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Physical Adsorption
Rare Gas Atoms on Solid Surfaces

Progress Report
for Period June 1, 1980 - May 31, 1981

Milton W. Cole
104 Davey Laboratory
The Pennsylvania State University
University Park, PA 16802

February 1981

Prepared for

The Department of Energy
under Contract DE-AS02-794ER10454

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ABSTRACT

This project has entailed investigation of three areas during the current term: physical adsorption, photostimulated field emission (PSE), and phonon reflection at interfaces. The principal effort has been directed toward understanding interactions associated with physical adsorption and the associated properties of a film. The specific topics pursued include the detailed form of the long range interaction, the configuration space wave function, and the interaction between adatoms. Experimental confirmation of the last two come from neutron scattering and thermodynamic measurements, respectively.

The research in PSE has yielded results which improve upon previous calculations. There is, however, a remaining disagreement with experiment; suggestions for the origin are discussed.

The phonon reflection work is directed toward understanding the role of surface roughness, an important factor in increasing the energy transmission across interfaces. A formalism has been developed which will be evaluated in the future.

I. INTRODUCTION

This report summarizes progress since June, 1980 in understanding several problems involving surfaces. During this period of support under contract DE-AS02-79ER10454, several problems have been addressed which are reviewed below. The principal thrust is focused at physical adsorption. Our major achievement has been to calculate from atomic scattering data a variety of thermodynamic and neutron scattering properties.¹ The measurements agree to an extent which is nearly unique in surface science. This reflects largely the sophistication and precision of the experiments.

Other research, concerning photostimulated field emission and phonon reflection at rough surfaces, is discussed below. The latter topic has only begun to receive attention.

The research has received approximately one-half of my effort, averaged on a twelve month basis. It is expected that this half-time devotion to the project will continue for the remainder of the term. Several students have also participated, partially sponsored by the contract; one Ph.D. was awarded (Carey Schwartz). Major effort was also expended by F. Toigo.

II. SUMMARY OF RESEARCH ACCOMPLISHED SINCE JUNE, 1980

The past eight months has involved extending research in areas investigated previously (physisorption and photostimulated field emission) and beginning an effort in a new area (phonon reflection at interfaces). Particularly valuable during this period was a collaboration with F. Toigo (University of Padua), who came to Penn State for six months under the auspices of this contract. This interaction continues in several areas.

A list of papers based on this research and seminars presented follows. The papers themselves are appended to this report.

A. Papers Supported by this Grant - Submitted After June 1, 1980

1. M. W. Cole, D. R. Frankl, and D. L. Goodstein, "Probing the He/Graphite Interaction," Reviews of Modern Physics, April 1981.
2. G. Vidali and M. W. Cole, "Effective Interaction Between He Atoms on a Graphite Surface," Phys. Rev. B22, 4661 (1980).
3. M. W. Cole and F. Toigo, "Quasi-two Dimensional Approach to States of an Adsorbed Atom," Phys. Rev. B, to be published.
4. C. Schwartz and M. W. Cole, "Transmission Coefficients for Field Emission," submitted to Solid State Comm.
5. G. Vidali and M. W. Cole, "Long Range Interaction Between a He Atom and a Semiconductor Surface," submitted to Surface Science.
6. W. E. Carlos, M. W. Cole, S. Rauber, G. Vidali, A. F. Silva-Moreira, J. Codona, and D. L. Goodstein, "Thermodynamic Implications of Band Structure Effects for Rare Gases on Graphite," in Ref. 2.

B. Seminars and Colloquia Presented Since June, 1980 Concerning This Work

New York University

Brown University (Chemistry)

Lehigh University

California Institute of Technology

M.I.T. (Chemical Engineering)

University of Rhode Island

University of Vermont

University of Arizona

Center for Nuclear Studies (Saclay, France)

University of Liege (Belgium)

University of Erlangen (Germany)

Technical University of Munich

University of Padua

University of Rome

National Italian Laboratory (Frascati)

C. Physical Adsorption

For the last ten years it has been appreciated that rare gases adsorbed on graphite represent a physical realization of a two-dimensional (2D) system.¹⁻³ This provides a strong stimulus for this research. A more general motivation is that other adsorption systems (having potential technological application, for example) may manifest some aspects of the behavior seen with graphite.⁴

In order to understand the many phenomena exhibited experimentally (commensurate and incommensurate solids, possible condensation, orientational epitaxy, and configurational ordering of molecules), theorists have made a variety of simplifying assumptions. Our work has been directed in part toward quantifying their validity or modifying them, where appropriate. Two problems of particular interest have been addressed:

1. What is the form of the interaction $V(\vec{r})$ between a single atom and a surface?
2. What are the interactions between two adsorbed atoms and the resulting properties of a film?

