PHYSICAL REVIEW B VOLUME 34, NUMBER 4 15 AUGUST 1986

Long-range interaction between rare-gas atoms or simple molecules and the surfaces of LiF, CaF_2, sapphire, and BN

M. Karimi
Physics Department, Utica College, Utica, New York 13502

G. Vidali
Physics Department, Syracuse University, Syracuse, New York 13244-1130

(Received 10 February 1986)

An atom or a molecule approaching a surface experiences an attractive potential given by $V(z)\sim -C_3/z^3$. We have computed C_3 for rare-gas atoms and simple molecules interacting with surfaces of various insulators. Our calculation utilizes (frequency-dependent) atomic polarizabilities and dynamic dielectric functions obtained from optical data. A comparison is made with C_3 values deduced from multilayer adsorption data on CaF_2. We show that a simple formula can be used to evaluate C_3 that utilizes readily available constants. We have also computed the long-range surface-mediated interaction between two adsorbed atoms on a surface. We then present a discussion on adsorption of adatoms on hexagonal BN as compared to that on a graphite substrate.

I. INTRODUCTION

Considerable attention has been devoted in recent years to the problem of calculating, possibly by *ab initio*, reliable atom (molecule) -surface potentials.[1] These efforts were motivated by the appearance of high-resolution experiments using the technique of atom beam scattering[2] as well as by the interest in studying two- or quasi-two-dimensional adsorbed films on substrates.[3] An important ingredient in such calculations is the long-range behavior of the interaction, i.e., the behavior that results when the incoming atom and the surface are well separated and no significant overlap of wave functions occurs. It has been shown[4] that the asymptotic part of the potential is

$$V(z)\sim -C_3/z^3\,, \tag{1}$$

where

$$C_3=(1/4\pi)\int_0^\infty \alpha(iE)\frac{\epsilon(iE)-1}{\epsilon(iE)+1}dE\,, \tag{2}$$

z is the atom-surface separation, $E=\hbar\omega$, and C_3 is a constant that depends on the dynamic atomic polarizability α and the dielectric response ϵ of the solid. The purpose of this paper is to calculate such constants for many atom (molecule) -surface systems of interest. We have considered the interaction of H, H_2, He, Ne, Ar, Kr, Xe, and CH_4 on the surfaces of sapphire, LiF, CaF_2, and boron nitride (BN). This choice was made for the following reasons.

Considerable attention has been given to the Kr-BN system;[5,6] we recall that *BN* has the same structure as graphite and similar lattice spacing with the difference that BN is an insulator and graphite is a semimetal. However, the existence of a commensurate-incommensurate phase transition (at about monolayer coverage) for Kr-graphite has not been observed unequivocally on BN.[5,6] Unfortunately, there has been no structural studies of adsorbates on BN to date. A reliable atom-surface potential is extremely useful to calculate key thermodynamics properties as has been demonstrated for rare-gas atoms on graphite.[7] Here we contribute to better understanding of this system by calculating the long-range part of the atom-surface interaction (the coefficient C_3) *and* the modification of the adsorbate-adsorbate potential due to substrate screening effects (for the coefficients C_{s1} and C_{s2}, see Sec. II). This latter effect has been evaluated to amount to 15–20% of the unscreened interaction for many rare gases adsorbed on graphite.[8]

In the case of He-sapphire, our motivation again is to calculate the long-range part of the interaction and then calculate the entire atom-surface potential (to be presented elsewhere). Such calculations should be helpful in interpreting recent low-temperature He desorption data from sapphire at low temperatures.[9]

Finally, we have calculated C_3 values for rare gases on LiF in order to compare these values with estimates obtained using a simple formula (see Sec. III). [Previously C_3 was calculated for the atoms (molecule) He, H, and (H_2).[10]] Results of the comparison show a close likeness, the two values (calculated and estimated) differing from each other by typically 5–10%, often within the limits to which C_3 is known because of uncertainties in optical data used to calculate the dielectric function.

The paper is organized as follows: in Sec. II the method employed to calculate C_3, and C_{s1}, C_{s2} from optical data is presented. In Sec. III the validity of the above-mentioned simple formula to evaluate C_3 is discussed. The presentation and discussion of the results are given in Sec. IV.

