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Long-Range Forces between Molecules and Metals

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Isotherms of oxygen, argon, neopentane, tetramethylsilane, and diethyl ether on optically flat gold surfaces have been determined over the range 0–70 Brunauer-Emmett-Teller) (BET) monolayers, corresponding to 0–220 Å. The results are found to imply a potential energy of interaction $U(Z)$ of the form $U(Z) = \alpha 1.74\times10^{-4} Z^{-2}$ erg/molecule, where α is the molecular polarizability and Z the distance from the surface. The possible source of the disagreement between the experimental results and the theoretical predictions of Margenau, Bardeen, and Lennard-Jones is briefly discussed.

INTRODUCTION

The potential energy $U(Z)$ of a molecule at distance Z from a conducting surface has been the object of extensive theoretical investigation. Lennard-Jones,[1] Margenau and Pollard,[2] and Bardeen[3] evaluate the energy of the interaction of the instantaneous dipole moment of the molecule with its image in the metal and so deduce a potential proportional to Z^{-3}. Mavroyannis[4] and Dzyaloshinskii *et al.*[5] obtain this result at distances where retardation is not important; a potential which varies as Z^{-4} is predicted at greater distances.[4-7] Prosen and Sachs[8] calculate the energy of an assembly of free electrons and ion cores in the field of an external molecule by means of second-order perturbation theory and arrive at a potential of the form $Z^{-2}\ln 2k_F Z$, where k_F is the magnitude of the Fermi wave vector.

The limiting form of the Frenkel-Halsey-Hill equation[9-10] provides a connection between $U(Z)$ and experimentally accessible quantities. The equilibrium vapor pressure of an adsorbed film of thickness Z is given by

$$\ln(P/P^0) = -[U(Z) - U'(Z)]/kT = -\Delta U(Z)/kT, \qquad (1)$$

where P^0 is the equilibrium vapor pressure of the bulk adsorbate and $U'(Z)$ the potential energy of a molecule at distance Z from a semi-infinite slab of bulk adsorbate. We have investigated the adsorption of methanol and diethyl ether on optically flat gold surfaces at coverages between 0 and 70 BET monolayers (corresponding to film thickness 0–220 Å). As found previously for the pseudospherical molecules neopentane and tetramethylsilane,[11] the limiting form of the potential at large values of Z is $U(Z) = \alpha C Z^{-2}$, where α is the molecular polarizability.

EXPERIMENTAL

The deposition of a small mass (Δm) on the surface of a quartz crystal of total mass m vibrating in a thickness shear mode produces a change (Δf) in the resonant frequency (f) given by

$$\Delta f/f = \Delta m/m \ . \qquad (2)$$

Since Δf can be measured with considerable accuracy, such a crystal constitutes a rather sensitive adsorption microbalance.[12,13] When the adsorbed film is sufficiently thick so that its density may be approximated by the density (ρ) of the bulk adsorbate, Eq. (2) may be rewritten in terms of the film thickness Z as $Z = (\rho_q t_q / 2K\rho f)\Delta f$, where ρ_q is the density of quartz, t_q is the thickness of the quartz crystal, and the "roughness factor" K is the ratio of the "true surface area" of the crystal to the geometrical area. The form of $\Delta U(Z)$ can thus be deduced directly from the very high coverage portion of the adsorption isotherm, the numerical evaluation of $\Delta U(Z)$ requires an independent determination of K.

There is experimental evidence in support of an inverse-cube law for the potential between molecules and nonmetals and reason to believe[14,15] that the Kirkwood-Muller formula[16] gives a qualitatively correct account of the magnitude of the interaction. We have attempted here to evaluate $\Delta U(Z)$ in the region where $U'(Z)$ is expected to be negligible and so characterize $U(Z)$ independently of an exact form for $U'(Z)$.