The principal tool used in answering the first of these is the analysis⁵⁻⁷ of atomic scattering data. Our initial work⁵ on this showed that the conventional description of the potential is inadequate. Specifically, if one assumes⁹ additivity of He-C pair interactions, i.e.,

$$V(\vec{r}) = \sum_i U(\vec{r} - \vec{R}_i) \quad , \quad (1)$$

(where the C atoms are at $\vec{R}_i$) then the pair potential $U(\vec{r} - \vec{R}_i)$ must be anisotropic (i.e., depends on the orientation of $(\vec{r} - \vec{R}_i)$), in contrast to the conventional assumption of isotropy. This anisotropy can be understood quantitatively in terms of dielectric properties of graphite.⁵ The result of including this variation is to increase substantially the lateral variation of $V(\vec{r})$. This conclusion, hinted at by the scattering data,^{9,10} led to our prediction¹¹ of moderately large band structure effects for He on graphite. The detailed confirmation^{12,13} of this prediction and others by thermodynamic measurements is discussed in our review article.¹

More recently, an ingenious neutron scattering measurement¹⁴ succeeded in determining the mean distance $\langle z \rangle = 2.85 \text{ \AA}$ of a ^4He atom from the top C layer of graphite. This datum motivated us to look at the problem of determining the wavefunctions for this potential. There is no difficulty in principle if one has sufficient computing power and patience. What we sought was a conceptually and computationally simple way to solve the problem. What emerged¹⁵ was a method analogous to the Born-Oppenheimer approach of molecular physics. Specifically, we generated a wavefunction of the form:

$$\psi(z, \vec{R}) = g_n(z; \vec{R}) h_n(\vec{R})$$

where $\vec{R} = (x, y)$ and z is the coordinate normal to the surface. Here $g_n(z; \vec{R})$

is an eigenfunction of a one-dimensional Schrodinger equation for motion perpendicular to the surface (at fixed $\vec{R}$):

$$\left[-\frac{\hbar^2}{2m} \frac{d^2}{dz^2} + V(z, \vec{R}) - E_n(\vec{R}) \right] g_n(z, \vec{R}) = 0 \quad .$$

Neglecting very small corrections (which are evaluated in Ref. 15), the local eigenvalue $E_n(\vec{R})$ becomes an effective potential energy for a 2D calculation:

$$\left[-\frac{\hbar^2}{2m} \nabla_{\vec{R}}^2 + E_n(\vec{R}) - E \right] h_n(\vec{R}) = 0 \quad ,$$

which may be solved to get the dispersion relation of adsorbed atoms.

The similarity to the Born-Oppenheimer method arises because the eigenvalues of perpendicular motion are widely spaced in the quantum regime. Thus these generate an effective potential for the relatively slowly varying lateral motion.

The results of this calculation agree very well with a more conventional approach.¹⁶ The advantage of the method is computational simplicity; the disadvantage (of the simplest version) is the neglect of mixing between distinct states of perpendicular motion. The latter is unimportant for low-lying states. With this technique we determined¹⁵ a mean distance $\langle z \rangle = 2.89 \text{ \AA}$, in excellent agreement with the experimental results.¹⁴ This further confirms the inadequacy of potentials proposed prior to the scattering experiments, which gave $\langle z \rangle = 3.25 \text{ \AA}$.¹⁷

As a result of this emerging quantitative description, we may perform a variety of new calculations of the properties of rare gases on graphite. One example is the problem of a submonolayer film. We have recently examined the case of He at low coverage,¹⁸ other systems are discussed in the proposal

for future work. Our calculation of the thermodynamic properties of He on graphite uses a 2D virial expansion. The work differs from the classic calculation of Siddon and Schick¹⁹ in two respects. The first is that we incorporate the effective mass enhancement (1.06 and 1.04 for ⁴He and ³He) appropriate to¹⁶ the substrate potential. The second difference is that we employed an effective 2D potential between adatoms which is about 20 percent less attractive than the free space He-He interaction. This arises in our calculation¹⁸ from an incorporation of both substrate screening and motion perpendicular to the substrate.²⁰ The former, which dominates, depends strongly on the assumed distance $\langle z \rangle$ from the substrate; the agreement described above for $\langle z \rangle$ gave us confidence in the value used.

