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Author
Nieuvenhuys, B.E.

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B. E. Nieuwenhuys

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ADSORPTION OF NOBLE GASES ON METALS

B. E. Nieuwenhuys*

Gorlaeus Laboratoria, Leiden, The Netherlands

SUMMARY

The objective of this review is to outline the present knowledge about adsorption of noble gases on metals. Due to the development of the ultrahigh vacuum technique and the recent availability of several surface techniques (LEED, Auger electron spectroscopy, field emission probe-hole microscopy) a number of physical adsorption studies on well-defined clean metal surfaces have appeared. These results are described and discussed in the light of theories dealing with the nature of the interaction of noble gases with metals.

SAMENVATTING

In dit artikel wordt ecn overzicht gegeven van de adsorptie van edelgassen op metalen. Pas de laatste jaren zÿn er dank zÿ de ultrahoogvacuumtechnick en nieuwe oppervlaktetechnieken (LEED, Auger elektronen spektroskopie en veldemissie probe-hole mikroskopie) voldoende experimentele gegevens over de binding tussen edelgassen en goed gedefinieerde schone metaaloppervlakken beschikbaar gekomen. Deze resultaten worden beschreven. De verschillende theorieën over de binding tussen edelgassen en metalen worden besproken en vergeleken met de experimentele gegevens.

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*Currently at the Inorganic Materials Research Division, Lawrence Berkeley Laboratory, University of California, Berkeley, California 94720

1. Introduction

When a gas molecule approaches a solid surface it experiences forces which may result in a greater concentration of gas molecules near the surface than in the gas phase. This phenomenon is called adsorption of the gas on the surface.

Conventionally adsorption is divided into two distinct types. In the first type, called physical adsorption the adsorbed molecule is bound to the surface by the weak van der Waals forces. The adsorption is similar in nature to the condensation of an inert gas on the surface of its own crystal or liquid. In the second type, termed chemisorption, a chemical bond is formed between the adsorbed molecule and the solid by sharing and/or transfer of electrons. While chemisorption is accompanied by large changes in electronic structure, physical adsorption is characterized by much weaker electronic perturbations, the electron sharing or transfer between the interacting species is absent.

Experimentally it is sometimes difficult to decide which kind of interaction is operating. Criteria based on the heat of adsorption e.g., have no general validity since heats of chemisorption are sometimes comparable in magnitude to heats of physical adsorption.

Theories of physical adsorption have developed over the past 45 years. Reliable experimental data in this field with well-defined surfaces, however, are still scarce. This may for a large part be attributed to the extremely clean conditions required for this kind of investigation: residual gas pressures below 10^{-10} Torr and extremely low levels of impurities in the gases and metals studied. Since the recent developments of techniques for the production of ultrahigh vacuum, for surface analysis, for characterization of solid surfaces and for studying adsorption processes, this interesting field has also become accessible to the experimentalist and an increasing number of papers about physical adsorption have appeared. For comprehensive reviews of all phases of physical adsorption the reader is referred to Refs. 1 through 6.

This work is concerned with the adsorption of the noble gases, He, Ne, Ar, Kr and Xe, on metals, an adsorption system which is conventionally described as a typical example of physical adsorption on metals. The main objective of this article is to give an insight into the present knowledge about: (1) the nature of the interaction of noble gases with metals, and (2) the configuration of the adsorbed noble gas atoms with respect to each other and to the substrate atoms.

First the different theories on the physical interaction of gases with solids are discussed and applied to the special case of noble gases on metals. Then in subsequent chapters experimental results are reviewed and compared with theoretical predictions. It will be shown that recent experimental results have brought about a new view on the nature of physical adsorption on metals.

2. Principles of van der Waals Interaction

2a. Dispersion Forces between Two Molecules

Let us first consider two molecules which are unable to form a chemical bond with each other, e.g., two Ar, Kr or Xe atoms. At a sufficiently low temperature these atoms condense to liquid or solid phases, illustrating that attractive forces, known as van der Waals forces, must exist between approaching molecules. The heat of sublimation of Xe, for instance, amounts to 3.8 kcal/mole.

A plausible explanation of the van der Waals attraction between two molecules having no permanent dipole moments was given by London in 1930.[7] Upon approaching the molecules experience electric forces induced by each other, because the molecules become virtually excited. This arises from the non-cancellation of repulsive and attractive forces between the molecules if excited in non-stationary states. These are the quantum-mechanical analogues of the classically induced dipole moments due to the rapidly changing positions of the electrons around the nuclei. Although the average electron charge on two molecules approaching each other will not change, the electron distribution changes such that the total energy is lowered. This kind of interaction is usually called a dispersion force or London interaction.

An additional interaction is present when one or both of the interacting pair of molecules possesses a permanent dipole moment. This kind of interaction is known as Debÿe and Keesom forces.

The potential energy of van der Waals interaction between two molecules separated by a distance R is usually expressed by the Lennard-Jones 6-12 potential law:

$$U(R) = - CR^{-6} + BR^{-12} \tag{1}$$

The first term accounts for the London attraction of mutually induced dipoles. Sometimes terms involving higher powers of 1/R are included, taking thus into account dipole-quadrupole ($\sim R^{-8}$) and quadrupole-quadrupole interactions ($\sim R^{-10}$). The second term in Eq. (1) is an approximate expression for the repulsion between the two molecules. The contribution of this last term becomes increasingly important at still smaller distance R.

When R_o corresponds to the distance between the molecules where U has a minumum value, Eq. (1) can be rewritten as

$$U = -C\left\{R^{-6} - 1/2\; R_o^6 R^{-12}\right\} \qquad (2)$$

The value of C is usually evaluated by means of one of the following formulae: The expression of London[7]

$$C_L = 3/2\; \alpha_1\alpha_2 \frac{I_1 I_2}{I_1 + I_2} \quad , \qquad (3)$$

The Slater-Kirkwood formula[8]

$$C_{SK} = \frac{3eh}{4\pi m^{1/2}} \frac{\alpha_1\alpha_2}{\left(\frac{\alpha_1}{N_1}\right)^{1/2} + \left(\frac{\alpha_2}{N_2}\right)^{1/2}} \quad , \qquad (4)$$

and the Kirkwood-Müller expression[9,10]

$$C_{KM} = 6mc^2 \frac{\alpha_1\alpha_2}{\left(\frac{\alpha_1}{\chi_1}\right) + \left(\frac{\alpha_2}{\chi_2}\right)} \quad . \qquad (5)$$

In these formulae α_1 and α_2 represent the polarizibilities, I_1 and I_2 the ionization enerties, χ_1 and χ_2 the diamagnetic susceptibilities of the atoms; e and m stand for the electronic charge and mass respectively; c is the velocity of light and h is Planck's constant.

These expressions show that the interaction increases with increasing polarizibility of the interacting molecules, or, according to quantum mechanics, the smaller the distance in energy levels between the first excited state and the ground state the stronger the interaction.

