LBL-28043
Preprint

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Submitted to Surface Science

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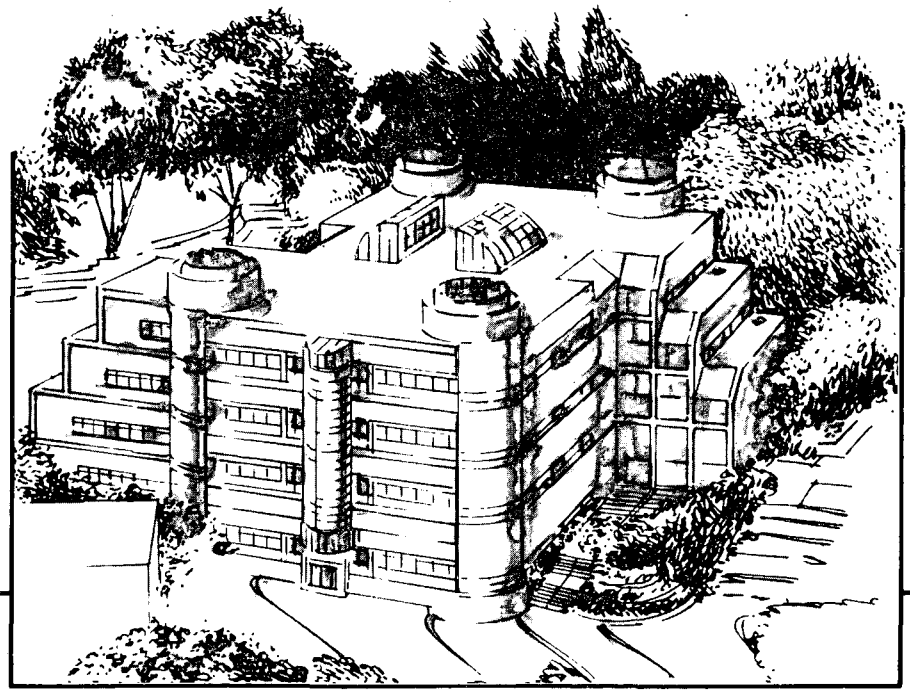
December 1989



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Prepared for the U.S. Department of Energy under Contract DE-AC03-76SF00098

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LBL-28043

KINETIC MODEL FOR COOPERATIVE DISSOCIATIVE CHEMISORPTION AND CATALYTIC ACTIVITY VIA SURFACE RESTRUCTURING

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"This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Science Division, of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098. The Fritz Haber Research Center is supported by the MINERVA Gesselschaft".

Abstract

A kinetic model for catalytic reactions involving metal surface restructuring is proposed and discussed. The model is an extension of the equilibrium model for cooperative dissociative chemisorption [I. Oppenheim and R.D. Levine, Chem. Phys. Letters 155, 168 (1989)]. The model provides a possible explanation as to: (a) why strong binding sites (e.g. those at high surface roughness) can also exhibit a high turnover rate resulting in efficient catalytic activity, (b) why bond breaking occurs preferentially over a narrow temperature range and, (c) why this range is lower for more open surfaces.

All these and other conclusions derive from the central result of the model that dissociative chemisorption of the physisorbed molecules is a cooperative process. It must, however, be emphasized that this behavior is due to the cooperative rearrangement of the substrate metal atoms upon the chemisorptive dissociation of the adsorbate and not to the weaker forces that may operate among the adsorbates.

The model is a kinetic one and depends on input from experiment. In particular, we take two general results as given. One is the well documented [G.A. Somorjai and M.A. Van Hove, Cat. Letters 1, 433 (1988)] restructuring of the surface upon bond breaking. The other, is that upon a bare, defect free, smooth surface, the probability for dissociative chemisorption of an isolated physisorbed molecule, is low, [B. Poelsema and G. Comsa, "Scattering of Thermal Energy Atoms", pg. 90 Springer Verlag (1989).]