II. CALCULATIONS

In order to calculate C_3 from Eq. (2), we need the atomic polarizability and dielectric function of the solid as a function of frequency; α and ϵ are evaluated at imaginary frequencies but are, of course, real numbers.

The atomic polarizability function can be approximated by

$$\alpha(iE)=\alpha_0/[1+(E/E_a)^2]\,, \tag{3}$$

as shown previously.[11] Here α_0 is the static polarizability and E_a is a characteristic absorption energy. For consistency, E_a has been chosen so as to give the known value of C_6 using

$$\begin{aligned} C_6&=(3/\pi)\int_0^\infty \alpha^2(iE)dE \\ &=\tfrac{3}{4}\alpha_0^2E_a^2\,. \end{aligned} \tag{4}$$

The result is that E_a is comparable to the ionization energies.[11] For H_2 we used the orientationally averaged polarizability.

To evaluate $\epsilon(iE)$, input of optical data is necessary. Typically reflectance data in the visible through the far ultraviolet region are analyzed to obtain ϵ_2, the imaginary part of the dielectric function. Using published values of ϵ_2 and the Kramers-Kronig relation,

$$\epsilon(iE)=1+(2/\pi)\int_0^\infty \frac{E'\epsilon_2(E')}{(E')^2+E^2}dE'\,, \tag{5}$$

$\epsilon(iE)$ can be computed. There are some difficulties associated with this procedure. First, ϵ_2 varies considerably from study to study due to uncertainties; nevertheless, the main features in ϵ_2 vs E are retained. The absolute and relative values of the maxima (corresponding to interband and/or intraband transitions, plasmon excitations, etc.) might vary from experiment to experiment. Fortunately, in order to obtain C_3 two integrals have to be performed; this ensures that minor details ϵ_2 vs E are not important. Of course, errors will occur if ϵ_2 from a set of data is consistently higher than another one. Second, optical data are usually taken in the visible and near-ultraviolet region (for the insulators under study). An extrapolation of $\epsilon_2(E)$ to higher frequencies is then necessary in order to perform the integral in Eq. (5) correctly. We found that data are typically available from the band gap up to 30 to 60 eV. We then extrapolated from the last value (up to 100 eV in most cases) using $\epsilon_2\sim 1/E^3$.[12] For LiF we have taken the data of Ref. 13, the same data used in Ref. 10; for sapphire, data is available for "corundum" samples[14] and we have also done calculations using data for "ruby" samples;[15] as expected, the ϵ_2 vs E curves differ considerably, due to chromium impurities in the latter. For CaF_2 we have used data of Ref. 15 while for BN, data up to only 30 eV was available.[16] Errors in C_3 connected with lack of complete data, etc., will be discussed in Sec. IV. For BN we have used the following equation:[17]

$$\epsilon(iE)=[\epsilon_{\|}(iE)\epsilon_{\perp}(iE)]^{1/2}\,, \tag{6}$$

to take into account the fact that BN, like graphite, has quite different dielectric responses parallel and perpendicular to the c axis.

When two adatoms interact on a surface, their gas-phase interaction is modified because of the electromagnetic screening of the van der Waals interaction via the substrate. In the case of the continuum model of the substrate, McLachlan derived the following expression for the change of the adatom-adatom interaction:[18]

$$\Delta V(r)=\frac{4C_{s1}}{r^6p^{3/2}}\left[\frac{1}{3}-\frac{L^2}{pr^2}\right]-\frac{C_{s2}}{r^6p^3}\,, \tag{7}$$

where L is the height of the adatoms from the reference plane of the substrate, $p=1+(4L^2/r^2)$, and r is their separation. The coefficients are

$$C_{s1}=(3/\pi)\int_0^\infty \alpha^2(iE)\frac{\epsilon(iE)-1}{\epsilon(iE)+1}dE\,, \tag{8}$$

$$C_{s2}=(3/\pi)\int_0^\infty \alpha^2(iE)\frac{[\epsilon(iE)-1]^2}{[\epsilon(iE)+1]^2}dE\,, \tag{9}$$

and can be readily evaluated once $\alpha(iE)$ and $\epsilon(iE)$ have been calculated. The perturbation ΔV has already been calculated for rare gases and methane on graphite.[8] The modified two-dimensional (2D) adatom-adatom potential is up to 20% shallower than the gas-phase counterpart.

