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Measurement of Molecule-Surface Binding Energies by a Time-of-Flight Diffusion Method*

F. Pollock, H. Logan,† J. Hobgood,‡ and J. G. Daunt

Physics Department and Cryogenics Center, Stevens Institute of Technology, Hoboken, New Jersey 07030

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A kinetic method for measuring the properties of solid surfaces is described, and results are reported for the binding of helium on copper and copper thickly plated with argon.

The purpose of this paper is to describe a technique for studying the properties of solid surfaces and to report the results of the initial investigations on atomic binding energy to surface sites using this method. The method uses kinetic rather than static measurements. In the first series of experiments we have measured characteristic times for the transit of a pulse of helium gas through a long narrow tube (tube diameter < mean free path for molecule-molecule collision). Keeping in mind that the arguments apply to other geometries, we shall use this one to fix our ideas. Provided the gas of the input pulse is sufficiently dilute, the molecules execute a one-dimensional random walk with each step terminating at the tube wall. The rate of transit down a tube depends on the diffusion constant for one-dimensional motion which is given by

$$D = \tfrac{1}{2}\overline{X}^2/\bar{\tau}, \tag{1}$$

where $\overline{X}^2 \sim (\text{diameter})^2$ is the mean square step length and is essentially temperature independent, and $\bar{\tau}$ is the mean step time which does depend on the temperature of the system. There are two contributions to $\bar{\tau}$. First, there is the kinetic part $\bar{\tau}_f$ depending on the temperature through the rms molecular speed. This part should vary as $T^{-1/2}$. For our geometry $\bar{\tau}_f \sim 10^{-5}$–$10^{-6}$ sec. The other, more interesting part, is the capture time on the surface. One expects that its principal temperature dependence will be exponential, and arguments can be made making this conjecture more precise. If, now, ξ is the probability that an incident particle will be captured and $\bar{\tau}_c$ the capture time, one can write for $\bar{\tau}$

$$\bar{\tau} = (1-\xi)\bar{\tau}_f + \xi(\bar{\tau}_f + \bar{\tau}_c) = \bar{\tau}_f + \xi\bar{\tau}_c. \tag{2}$$

Thus, any characteristic time of the diffusion process will depend on $\bar{\tau}_f$ and the product $\xi\bar{\tau}_c$.

An analysis of the adsorption-desorption process can be made analogous to the Einstein treatment of the adsorption and emission of radiation by atoms. Here, since the processes depend on surface and molecular properties and the temperature of the system, we may consider a system in equilibrium at temperature T, consisting of a gas of N_0 molecules of interest in a volume V, surrounded by a surface made of the solid of interest whose area is A. We assume a single binding energy per site of W $(W > 0)$ and ν sites per unit area. The density of atoms both in the gas and on the surface is low so that molecule-molecule interactions may be safely neglected.

We then have a simple problem in statistical mechanics. The density of particles on the surface is

$$\sigma = Z^{-1} N_0 \nu \exp(W/kT), \tag{3}$$

where Z is the single-particle partition function. The gas density is

$$\rho = \frac{N_0}{Z}\frac{1}{(2\pi\hbar)^3}\int \exp\left(\frac{-p^2}{2mkT}\right) d^3p \tag{4}$$

From elementary kinetic theory, the flux of molecules striking the surface is

$$j = \tfrac{1}{4}\rho\bar{\upsilon}, \tag{5}$$

where $\bar{\upsilon}$ is the rms molecular speed, and the number captured per unit time per unit area is, by definition of the capture probability ξ,

$$d\sigma/dt_{\text{adsorption}} = \tfrac{1}{4}\xi\rho\bar{\upsilon}. \tag{6}$$

From the definition of the mean lifetime τ_c we have

$$d\sigma/dt_{\text{desorption}} = -\sigma/\bar{\tau}_c. \tag{7}$$

Detailed balance then gives

$$\xi\bar{\tau}_c = \frac{4\sigma}{\upsilon} = \frac{(2\pi\hbar)^3}{2\pi m}\frac{\nu}{k^2T^2}e^{W/kT}, \tag{8}$$

which is the result we sought and which has the interesting property that while ξ and $\bar{\tau}_c$ separately depend, sensitively perhaps, on dynamical details of the molecule-surface interaction, their product depends only on gross properties—the binding energy, the density of sites, and the molecular mass.[1]

