epsilon_m{}^a - \epsilon_n{}^b)},$$
$$m, n \neq 0, \quad (1)$$

where $f_m{}^a$ is the oscillator strength for the electric-dipole transition from the ground state of A to the mth excited state and $f_n{}^b$ is the oscillator strength of the electric-dipole transition from the ground state of B to the nth excited state and where $\mathbf{S}'$ denotes a summation over discrete level plus an integration over the continuum.

The problem of evaluating C_{ab} therefore reduces to the determination of the oscillator strengths of the individual atoms. Unfortunately when experimental data on oscillator strength is available, it is often incomplete and subject to experimental error and in general theoretical calculations yield values of uncertain accuracy. However, oscillator strengths satisfy the Thomas-Kuhn sum rule

$$\mathbf{S}_t{}' f_t = N, \quad (2)$$

where N is the number of atomic electrons and from experimental measurements of the refractive index and Verdet constant we can often obtain accurate values of the oscillator strength sums[15]

$$S(k) = \mathbf{S}_t{}' f_t (\epsilon_0 - \epsilon_t)^k, \quad (3)$$

for $k = -2$, -4, and -6.

Our procedure[5] consists of selecting a set of oscillator strengths from the available experimental and theoretical data and adjusting this set so that it satisfies the

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sums $S(k)$ for $k=0$, -2, -4, and -6, this adjusted set is then used in Eq. (1) to obtain C_{ab}. Although the accuracy of these adjusted oscillator strengths for any individual transition is not high, the control exerted by the oscillator strength sums prevents serious error entering into the evaluation of Eq. (1).

RESULTS AND DISCUSSION

In our calculations we used for the oscillator strengths of helium, a very accurate set proposed by Dalgarno and Stewart.[14] This set satisfies certain other sum rules and reproduces the experimental refractive index and Verdet constant data very accurately.

We used the recently measured experimental photo-absorption data of neon,[8] argon,[9,10] krypton[11,12] and xenon[9,13] to derive the continuous oscillator strengths and some of the discrete oscillator strengths for these gases. For neon[16] and argon[17] there are available Hartree-Fock calculations of the oscillator strengths of the resonance lines. No theoretical calculations have been carried out for the oscillator strengths of the resonance lines of krypton and xenon and we adopted the experimental values suggested by Koch from an analysis of his refractive-index data.[18]

These sets of oscillator strengths were then adjusted slightly so that they satisfied the Thomas-Kuhn sum rule and so that they reproduced the experimental Verdet constant[19] data and refractive-index data for neon,[20] argon,[21] krypton[18] and xenon.[18]

We have used these adjusted sets of oscillator strengths to compute C_{ab} for all pairs selected from helium, neon, argon, krypton, and xenon. These are tabulated in Table I. The value for He-He has been derived earlier by Dalgarno and Kingston[5] and the neon and argon values supersede the estimates of Dalgarno and Kingston.[5]

The absolute error in C_{ab} is certainly less than 10% and it may be much smaller. For neon and argon our previous calculations agree with the present results to better than 5%. Since the oscillator strengths for neon and argon which were used in the previous calculations were very inaccurate, it is seen that the control exerted on the oscillator strengths by making them satisfy the sum rules is sufficient to give us accurate values for C_{ab}. Previous calculations by Slater and Kirkwood[22] for C_{aa} between inert gas atoms agree remarkably well with the present calculations, their method gives the values 1.56, 8.3, 73, 135, and 285 for the long range interaction constant between He-He, Ne-Ne, A-A, Kr-Kr, and Xe-Xe, respectively.[2]

The results of the present calculations disagree with

TABLE I. Values of C_{ab} for the inert gases in atomic units.[a]

b \ a	He	Ne	Ar	Kr	Xe
He	1.456	3.01	9.63	13.5	18.7
Ne	3.01	6.31	19.7	27.4	37.7
Ar	9.63	19.7	65.4	92.3	131
Kr	13.5	27.4	92.3	131	186
Xe	18.7	37.7	131	186	269

[a] The leading terms in the long-range interaction energy $-C_{ab}/R^6$ is in atomic units if R is measured in atomic units a_0.

currently accepted values of C_{ab} derived from such experimental data as viscosity,[1] second virial coefficients,[1] and low-energy elastic scattering.[23] For example, values of C_{aa} for the long-range interaction between He-He, Ne-Ne, A-A, Kr-Kr, and Xe-Xe derived from viscosity data are 1.7, 9.7, 114, 243, and 587, respectively.[1] These are almost a factor of 2 greater than the values in Table I. This disagreement between theory and experiment may not be as serious as it seems for the long-range interaction energy cannot be determined uniquely by the present experimental viscosity data. Moreover Guggenheim and McGlashan[24] have made a careful examination of a wide range of experimental data on argon and have shown that an interaction potential between two argon atoms which has a long-range interaction constant C_{A-A} of 68 reproduces a large range of experimental data. This value is in excellent agreement with the present calculations.

There is also serious disagreement between the present calculated values of C_{ab} and the experimental values derived from low-energy elastic-scattering cross sections. These experimental values[23] of 26, 63, 188, 210, and 377 for the long-range interaction constants between He-A, Ne-A, A-A, Kr-A, and Xe-A are not only three times greater than the present calculated values but also more than 50% greater than the values of C_{ab} derived from experimental viscosity and second virial coefficient data. Here again the disagreement between theory and experiment is not as serious as it seems for since the experimental cross section is proportional to $(C)^{2/5}$ an error of 40% in the measured elastic-scattering cross section could easily account for the difference between theory and experiment.

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