Prediction of Physisorption Interaction Energies: He on Metals

G. G. Kleiman

Physics Department, Research Laboratories, General Motors Corporation, Warren, Michigan 48090

and

Uzi Landman

Xerox Research Laboratories, Webster, New York 14580

(Received 4 June 1973)

Microscopic calculations of noble-gas adsorption on metals result in an *ab initio* determination of the interaction energy in agreement with available experimental data. An adequate determination of the attractive interaction energy using a local–dielectric-function formalism requires an accurate description of the dynamic polarizability of the incident atom. The repulsive contribution to the interaction energy was evaluated via the density-functional method. Systematics of He physisorption on various metals are reported.

The adsorption of gases on metal surfaces is one of the most relevant and intriguing problems in surface science, in view of the catalytic properties of some metallic surfaces and the complexity of the system.[1] Customarily in the literature, binding-energy magnitudes provide a distinction between physical (10^{-2} eV) and chemical (several electron volts) adsorption. Physisorption has been suggested as a precursory stage to chemisorption and hence is of interest in the evaluation of the adsorption mechanism.[1] In the case of noble gas atoms adsorbed on metals, physisorption is the main form of interaction, rendering these systems particularly attractive for the study of physisorption processes. Physical adsorption is usually considered to arise from the presence of Van der Waals forces.[2] A number of quantum mechanical and semiclassical attempts to calculate physisorption interaction energies have been suggested in the literature, and have been reviewed by several authors.[2b,3] Earlier attempts to account for both the repulsive and attractive terms of the interaction follow the scheme (or a variation thereof) originally suggested by Pollard.[4] In this method the Van der Waals contribution is described by classical dipole-dipole interactions between the constituents of the system, and the repulsive term is treated by employing a Heitler-London coupling scheme which assumes by construction the creation of a one-elec-

tron bond between a localized surface-state orbital and the adsorbate valence orbitals. As was pointed out by several investigators,[3] the adequacy of such an approach is limited, because of interactions of the adsorbate and metal electrons which are of the same order as the bonding interaction and the unrealistic description of the metal surface states employed in the calculations.

The objective of the present work is to construct a consistent microscopic quantum mechanical formulation which is based on, and conforms with, modern techniques which provide adequate description of the isolated components, and to examine the systematic variations of the interaction energy of He atoms adsorbed on metal surfaces as a function of the parameters characteristic to the atom and metal under study. The calculation of the Van der Waals interaction energy proceeds by adoption of the formulation of Dzyaloshinskii, Lifshitz, and Pitaevskii.[5] According to the above theory, Van der Waals forces originate from the electromagnetic-field fluctuations in the solid, extending beyond its boundaries, which induce spontaneous fluctuations in the atom. Since the wavelengths of the field fluctuations are much longer than the interparticle spacing, the solid is considered as a uniform continuous medium. The expression for the interaction energy derived from the above theory is given by

$$E_{vw}(d) = \lim_{N_0 \to 0} \frac{kT}{8\pi d^3} \sum_{n=0}^{\infty} \left(\frac{2\xi_n d}{c}\right)^3 \int_1^\infty \frac{p^2 \, dp}{N_0} (F_1^{-1} + F_2^{-1}), \tag{1a}$$

$$F_i = Y_i^2 \exp\left(\frac{2p\xi_n d}{c}\right) - 1 \quad (i=1,2), \quad Y_1 = \frac{(S_M + p)(S_A + p)}{(S_M - p)(S_A - p)}, \quad Y_2 = \frac{(S_M + p\epsilon_M)(S_A + p\epsilon_A)}{(S_M - p\epsilon_M)(S_A - p\epsilon_A)}, \tag{1b}$$