The pre-exponential factor in (8) is very small compared with $\bar{\tau}_f$ for all interesting temperatures. The consequence of this is that one must operate at temperatures much lower than W/k to detect the effect of capture time. As a result the time of transit of the pulse is extremely sensitive to both the temperature and the binding energy. Typically, binding energies between 100 and 200°K require operating at temperatures between 5 and 11°K. With the use of noble gases we have then a very sensitive yet gentle probe of surface properties, especially since mass spectrometry makes possible the detection of a very low density of molecules.[2]

The experimental arrangement is simple. In our initial experiments the transit tube was of copper, 400 cm long and 0.32 cm i.d., which could be maintained isothermally at any temperature in the range 4.2 to 77°K. Helium gas could be injected into one end of the tube, at a temperature equal to that of the tube. For a measurement, a square step pulse of helium of approximately 10 cm width is introduced into one end of the evacuated tube and the time noted. The number of particles in the pulse is sufficiently small as to justify the neglect of molecule-molecule interactions both in the gas and on the surface. A mass spectrometer, in this case a standard leak detector, measures the flow of helium from the other end of the tube and the signal is displayed on a chart recorder. Typical transit times, measured to the half-height of the leading edge of the pulse, range from about 9 sec at 15°K to about 10 min or more at the low-temperature end of the range. Figure 1 shows a typical output signal. The output pulse shape is found to agree quite well with the results of one-dimensional diffusion theory with small discrepancies that are temperature dependent, i.e., at high temperatures it is slightly narrower than theory predicts, while it is wider at low temperature. This effect is not yet completely understood, but does not seem to affect the shape of the leading edge of the output pulse from which the data are taken.

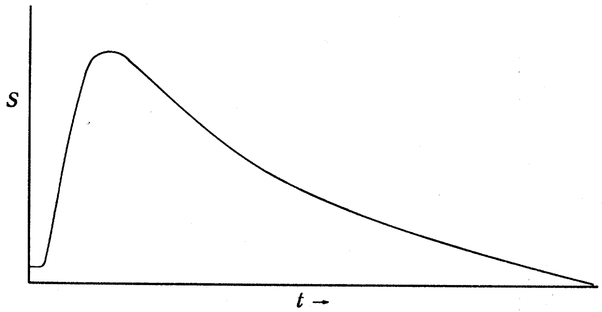

FIG. 1. The output response signal from the gas detector. S is the signal strength, t is the time.

The most convenient quantity to measure seems to be the time of arrival of the half-maximum on the rising slope of the output curve. From the previous considerations we can write

$$t_{1/2} = \alpha/\sqrt{T} + (\beta/T^2)e^{W/kT}, \tag{9}$$

where a small constant term due to lead-in and lead-out delays is neglected. In Fig. 2 we show a typical curve for half times, $t_{1/2}$, on the bare copper surface of the transit tube (which presumably has an oxide coating and perhaps other impurities). In Fig. 3 we plot for two cases, He on bare copper and He on argon-plated copper, $T^2(t_{1/2} - \alpha/\sqrt{T})$ vs $1/T$, from the slope of which we can infer the binding energy values. For the