For a discussion of the dispersion force interaction between molecules the reader is referred to reviews of Margenau,[11] Hirschfelder et al.,[12] Pitzer,[13] Salem,[14] Mavroyannis et al.[15] and Margenau et al.[16]

2b. Atoms Adsorbed on Insulators

So far only the van der Waals interaction between two molecules has been considered. For calculating the dispersion energy U of a single atom in the neighborhood of a solid, it is generally assumed that U is the resultant of all the interactions U_i occurring between the single gas atom and each of the surface atoms i, i.e.,

$$U = \sum_i U_i(R_i) = \sum_i U_{i_{\text{attr.}}}(R_i) + \sum_i U_{i_{\text{rep.}}}(R_i) \tag{6}$$

where U_i is the interaction energy of the gas-atom with the i^{th} atom of the surface at a distance R_i between gas and surface atom. The individual U_i can then be calculated by means of Eqs. (1) through (5).

This additive pair-wise interaction approximation is justified in the case of the attraction term which is obtained from quantum mechanical perturbation theory as the second order contribution. For the repulsion term, however, there is no theoretical justification for additivity. Nevertheless, the assumption of pairwise additivity is often satisfactory for many calculations of the gas-solid interaction.

In the case of a semi-infinite solid a simple expression for the potential energy of an atom at a distance r from the surface can be obtained by replacing the summation in Eq. (6) by a volume integration:

$$U(r) = -\frac{1}{3}\pi\rho\left(\frac{C}{2r^3} - \frac{B}{15r^9}\right) \tag{7}$$

where ρ is the atom density in the solid. The minimum value for U, U_o, is obtained when the atom is at the equilibrium distance r_o from the surface. Then,

$$\left(\frac{\partial U}{\partial r}\right)_{r=r_o} = 0 \quad ,$$

and Eq. (7) can be rewritten as

$$U(r) = -\frac{\pi\rho C}{6r_o^3}\left\{\left(\frac{r_o}{r}\right)^3 - 1/3\left(\frac{r_o}{r}\right)^9\right\} \tag{8}$$

The variation of the potential energy with the distance r is shown schematically in Fig. 1. It can directly be seen from Eq. (8) that

$$U_o = \frac{\pi\rho C}{9r_o^3} \tag{9}$$

U(r) can be calculated from Eq. (8) for any value of r by using reasonable values for r_o and C (C e.g., by means of Eq. (3), (4) or (5)). It is not the purpose of this article to review here all these kinds of calculations. We mention here only calculations of Ricca et al.[17] for noble gas atoms adsorbed on different sites of various crystal planes of a solid Xe crystal. Using a variational method they calculated for U_o of He on the (100) face of a face centered cubic Xe crystal a value of -340×10^{-16} erg, on the (110) face -349×10^{-16} erg and for the (111) face -270×10^{-16} erg. This illustrates that large differences can be expected in adsorption behavior between various planes of a solid crystal.

The variation of potential energy over the surface of a single crystal plane, as calculated by Ricca et al. is also interesting. Figure 2 shows the (100) face of a Xe lattice. The potential energy of a He adatom on the square site A amounts to -340×10^{-16} erg, on the saddle site B -209 and on the site C directly above a Xe atom, only

-135 erg. The differences are much smaller for the sites on the smoother (111) plane.

These results of Ricca et al. show that the residence time of physically adsorbed atoms may be especially large on certain surface sites and that the heat of adsorption will exhibit a large variation with the surface structure of the adsorbent.

2c. Physical Adsorption on Metals

There are also theories dealing specifically with the dispersion interaction of gases with metal surfaces.

Lennard-Jones[18] assumed a metal as an ideally polarizable system because of the mobility of the fluid of conduction electrons. He considered the interaction between an adsorbed molecule and the surface as a Coulomb attraction between the instantaneous charge distribution of the molecule and its classical image in the conductor which is induced by the fluctuating dipole in the molecule. For the interaction of an inert gas molecule with a metal surface he found the following expression for the interaction energy:

$$U_L = -\frac{mc^2\chi}{2r^3} \tag{10}$$

where m stands for the mass of an electron, c for the velocity of light and χ for the diamagnetic susceptibility of the molecule.

Bardeen[19] corrected the Lennard-Jones theory by taking into account the interaction of the electrons in the metal. He obtained the following expression:

$$U_B = -\frac{\alpha k e^2}{16 r_e\left(1 + \frac{k e^2}{2 r_e I}\right)} \frac{1}{r^3} \qquad (11)$$

where e is the charge of an electron, k is a numerical constant approximately equal to 2.5, r_e is the radius of a sphere in the metal containing one conduction electron, α is the polarizability and I the ionization energy of the gas molecule.

Margenau and Pollard[20] noted that a metal cannot actually be considered to be ideally polarizable because of the finite relaxation time of the electrons which cannot maintain an electrical image of the continuously fluctuating charge distribution in the molecule. They calculated the interaction energy by considering the interaction of the adsorbed molecule with infinitesimal elements in the metal surface and by summing over these elements. Their result is

$$U_{mp} = -\frac{e^2\alpha}{16 r^3}\left(\frac{k}{r_e} - \frac{hn}{\pi m \nu_o}\right) \qquad (12)$$

where n is the density of conduction electrons in the metal and ν_o the characteristic resonant frequency of the molecule.

Prosen and Sachs[21] used second-order perturbation theory for their calculation of the interaction energy, resulting in

$$U_{ps} = \frac{N_A \alpha e^2 k_m^2}{8\pi^2} \frac{\ln (2 k_m r)}{r^2} \qquad (13)$$

with

$$k_m = (3\pi^2 \rho)^{1/3} \qquad (14)$$

ρ being the electron density in the metal.

More recently the following expression was derived by Mavroyannis:[22]

$$U_m = \frac{N_A \hbar e}{m^{1/2}} \frac{\alpha^{1/2} n^{1/2}}{8r^3} \frac{\hbar \omega p/\sqrt{2}}{\left(\frac{n}{\alpha}\right)^{1/2} \frac{\hbar e}{\sqrt{m}} + \hbar \omega p/\sqrt{2}} \qquad (15)$$

where ωp is the plasma frequency of the metal.

A discussion of these different approaches can be found e.g., in the review of Margenau and Kestner.[16]

It is important to note that in Eqs. (10) through (15) the solid is considered as a uniform structureless medium. The influence of the of the surface structure on the bonding has not been taken into account. We saw, however, in Section 2b that an important variation of the binding energy with the crystal plane can be expected. Further, Eqs. (10) through (15) give only the attractive part of the interaction, the repulsive forces have been omitted. This is a rather serious omission for small values of r. Useful expressions for the repulsive interaction between a solid and a gas molecule in a manner analogous to that of the attractive part are not available. As Fig. 1 already shows it may be expected that the contribution of repulsive forces is of the order of a third to a half of the attractive interaction at the equilibrium distance.