1. Introduction

There is a great deal of experimental evidence from modern surface science studies to indicate that adsorbed atoms on transition metals are held with higher binding energy at more open surface sites with lower packing density, at atomic height steps and at kinks for example. This is shown for adsorbed hydrogen on the flat platinum (111) and the stepped and kinked Pt surfaces (Figure 1a) by temperature programmed thermal desorption (Figure 1b) where the temperature at which the maximum rate of desorption is obtained increases as (111) < steps < kinks [1]. Catalytic reaction studies indicate that these high binding energy sites also have superior catalytic activity for reactions that involve H-H, C-H or C-C bond breaking [2]. For example reactive scattering studies using mixed H_2 and D_2 molecular beams show that the H_2/D_2 exchange probability is about 90% at an atomic step under appropriate reaction conditions [3] while it is at least three orders of magnitude lower on the flat Pt(111) surface that is largely free of defect sites [4].

Another well recognized finding that comes from surface studies is that upon heating, bond breaking occurs in a narrow temperature range. X-ray photoelectron spectroscopy studies revealed that dinitrogen dissociates on the iron surfaces in the 125-130K temperature range thus going from a physisorbed molecular to a chemisorbed atomic state by forming strong Fe-N bonds [5]. Figure 2 shows the sequential dehydrogenation of alkenes as the temperature is increased [6]. Hydrogen evolves from the chemisorbed organic molecules in well-defined temperature ranges leaving behind partially dehydrogenated fragments. The temperature of chemical bond breaking is characteristic of the adsorbate-substrate system.

Lastly, it is well-documented by experiments that the bond breaking of adsorbed molecules shift to lower temperatures on rough, more open surfaces.

For example, [7] ethylene looses its first hydrogen atoms at 280 K on the flat Ni(111) crystal face. On a stepped nickel surface, however, the onset temperature range of C_2H_4 dehydrogenation is 150 K.

We consider a simple kinetic model which addresses these experimental findings. The three questions [8] of surface catalytic activity identified during studies of transition metals are: (a) why is there higher activity at rougher, (that is, more open) surfaces, (b) why does bond breaking occur over a narrow temperature range and, (c) why is this temperature range lower for more strongly binding sites. An equilibrium model providing a possible answer to the nature of the narrow temperature range has recently been provided [9]. The model did not, however, address the question of high turnover rate on rough surfaces which is essential for efficient catalytic activity. We do so here, by proposing a kinetic scheme whose equilibrium (that is, steady state) solution is the one previously [9] discussed. It is a direct implication of the mechanism discussed here and earlier [9] that efficient dissociative chemisorption on transition metal surfaces is a cooperative process. We show that this cooperative behavior makes it possible to have both tight binding to the surface <u>and</u> a high desorption rate, provided one operates at the optimal temperature range for surface bond breaking.

The recent work [10,11] on the experimental and theoretical correlation between surface restructuring and roughness (=1/packing density) of metals enables us to also address our third question: why does catalytic chemistry occur at lower temperatures at more open surface sites.

The model we consider is very highly idealized. It is not meant to reproduce any particular experimental system. Rather, our intention is to identify a set of minimal physical assumptions that can account for the common, most prominent features, of a large class of catalytic processes that occur on metal surfaces.

The model to be presented is a kinetic scheme, where the rates of adsorption and desorption of homonuclear diatomic molecules are explicitly taken into account. We shall furthermore distinguish between desorption of the original molecule and the desorption of a "reacted" molecule. Only the simplest kind of "reaction" will be allowed, namely exchange of atoms, e.g. $H_2+D_2 \rightarrow 2HD$ [3,4]. In our schematic model we allow only one type of diatomic molecule. Reaction is said to occur when the two atoms bound in the desorbed diatomic molecule formed on the surface due to dissociation of two distinct diatomics. This we shall call "non-geminate" recombination.