The apparatus used in this work is illustrated schematically in Fig. 1. A 5-MHz AT-cut quartz

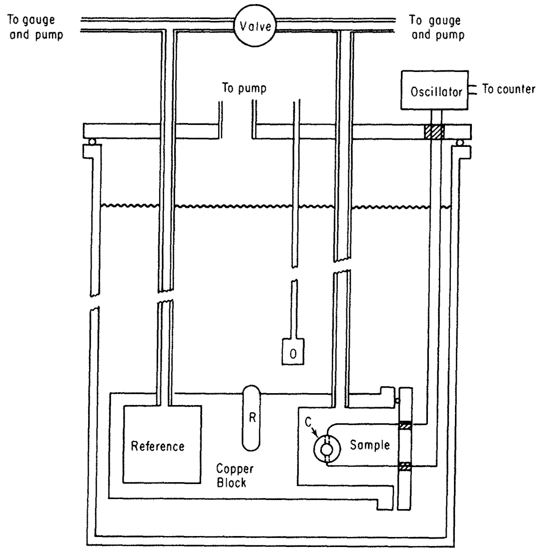

FIG. 1. Schematic diagram of the apparatus. *C* is the quartz crystal, *R* a platinum resistance thermometer, *O* an oxygen vapor-pressure thermometer which, in conjunction with a large-bore mercury manometer, an electronic relay and a solenoid valve in the pumping system provides the primary temperature control for the low-temperature isotherms. Except at liquid-nitrogen temperature the portion of the apparatus illustrated here is enclosed by a second constant-temperature bath.

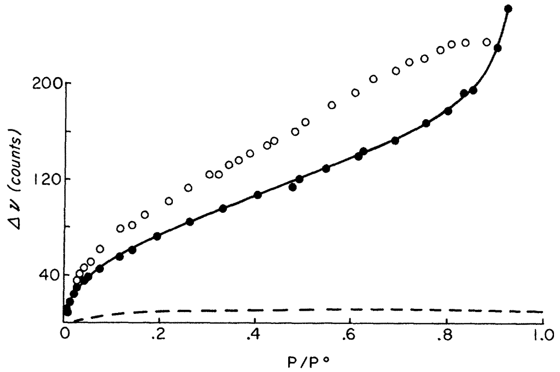

FIG. 2. Frequency shift in counts (1 count = 0.02 ppm) versus relative pressure for oxygen at 77.6 °K (solid circles) and argon at 72.6 °K (open circles). The broken line represents the net correction for hydrostatic pressure and aerodynamic drag which has been applied to the oxygen isotherm.

crystal is suspended in an evacuated "sample chamber" in a copper block immersed in a constant-temperature bath. Liquid or solid adsorbate is distilled into the reference chamber and P/P^0 is varied by opening the valve connecting the two chambers. $P^0 - P$ is determined by a quartz spiral Bourdon gauge and Δf by a Hewlett-Packard 5245 frequency counter. Adsorption isotherms (Δf versus P/P^0) for oxygen, argon, ether, and methanol are given in Figs. 2–4.

In addition to the effect of adsorption, the presence of the adsorbate vapor changes the resonant frequency of the crystal directly since the shear moduli of quartz depend on the hydrostatic pressure. Moreover, the equivalent resistance of the crystal is altered by aerodynamic drag and possibly by acoustic radiation by modes with longitudinal character coupled to the fundamental shear. The effect of hydrostatic pressure can be calculated directly from the third-order elastic constants of quartz[13,17] or estimated from the effect of a gas of low acoustic impedance on the resonant frequency. The results of both methods are in good agreement. The effect of aerodynamic drag is deduced from the observed frequency change when the pressure of a number of gases which are not significantly adsorbed at room temperature (He, Ne, N_2, Ar, CO_2, Kr, Xe) is varied. The results in Figs. 2–4 have been corrected for both of these effects. The magnitude of the correction (broken line) is also displayed. For values of P/P^0 close to one, the region of primary interest in this work, the small and slowly varying aerodynamic correction does not limit the accuracy with which the slope of the rapidly varying high-coverage portion of the isotherm can be characterized.