III. A SIMPLE FORMULA

As mentioned above, one of the main problems in calculating C_3 is to find reliable data for $\epsilon_2(E)$. Hoinkes[19] has introduced the following formula: $C_3^H=k_c\alpha_0(\epsilon_0-1)/(\epsilon_0+1)$, where $k_c=1400$ meV and ϵ_0 is the static dielectric constant (evaluated at ~ 0.58 μm). It was shown previously[11] that Hoinke's formula gives a crude estimate for C_3. We have found that C_3^H is typically 10–15 % lower than the calculated value for He on any of the substrates under consideration, about 10% higher for Kr and often 30% or more off for other gases. It is customary to introduce the following definition:

$$g(iE)=\frac{\epsilon(iE)-1}{\epsilon(iE)+1}\,. \tag{10}$$

Then, according to Ref. 11, one can approximate Eq. (10) with

$$g(iE)=g_0/(1+E^2/E_a^2)\,, \tag{11}$$

where g_0 can be obtained by approximating $\epsilon(0)$ with $\epsilon_1(0)$:[20]

$$g_0\approx\frac{\epsilon_1(0)-1}{\epsilon_1(0)+1}\,, \tag{12}$$

where

$$E_s=E_p/(1+g_0)^{1/2}\,, \tag{13}$$

E_p is the plasmon frequency

$$E_p=\hbar(4\pi n_{\text{eff}}e^2/m)^{1/2}\,, \tag{14}$$

and n_{eff} is the effective number density of electrons that participate in the optical transitions. If one substitutes Eqs. (3) and (11) in Eq. (2), one can evaluate the integral analytically. The result is

$$C_3=\frac{\alpha_0g_0}{8}\frac{E_sE_a}{E_s+E_a}\,. \tag{15}$$

In many cases it is easy to evaluate C_3 from the above formula, since dielectric constants and plasmon frequen-

TABLE I. Values of g_0 and E_s coming from fits of Eq. (11) to Eq. (10), column A. In Column B available data for g_0 and E_s are given. We have taken ϵ_1 values at $\lambda \sim 0.58$ μm from Ref. 23, E_p values from electron-energy-loss data (Refs. 22 and 14) and used Eqs. (12) and (13). The last row gives estimates of C_3 for He using parameters from column A and column B. Entries in parentheses are for ruby.

	LiF		CaF_2		Al_2O_3		BN
	A	B	A	B	A	B	A
g_0	0.31	0.32	0.33	0.34	0.49 (0.36)	0.52	0.38
E_s (eV)	20.1	21.7	28.4	20.1	21.8 (31.2)	22.5	19.3
C_3 (meV Å^3)	92	93	118	101	151 (135)	167	110

TABLE II. C_3 (meV Å^3), C_{s1} (meV Å^6), C_{s2} (meV Å^6) values for atoms or molecules on LiF. Optical data from Ref. 13 were used.

	H	H_2	He	Ne	Ar	Kr	Xe	CH_4
C_3	192	261	93	192	626	882	1314	884
C_{s1}	1055	1791	181	742	9177	19 180	45 040	19 610
C_2	300	496	45	177	2427	5191	12 460	5346

TABLE III. Same as for Table I, but for CaF_2. Optical data from Ref. 15.

	H	H_2	He	Ne	Ar	Kr	Xe	CH_4
C_3	228	314	117	246	768	1071	1579	1070
C_{s1}	1195	2049	217	903	10 690	22 140	51 550	22 580
C_{s2}	379	635	61	244	3176	6720	15 940	6890

TABLE IV. Same as for Table I, but for Al_2O_3. Optical data are from Ref. 14 (corundum) and Ref. 15 (ruby).

	H	H_2	He	Ne	Ar	Kr	Xe	CH_4
				Corundum				
C_3	336	458	165	342	1104	1552	2306	1555
C_{s1}	1820	3101	318	1308	15 980	33 300	77 970	34 020
C_{s2}	817	1357	125	496	6690	14 250	34 060	14 660
				Ruby				
C_3	253	348	132	277	855	1191	1754	1189
C_{s1}	1319	2260	240	1002	11 800	24 420	56 860	24 900
C_{s2}	462	773	74	297	3859	8160	19 400	8380

TABLE V. Same as for Table I, but for BN. Optical data are from Ref. 16.

