

Kinetics of Adsorption on Stepped Surfaces and the Determination of Surface Diffusion Constants

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Nitrogen adsorption on stepped W(110) surfaces is examined to illustrate a theory of surface kinetics. Experimental findings by Besocke *et al.* have shown that nitrogen chemisorbs dissociatively only at the step corner sites of a W(110) surface. Thus the rate of dissociation reveals the mobility of nitrogen and its interaction with the surface. Using continuous-time-random-walk theory, we obtain the probability that molecules reach the step corner sites as a function of time. A kinetic model of nitrogen dissociation is proposed to calculate a coverage function that is in good agreement with experiment. The surface diffusion constant of nitrogen molecules is obtained and is in accordance with previous observations that nitrogen molecules are first weakly physisorbed on the W(110) terrace. Finally, the coverage functions for different step densities are predicted.

KEY WORDS: Surface diffusions; random walks; lattices; periodic traps; dissociation.

1. INTRODUCTION

The migration of foreign molecules on surfaces, especially on metal or transition metal surfaces,⁽¹⁾ is an important process in indirect chemisorption and heterogeneous catalysis. In these processes, there are "active sites"^(2,3) associated with some specific surface locations and adsorbed molecules are usually required to perform random walks to reach those sites before certain reactions can occur.⁽⁵⁾ Thus by knowing how quickly molecules drift onto those active sites, one may deduce the properties of surface diffusion and obtain information (such as activation energy) about the interaction of molecules with the surface. The study of the mobility of

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molecules on surfaces is related to a quasi-two-dimensional problem of interest in statistical mechanics. While the description of molecular migration is of a microscopic nature, the experimental measurements, such as coverage functions, are largely macroscopic. Thus a theoretical fit of experimental data requires using the average properties of the interaction of molecules with surfaces.

Experimental findings by Besocke *et al.*⁽⁴⁾ reveal that nitrogen dissociation on stepped W(110) surfaces occurs only at the step corner sites. Stepped surfaces are high-index surface planes with an orientation close to a low-index one. The number of steps is simply related to the inclination angle towards the low-index plane and its step direction. Thus the steps, being equally spaced, constitute a periodic array of low-index terraces separated by monoatomic steps. In the experiment two types of step direction are used, namely, [001] and $[\bar{1}10]$ steps, with almost equal step densities.³ It is found that [001] steps yield higher initial coverage of surfaces than $[\bar{1}10]$ steps; nevertheless, saturation coverages depend on the step densities and not on the step structures. We shall use this example to illustrate the migration of molecules on surfaces and describe it by continuous-time-random-walk (CTRW) theory.⁽⁶⁻¹⁰⁾ The "active sites" in this type of indirect chemisorption are step corner sites.

In preparation for our derivation of a kinetic description of nitrogen dissociation let us summarize the role of step structures. In the gas phase the N_2 molecule is held together by a triple bond. When attached to a [110] terrace one might suppose that each nitrogen atom is attached to a tungsten atom by a single bond with the N_2 molecule being held together with a double bond. The attachment to the surface is sufficiently weak that surface migration is easy,^(5,11) but dissociation on a [110] surface does not occur (as compared with a [001] surface⁽¹¹⁻¹⁵⁾). On the other hand at a step corner site an individual nitrogen atom may place itself at a point equidistant from three tungsten atoms bonding with each in a manner preferred over an $N-N$ bonding so that dissociation occurs at the corner.

The kinetic process of nitrogen adsorption is thus two-staged. First, a nitrogen molecule approaching the [110] terrace from the gas phase meets the surface, is accommodated into an appropriate state, and is weakly physisorbed⁽⁵⁾ on the surface. Next, such a molecule migrates randomly with negligible activation energy to reach a step corner site where dissociation occurs. Since the surface coverage of nitrogen atoms starts with the occupation of step corner sites, we describe the rate of such occupation in Section 2, based on the model first given by Singh-Boparai *et al.*⁽¹¹⁾

³ Since microscopically there must be integer number of atoms on the terrace, only approximate equal step density is possible.

The central feature of the problem is to calculate the probability that a molecule will arrive at the step corner sites after the exposure of the surface to nitrogen. The CTRW theory is appropriate to describe molecular migration on surfaces. In Section 3, we ask more generally: what is the probability that a random walker will arrive at a specific line of periodic corner traps, given an initial position on the surface and a waiting-time distribution function $\psi(l, t)$ for a walker to make successive jumps from site to site? This problem will be solved exactly in Section 3.