3. Brief Survey of Calculated and Experimental Heats of Adsorption

In this chapter we shall discuss in subsequent sections what may be expected from dispersion force interaction for (a) the heat of adsorption of Xe on different transition metals, (b) the dependence of the heat of adsorption on the surface structure of the metal and (c) the dipole moment of the adcomplex. Further relevant experimental data are introduced in these sections and compared with the results calculated from the dispersion force theories.

3a. The Heat of Adsorption of Xe on Different Transition Metals

Let us first try to calculate absolute values for the heat of adsorption arising from dispersion forces for Xe adsorbed on a metal surface. The first problem encountered in this kind of calculations is which value has to be taken for r_o, the equilibrium distance between Xe and the metal. As pointed out by de Boer[23] there is a large uncertainty in r_o and, thus, in the values for the heat of adsorption Q, calculated by means of Eqs. (10) through (15), all of which vary as r^{-3} (except that of Prosen and Sachs).

Taking for r_o the sum of the metallic radius and the van der Waals radius of the adsorbate, values for Q have been calculated from Eqs. (10) through (15) by Chon et al.[24] and by Mavroyannis[22] for He, Ne, Ar and Kr on Pt. The values obtained from Eqs. (11) through (15) appear to be in reasonable agreement with those found by experiment on platinum black.[24] Accepting these values for r_o we have calculated Q from Eqs. (11) through (15) for Xe on five transition metals, viz Au, Cu, Ni, Pt and Rh.[25] The numerical values for Q following from Eq. (13) and (15) are given in Table I. Values calculated from Eq. (11) and (12), not shown in this table, are somewhat smaller than those obtained from Mauroyannis' equation. On the other hand, much higher values are obtained by using Eq. (13).

Nieuwenhuys, van Aardenne and Sachtler[25] determined the heat of adsorption on films evaporated in ultrahigh vacuum of the metals mentioned above using adsorption isotherms (obtained via work function measurements) at different temperatures. These values for equal coverages have been compiled in Table I.

It appears that the values Q_M, following from Eq. (15) (and also from Eqs. 11 and 12) are much lower than the experimental values Q_{exp}. The large differences between Q_{exp} and Q_M cannot be attributed to the uncertainty in r_o since Q_M is fairly constant on the metals considered while Q_{exp} on Rh e.g., is nearly twice that on Au. $Q_{P.S.}$ (from Eq. (13)) is about equal to Q_{exp} for Xe on Cu, Ni and Au while on Pt and Rh it is lower than Q_{exp} by more than 3 kcal/mole.

It was discussed previously that no unambiguous values for Q_{disp} can be calculated by means of the presently available theories on van der Waals adsorption. This is caused by the approximations required in the theoretical approach in order to get useful equations for Q, by the uncertainty of the contribution of Q_{rep} and by the uncertainty in r_o. Yet, we have to conclude that there exists a large discrepancy between theory and experiment: none of the present dispersion theories can explain the large variation in the heat of adsorption with the transition metal.

3b. The Dependence of the Heat of Adsorption on the Surface Structure of the Metal

In Section 2b it was shown that the heat of physical adsorption may depend on the surface structure of the adsorbent. Unfortunately, Eqs. (10) through (15) ignore completely the actual structure of the metal. Therefore, several authors used the additive pair-wise interaction approximation for calculating the heat of adsorption on different crystal planes. In Table II are shown values for the heat of adsorption of Xe on several crystal planes of Rh, as calculated by Ehrlich.[26] Absolute values determined in this way are open to doubt since the uncertainties in B and C in Eq. (7). Moreover, there is some doubt about the general validity of this approach because of the collective behavior of the electrons in metals. However, it has been mentioned in Section 2c that the response of electrons in a metal at high frequency is not instantaneous. At very high frequencies metals behave more like insulators than real metals, so that the pairwise interaction model will probably be reasonably valid, certainly if only the order in heat of adsorption on different crystal faces is requested.

Bacigalupi and Neustadter[27,28] calculated the order in heat of adsorption of several gases on different planes for various face- and body-centered-cubic metals. For Xe on Pt, Rh and Ir we may expect from their data: $Q_{210} > Q_{110} > Q_{100} > Q_{111}$ and for Xe on W: $Q_{411} > Q_{210} > Q_{111} > Q_{100} > Q_{110}$.

It is interesting to compare these calculations with experimental data. Table III shows the available data for the heat of adsorption of Xe on different single crystal planes of several metals. Q_{max} and Q_{min} correspond to the heat of adsorption at low and high coverage, respectively. Experimental data on the heat of adsorption of Xe on several crystal faces of a single metal are limited to W, Pt and Ir, all values obtained by field emission probe-hole microscopy. The methods used by the different investigators does not allow the determination of the heat of adsorption with an accuracy better than 1-2 kcal/mole. The error in the relative heat of adsorption is, however, very small, below 0.2 kcal/mole.

The differences between Q_{max} on the various crystal planes of Pt and Ir are small, in the order of 10%. This proves that the variation in the Q values given in Table I are merely caused by different metallic properties and not by a different abundance of crystal planes on the surface of the polycrystalline films used in these experiments.

The order in initial heat of adsorption is not in agreement with the order predicted by the pairwise interaction model: Q_{max} on the close-packed faces (111) and (100) of Pt and Ir is larger than on the rougher faces (110) and (210). This holds also for Xe on W where Q_{max} is higher on the closest-packed (110) face of W than on the (100), (111) and (210) faces.[30]

3c. The Dipole Moment of the Adcomplex

Mignolet[37] discovered in 1950 that Xe adsorption produces a large decrease in the work function of transition metals, i.e., the Xe-metal bond is characterized by a considerable dipole moment with the positive end directed away from the metal. This was confirmed by other investigators.[30-42] Some characteristic values have been compiled in Table IV. It is interesting to note that the decrease in work function is large on transition metals, small on metals such as Zn, and zero on alkali metals.

A change in the work function ϕ of a metal, $\Delta\phi$, is related to the number N of adsorbed molecules per unit area and the dipole moment μ of the adcomplex:

$$\Delta\phi = -4\pi N\mu \tag{16}$$

Generally the dipole moment decreases with increasing coverage as a result of depolarization of an adatom by the neighboring adatoms. In Table I some values are given for the estimated dipole moment normal to the surface in the limit of zero coverage, estimated from the observed change in work function by means of the Topping equation.

Table III shows values for the work function reductions on different crystal planes. The magnitudes of the work function decrease are relatively large on all crystal planes. The highest values on W and Ir have been reported for the closest-packed faces, thus (111) and (100) for the fcc metal Ir and (110) for the bcc metal W. There is some doubt on the absolute values of the work function reduction on the close-packed faces as determined by the Fowler-Nordheim relation in field emission microscopy, the order is, however, probably correct.[30]

In Section 1 physical interaction between two atoms was defined as an interaction in which electron sharing and electron transfer between the atoms is absent. The observed dipole moments look, therefore, incompetible with dispersion force interaction. Antoniewicz[43] pointed out that a small decrease in work function may be expected. This is a result of the tendency of the orbital electrons of the adatom to move towards its image charge, hence the electron concentration on Xe will be somewhat larger in the direction of the metal than in the opposite direction. It is difficult to estimate which value for the dipole moment may be expected from this effect. Due to the nature of dispersion forces it cannot be a large effect. We saw, however, that the observed decrease in work function is very large, comparable to that of alkali atoms adsorbed on transition metals where, as generally assumed, the bond has a strong ionic character. Moreover, adsorption of Xe on alkali metals does not bring about any detectable change in the work function,[38-41] what is also hard to reconcile with the model of Antoniewicz.