$$S_j = (\epsilon_j - 1 + p^2)^{1/2} \quad (j=A,M), \tag{1c}$$

where N_0 is the density of adsorbed atoms,[2b] and d is the distance separating the atom and metal plane. The summation in Eq. (1a) is taken over integral values of n, the $n = 0$ term given half weight; and $\xi_n = 2\pi nkT/\hbar$, where k is Boltzmann's constant, T the absolute temperature, and c the velocity of light in vacuum. The dynamic dielectric functions ϵ_A and ϵ_M are the atomic and metallic dynamic functions, respectively, evaluated on the imaginary frequency axis $\omega = i\xi_n$, i.e., $\epsilon(i\xi_n)$. In the present calculation a dispersionless dielectric function was used for the metal, i.e., $\epsilon_M(i\xi_n)$ $= 1 + \omega_p^2/\xi_n^2$, where ω_p is the plasma frequency, characteristic of the metal, $\omega_p = (4\pi Ne^2/m)^{1/2}$, with N the electron volume density.[6] For the range of distances of interest in our problem the interaction energy may be shown to be practically independent of temperature.[7] In Fig. 1 attractive interaction energies for values of plasma frequency which span the range of most common metals[8] are shown for three modes of atomic excitations.[9] The importance of including the complete excitation spectrum of the atomic species responding to the electromagnetic fluctuating field, especially at small distances, is evident from the figure. Approximations which treat the entire excitation spectrum by means of averages result in upper- and lower-bound estimates to the attractive energy.[10] The systematic increase in attraction correlated with the increase in the plasma frequency of the metal is also demonstrated.

Since correlation and exchange contributions to the interaction energy are included in the term discussed above,[11] the repulsive contribution originates from the change in the electronic kinetic energy of the many-electron atom-metal surface system. To evaluate the change in kinetic energy a planar "jellium" model of the surface is used in conjunction with the extended Thomas-Fermi version of the density-functional formalism.[12] The change in kinetic energy ΔT of the system in
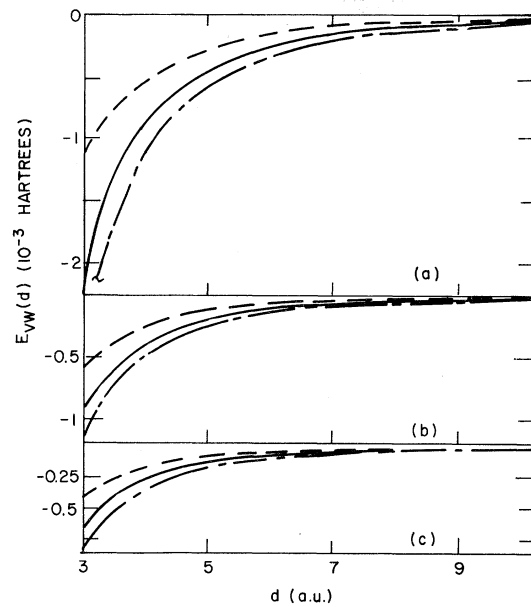

FIG. 1. Van der Waals interaction energies of He adsorbed on metals. Results are shown for three metals, characterized by $\hbar\omega_p = 10$, 20, and 30 eV (dashed, solid, and dash-dotted curves, respectively). Three excitation modes of the atom are considered: (a) twelve discrete ground-state excitations and transitions to the continuum, (b) twelve discrete ground-state excitations, (c) only the first excitation is included.

interaction is given by

$$\Delta T[n_C] = T_d[n_C] - T_\infty[n_A, n_M], \tag{2}$$

where T_d and T_∞ are the kinetic energies of the atom and metal electrons at a distance d and at infinite separation, respectively. n_C, n_A, and n_M are the electron number densities of the combined atom-surface system, isolated atom, and metal, respectively. For the case of slowly varying electronic densities one may perform an expansion of $T[n_C]$ in successive orders of the gradient operator which to first order in perturbation theory yields the following expression for ΔT:

$$\Delta T \simeq \int d^3r\, n_M \left[0.5(3\pi^2)^{2/3}(n_A^{2/3} - n_M^{2/3}) + \frac{1}{72}\left(\frac{(\nabla n_A)^2}{n_A^2} - \frac{(\nabla n_M)^2}{n_M^2} - \frac{2\nabla^2 n_A}{n_A} + \frac{2\nabla^2 n_M}{n_M}\right)\right]. \tag{3}$$

Rather than using the density functional for the variational solution of the number density, we use a parametrized form for n_M,[12b] and a screened atomic charge density:

$$n_M = \tfrac{1}{2}n_+\{1 + (z/|z|)[1 - \exp(-\beta|z|)]\}, \tag{4}$$

$$n_A = \sum_{i=1}^{2} |\psi_i(\vec{r})|^2, \tag{5}$$

where n_+ is the positive jellium charge density,[13] β is a variational parameter,[12b] and $\psi_i(\vec{r})$ are

hydrogenic wave functions with parametrized screening λ.[14] z is the coordinate normal to the surface.