Since the experiment of surface exposure to N_2 involves a small amount of oxygen, we compare the theoretical calculations with the experimental values extrapolated to the oxygen-free limit. In this fitting, only the average jumping rate W of nitrogen molecules and the dissociation rate C at the step corner sites are used. The diffusion constant of nitrogen molecules that we will calculate from these quantities is rather small. This is consistent with other observations that nitrogen molecules are first weakly physisorbed and form a precursor state.

2. KINETIC MODEL OF NITROGEN ADSORPTION ON STEPPED W[110] PLANE

A proper kinetic model of nitrogen adsorption on stepped tungsten surfaces has been proposed by Singh-Boparai *et al.*⁽¹¹⁾ Nitrogen molecules impinging on the surface are either elastically scattered back into the gas phase or are rapidly equilibrated at the incident sites as they enter positions of minimum potential energy.⁽⁵⁾ Thus nitrogen molecules first form weakly physisorbed precursors and then perform random walks on the surface along equipotential paths. Once a molecule arrives at any step corner site, it is dissociatively adsorbed and subsequently one of the adatoms migrates back onto the terrace. When all the step corner sites are occupied, the dissociation process is stopped. Let us use $\theta(t)$ to denote the fraction of occupation of a typical step corner "line" of N available sites. The rate of occupation at time t of a step corner line depends on the probability that a molecule is available at the step site, $F(t)$, and the probability that the step site is available after the nitrogen exposure at time $t = 0^+$. Thus the occupation function $\theta(t)$ satisfies

$$\frac{d\theta(t)}{dt} = C \cdot F(t) \cdot [1 - \theta(t)] \quad (1)$$

where we have normalized total occupation to unity. C is the dissociation rate constant and may be further factored into two parts: $C = C_1 C_2$, where C_1 is the conversion rate from the gas phase into nitrogen precursors and is proportional to the pressure of the nitrogen exposure. In an experiment,

this pressure is kept constant and we further assume this rate to be independent of the degree of occupation of the surface by the chemisorbed layer. The coefficient C_2 measures the accommodability of step corner sites to dissociated nitrogen atoms and is thus structure dependent. We shall discuss this further in Section 4 with respect to coverage functions. Since experiments only yield a macroscopic estimate of nitrogen coverage, of the order of 10^{14} atom/cm², and the step density is of the order of 10^6 /cm, both $\theta(t)$ and $F(t)$ are for an averaged step-corner and do not depend on specific locations.

Generally the rate equation should also contain a loss term. The omission of this term is based on the assumption that once nitrogen dissociates, one of the adatoms continues to occupy a step corner site and the other makes only a few limited jumps until it also becomes tightly bound. Indeed, experimental evidence⁽¹⁶⁾ supports this assumption in that at room temperature the diffusion constant of the chemisorbed atom is only 7×10^{-18} cm²/sec. Thus it is reasonable to assume⁽¹¹⁾ that the more energetic of the two dissociated atoms migrates only to a nearest neighbor on the terrace and there is very little probability that the atom will migrate further to occupy another site on a step corner.

3. CTRW THEORY OF MIGRATION OF MOLECULES ON SURFACES

The calculation of the probability $F(t)$ that a molecule will arrive at a step corner site at time t after nitrogen exposure, becomes the central problem in the determination of the occupation function $\theta(t)$ in Eq. (1). This problem may be properly approached through a CTRW model on a [110] surface with periodic traps.

Let us start with a more general question by asking: what is the probability $P(\mathbf{l}_t, t)$ of a molecule arriving at step corner sites \mathbf{l}_t at time t , given an initial position \mathbf{l}_0 at $t = 0^+$? Here we assume the molecular mobility on the surface to be described by CTRW model on a discrete lattice of points

$$\mathbf{l} = l_1 \mathbf{a}_1 + l_2 \mathbf{a}_2 \quad (2)$$

with l_i equal to an integer and $\{\mathbf{a}_i\}$ the primitive translation vectors. For convenience, we restrict the molecules to a finite two-dimensional lattice of N^2 unit cells with periodic boundary conditions. The step corner sites are located periodically at positions \mathbf{l}_t and are collectively members of a set L .