4. Alternative Bonding Models for Noble Gases on Transition Metals

It was shown in Section 3 that there exists an appreciable disagreement between the experimental data and the expectations from dispersion force binding: The relative high heat of adsorption of Xe on Pt and Rh, the order in the heat of adsorption on different crystal planes of Pt, Ir and W and the large dipole moment are incompatible with dispersion force interaction. Hence, we have to conclude that the adsorption of noble gases on metals cannot be described in terms of mere dispersion forces. In this chapter we shall discuss other approaches which, of course, have to incorporate the results of Chapter 2.

4a. Electric Polarization of Adatoms by the Surface

A model frequently used for explaining the large dipole moment assumes a dispersion force interaction to which an additional interaction term is added which is due to a classical polarization of the adsorbate in a hypothetical surface field.[44-47] This field would arise from the Helmholtz double layer at the metal surface. This model was recently critized on the basis of the data described in Section 3.[25] The authors rejected the model for the following reasons:

(1) The dipole moment of an adatom polarized by an electric field F is given by

$$\mu = \alpha F \tag{17}$$

The heat of adsorption arising from this interaction, additional to dispersion forces

$$Q = Q_{disp} + Q_{pol} \tag{18}$$

is then

$$Q_{pol} = \frac{1}{2} \mu F \tag{19}$$

From Eqs. (17) and (19) it follows that

$$Q_{pol} = \frac{1}{2} \mu^2/\alpha \tag{20}$$

The values for Q_{pol} emerging from Eq. (20) have been compiled in Table I In this calculation $\alpha = 4.0\mathring{A}^3$, the polarizability of Xe in the gaseous state, while for μ the values mentioned in Table I were taken. The electrostatic contribution to the bonding would be only 5-10% of the total heat of adsorption. Clearly, the numbers for Q_{pol} in combination with Q_{disp} cannot explain the much higher heat of adsorption of Xe on Rh and Pt in comparison with Xe on Au and Cu.

(2) The model has to explain why its contribution to the bonding would be larger on the smooth crystal planes were both the work function reductions and the heat of adsorption are larger than on other planes of W[30] and Ir.[33] It is generally assumed that on smooth planes the electric double layer, conventionally ascribed to a "spill-over" of electrons has its negative sign at the outside. It is, therefore, difficult to reconcile the observed sign of the dipole moment with the direction of this electric surface field. Only a deep penetration of the big Xe molecules into the double layer, and thus in the electron sea at the metal, could cause a work function decrease. Such a penetration is, however, incompatible with the basic principles of van der Waals interaction.

4b. Charge-Transfer Model

This model is based on Mulliken's charge transfer no-bond theory of organic charge transfer complexes.[48] It assumes chemical bond formation by a partial electron transfer from adsorbate to metal. It seems that Mignolet[49] was the first to realize the importance of this type of bonding in the metal Xe interaction. The theory was later elaborated and applied by Gundry and Tomkins,[50] Engel and Gomer[30] and Nieuwenhuys, von Aardenne and Sachtler.[25] The electronic charge per Xe adatom must be in the order of 0.05-0.10 in order to explain the observed work function changes.[30,32]

Just as done before for dispersion forces and electrostatic contributions we shall try to calculate the heat of adsorption Q_{CT} arising from this interaction and compare it with the heat of adsorption found experimentally.

Charge transfer states are formed by electron transfer from Xe to states k in the metal above the Fermi level. The theory gives the following equation for the heat of adsorption Q_{CT} and the dipole moment μ of adsorbed Xe:[25]

$$Q_{CT} = \sum_k \beta_k^2/(H_k - H_o) \qquad (21)$$

and

$$\mu = 2er \sum_k \beta_k^2/(H_k - H_o)^2 \qquad (22)$$

where β_k corresponds to the energy of interaction between the unperturbed, no-bond state and a charge transfer state; H_o is the energy of the unperturbed no-bond state and H_k the energy of a charge transfer state

(Xe^+, metal$^-$). In order to calculate Q_{CT} the interaction integrals β must be replaced by an expression which contains experimentally known terms. The following approximate expression can be derived for Q_{CT}:[25]

$$Q_{CT} = \frac{(Ig - \phi - e^2/4r)}{4\pi Ner} \quad (-\Delta\phi) \tag{23}$$

In the derivation of this equation any contribution was neglected of charge transfer from metal states below the Fermi level to an excited state of the inert gas atom. Xe has excited states at -3.7 and -3.8 eV relative to the vacuum level;[30] thus levels of about 1.4 eV from the Fermi level of a low work function surface of Pt. Some contribution of "back donation" of electrons to Xe may, therefore, be expected. In first approximation the neglect of back donation is probably reasonable in view of the large decrease in work function by Xe adsorption.

Values for Q_{CT} calculated from $\Delta\phi$ using Eq. (23) are given in Table I. For r and $\Delta\phi$ the values mentioned in this table have been taken. It appears that the calculated values of Q_{CT} combined with a contribution of dispersion forces in the order of 2 kcal/mole (as predicted by Mavroyannis, Eq. (15)) can explain the measured heats of adsorption.

Equation (23) shows that an electron transfer to the metal as required in the CT model is favored by a high work function of the adsorbing surface. The relatively large heat of adsorption on the (111) and (100) regions of a Pt (Ref. 34) and Ir (Ref. 33) tip or the (110) region of a W tip[30] can thus easily be rationalized in the CT model.

The large dipole moment, the high heat of adsorption, the relationship[25] between heat of adsorption and dipole moment on different transition metals, and the relatively high heat of adsorption on high work function planes suggest that charge transfer bonding play an important role in noble gas adsorption on transition metals.

A more direct evidence for CT binding could possibly be obtained by means of photo and field emission electron spectroscopy. Only two studies of noble gas adsorption by means of electron spectroscopy are known to the author: a field emission study by Lea and Gomer[29] and a X-ray photoemission study by Yates and Erickson.[51]

Lea and Gomer measured the total energy distribution of electrons field emitted from different crystal planes of W as a function of Kr coverage. They were unable to detect a direct evidence for charge transfer, neither for donation of electrons, nor for back donation of electrons to excited levels of Kr. It is, however, interesting that the "Swanson hump",[52] characteristic for the electron energy distribution of the (100) plane, disappears upon Kr and Xe adsorption. The "Swanson hump" which is generally attributed to specific surface states, disappears upon chemisorption of gases.[53] Since it would be surprising if surface states could be modified by dispersion forces, Lea and Gomer concluded that their results yield indirect evidence for charge transfer bonding.