Total-interaction-energy curves for the adsorption on free-electron metals, obtained by addition of E_{vw} and the repulsive interaction, are shown in Fig. 2(a). The systematic increase in both the depth and the equilibrium distance of the
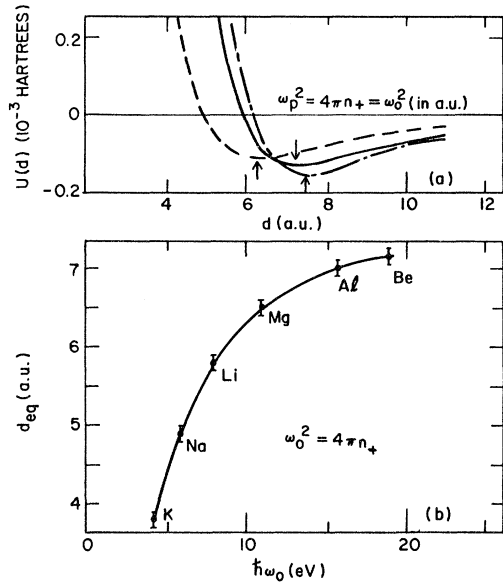
FIG. 2. (a) Total interaction energies of He adsorbed on metals characterized by $\hbar\omega_p = 10$, 20, 30 eV (dashed, solid, and dash-dotted curves, respectively). Corresponding values of the metal charge-density screening parameter β, taken from Ref. 12b are 1.22, 1.27, and 1.34, respectively. Vertical arrows indicate the position of the minimum. (b) Equilibrium position, d_{eq}, of physisorbed He atoms on "free-electron" metals. The monotonic increase of d_{eq} as a function of the plasma frequency is illustrated. Error bars represent the uncertainty in the numerical distance mesh.

physisorption well, as a function of the plasma frequency of the metal, is clearly demonstrated. The monotonic increase in equilibrium distance is further illustrated for adsorption on a number of "free-electron" metals in Fig. 2(b). This trend is in contrast with the result derived for the adatom equilibrium position on the basis of the sum-of-atomic-radii rule.[2b,10]

Results of calculations for the adsorption energies on representative free-electron and transition metals are shown in Figs. 3(a) and 3(b), respectively. These values agree well with the results of He scattering experiments.[15] According to the present method the total-interaction curve is determined in an *ab initio* fashion, whereas in some other methods[2b,10] the position of equilibrium is preassumed (the sum of atomic radii). The energies obtained by Mavroyannis[10] are derived on the basis of the Van der Waals interaction alone, neglecting the repulsive term, and thus do not predict a minimum in the interaction-energy curve. The systematic observation that the potential minimum does not occur at a dis-
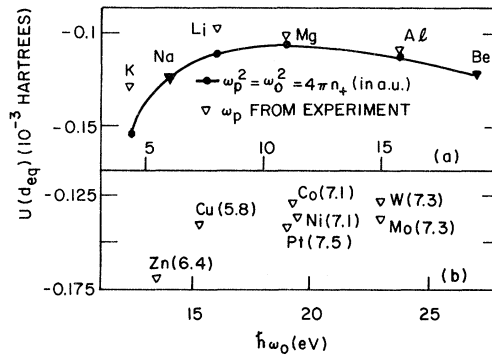

FIG. 3. (a) Physisorption energies for He adsorbed on "free-electron" metals. The decrease of $-U(d_{eq})$ for small electron densities reflects the sharp increase in d_{eq} at these densities. The increase in $-U(d_{eq})$ for high electron densities is a result of the slow variation of d_{eq}. (b) Physisorption energies for representative transition metals. The absence of a systematic dependence on ω_0 reflects the lack of a simple relationship between ω_p and ω_0 for these metals (Ref. 13). Values of d_{eq} in atomic units are given in parenthesis. Triangles in both (a) and (b) represent energies calculated with plasma frequencies measured in electron energy-loss experiments (Ref. 8).

tance equal to the hard-sphere radius of the metal-ion-gas-atom system, but rather at larger distances [see also Fig. 2(b)], indicates the necessity for a complete theory which includes both the attractive and repulsive terms. Such a theory, subject to the approximations and assumptions indicated above, with the neglect of mutual interadsorbate interactions has been used in this study. Consequently, a systematic dependence of the interaction energy on parameters characterizing the metal surface and adsorbed atom were derived.[16] A more detailed discussion of the model and results for the adsorption of other noble gases on metal surfaces will be given in a forthcoming publication.

[1]G. C. Bond, *Catalysis by Metals* (Academic, New York, 1962).

[2a]D. M. Young and A. D. Crowell, *Physical Adsorption of Gases* (Butterworths, London, 1962).

[2b]A. D. Crowell, in *The Solid-Gas Interface*, edited by E. A. Flood (Marcel Dekker, New York, 1967), Vol. 1.