We follow the formulation of CTRW theory developed by one of the authors and his colleagues⁽⁶⁻¹⁰⁾ by evaluating $R(\mathbf{l}, t)$, the probability density that a molecule just arrives at \mathbf{l} at time t if it is started at \mathbf{l}_0 at $t = 0^+$. The

governing integral equation for $R(\mathbf{l}, t)$ has the form

$$\begin{aligned}
 R(\mathbf{l}, t) = & \sum_{l'} \int_0^t \psi(\mathbf{l} - \mathbf{l}', t - \tau) \cdot R(\mathbf{l}', \tau) d\tau \\
 & - \sum_{l_i \in L} \int_0^t [\psi(\mathbf{l} - \mathbf{l}_i, t - \tau) - \psi_t(\mathbf{l} - \mathbf{l}_i, t - \tau)] R(\mathbf{l}_i, \tau) + R_0(\mathbf{l}, t)
 \end{aligned}
 \tag{3}$$

where $\psi(\mathbf{l}, t)$ is the probability density that a displacement \mathbf{l} occurs at time t at nontrapping sites. For the purpose of generalization and to include the case that step structures are not totally effective as dissociation centers, there is a small probability that molecules once arrived at the step corner sites are slowly released without being dissociated. $\psi_t(\mathbf{l} - \mathbf{l}_i, t)$ represents such a transition probability density to its neighboring sites at time t . Both the ψ and ψ_t functions describe arbitrary interactions. Note that we have assumed that the transition onto a step corner site is the same as that for the terrace even though the step structure may act as a stronger attraction center than other trap-free sites.

The probability of a molecule being found at \mathbf{l}_i at time t , starting from \mathbf{l}_0 at $t = 0^+$ is the propagator $P(\mathbf{l}_i, t)$. Its Laplace transform $P(\mathbf{l}_i, u)$ is related to $R(\mathbf{l}_i, u)$ by

$$P(\mathbf{l}_i, u) = R(\mathbf{l}_i, u) \cdot [1 - \psi_t(u)] / u
 \tag{4}$$

Since the initial position \mathbf{l}_0 may be anywhere on the surface lattice sites, including the step corner sites, we take the average over all possible \mathbf{l}_0 values. In addition, the step corner densities are of the order of $10^6/\text{cm}$, and we are not interested in any specific step corner sites but in an averaged step corner site. Thus the probability of a molecule being found on any step corner site for any initial position is $\langle P(t) \rangle$, whose Laplace transform can be written as

$$\langle P(u) \rangle = \frac{\frac{1}{u} \cdot \frac{1 - \psi_t(u)}{1 - \psi(u)}}{\sum_{i=1}^m \frac{1 - \Lambda_i(t \cdot k_m, 2\pi, u)}{1 - \Lambda(t \cdot k_m, 2\pi, u)}}
 \tag{5}$$

where

$$\Lambda(\mathbf{K}, u) = \sum_l \int_0^\infty \psi(\mathbf{l}, t) e^{-i\mathbf{K} \cdot \mathbf{l}} e^{-ut} dt
 \tag{6}$$

$$\psi(u) = \Lambda(2\pi, 2\pi, u)
 \tag{7}$$

and similarly for $\psi_t(u)$. The expression of $\langle P(u) \rangle$ in Eq. (5) is evaluated for

arbitrary interactions with step corner sites parallel to the x direction of periodicity at every m lattice site.

Let us now evaluate $\langle P(t) \rangle$ for cases of special interest. The restriction of local probability conservation requires that

$$\int_0^\infty \sum_l \psi(\mathbf{l}, t) dt = 1 \quad (8)$$

where a useful form of $\psi(\mathbf{l}, t)$ may be written as⁽⁷⁾

$$\psi(\mathbf{l}, t) = W(\mathbf{l}) \exp -t \sum_l W(\mathbf{l}) \quad (9)$$

and $W(\mathbf{l})$ is the jumping rate from the origin to a distance \mathbf{l} . The exponential form of $\psi(\mathbf{l}, t)$ in Eq. (9) makes the solution of the random walk equation, Eq. (3), equivalent to exactly solving a master equation for periodic line traps. We further assume that a molecule only moves to its nearest neighbor in each jump, that the surface of interest is a [110] surface of a BCC lattice, and that the step corner structures are totally effective in dissociating nitrogen molecules upon their arrival ($\psi_i = 0$). We have finally

$$\langle P(t) \rangle = 1 - \sum_{j=1}^{m/2} \frac{2}{m^2} \cot^2 \frac{(2j-1)\pi}{2m} \exp[-8Wt \sin^2(2j\pi/2m)] \quad (10)$$

We note that $\langle P(t) \rangle$ depends only on the step density $1/m$ and on the jump rate to nearest neighbors, W .