Yates and Erickson found a considerable shift (2.1 eV) in the binding energy of the Xe core $3d_{5/2}$ level when Xe is adsorbed on a W (111) plane. A similar shift was found for Xe adsorbed on or imbedded in a Pt polycrystalline rod.[54] They argued that a small increase or the $3d_{5/2}$ energy level could be expected on electrostatic grounds since the dipole moment has its positive pole outwards. The observed shift was, however, in the opposite direction. They attributed the shift to core hole/extra-atomic relaxation processes.

The present data from X-ray photoemission and field emission electron spectroscopy do not thus yield direct evidence for the bonding mechanism. It can be expected that in the near future more studies by means of electron spectroscopy will appear which may provide more detailed information about the noble gas-metal bonding.

5. Some General Remarks on the Bonding of Adsorbed Inert Gases

Surveying all experimental data available at the moment we can conclude that the bonding between Xe and transition metals is satisfactorily described by the charge transfer model. According to the definitions of physical and chemical adsorption as given in Section 1, the adsorption of Xe on transition metals may be considered as a weak chemisorption.

This work is merely devoted to adsorption of noble gases on metals. It has to be noted here that the charge transfer model may generally be applied to weak chemisorption systems, e.g., N_2 adsorption on group VIII b and c metals and CO adsorption on Cu, Ag and Au. These adsorption systems are characterized by heats of adsorption in the order of 10 kcal/mole. Some authors explained the bonding in terms of physical adsorption.[55,56] Recent data,[57] however, show that the interaction is of a chemical nature. Nieuwenhuys et al.[57] describe the bonding as a donation of electrons from the $3\sigma_g$ orbitals of the N_2 molecules to the metal stabilized by back donation of electrons from the metal d-band into the vacant degenerate 1 πg antibonding orbitals of N_2. While the back donation of electrons in the Xe-metal bond play only a minor role as suggested by the large work function decrease, it is of considerable importance in the N_2-metal and CO-metal bond. This is directly demonstrated by the work function changes: on some faces of Rh, e.g., the work function increases by N_2 adsorption.[58]

The description of the interaction of Xe with transition metals in terms of a weak chemical bonding is in line with the newly realized chemical reactivity of noble gases: a large number of noble gas compounds are known now.[59,60] Especially Xe compounds with fluorine are remarkably stable. XeF_2 e.g., has an enthalpy of formation of -37±10 kcal/mole with an average bond energy between Xe and F of 39±10 kcal/mole. In XeO_3, although on endothermic compound with enthalpy of formation of +96±2 kcal/mole, the Xe-O bond energy is still 28 kcal/mole.

6. Configuration of Adsorbed Molecules on Metal Surfaces

In this section we shall discuss the arrangement of noble gas adatoms on single crystal surfaces. Adsorption of inert gases has been used over many years in order to determine the surface area of polycrystalline metal samples. It is generally assumed in these calculations that the inert gas atoms do not feel an influence of the geometry of the surface. The packing in the adsorbed layer would resemble the closest-packed layer as is formed in the condensed phase of the particular gas. A value of 16.8Å^2 is e.g., often assumed for the area of a Xe adatom corresponding to the value in the densely packed plane of a Xe crystal.

Results obtained in the last 15 years cast doubt on the general correctness of this procedure. Field emission experiments revealed that adsorption of Xe, Kr and Ar on W display a large crystal face specificity.[44,61,62] The field emission results indicate also that the diffusion rate of Xe at 78K is already large enough for the establishment of a diffusional equilibrium distribution of Xe over the whole tip surface. Further the heat of adsorption of Xe at low coverage appeared to be higher on (411)-(611) regions on W where the adatoms fit perfectly into the substrate structure than on (111) faces where Xe is less coordinated.[44,62] Comparable results were obtained on Mo,[63] just as W a metal with the bcc structure, on Re (Ref. 64) with the hcp structure and on Rh[26] with the fcc structure. Apparently Xe adsorption is highly localized on these metal surfaces at 78 K. The adsorbed atoms jump rapidly from site to site until they have found the most favorable sites where their time averaged residence is much larger than on other faces. More recent measurements on individual crystal faces of Pt (Ref. 34) and Ir (Ref. 33), both having the fcc structure, are in agreement with this view. As shown in Table III, the initial heat of adsorption is especially large on the (321) tip areas of these metals, and just on these planes sites are available where Xe atoms have a very good coordination with metal atoms.

While site adsorption plays an important role at low coverage, one may imagine two processes at high coverage:

I. The formation of a two-dimensional close-packed Xe layer. When all favorable sites have been occupied, Xe adsorption proceeds via less favorable sites. Usually the formation of a close-packed layer will require a rearrangment of the already adsorbed Xe atoms, so that a part of the Xe atoms must leave their low-energy sites.

II. Adsorption is finished when the favorable sites have been occupied. The Xe layer will in most cases be appreciably less densely packed than in bulk Xe.

One may expect that the occurrence of I or II depends on the crystal face, the heat of adsorption and the temperature of the surface. Further, not only adsorbate-metal but also adsorbate-adsorbate interaction will play a role in the arrangement of the adatoms at high coverage. This is because the adsorbate-adsorbate interaction may be attractive due to dispersion attraction or repulsive as a consequence of the mutual repulsion between electric dipoles on the surface (see Section 3c). Clearly, the former favors the formation of a close-packed layer. Most data obtained on single crystal planes indicate that the latter is more important than the former for Xe on crystal planes of Pd,[35] W,[30] Pt,[34] and Ir (Ref. 33) since the heat of adsorption decreases with increasing coverage.

We shall review now the experimental results relevant for a discussion of the two alternative possibilities I and II. Some observations obtained with polycrystalline metal films support II. Ponec and Knor[65] reported that the number of adsorbed Xe atoms in a monolayer on a Ni film is in no way smaller than the number of adsorbed Kr atoms on the film while Xe has a much larger atomic radius than Kr. Brennan and Graham[66] found that the ratio of the monolayer capacities for these two gases on films of several metals is close to unity.

A more direct evidence for I or II is obtained by means of low energy electron diffraction. The first observations were reported by Lander and Morrison[67] on the (0001) basal plane of graphite. They observed for monolayer coverage at a temperature of 90K extra diffraction spots corresponding to a ($\sqrt{3}\times\sqrt{3}$ R30°) structure which is consistent with a dense hexagonal arrangement of the adatoms in complete registry with the substrate structure. On this plane close-packing and site adsorption are combined resulting in a Xe area of 15.7$\mathring{A}^2$ which is somewhat smaller than the area of 16.8$\mathring{A}^2$ in solid Xe. Suzanne et al.[68,69] confirmed these results for Xe on the (0001) face of graphite. Dickey, Farrell and Strongin[70,71] found a similar behavior for Ar and Kr condensed on a (100) plane of the bcc metal Nb: crystallization of Ar(111) and Kr(111) layers in full registry with the uderlying substrate surface which is possible due to a very small compression of the Xe-Xe distance compared to bulk Xe. They also succeeded in obtaining LEED patterns of Ne, several layers thick, condensed on this plane. The pattern observed was similar to those for Ar and Kr despite the 18% lattice mismatch between the Ne(111) and the Nb(100) face. Xe condenses with the (100) face parallel to a Nb(100) substrate and is slightly out of registry with the substrate. When this layer was annealed pure (111) crystallites could be grown. Ignatiev et al.[72,73] condensed Xe on a Ir(100) plane at 55K. Here the Xe crystals grew epitaxially with the (111) face of Xe parallel to the substrate face. The measured lattice spacing is very close to the value obtained from X-ray data on solid Xe. Multilayer formation is not observed at a substrate temperature of 78K.