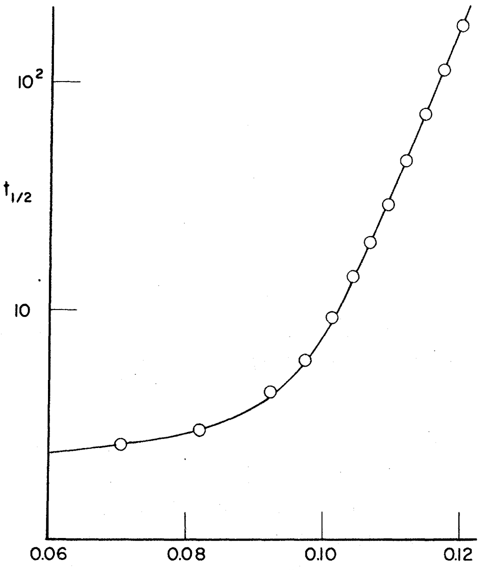

FIG. 2. The time of arrival of the half-maximum, $t_{1/2}$, as a function of the reciprocal of the absolute temperature. A unit of time here is 3.75 sec.

second case the tube was coated with approximately twenty layers of argon. The binding energies so obtained are $W_{\mathrm{He,Cu}}=177°\mathrm{K}$ and $W_{\mathrm{He,Ar}}=102°\mathrm{K}$.

Repeated measurements on the two substrates give values that vary by roughly 5%, most of which variation is probably due to incomplete reproducibility of the temperature of the tube from run to run. We have been able to hold the temperature of the transit tube, as measured by a gas-bulb thermometer, constant usually to within less than one part per thousand. Time measurements at the low temperature are generally accurate to within 2%, while at the highest temperatures the error is probably less than 10%. This latter error is important in determining the coefficient in the $T^{1/2}$ term, but unimportant for low temperatures which are the data used for the energy determination.

It is difficult to find experimental results with which to compare our findings. Ordinary thermostatic measurements require significant coverages, because of absolute or relative signal problems. An extrapolation to zero coverage of the results of Daunt and Lerner[3] for the isosteric heat of adsorption of helium on copper is roughly consistent with our results.[4] For the argon coating Novaco and Milford[5] have calculated an expected binding energy for helium on the 100 face of argon and find 100°K in very good agreement with our result of 102°K. It should be pointed out that in our derivation of Eq. (8) we assumed only one binding state. The extension to the more general case is straightforward. In particular, except for very closely spaced levels only the most tightly bound state contributes significantly to the average sticking time. In the case of argon plating, presumably a collection of crystallites exposing some fraction of each of the crystal faces would be formed. We should expect then to see the binding on the face that binds most strongly, which from theoretical considerations is the (100) face.

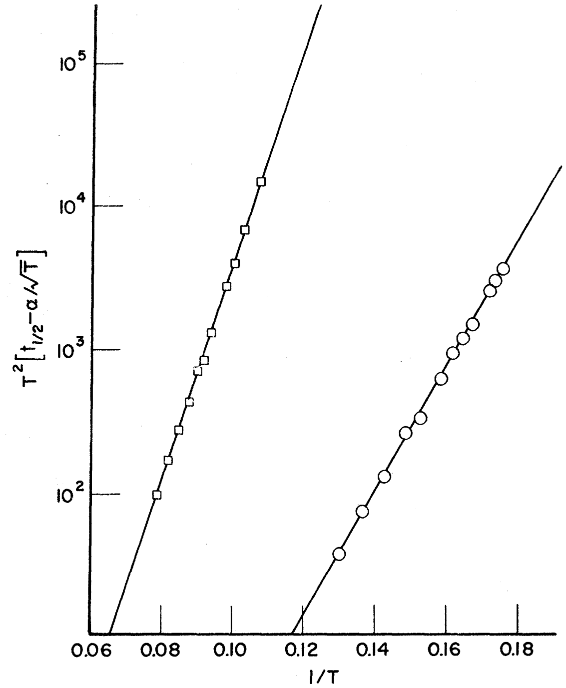

FIG. 3. $T^2[t_{1/2}-\alpha/\sqrt{T}]$ versus the reciprocal of the absolute temperature. The squares represent the data for He on bare copper, the circles those for He on argon-plated copper.