The crystals were polished flat and parallel to better than $\frac{1}{4}$ fringe of green light. The evaporated gold films were sufficiently thick (at least 3000 Å) so that interaction between an adsorbed molecule and the underlying quartz should not be important. The system was degassed for 72 h at 10^{-8} Torr and

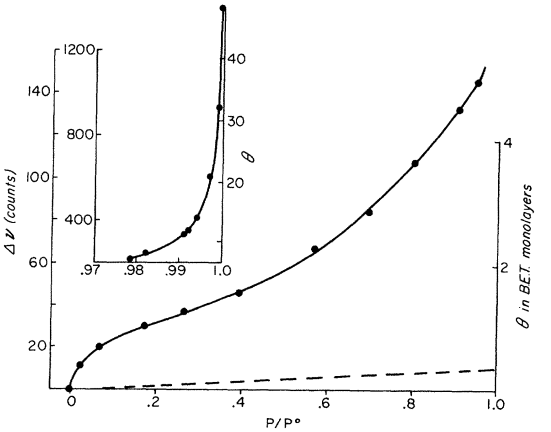

FIG. 3. Frequency shift in counts and coverage in BET monolayers versus relative pressure for methanol adsorbed on gold at 0 °C. The broken line represents the net correction.

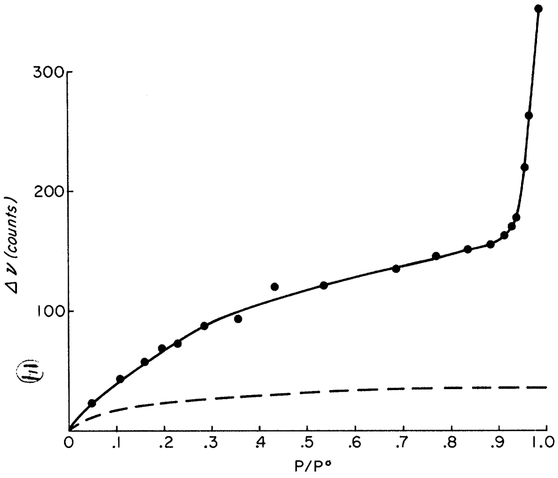

FIG. 4. Adsorption isotherm for ether on gold at 0 °C.

170 °C before each series of experiments. The adsorbate was dried over a molecular sieve, outgassed by repeated freezing and thawing in vacuum, and distilled into the reference chamber. The temperature control may be checked by replacing the AT-cut crystal with a crystal (Y-cut) which has a high-temperature coefficient of frequency. Temperature excursions and drift in the course of a "run" do not exceed 0.001 °C.

At the highest values of P/P^0, it is necessary that the entire experimental volume be at the same temperature. The upper limit of P/P^0 attained in this work (0.9993) is set by the presence of a small temperature gradient in the line connecting the block to the gauge rather than by the sensitivity of the differential pressure measurement or by the temperature control in the sample and reference chambers.

RESULTS

A. Low Coverage

The frequency shifts at BET monolayer coverage (Δf_m) are listed in Table I for the various adsorbates investigated. From Eq. (2) and Δf_m, the number of moles adsorbed at BET monolayer coverage is deduced and if the area of the adsorbed molecule is presumed to be known the surface area of the gold film and the roughness factor can be calculated. The molecular areas A_m given in Table I are calculated from the bulk density of the liquid or solid adsorbate assuming hexagonal close packing. The areas A'_m are taken from the compilation by McClellan and Harnsberger[18] of molecular cross sections derived from adsorption isotherms. The roughness factor computed from either set of areas is one within experimental error ($K = 1.1 \pm 0.2$).

The low value of K is not unexpected. Gold films evaporated onto optically flat quartz surfaces have been found to be optically flat, crystalline,[19] and smooth within the resolution of a scanning electron microscope although a high density ($\sim 10^{11}/\mathrm{cm}^2$) of lattice defects is to be expected.[20]

The isotherms themselves are not qualitatively different from those commonly obtained on high specific-area substrates. They do not display the step-wise structure at low coverage which is found[21] for the inert gases on graphitized carbon black and other microscopically uniform surfaces nor would it be expected that vacuum evaporation would produce an atomically flat surface. However, the very

TABLE I. Frequency shifts at monolayer coverage (Δf_m) and roughness factors.