Xe adsorption up to monolayer coverage was studied at a temperature of 78K on Pd(100) by Palmberg[35] and on Cu(111), (100), (110) and Ag(111), (110) and (211) by Chesters and Pritchard.[36] Their LEED observations indicate that a monolayer coverage the adatoms are close-packed on these surfaces. The surface area per Xe adatom in a complete monolayer is about 17Å^2 in each of these surfaces resembling the area in bulk Xe. Site adsorption was observed on Cu(111). The overlayer was not in registry with the substrate on Cu(100). On all other faces the Xe layer was epitaxially related to the substrate without true site adsorption. The difference between Cu(111) and Ag(111) is interesting. The lattice packing model would predict an adatom area for Xe of 16.9Å^2 on Cu and 21.5Å^2 on Ag, comparing with 16.8Å^2 on solid Xe. Site adsorption was observed on Cu(111) but not on Ag(111) where an area per adatom of 17.5Å^2 was found. Apparently close-packing is preferred.

The general conclusion which can be drawn from the LEED results is that the packing of Xe on the low index surfaces studied is, at least at monolayer coverage, more governed by the adatom size than by lattice packing. This is clearly in variance with the earlier results on polycrystalline films. Films have poorly defined surfaces, not only atomically smooth but also open faces contribute to the surface while the LEED observations were carried out on relatively smooth faces. Relevant to this apparent controversy are recent results of Nieuwenhuys et al.[33,34] obtained by field emission probe-hole microscopy. They observed that the decrease in heat of adsorption with coverage (ΔQ) is significantly different on the various crystal faces of Pt and Ir tips. Some values for ΔQ are given in Table III. Apparently the repulsion between Xe adatoms at monolayer coverage depends on the crystal face. This cannot merely be attributed to differences in the dipole moment: On (210) e.g., ΔQ is smaller than on (321) while the change in work function ($\Delta\phi$) is larger on (210). ΔQ is very small on the (210) regions, indicating a very small repulsion between the adatoms. Apparently, no close-packed layer is formed on this plane and only a part of the favorable sites becomes occupied. On (321) the sites are even more favorable than on (210). When all these sites have been occupied the Xe-Xe distance approaches that of a close-packed layer in one dimension only, causing a larger Xe-Xe repulsion than on (210). A localization of the adatoms on single sites is less favorable on the smooth regions (111) and (100). A close-packed Xe layer is presumably formed on these planes, as here ΔQ is large.

It may be concluded from all available data that a close-packed Xe layer is formed at high coverage on the smooth faces while on the faces possessing suitable sites for Xe site adsorption is preferred to the formation of a close-packed Xe layer.

Conclusions

1. Experimental data on the adsorption of noble gases on transition metals are incompatible with an interaction entirely due to dispersion forces.

2. All available data point to a weak chemical interaction of xenon with transition metals, as is properly described in the charge transfer model.

3. LEED experiments prove that noble gases form at monolayer coverage a densely packed Xe layer on close-packed planes of metals.

4. Field emission experiments show that Xe adsorption depends strongly on the exposed crystal face of the transition metal. Site adsorption is preferred to the formation of a close-packed layer on rough faces possessing favorable sites for the noble gas.

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References

1. D. M. Young and A. D. Crowell, Physical Adsorption of Gases (Butterworths, London, 1962).
2. S. Ross and J. P. Olivier, On Physical Adsorption (Wiley, New York, 1964).
3. E. A. Flood, ed., The Solid-Gas Interface (M. Dekker, New York, 1967).
4. R. A. Pierotti and H. E. Thomas, Surface Colloid Science IV, 93 (1971).
5. J. P. Hobson, CRC Critical Reviews in Solid State Sciences 221 (1974).
6. F. Ricca, ed., Adsorption-Desorption Phenomena (Academic Press, London, 1972).
7. F. London, Z. Phys. Chem. B11, 222 (1930).
8. J. C. Slater and J. G. Kirkwood, Phys. Rev. 37, 682 (1931).
9. J. G. Kirkwood, Phys. Z. 33, 57 (1932).
10. A. Müller, Proc. Roy. Soc. A 154, 624 (1936).
11. H. Margenau, Rev. Mod. Phys. 11, 1 (1939).
12. J. O. Hirschfelder, C. F. Curtiss and R. B. Bird in Molecular Theory of Gases and Liquids (John Wiley and Sons, New York, 1954).
13. K. S. Pitzer, Adv. Chem. Phys. 2, 59 (1959).
14. L. Salem, Mol. Phys. 3, 441 (1960).
15. C. Mauroyannis and M. J. Stephen, Mol. Phys. 5, 629 (1962).
16. H. Margenau and N. R. Kestner, Theory of Intermolecular Forces (Pergamon Press, NY, 1969).
17. F. Ricca, C. Pisani and E. Garrone in Adsorption-Desorption Phenomena, F. Ricca, ed. (Academic Press, London, 1972), p. 111.