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†Permanent address: Wagner College, Staten Island, N. Y. 10301.

‡Permanent address: State University of New York at Binghamton, Binghamton, N. Y. 13901.

[1] Throughout this discussion it has been assumed that the diffusive process is so slow that the system is locally in equilibrium.

[2] It has been pointed out that quite a long time ago similar experiments were attempted. The earlier attempts were limited chiefly by detection techniques and small

amounts of input gas could not be used. See J. de Boer, *The Dynamical Character of Adsorption* (Oxford Univ. Press, Oxford, England, 1968), 2nd ed.

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Stark Ladders for Finite, One-Dimensional Models of Crystals

William Shockley
Bell Telephone Laboratories, Murray Hill, New Jersey 07974, and Stanford University,
Stanford, California 94305

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Application of the methodology of analysis of Shockley surface states confirms the existence of Wannier's Stark ladders of energy levels in finite crystals for wave functions that decay exponentially towards both edges of the crystal and shows that the perfectly regular energy intervals will be minutely disturbed by tunneling effects. If phonon scattering is neglected, coherent oscillations of electrons associated with specified energy bands are predicted.

Conflicting conclusions have been reached about the solutions of Schrödinger's equation for an electron in a potential

$$U(x) = V(x) - Fx = U(x+a) + w, \tag{1}$$

where F is the force exerted by a uniform electric field, a is the lattice constant for the periodic potential $V(x)$, and $w = Fa$. Wannier[1] noted that an energy eigenfunction $\psi(x)$ of energy E when translated by $-a$ satisfies what we shall call Wannier's theorem,

$$H\psi(x+a) = (E+w)\psi(x+a), \tag{2}$$

and predicted a Stark ladder of levels of spacing w. Zak and Rabinovitch have disputed this conclusion on a number of grounds, most recently by computing energy levels in a "Mathieu-type model crystal" of finite size and failing to find Stark-ladder distributions.[2] As they have noted, Wannier's theorem must fail if boundary conditions destroy translational symmetry. (They do not treat the "transformer secondary" model that preserves translational symmetry.[3]) We shall show that Wannier's theorem fails negligibly for those wave functions, not included in Ref. 2, for which the boundary conditions affect only the small exponential tails of ψ in the energy gaps.

We use the methodology[4] of Shockley surface-state analysis to define idealized Stark-ladder (ISL) wave functions and levels of energy (usually *not* eigenfunctions or eigenenergies) for the time-independent Schrödinger equation. For simplicity, we restrict our considerations to "uncrossed"[4] energy bands arising from a $V(x)$ that has a symmetric potential well at the center of each unit cell. This "uncrossed-symmetric-well" (USW) case requires[4] for $F=0$ that the wave functions at top and bottom of the lowest band be even or "gerade" functions about the cell center; at the band bottom, ψ is periodic with no nodes; at the band top, ψ has nodes at cell edges and alternates in sign from cell to cell. At the limits of the next band, ψ is odd or "ungerade" about the cell center; at the band bottom, ψ has zero slope at the cell edges and, at the band top, it has nodes at the edges, and for $F=0$ averages 1.5 nodes per cell through the band. Even and odd bands alternate as energy increases with one more node per cell for each higher band.

Of particular importance in this ISL analysis, as was the case for surface states, are the two linearly independent wave functions in the forbidden bands or energy "gaps" of the form

$$\psi_\pm(x+a) = f^{\pm 1}\psi_\pm(x). \tag{3}$$

In the lowest gap below the first band, $f > 1$ and ψ has no nodes. The next gap has $f = -|f| < -1$ and has one node per cell so that the node spacing is exactly equal to the lattice constant a; the node positions shift in the cell as the energy varies in the gap. The next gap has two nodes per cell, etc. In the energy bands, f has the Bloch-function form of $\exp(\pm ika)$.

We next consider a crystal of finite length