In deriving Eq. (10) we have assumed that the surface is a [110] plane and that step corner sites are parallel to the [001] direction (Fig. 1). The corresponding probability for other step directions may also be easily derived from Eq. (10). For example if the step direction is perpendicular to [001], that is, in the $[\bar{1}10]$ direction (Fig. 1), then the probability is the same as in [001], that is

$$\langle P_{[\bar{1}10]}(t) \rangle = \langle P_{[001]}(t) \rangle \quad (11)$$

and if the step direction is in $[\bar{1}\bar{1}\bar{1}]$ (see Fig. 1), then the probability of reaching the step sites is half as fast. That is,

$$\langle P_{[\bar{1}\bar{1}\bar{1}]}(t) \rangle = \langle P_{[001]}(2t) \rangle \quad (12)$$

Finally, in the nitrogen exposure experiment, molecules strike the surfaces continuously; therefore at time t after the exposure, the probability of reaching step sites is the integrated sum of $\langle P(t) \rangle$, which has the form

$$F(t) = \frac{1}{t} \int_0^t \langle P(t-\tau) \rangle d\tau \quad (13)$$

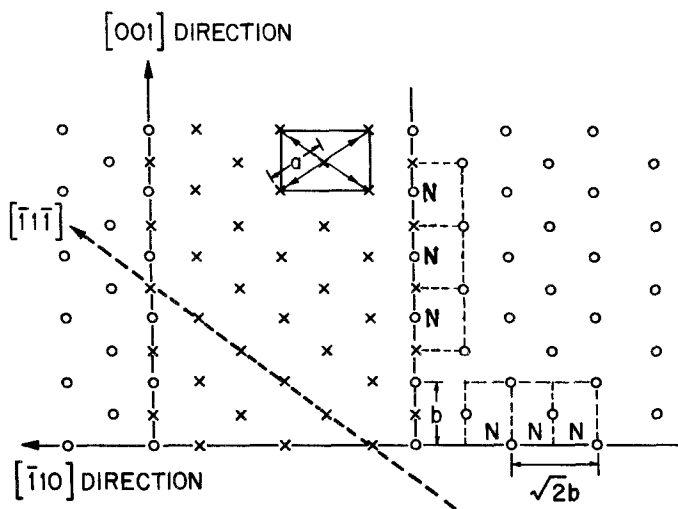


Fig. 1. Stepped surface of a (110) plane of a BCC lattice with step density = $1/m$ is illustrated. The case of $m = 6$ and [001] step direction are shown. Other step directions, such as $[\bar{1}10]$ and $[\bar{1}\bar{1}\bar{1}]$, are also marked. Circles and \times 's indicate different layers of tungsten atoms. The nearest neighbor distance is $a = 2.238$ Å. On the right-hand side, the N 's indicate nitrogen atoms. The accommodability of nitrogen atoms with respect to [001] and $[\bar{1}10]$ step directions is shown. A step length of b accommodates one nitrogen atom in the [001] step direction, while a step length of $\sqrt{2} \cdot b$ accommodates two in $[\bar{1}10]$.

4. CALCULATIONS OF NITROGEN COVERAGE

We have assumed that step structures are totally effective in dissociating nitrogen molecules regardless of step direction on a $W(110)$ plane. However, the dissociation rate coefficient C does depend on the step geometry, as was discussed in Section 2. From the saturation coverage data, experiment has shown that the ratio of total coverage to the number of step corner sites is 2 to 1 in the [001] step direction. This is consistent with the Singh-Boparai model⁽¹¹⁾ in which for each nitrogen molecule chemisorbed, one of the adatoms remains at the step site while the other migrates to its neighbor on the terrace. In the case of the $[\bar{1}10]$ step direction, the step corner sites/total coverage ratio is 1/4. This suggests that the dissociation rate constant C satisfies the relation $C_{[\bar{1}10]} = (1/2)C_{[001]}$. Since the coefficient C is also a measure of accommodability of the step structures with respect to the nitrogen atoms we illustrate the relationship of nitrogen atoms with step corner sites of [001] and $[\bar{1}10]$ directions in Fig. 1. In the [001] step direction, each [001] site can accommodate one nitrogen atom while in the $[\bar{1}10]$ step direction two nitrogen atoms are accommodated.