18. J. E. Lennard-Jones, Trans. Faraday Soc. 28, 334 (1932).

19. J. Bardeen, Phys. Rev. 58, 727 (1940).

20. H. Margenau and W. G. Pollard, Phys. Rev. 60, 128 (1941).

21. E. J. R. Prosen and R. G. Sachs, Phys. Rev. 61, 65 (1942).

22. C. Mavroyannis, Mol. Phys. 6, 593 (1963).

23. J. H. de Boer, *The Dynamical Character of Adsorption* (Clarendon Press, Oxford (1953).

24. H. Chon, R. A. Fischer, R. D. McCammon and J. G. Aston, J. Chem. Phys. 36, 1378 (1962).

25. B. E. Nieuwenhuys, O. G. van Aardenne and W. M. H. Sachtler, Chem. Phys. 5, 418 (1974).

26. G. Ehrlich, Technical Report General Electric S-68-1125 (1968).

27. R. J. Bacigalupi and H. E. Neustadter, Surface Science 19, 396 (1970).

28. H. E. Neustadter and R. J. Bacigalupi, Surface Science 6, 246 (1967).

29. C. Lea and R. Gomer, J. Chem. Phys. 54, 3349 (1971).

30. T. Engel and R. Gomer, J. Chem. Phys. 52, 5572 (1970).

31. J. Nikliborc and Z. Dworecki, Acta Phys. Polon. 32, 1023 (1967).

32. M. J. Dresser, T. E. Madey and J. T. Yates, Jr., Surface Science 42, 533 (1974).

33. B. E. Nieuwenhuys and W. M. H. Sachlter, Surface Science 45, 513 (1974).

34. B. E. Nieuwenhuys, D. Th. Meÿer and W. M. H. Sachtler, Phys. Stat. Sol. A 24, 115 (1974).

35. P. W. Palmberg, Surface Science 25, 598 (1971).

36. M. A. Chesters, M. Hussain and J. Pritchard, Surface Science 35, 161 (1973).

37. J. C. P. Mignolet, Disc. Faraday Soc. 8, 105 (1950).

38. D. F. Klemperer and J. C. Snaith, Surface Science 28, 209 (1971).

39. J. C. P. Mignolet, in Chemisorption, W. E. Garner, ed. (Butterworths, London, 1957), p. 118.

40. Th. G. J. von Oirschot and W. M. H. Sachtler, Ned. Tÿdschrift Vacuumtechn. 8, 96 (1970).

41. D. F. Klemperer and J. C. Snaith, Surface Science 45, 318 (1974).

42. B. E. Nieuwenhuys, R. Bouwman and W. M. H. Sachtler, Thin Solid Films 21, 51 (1974).

43. P. R. Antoniewicz, Phys. Rev. Lett. 32, 1424 (1974).

44. G. Ehrlich and F. G. Hudda, J. Chem. Phys. 30, 493 (1959).

45. G. Ehrlich, Adv. Catalysis 14, 255 (1963).

46. P. G. Hall, Chem. Commun. 877 (1966)

47. J. Müller, Surface Science 42, 525 (1974).

48. J. Mulliken, J. Am. Chem. Soc. 74, 811 (1952).

49. J. C. P. Mignolet, J. Chem. Phys. 21, 1298 (1953).

50. P. M. Gundry and F. C. Tompkins, Trans. Faraday Soc. 56, 846 (1960).

51. J. T. Yates, Jr. and N. E. Erickson, Surface Science 44, 489 (1974).

52. L. W. Swanson and L. C. Crouser, Phys. Rev. 163, 622 (1967).

53. J. W. Gadzak and E. W. Plummer, Rev. Mod. Phys. 45, 487 (1973).

54. N. E. Erickson, J. Vac. Sci. Technol. 11, 226 (1964).

55. R. V. Culver, J. Pritchard and F. C. Tompkins, Z. Electrochem. 63, 741 (1959).

56. R. van Hardeveld and A. van Montfoort, Surface Science 4, 396 (1966).

57. B. E. Nieuwenhuys, D. Th. Meÿer and W. M. H. Sachtler, Surface Science 40, 125 (1973).

58. A. Hoek and B. E. Nieuwenhuys, to be published.

59. J. H. Holloway, Noble Gas Chemistry (Methuen, London, 1968).

60. H. H. Hyman, ed. Noble Gas Compounds (University Chicago Press, Chicago, 1963).

61. R. Gomer, J. Chem. Phys. 29, 441 (1958).

62. W. J. M. Rootsaert, L. L. van Reÿen and W. M. H. Sachtler, J. Catalysis 1, 416 (1962).

63. G. Ehrlich, Brit. J. Appl. Phys. 15, 349 (1964).

64. K. Ishizuka, J. Res. Inst. Catalysis, Hokkaido Univ. 15, 95 (1967).

65. V. Ponec and Z. Knor, Coll. Czech. Chem. Comm. 27, 1091 (1962).

66. D. Brennan and M. J. Graham, Phil. Trans. Roy. Soc. London A258, 325 (1965).

67. J. J. Lander and J. Morrison, Surface Science 6, 1 (1967).

68. J. Suzanne, J. P. Coulomb and M. Bienfait, Surface Science 44, 141 (1974).

69. J. Suzanne, J. P. Coulomb and M. Bienfait, Surface Science 47, 204 (1975).

70. J. M. Dickey, H. H. Farrell and M. Strongin, Surface Science 23, 448 (1970).

71. H. H. Farrell, M. Strongin and J. M. Dickey, Phys. Rev. B 6, 4703 (1972).

72. A. Ignatiev, J. B. Pendry and T. N. Rhodin, Phys. Rev. Lett. 26, 189 (1971).

73. A. Ignatiev, A. V. Jones and T. N. Rhodin, Surface Science 30, 573 (1972).

Table I. Xe adsorption on metal films annealed at room temperature. For a legend of the symbols, see Table V.

Metal	r_o(Å)	$-\Delta\phi$(V)	μ_o(Debye)	$Q_{exp}\left(\frac{kcal}{mole}\right)$	$Q_M\left(\frac{kcal}{mole}\right)$	$Q_{P.S.}\left(\frac{kcal}{mole}\right)$	$Q_{pol}\left(\frac{kcal}{mole}\right)$	$Q_{CT}\left(\frac{kcal}{mole}\right)$
Au	3.62	0.52	0.36	4.6	2.9	4.0	0.2	2.7
Cu	3.46	0.63	0.43	5.2	2.8	5.8	0.3	3.9
Ni	3.43	0.82	0.56	6.4	2.9	6.3	0.6	4.8
Pt	3.56	0.95	0.65	7.6	3.4	4.6	0.8	4.8
Rh	3.52	1.08	0.74	8.7	3.2	5.0	1.0	6.1

Table II. Lennard-Jones interaction energies Q on Rh as calculated by Ehrlich.[26]

Plane	Q (kcal/mole)
(100)	8.6
(110)	9.2
(311)	9.6
(210)	9.6
(320)	10.2
(531)	10.5
(321)	11.0

Table III. Work function changes and heats of adsorption of Xe on single crystal planes. For a legend of the symbols, see Table V.

	ϕ^a(V)	$\Delta\phi^b$(V)	$\Delta\phi^c$(V)	$\Delta\phi^d$(V)	$Q_{max}{}^b\left(\frac{kcal}{mole}\right)$	$Q_{max}{}^b\left(\frac{kcal}{mole}\right)$	$Q_{min}{}^b\left(\frac{kcal}{mole}\right)$
W (110)	5.8	2.4	1.5		9.2		
(210)		1.4			6.4		
(100)	4.9	1.35	0.9		5.9		
(111)	4.7	1.13	0.6	1.1	5.9	9.3	9.3
(211)	5.0	0.92	1.0		6.5		
(611)			1.1				
(320)			0.6				

	Φ(V)	$\Delta\phi$(V)	$Q_{max}\left(\frac{kcal}{mole}\right)$	$Q_{min}\left(\frac{kcal}{mole}\right)$
Ir^e (111)	5.8	1.8	7.5	6.5
(100)	5.7	1.6	7.5	6.5
around (110)	5.0	0.8	7.0	6.3
(210)	5.0	1.3	7.2	6.7
(331)	5.4	1.1		
(321)	5.4	1.0	7.8	7.0

Table III. Continued.