	H	H_2	He	Ne	Ar	Kr	Xe	CH_4
C_3	218	296	105	216	707	997	1487	1000
C_{s1}	1209	2044	204	836	10 410	21 820	51 380	22 330
C_{s2}	398	653	58	228	3159	6790	16 370	7000

cies are often readily available. For semiconductors (Si, Ge, and GaAs) and insulators (NaCl, LiF, and MgO) it was shown[11,21] that E_s obtained from electron-energy-loss experiments would give C_3 values within 5–10% of the C_3 calculated using optical data. In case E_s values are not easily available, one can estimate the number of effective electrons that are optically active. We can check this procedure for Al_2O_3. There are 6 valence electrons from Al_2 and 18 from O_3, or an average of 4.8 electrons per atom. This gives $E_p = 27.8$ eV,[22] and, from formula (13), $E_s = 22.5$ eV; this can be compared with $E_s = 21.8$ eV of Table I (see Sec. IV) obtained by fitting Eq. (11) to Eq. (10). Analogously one can find E_s for the other substrates (Table I, columns B). g_0 can also be easily found in the literature.[23] We can then use Eq. (15) to calculate C_3. We fitted Eq. (12) to Eq. (10) and determined g_0 and E_s (Table I, columns A) differ somehow from the values in columns B. However, C_3 is moderately sensitive to E_s. The values of C_3 so obtained, columns A and B, are in reasonable good agreement with the full calculation of Tables II–V (see Sec. IV).

IV. RESULTS AND DISCUSSIONS

In Tables II through V, we report the results of our calculations for C_3, C_{s1}, and C_{s2} for LiF, CaF_2, corundum, ruby, and BN. In all cases ϵ_2 optical data have been extrapolated at higher energies. C_3 values were also calculated without any high-frequency extrapolation and we found that these latter values are typically 5% below the ones in which ϵ_2 was extrapolated, except for BN for which the discrepancy rises to 20%.

We would like to comment now on the results obtained for boron nitride. We find that C_3 for BN is typically 40% smaller than for graphite.[11] Does that mean that the atom-surface potential is comparably smaller? Not necessarily. In fact, calculations performed so far with different methods and using different sets of data[24] give an atom-surface potential that is about 10–15% less than for graphite. While we recognize the fact that the experimental and theoretical work for adsorption on BN is not as rich and thorough as for graphite and that uncertainties lie in the determination of C_3 for BN, we might venture in speculating that the somewhat unexpected deep potential for BN might be caused by a shorter-range repulsion, allowing the incoming atom to sample more of the attractive part [Eq. (1)]. At present we are exploring this conjecture.

As far as C_{s1} and C_{s2} are concerned, we can estimate their effect on the Kr-Kr potential when Kr is adsorbed on boron nitride. Since L in Eq. (7) is referenced to a plane delimiting the continuum solid, we subtract half the interplane distance in BN (~ 3.33 Å) from the value of the height of Kr on the basal plane of BN: $L = 3.48 - 3.33/2 = 1.8$ Å, where we have used the value of the minimum of the Chang-Crowell Kr-BN potential.[24] Contrary to the adatom-graphite case, there is no solid evidence to confirm the height of an adatom above the basal plane of BN. Therefore, we cannot take this $L = 1.8$ Å too seriously; we recall that for Kr-graphite $L \sim 1.6$ Å. By using Eq. (7) for $L = 1.6 - 1.8$ Å we conclude that the well depth of the Kr-BN potential is reduced by about 10%, a somewhat smaller effect than for the corresponding graphite case.[8] It will be interesting to explore this aspect further, as, for example, in connection with recent theoretical work on the two-dimensional liquid-vapor critical point.[25]

Finally, we have compared[26] our C_3 for He on CaF_2 with the value obtained by Sabisky and Anderson based on analysis of a multilayer film of He on CaF_2:[27] our value of 117 meV Å^3 is in good agreement with their value of 103 meV Å^3, the difference due probably in neglecting the compression of the first layers of liquid He.[17,21]

ACKNOWLEDGMENTS

We would like to thank Professor M. Cole and Professor R. Mamy for helpful discussions. This work was supported in part by the Petroleum Research Fund of the American Chemical Society and Research Corporation.