To make the model analytically soluble we take the "surface" to be one dimensional. This is not an inherent limitation of the work. More realistic two dimensional treatments are possible using either the "quasichemical" approximation [12] to generate analytical results or via Monte Carlo numerical simulations. Such computations can also remove the restriction, made in the present model, of no diffusion of the physisorbed molecules.

a) Description of the Model Assumptions

There are two essential assumptions of the proposed model. One is that there is adsorbate-induced restructuring of the clean surface concomitant with bond breaking [8,9,13]. Ours is not a dynamical theory so that we cannot address the question of does bond breaking drive the surface restructuring or vice versa. We do, however, make an assumption about this process for which we lack any extensive experimental evidence*. The second assumption is motivated by the following physical consideration: The reconstruction of the surface which is concomitant with bond breaking requires the displacement of the surface metal atoms from their equilibrium positions for the bare surface.

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*For the available results see the references discussed in [9] and also [13].

Suppose now we have just one single physisorbed molecule on an otherwise bare, defect-free surface. The dissociative chemisorption of this isolated molecule will be accompanied by a very local restructuring of the surface. The surface atoms further away will still not restructure and hence the dissociation of a strictly isolated molecule will cause local strain which can only be alleviated either by further restructuring or by recombinative desorption of the isolated chemisorbed molecule. A further restructuring will be possible when a second molecule dissociates on a surface site near the first one. The strain will be further removed when a third molecule dissociates nearby, etc. The result is that for a surface with a finite coverage of physisorbed molecules, once reconstruction starts it can proceed to completion. On the other hand, we are not necessarily discussing a saturation coverage of the surface. It is known from the study of clean surfaces that the reconstruction of the bulk structure can be several layers deep. Hence, a strain on a surface atom can be manifested several sites away, so that different molecules need not chemisorb at adjacent sites for the cooperative behavior to be manifested.

It would clearly be desirable to have additional experimental (or computational) support for our physical considerations*. Unfortunately, this is not going to be easy. The experimental work is complicated by the inevitable presence of surface defects whereas our assumption has to do with the dissociation on an ideal defect-free bare surface. The computational work is complicated by the need to consider a fairly large cluster of atoms so that local strain and its relaxation by the dissociation of additional molecules can be evident.

We now explicitly state the second assumption of the model as it has a key role in generating the implications: We assume that <u>a single molecule on an otherwise bare surface has a low probability for dissociation</u>. The probability is low (by a factor γ, $\gamma \ll 1$) as compared to that for a molecule to

dissociate when there are nearby dissociated molecule on the surface, at the same temperature for both cases. It is necessary to state that the model does not include any direct lateral forces between the absorbed molecules. The cooperative behavior that we are predicting is due to the forces between the surface atoms and the changes in these forces when a molecule dissociates and thereby changes the chemical environment at the surface. There are grounds (e.g. [14]) for assuming that the adsorbate-adsorbate interaction energies are much weaker then the adsorbate-substrate interaction energies which drive the restructuring. It is intended, however, to further refine the model by including, in future work, the effects of direct adsorbate-adsorbate coupling.

b) Equilibrium Dissociative Chemisorption

The mathematical model corresponds to a linear array of sites. Each site can be either bare (and by bare we include a site on which a molecule is physisorbed) or restructured due to the dissociative chemisorption of a diatomic molecule on that site. The first process we consider is the dissociation of a single molecule on an otherwise bare surface leading to local reconstruction. In a very symbolic fashion we can write this as:

$$\begin{array}{c} A_2 \\ + \\ ..S\text{-}S\text{-}S\text{-}S\text{-}S\text{-}S.. \end{array} \rightleftharpoons \begin{array}{c} A\ \ A \\ 1\ \ 1 \\ ..S\text{-}S\text{-}S'\text{-}S'\text{-}S\text{-}S\text{-}S.. \end{array} \qquad \text{(I)}$$

where S and S' are surface atoms without and with modified forces. The other process we explicitly introduce is the dissociation of A_2 in the vicinity of an already dissociated molecule

$$\begin{array}{c} A\ \ A \\ 1\ \ 1\ \ +A_2 \\ ..S\text{-}S'\text{-}S'\text{-}S\text{-}S\text{-}S.. \end{array} \rightleftharpoons \begin{array}{c} A\ \ A\ \ A\ \ A \\ 1\ \ 1\ \ 1\ \ 1 \\ ...\ S\text{-}S'\text{-}S'\text{-}S'\text{-}S'\text{-}S.. \end{array} \qquad \text{(II)}$$

*For some available evidence see [13].