A Substance	B Temp (°C)	C Δf_m (counts)	D A_m (Å^2)	E K (from Column D)	F A''_m Average of experimentally determined areas (Å^2)	G K (from Column F)
Argon	−200.8	43.9	13.8	0.8	14.7	0.9
Oxygen	−193.8	58.1	12.1	1.1	13.6	1.2
Neopentane	0	21.5	36.5	0.6	53.3	0.9
Neopentane	19	28.6	36.5	0.8	53.3	1.1
Tetramethyl-silane	19	49.0	40.4	1.1	...[a]	...[a]
Diethylether	0	60.2	33.8	1.4	34.0	1.4
Diethylether	19	71.9	33.8	1.7	34.0	1.4
Methanol	0	29.3	18.0	0.9	21.9	1.1
Methanol	19	29.4	18.0	1.1	21.9	1.1

[a] No data available.

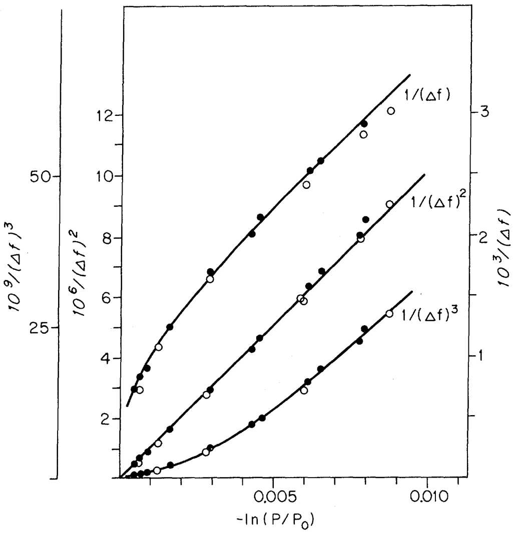

FIG. 5. Inverse powers of the frequency shift (in counts) versus $\ln(P/P^0)$ for methanol adsorbed on gold at 0 °C (open circles) and 19 °C (solid circles).

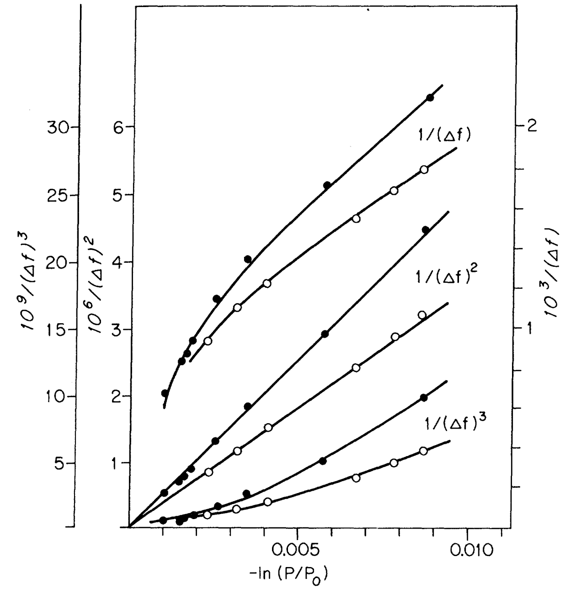

FIG. 6. Inverse powers of the frequency shift (in counts) versus ln (P/P^0) for ether at 0 °C (open circles) and 19 °C (solid circles).

low value of the roughness factor does indicate that on any larger scale the surface is effectively uniform.

In contrast to the sharp upturn at high relative pressure which characterizes the isotherms obtained with liquid adsorbates, the isotherm of solid argon approaches a limiting value of approximately 5 BET monolayers. Bowers[22] finds a limit of three layers for solid argon adsorbed on aluminum and Singleton and Halsey[14] observe a similar effect for solid Kr on graphite and suggest that the phenomenon should occur generally when the lattice spacings of the substrate and the adsorbed species are not compatible.