The results of our calculations agree well with data for ³He, explaining a systematic discrepancy existing when the free space interaction was used. In the case of ⁴He, the situation is less clear because the model employed is not strictly valid in the relevant regime ($T \gtrsim 3$ K). Specifically, the single particle band structure effects become important and the effective mass approximation no longer suffices.²¹

One other research area which has been investigated concerns the asymptotic part of the van der Waals interaction. This can be written²²

$$V \sim -C_3 z^{-3}$$

$$C_3 = (4\pi)^{-1} \int_0^{\infty} dE \alpha(iE) g(iE)$$

$$g(iE) = [\epsilon(iE) - 1] / [\epsilon(iE) + 1]$$

The coefficient C_3 thus depends on the polarizability of the atom and dielectric

function of the solid, both evaluated on the imaginary energy axis. In view of recent and forthcoming experiments on atomic scattering from semiconductor surfaces, we have calculated²³ C_3 for the case of He interacting with Ge, Si, GaAs, and diamond. This extends previous work for graphite,^{24,25} alkali halides,²⁵ and metals.²⁶

The utility of a C_3 calculation is that this number provides estimates for various properties of bound states. These include a direct relation to the spectrum of weakly bound states,²⁷ an approximate empirical relation to the depth of the attractive potential,⁷ and provides the basis for ab initio calculations of the full potential.²⁸⁻³⁰ These questions are discussed more fully in the proposal for future research.

D. Photostimulated Field Emission

The capability of field emission and photoemission in probing electronic properties at surfaces is well known. Recently, effort has been devoted to combining these two techniques.^{31,34} Specifically, one illuminates a field emission tip with a laser and measures the I-V characteristics. The great potential of this experiment lies in the significant contribution to I of states which lie several electron volts above the Fermi level but below the zero field vacuum level. The emission probability from these states is very sensitive to the form of the potential at the surface, a problem of fundamental interest.

We have performed a series of calculations, most of which are not yet published. These include an exploration of the triangular barrier model in photostimulated field emission³⁴ (PSE) (which is much too crude), calculations of barrier transmission coefficients for realistic potentials,^{3,5} and a moderately realistic calculation of PSE.³⁶

The triangular barrier calculation yielded results which were a slight improvement of work by Bagchi³⁷ for the same model (because he made a simplifying approximation). The transmission coefficient calculation³⁵ found corrections to the WKB-like results which might have general application, including field emission. The full-blown PSE calculations³⁶ are the most sophisticated to date. Extensive numerical calculations were required because we felt that a realistic treatment of the potential was an essential ingredient of a quantitative theory.

Our results, unfortunately, were not in agreement with the fascinating data of Lee and Reifenberger³¹ (which had stimulated our interest in this problem). The latter exhibit intriguing oscillations in the field dependence of the current I ; these did not appear in the results of our calculation.

In order to put this work in context, it should be described as analogous to "surface effect" calculations of photoemission.³⁸ We did not treat the absorption matrix element as a constant.³⁹ One possible source of error may well be, however, our assumption (which is common³⁸) of a transverse field. This would certainly be erroneous at high photon energy;⁴⁰ the nature of the error at lower energies is less well established, but certainly present. Another possibility is the omission of dynamic corrections to the image potential.⁴¹ Because of our simplifications, the calculation is to be regarded as only qualitative.

We had initiated our work on this problem with an idea about the origin of the experimentally observed³¹ oscillatory behavior. Specifically, the latter seemed quite similar to oscillations observed in thermionic emission (so-called "periodic deviations"), which have been explained as interference phenomena manifested in the transmission coefficients.⁴² We found, however, that this behavior disappears in the limit of the high electric fields

($> 0.1 \text{ V/\AA}$) which are relevant to PFE. Thus our suspicion was unfounded. Alternative hypotheses involve our neglect of the longitudinal part of the electromagnetic field or dynamical corrections to the image potential.

E. Phonon Transmission and Reflection at Rough Surfaces

When a sound wave is incident upon an interface between a solid and a liquid, it produces in general both refracted and reflected components. Since these waves carry energy, the problem of heat transmission is directly related to the relative intensities of these components. This view is the basis for the acoustic mismatch theory of thermal boundary resistance.⁴³ This theory has dramatic implications when the liquid is He because the ratio of solid to liquid acoustic impedances is then of order 100. It has been found for He, however, that this theory fails by more than an order of magnitude for temperature $T \approx 1 \text{ K}$.⁴⁴⁻⁴⁵ The discrepancy is greatest for such light quantum systems⁴⁶, but exists to some extent for more classical fluids.⁴⁷

Recently a number of sophisticated experimental techniques have been employed to probe this phenomenon. These use the fact that a sound wave propagates ballistically in a pure crystal at low T . The experimental results^{48,49} indicate that surface imperfection contributes significantly to the discrepancy with theory. Unfortunately, to quote Ref. 47, the theoretical problem of the effect of roughness on sound transmission is "confused...a more realistic theory would be helpful."

This situation has stimulated us to examine the problem. Working in collaboration with Flavio Toigo, I have developed an approach to computing the reflection and transmission at a rough surface (see proposal). The extensive numerical work required to achieve a solution has not begun.

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