The equilibrium constants for these two reactions are assigned the values γs and s respectively. s will vary with temperature in the usual fashion

$$s = \exp(-\Delta G_2^0/RT) \tag{1}$$

Here ΔG_2^0 is the standard free energy change for the dissociative chemisorption of A_2 on a restructured surface

$$\Delta G_2^0 = 2\mu^0_{A:S'} - \mu^0_{A_2:S'} \tag{2}$$

The subscripts on the chemical potentials indicate that the dissociation is on a restructured surface. Similarly

$$\gamma s = \exp(-\Delta G_1^0/RT) \tag{3}$$

with

$$\Delta G_1^0 = 2\mu^0_{A:S'} - \mu^0_{A_2:S} \tag{4}$$

It follows from (1)-(4) that

$$\gamma = \exp(-\Delta G_3^0/RT) \tag{5}$$

where $$\Delta G_3^0 = \mu_{A_2:S'} - \mu^0_{A_2:S} \tag{6}$$

is the strain free energy of the surface when it restructures without concomitant chemisorption [9]. ΔG_3^0 will usually be large (compared to RT) and positive so that $\gamma \ll 1$. In physical terms we can say that $K_1(\equiv\gamma s)$ is small compared to $K_2(\equiv s)$ since the rate of the reverse reaction (recombinative desorption) is much higher as this will alleviate the surface strain energy.

In our idealized model, the local strain caused by the surface restructuring concomitant with the dissociation of an isolated molecule is alleviated by the dissociation of one near neighbor. A third, fourth etc. A_2 molecules which dissociates next to a pair of dissociated molecules will have s as the value of the equilibrium constant. If neighboring molecules are not available the recombinative desorption rate of the isolated species will be large because of the local strain. Rather than discussing local strain we

can also state our assumption as : the free energy of dissociative chemisorption of an isolated molecule, i.e. $-RT\,\ell n\,(\gamma s)$ is less negative (since $-RT\,\ell n\,\gamma > 0$) then the free energy, $-RT\,\ell ns$, of dissociative chemisorption of a finitely covered surface [9]. We reiterate that this is not due to any direct adsorbate-adsorbate interaction. If such are important - the model needs to be modified so as to include them, and we intend, in future work, to do so. The temperature To for which $s = 1$ will be shown to define the optimal range of activation. Since

$$\partial \ell ns\ s/\partial(1/T) = -\Delta H^{o}/R,$$

surfaces with a higher heat of desorption will, other things being equal, have a lower temperature where $s = 1$.

c) Summary

When a diatomic molecule dissociates on a surface site, the two adjacent sites can be either bare or occupied. If both are bare, the equilibrium constant is γs. If one or both are occupied, the equilibrium constant is s. The free energy and hence the state of the system is thus specified by two numbers: n, the total number of chemisorbed molecules and m the number of chemisorbed molecules that follow a bare surface site. The value of m is thus the number of disjoint regions covered continuously by dissociated molecules. m is necessarily small when n is either small or comparable to the number, N, of surface sites. The less expected result [9], is that $\langle m \rangle$ will have a maximal value, large compared to unity, when $s \simeq 1$ provided that γ is small.

2. Kinetic Model for Cooperative Dissociative Chemisorption

The first kinetic scheme we consider is meant to exclude chemical reactions. We consider a linear set of N sites with n chemisorbed molecules. Of these n, m molecules are placed so as to follow a bare surface site. Of

course, $m < n$. Note that N is not the number of surface atoms since dissociative chemisorption requires at least two surface atoms per A_2 molecule.N is the largest number of A_2 molecules that can be chemisorbed on the surface. Let k_{-0}/k_0 be the rate constants for chemisorption/desorption of a molecule without any near neighbors. This corresponds to the change of state $(n-1, m-1) \rightleftharpoons (n, m)$ since an isolated bare site is occupied/created. Let k_{-1}/k_1 be the rate constants for chemisorption/desorption of a molecule which has a left or right near neighbor. This corresponds to the change of state $(n-1, m) \rightleftharpoons (n,m)$ since m is unchanged in such a process.