The experimental nitrogen coverage function as a function of time is performed at a very low pressure (10^{-8} torr).⁽⁴⁾ Thus during the long duration of the experiment, oxygen contamination is unavoidable. In order to make comparisons, we extrapolate the data of nitrogen exposure at any time to the oxygen-free limit in accordance with the trends of the corresponding saturation cases which are experimentally available. The results are shown in Fig. 2.

To obtain the best fits, we have used the values of the two parameters $C_{[001]} = 2$ and $W = 0.5$ jumps/sec. The coverage functions $\Theta(t)$ are evaluated according to

$$\Theta_{[001]}(t) = \frac{2}{m} \cdot \theta_{[001]}(t) \quad (14)$$

in the case of the [001] step direction and

$$\Theta_{[\bar{1}10]}(t) = \frac{4}{\sqrt{2} \cdot m} \cdot \theta_{[\bar{1}10]}(t) \quad (15)$$

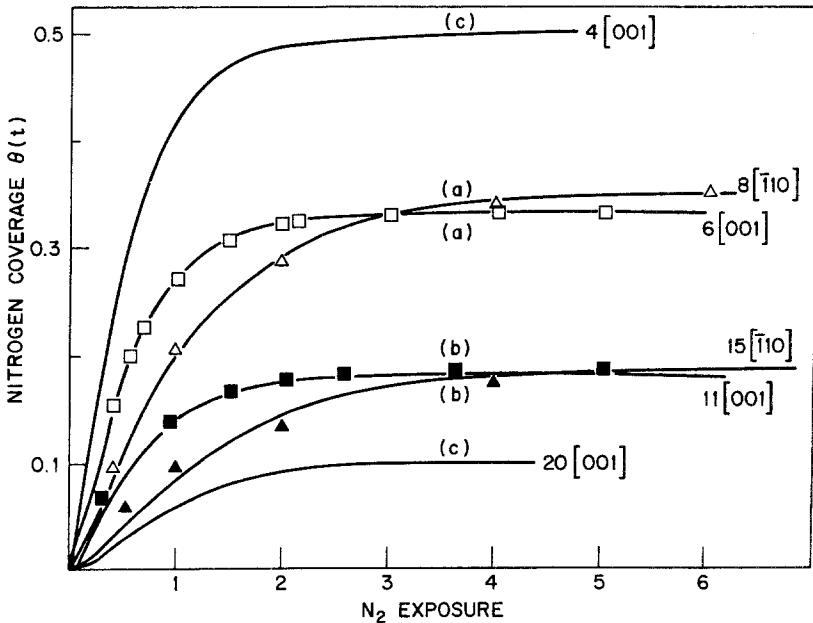


Fig. 2. Nitrogen coverage as a function of nitrogen exposure. The horizontal axis is in Langmuir scale $[L]$, where $1[L]$ corresponds to 100 sec at the experimental pressure of 10^{-8} torr. In the theoretical fitting (solid line), $1[L]$ corresponds to $50W \cdot t$. The squares and triangles indicate extrapolated experimental data in the oxygen-free limit. $6[001]$ indicates $m = 6$ and $[001]$ step direction. The results of $4[001]$ and $20[001]$ are predicted values (curves c). The two curves in case a (or b) correspond to approximately equal step density (see text).

in the case of the $[\bar{1}10]$ step direction. The $\sqrt{2}$ factor in Eq. (15) is due to the fact that the lattice spacing in the $[\bar{1}10]$ step direction is $\sqrt{2}$ times larger than that of $[001]$.

Since the comparison of two different step structures is by approximately equal step density only, we have in case (a) of Fig. 2 $m = 6$ in the $[001]$ step direction with step density $= 7.45 \times 10^6/\text{cm}$ (9.46°) and $m = 8$ in the $[\bar{1}10]$ step direction with step density $= 7.89 \times 10^6/\text{cm}$ (10°).