B. High Coverage

At very high relative pressure $\ln(P/P^0) \cong (P-P^0)/P^0 = \Delta P/P^0$. If it is assumed that $\Delta U(Z)$ can be expressed as $\Delta U(Z) = CZ^{-n}$, C and n can be deduced from a plot of $\ln(P/P^0)$ versus Z^{-n} for various choice of n (Figs. 5 and 6) or by least squares from $\ln(\Delta P/P^0) = n \ln Z + \ln(C/kT)$ (Table II). Reference to Figs. 5 and 6 or Table II indicates that the correct choice of n is 2 in accord with the results previously obtained for neopentane and tetramethylsilane[11] which are also given in Table II.

The lowest coverage point in Fig. 5 corresponds to 36-Å film thickness or approximately 11 BET monolayers for methanol, 60 Å or 10 layers for ether. $U'(Z)$ as calculated from the Kirkwood-Muller formula is less than 2% of the experimental $\Delta U(Z)$ at this lowest coverage and becomes proportionately less important at higher coverage.

TABLE II. Constants in expressions for the potential energy per molecule, $U(Z)$ as a function of distance (Z). The molecular polarizability α is also given.

	$U(Z) = CZ^{-n}$			$U(Z) = C'' Z^{-2} \ln 2k_F Z$		
	$10^{29}C$ erg cm^2	$10^{-4}C/\alpha$ erg cm^{-1}	n	$10^{29}C''$ erg cm^2	$10^{29}\alpha e^2 k_F^2/8\pi^2$ erg cm^2	$10^{25}\alpha$ cm^3
Neopentane	17.2	1.72	1.97	3.65	42	99.7[a]
Tetramethylsilane	21.4	1.69	2.00	4.06	53	127[b]
Ether	16.1	1.84	1.95	2.96	37	87.3[a]
Methanol	5.52	1.71	2.01	1.27	14	32.3[a]

[a] *Handbook of Chemistry and Physics* (Chemical Rubber Co., Cleveland, 1968).
[b] K. Frei and H. J. Bernstein, Chem. Phys. 37, 1891 (1962).

Thus the behavior of $\Delta U(Z)$ is essentially that of $U(Z)$. The near equality of the values of C/α for the various adsorbed molecules (2nd column of Table II) suggests that the potential energy of interaction is, within the accuracy of these experiments, proportional to the polarizability.

For large Z, $\ln(2k_F Z)$ is not a rapidly varying function of Z, so data which can be expressed by an inverse-square potential can also be accommodated to the form proposed by Prosen and Sachs. The constants C'' in $U(Z) = C''Z^{-2}\ln(2k_F Z)$ are given in Table II. The experimental values of C'' are considerably smaller than those predicted from Prosen and Sachs's result ($C'' = -\alpha e^2 k_F^2/8\pi^2$).

C. Moderate Coverage

As the thickness of the film is decreased, the relation between Δf and Z, resting as it does on the assumed equality of the density of the adsorbed layer and the bulk liquid density, becomes less exact and, except for surfaces which are flat on an atomic scale, the thickness of the film is itself less precisely defined. $U'(Z)$ the "self-interaction energy" of the adsorbate, although significantly smaller than $U(Z)$, makes a relatively larger contribution to $\Delta U(Z)$ at low coverage and any inadequacy of the semiempirical formula used to estimate $U'(Z)$ will begin to be reflected in $U(Z)$. We have therefore based the values of the parameters in Table II on results at $P/P^0 > 0.99$ corresponding to coverage greater than 10 BET monolayers. However previous studies of multilayer adsorption on metals[22,23] have terminated at lower coverage and it is between 2 and 10 monolayers that comparison with the results of other experimental techniques is possible.

Bowers[22] has studied the adsorption of oxygen, nitrogen, and argon on aluminum at relative pressures between 0 and 0.985. He finds that a potential which varies as Z^{-3} gives a satisfactory account of the oxygen and nitrogen isotherms between 2 and 5 BET monolayers. Only one point at coverage higher than 5 layers on the oxygen and nitrogen isotherms was obtained. In either case the one high coverage point would imply a potential which did not fall off with increasing distance as rapidly as Z^{-3}. The argon isotherm obtained above the melting point of bulk argon is consistent with an inverse-cube dependence of the potential energy on coverage between 2 and 7 layers. Pierotti and Halsey[23] have investigated the adsorption of krypton on sodium, iron, copper, and tungsten between 0 and 4 layers. They find that the Frenkel-Halsey-Hill equation with a potential energy calculated from the Kirkwood-Muller formula gives a satisfactory description of the isotherms.