		ϕ(V)	$\Delta\phi$(V)	$Q_{max}\left(\frac{kcal}{mole}\right)$	$Q_{min}\left(\frac{kcal}{mole}\right)$
Pt[f]	(111)	5.9		7.6	6.3
	(100)	5.8	0.96	7.5	6.4
around	(110)			7.1	6.4
	(210)	5.2	1.1	7.2	6.8
	(321)	5.4	0.9	7.8	6.9
	(311)	5.5	0.9		

		ϕ(V)	$\Delta\phi$(V)	$Q_{max}\left(\frac{kcal}{mole}\right)$	$Q_{min}\left(\frac{kcal}{mole}\right)$
Cu[g]	(111)		0.48		
	(100)		0.47		
	(110)		0.61		
Ag[g]	(111)		0.44		
	(110)		0.45		
	(211)		0.45		
Pd[h]	(100)		0.94	7.6	6.4

a	Ref. 29
b	Ref. 30
c	Ref. 31
d	Ref. 32
e	Ref. 33
f	Ref. 34
g	Ref. 36
h	Ref. 35

0 0 0 0 4 3 0 6 2 0 3

Table IV. Changes in work function brought about by Xe adsorption at 78K on films annealed at room temperature.

Metal	$-\Delta\phi$(V)	Reference	Metal	$-\Delta\phi$(V)	Reference
Na	0.00	38	Ni	0.85	39
K	0.00±0.02	39		0.82	25
	0.00±0.02	40	Pd	1.08	42
Ca	0.00	39	Pt	0.95	25
Cs	0.00±0.01	41	Cu	0.67	39
				0.61	38
Ti	0.84	39		0.63	25
Cr	0.95	39	Ag	0.71	42
Fe	0.66	39	Au	0.52	42
	0.60	38	Zn	0.21	39
Ru	0.98	42	Hg	0.23	39
Rh	1.08	42	Sn	0.0±0.01	41
Ir	1.03	42	Se	0	39

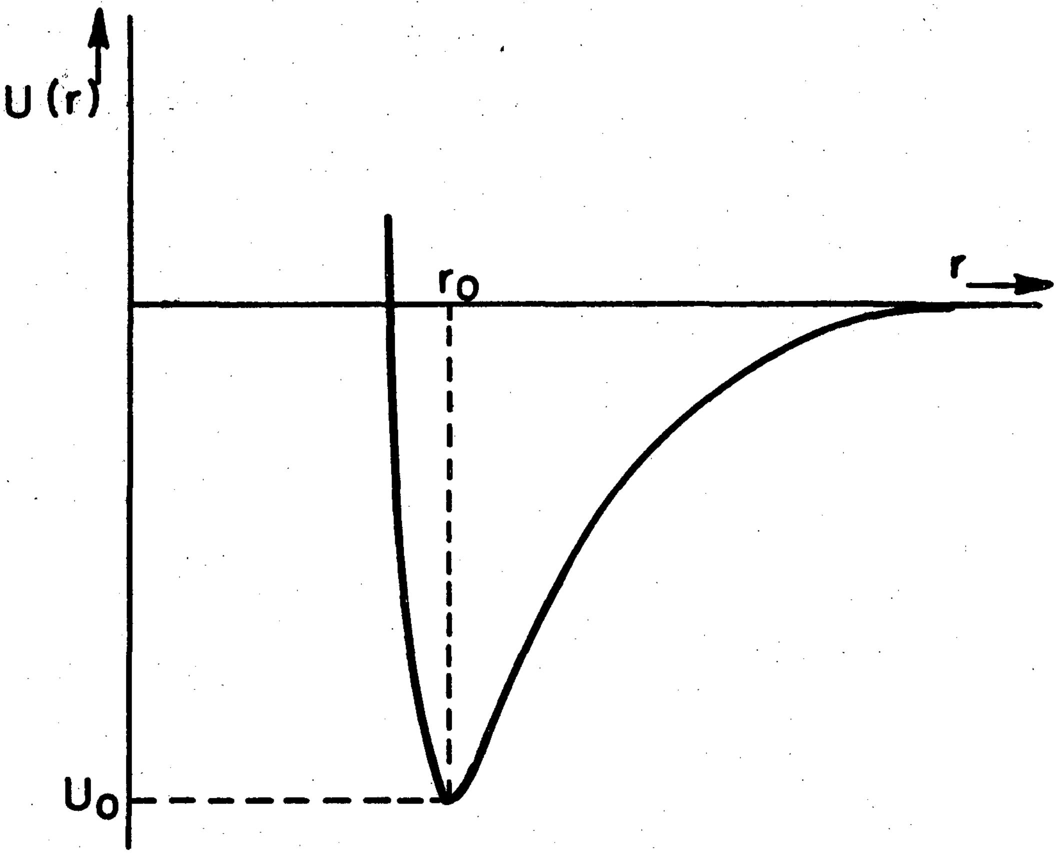
Table V. List of symbols used in the tables.

Q	heat of adsorption
Q_{exp}	experimentally heat of adsorption
Q_{disp}	contribution of dispersion forces to Q
Q_{pol}	contribution of induced polarization to Q
Q_{CT}	contribution of charge transfer bonding to Q
Q_M	Q_{disp} calculated from the equation of Mavroyannis (Eq. (15))
Q_{PS}	Q_{disp} calculated from the equation of Prosen and Sachs (Eq. (13))
Q_{max}	heat of adsorption at low coverage
Q_{min}	heat of adsorption at high coverage
Q	work function of the bare metal
$\Delta\phi$	change in work function by Xe adsorption at full coverage
μ	dipole moment
μ_o	dipole moment at very low coverage
R	distance between two molecules
r	distance between an adatom and a solid surface
r_o	equilibrium distance between adatom and surface

Figure Captions

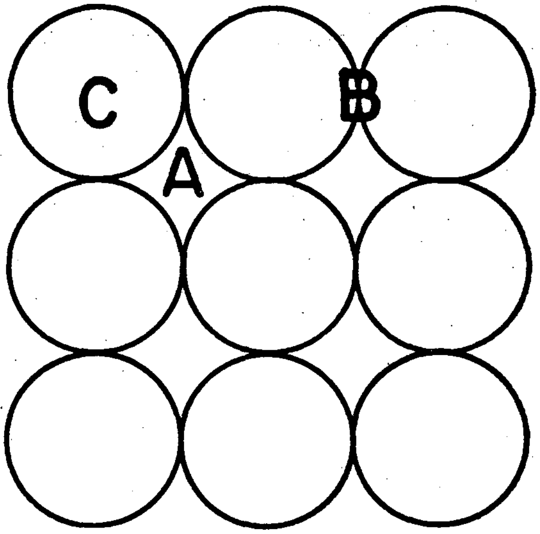
Fig. 1. Change in potential energy U(r) of a molecule as a function of the distance r from the surface.

Fig. 2. A schematic drawing of the (100) plane of a fcc lattice.



XBL 756-1620

Fig. 1



XBL756-6596

Fig. 2

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BERKELEY, CALIFORNIA 94720