---

[1] V. Celli, D. Eichenauer, A. Kaufhold, and J. P. Toennies, J. Chem. Phys. **83**, 2504 (1985).

[2] D. R. Frankl, Prog Surf. Sci. **13**, 285 (1983).

[3] L. W. Bruch, Surf. Sci. **125**, 194 (1983); I. P. Batra, *ibid.* **148**, 1 (1984); *Ordering in Two Dimensions*, edited by S. K. Sinha (North-Holland, Amsterdam, 1980).

[4] E. M. Lifshitz, Zh. Eksp. Teor. Fiz. **29**, 94 (1954) [Sov. Phys.—JETP **2**, 73 (1956)]. Retardation modifies this result for $z > 100$ Å.

[5] N. Dupont-Pavlovsky, C. Bockel, and A. Thomy, Surf. Sci. **160**, 12 (1985) and references cited therein.

[6] J. Regnier, A. Thomy, and X. Duval, J. Colloid. Interface Sci. **70**, 105 (1979); J. C. Noiray, M. Obadia, and J. P. Romagnan, Surf. Sci. **122**, 330 (1982).

[7] M. W. Cole, D. R. Frankl, and D. L. Goodstein, Rev. Mod. Phys. **53**, 199 (1981); see also G. Vidali and M. W. Cole, Phys. Rev. B **29**, 6736 (1984).

[8] S. Rauber, J. R. Klein, M. W. Cole, and L. W. Bruch, Surf. Sci. **123**, 173 (1982).

[9] D. L. Goodstein, R. Maboudian, M. Sinvani, F. Scaramuzzi, and G. Vidali, Phys. Rev. Lett. **54**, 2034 (1985).

[10] L. W. Bruch and H. Watanabe, Surf. Sci. **65**, 619 (1975).

[11] G. Vidali and M. W. Cole, Surf. Sci. **110**, 10 (1981).

[12] J. D. Jackson, *Classical Electrodynamics* (Wiley, New York, 1975).

[13] K. K. Kao, T. J. Moravec, J. C. Rife, and R. N. Dexter, Phys. Rev. B **12**, 5937 (1975).

[14] E. T. Arakawa and M. W. Williams, J. Phys. Chem. Solids **29**, 735 (1968).

[15] G. Stephan, J.-C. Lemonnier, and S. Robin, J. Opt. Soc. Am. **57**, 486 (1966).

[16] R. Mamy, J. Thomas, J. Jezequel, and J.-C. Lemonnier, J. Phys. (Paris) Lett. **42**, 473 (1981); R. Mamy (private communication).

[17] G. Vidali, M. W. Cole, and C. Schwartz, Surf. Sci. **87**, L272 (1979); T. Kihara and N. Honda, J. Phys. Soc. Jpn. **20**, 15 (1965); L. W. Bruch and H. Watanabe, Surf. Sci. **65**, 619 (1977).

[18] A. D. McLachlan, Mol. Phys. **7**, 381 (1964).

[19] H. Hoinkes, Rev. Mod. Phys. **52**, 933 (1980).

[20] $\epsilon_1(0)$ differs from the dielectric constant because of low-frequency optical phonons; these, however, contribute neglibly to $\epsilon(iE)$.

[21] S. Chung and M. W. Cole, Surf. Sci. **145**, 269 (1984).

[22] D. Pines, Rev. Mod. Phys. **28**, 184 (1956); this reference gives also $E_p = 23$ eV from electron-energy-loss data.

[23] Landölt-Bornstein, *Optische Konstanten* (Springer-Verlag, Berlin, 1962).

[24] A. Patrykiejew, M. Jaroniec, and A. W. Marczewski, Chem. Scr. **22**, 136 (1983); A. D. Crowell and C. O. Chang, J. Chem. Phys. **43**, 4364 (1965). Data are in A. C. Levy, T. R. Rybolt, and R. A. Pierotti, J. Colloid. Interface Sci. **70**, 74 (1979), and Ref. 5 (and references cited therein).

[25] J. R. Klein and M. W. Cole, Faraday Discuss. Chem. Soc. **80**, 1 (1985).

[26] See Refs. 17 and 21 for how multilayer adsorption data are analyzed in terms of C_3.

[27] E. S. Sabisky and C. H. Anderson, Phys. Rev. Lett. **30**, 1122 (1973).