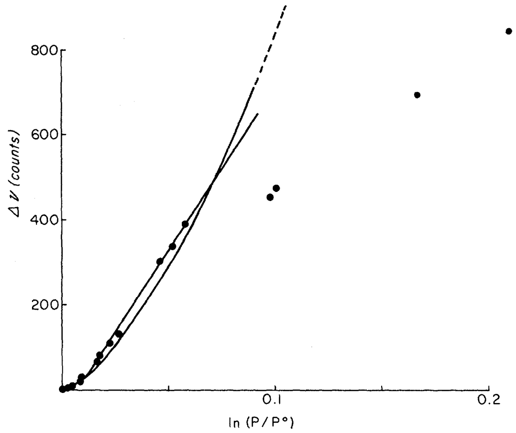

FIG. 7. Inverse cube of the frequency shift versus $\ln(P/P^0)$ for methanol at 0 °C. The broken curve is calculated from the potential constants given in Table II.

Our results at intermediate coverages are given, in the form of a plot of $(1/\Delta f)^3$ versus $-\ln(P/P^0)$ for methanol, in Fig. 7. The results for ether are essentially the same. The values of $-\ln(P/P^0)$ calculated from $U(Z) = CZ^{-2}$ are given as the broken curve in Fig. 7. It will be noted that over a restricted range of about 4 or 5 monolayers we could give a reasonable account of our isotherms with a potential proportional to Z^{-3} (solid line in Fig. 7). Over a wider range of distances it does not seem possible to fit our data with a simple-inverse-power potential. Thus there is no direct contradiction between the results given here and the experimental results of Bowers or Pierotti and Halsey. However, our conclusion is that at coverages below 9 BET monolayers, no potential of the form CZ^{-n} is completely satisfactory. At high coverage, the inverse-square potential gives a good account of the data over a wide range of distances (at least 9–50 layers).

Any unique properties of the van der Waals interactions of metals are presumably associated with the presence of a quasi continuum of excited electronic states immediately adjacent to the ground state and it is in the long-wave low-energy excitations and thus in the long-range interactions that might be expected to differ qualitatively from valence crystals. However, whatever the peculiarities due to the presence of the conduction electrons, the interaction with the ion cores in accord with the conventional theory of van der Waals forces is expected to vary with distance at least as rapidly as Z^{-3}. Thus if Z^{-2} or $Z^{-2}\ln(2k_F Z)$ correctly give the form of the potential energy at large values of Z, at shorter distances a more complex dependence is to be expected.

DISCUSSION

The lowest-lying electronic transitions of the molecules studied here are between 1500 and 2000 Å. The error introduced by neglecting terms higher than first order in R/λ should not be large. Mavroyannis[4] has shown that when, as in these experiments, the molecule is immersed in a medium of dielectric permeability ϵ', the interaction energy between molecule and metal is diminished by a factor $(\epsilon-\epsilon')/(\epsilon+\epsilon')$ as compared to $(\epsilon-1)/(\epsilon+1)$ in a vacuum. If this modification is made when appropriate it is not likely that there is any error in the connection established in Refs. 1–7 between the frequency-dependent electric and magnetic susceptibilities of the metal and the van der Waals interaction. The source of the apparent discrepancy between theory and the experimental form of the potential is best sought in the theoretical expression for the dielectric permeability $\epsilon(\omega)$ of the metal surface.

The difference between the approach of Prosen and Sachs and that of the other workers lies in the inclusion, implicit in their procedure of Fourier-transforming the perturbing potential and expanding the resulting integrals, of a dependence of response on wave vector. The treatment of Prosen and Sachs neglects electron-electron interaction in the metal and it is not surprising that it overestimates the total attractive interaction. On the other hand, it does give a dependence of the potential energy on distance at large distances qualitatively in accord with these experiments.

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