[3]K. F. Wojciechowski, in *Progress in Surface Science*, edited by S. G. Davison (Pergamon, New York, 1972),

Vol. 1.

[4]W. G. Pollard, Phys. Rev. 60, 578 (1941).

[5]I. E. Dzyaloshinskii, E. M. Lifshitz, and L. P. Pitaevskii, Advan. Phys. 10, 165 (1961).

[6]When a general, momentum-dependent dielectric function of the metal is used, Eq. (1a) remains the same, with the replacement of F_1 and F_2 by the corresponding dispersion relations derived from the solution of Maxwell's equation. Calculations of physisorption energies which demonstrate the effect of dispersion in the metal were performed by the present authors and will be reported elsewhere.

[7]E. M. Lifshitz, Zh. Eksp. Teor. Fiz. 29, 94 (1955) [Sov. Phys. JETP, 2, 73 (1956)].

[8]D. Pines, Elementary Excitations in Solids (Benjamin, New York, 1964).

[9]Atomic spectroscopic parameters used in the calculation were taken from W. L. Wiese, M. W. Smith, and B. M. Glenon, Atomic Transition Probabilities, U.S. National Bureau of Standards, National Standards Reference Data Series—4 (U.S.G.P.O., Washington, D.C., 1966), Vol. 1. The continuum oscillator strength was determined by curve fitting following S. S. Huang, Astrophys. J. 108, 354 (1948).

[10]C. Mavroyannis, Mol. Phys. 6, 593 (1963).

[11]J. Bardeen, Phys. Rev. 58, 727 (1940).

[12a]P. Hohenberg and W. Kohn, Phys. Rev. 136, B864 (1964).

[12b]J. R. Smith, Phys. Rev. 181, 522 (1969).

[13]Calculated plasma frequencies used in the evaluation of the repulsive interaction, with the "valency" number from J. Schmit and A. A. Lucas, Solid State Commun. 11, 419 (1972), are denoted hereafter by ω_0. Values of the plasma frequency obtained from high-energy electron-transmission loss experiments used in the calculation of E_{vw} are denoted by ω_p (Ref. 8).

[14]In the calculations presented in this paper $\lambda = \frac{16}{27}$ [see L. I. Schiff, Quantum Mechanics (McGraw-Hill, New York, 1955)]. A more detailed discussion is given by G. G. Kleiman and U. Landman, to be published.

[15]R. Sau and R. P. Merrill, Surface Sci. 34, 268 (1973).

[16]In comparing our theoretical adsorption energies and equilibrium positions with experimental measurements, we have neglected the contribution due to the zero-point motion of the adatom. This correction is not anticipated to modify our results significantly.

Temperature Dependence of Multiphonon Absorption*

J. A. Harrington and M. Hass
Naval Research Laboratory, Washington, D.C. 20375
(Received 2 May 1973)

The temperature dependence of multiphonon absorption in NaF, NaCl, and KCl was studied from room temperature to near the melting point at a wavelength of 10.6 μm. A large discrepancy was noted between the experimental results and those predicted using the usual expressions based upon temperature-dependent Bose-Einstein population factors and temperature-independent transition matrix elements.

In this Letter, experimental measurements of the temperature dependence of the multiphonon lattice absorption in NaF, NaCl, and KCl are presented, which differ markedly from those expected by application of the usual simple expressions based upon consideration of phonons as bosons. This suggests that there are some inadequacies in the approach which have not been evident in previous measurements. In earlier work,[1,2] the simple expressions based upon Bose-Einstein population factors have appeared to be satisfactory to explain the temperature dependence of multiphonon absorption. However, practically all of the previous investigations in this area have involved lower-order processes at lower temperatures. The present work is primarily concerned with higher-order processes at higher temperatures in which the temperature dependence is expected to be much greater.

The usual expressions for the temperature dependence of multiphonon processes can be written in terms of the energies of the various phonons participating in the process. For higher-order processes this can be quite complicated, but Sparks and Sham[3] pointed out that a T^{n-1} law would be expected to hold (if some average phonon frequency is assumed) in the high-temperature limit, where n is the number of phonons participating in the process. Similar results were obtained by Rosenstock,[4] who employed a Debye spectrum for the crystal, and by Hardy and Agrawal,[5] using an Einstein oscillator-type model. Under this latter approach,[5] the contribution to the multiphonon absorption coefficient β at high temperatures will be dominated by the contribution

$$(\bar{n} + 1)^n - (\bar{n})^n, \tag{1}$$