The probability functions $F_{[001]}(t)$ and $F_{[\bar{1}10]}(t)$ obtained from Eq. (13) are functions of the dimensionless product Wt . It is interesting to note that $F_{[001]}(t) \approx F_{[\bar{1}10]}(2t)$. That is, for approximately equal step density, nitrogen molecules arrive at the $[\bar{1}10]$ step only about half as fast as they arrive at the $[001]$ site. In addition to this, we have the relation $C_{[001]} = 2 \cdot C_{[\bar{1}10]}$. Consequently, the occupation functions are such that $\theta_{[\bar{1}10]}(t) \approx \theta_{[001]}(2t)$. The result is that during the short time period of nitrogen exposure, the coverage function in the $[\bar{1}10]$ direction grows approximately half as fast as that in the $[001]$ direction. The saturation coverages are $\Theta_{[001]} = 1/3$ and $\Theta_{[\bar{1}10]} = 1/2\sqrt{2}$, respectively.

Similarly, in case (b) of Fig. 2, we have $m = 11$ in the $[001]$ direction with step density $= 4.06 \times 10^6/\text{cm}$ (5.19°) and $m = 15$ in the $[\bar{1}10]$ direction with step density $= 4.21 \times 10^6/\text{cm}$ (5.38°). (Note that in the paper by Besocke *et al.*, $m = 12$ and $m = 16$ are used, respectively, to arrive at similar step densities.) The behavior of coverage functions is similar to case (a), with saturation coverage $\Theta_{[001]} = 2/11$ and $\Theta_{[\bar{1}10]} = 4/15\sqrt{2}$, respectively.

In case (c) of Fig. 2, we have predicted the coverage functions for $m = 4$ and $m = 20$ in the $[001]$ step direction.

The value of the jumping rate W obtained in Eq. (9) can be used to evaluate the diffusion constant of nitrogen molecules on $W(110)$ at room temperature. Since the nearest-neighbor distance $a = 2.238 \text{ \AA}$ (see Fig. 1), the diffusion constant is given by

$$D_{N_2} = a^2 \cdot W = 2.5 \times 10^{-16} \text{ cm}^2/\text{sec} \quad (16)$$

Comparing this with the diffusion constant of chemisorbed nitrogen atoms which has the value⁽¹⁶⁾

$$D_N = 7 \times 10^{-18} \text{ cm}^2/\text{sec}$$

we find that nitrogen molecules are approximately 36 times more mobile than chemisorbed atoms. Because the value of the jumping rate W is very small, we conclude that nitrogen molecules are weakly physisorbed.

6. CONCLUSIONS

We present a CTRW theory that is appropriate for dissociation or chemical reactions which are associated with active sites on the surfaces. In

particular, a kinetic model for nitrogen dissociation on step corner sites is used to illustrate the theory. It is found to be in good agreement with the extrapolated experimental data of nitrogen exposure.

The occupation equation of step corner sites [Eq. (1)] so proposed presents a new theory for indirect chemisorption. Step structures of a $W(110)$ surface are all capable of dissociating nitrogen molecules because they act as hard barriers and additional attraction centers to halt nitrogen molecules which are already weakly physisorbed on the terrace. While the ability of step corner sites to dissociate N_2 molecules is independent of the direction of step structures, the carrying character of the terraces depends upon lattice orientation as does the dissociation rate.

The probability of a random walker being found on a periodic array of step sites is solved exactly.

The occupation functions for two different step directions, namely, $[001]$ and $[\bar{1}10]$, with almost equal step densities, exhibit $\theta_{[001]}(t) \approx \theta_{[\bar{1}10]}(2t)$ behavior. This is explained by the dissociation rate and the probability function $F(t)$ as discussed in Section 4.

The mobility of nitrogen molecules is very small. This is in accordance with previous observations that nitrogen molecules are in precursor state on the $W(110)$ terrace. Due to this, the step corner structures act effectively as dissociation centers. On this terraced structure, we not only have an example of a random walk with periodically placed traps but we also have a structure with accurately measured distances. Hence an experiment that yields hopping rates allows us to determine surface diffusion constants in a manner somewhat simpler than that exploited in field emission microscopy.

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