In this section we exclude the possibility of non-geminate recombination by not allowing molecules to desorb when they have near neighbors on both sides. This will, however, be allowed in the next section.

Consider many replicas of the system so that there is a distribution in the values of m and n. Let X(n,m) be the number of systems in the state (n,m). Then

$$\begin{aligned} dX(n,m)/dt = & -(k_0+k_1)X(n,m) \\ & +k_{-0}\, X(n-1, m-1) \\ & +k_{-1}\, X(n-1, m) \end{aligned} \tag{7}$$

The first term in (7) is the loss term due to geminate desorption. The next two terms are due to chemisorption with and without new surface reconstruction respectively.

We define a 'configuration' of a surface as any particular arrangement of the n A_2 molecules on the N surface sites. When $n < N$, there can be more than one configureation for a given n and N. Configurations are counted in the appendix. Here we simply define g(n,m) as the number of possible configurations of the system for a given n and m [15]. It is clear that

$$\sum_m g(n,m) = \binom{N}{n} \tag{8}$$

where the sum is the number of ways n molecules can be placed on N sites.

Another result that is useful below is the mean value of m for a completely random arrangement of n molecules on the N possible lattice sites

$$\langle m\rangle_{random} = \sum_m mg(n,m)/\sum_m g(n,m)$$

$$= n(N-n)/N \qquad (9)$$

To prove (9), note that the probability of having the i'th site vacant is (N-n)/N and that the probability of having the i+1 st site occupied is n/N. The probability of a particular site to be unoccupied and followed by a site that is occupied is $n(N-n)/N^2$. There are N possible sites, QED. The explicit form for g(n,m) is discussed in an appendix.

It follows from detailed balance [16] that

$$k_{-0}/k_0 = g(n,m)s/g(n-1,\ m-1) \qquad (10.0)$$

and

$$k_{-1}/k_1 = g(n,m)s/g(n-1,\ m) \qquad (10.1)$$

It should be emphasized that the ratios should not be just γs and s respectively. The latter are the equilibrium constants per site while the rate constants as defined in our kinetic scheme (7), are per state of the chain.

Using (10.0) and (10.1) in the kinetic scheme (7), one readily verifies that the steady state solution is

$$X(m,n)1_{eq} = Xg(m,n)\gamma^m s^n/Q \qquad (11)$$

where X is the total number and Q is the partition function

$$Q = \sum_{nm}\sum g(m,n)\gamma^m s^n \qquad (12)$$

The mean numbers, $\langle n\rangle$, of molecules on the surface and $\langle m\rangle$, of regions of neighboring molecules have been evaluated in [9] using the transfer matrix method [12,15,17]. In the limit $N\gamma^{1/2} \gg 1$ the result is

$$\langle n\rangle \equiv \sum_{nm}\sum n\ X\ (n,m)/X \qquad (13)$$

$$= N\left(1 + \frac{s-1+2\gamma}{[(1-s)^2+4\gamma s]^{1/2}}\right)1/2$$

$\langle n\rangle = N/2$ at $s=1$ and the transition in the value of $\langle n\rangle$ from 0 to 1 occurs in the narrow temperature range $1-2\gamma^{1/2}<s<1+2\gamma^{1/2}$, cf Figure 1 of [9]. $\langle m\rangle$ is found to have a low value outside the indicated range, $\langle m\rangle = N\gamma s/[(1-s)^2+4\gamma s]^{1/2}$, (14) reaching its maximal value of $N\gamma^{1/2}/2$ at $s = 1$. Of particular interest to us is the mean number of dissociated (i.e., chemisorbed) molecules per aggregate

$$\langle n\rangle/\langle m\rangle = (2\gamma s)^{-1}\{[(1-s)^2+4\gamma s]^{1/2}+s-1+2\gamma\} \qquad (15)$$

which is large ($=1+\gamma^{-1/2}$) compared to unity at $s=1$. This high value of $\langle n\rangle/\langle m\rangle$ at the temperature range where $s \simeq 1$ will be the key feature in explaining the high turnover rate for catalytic activity. The result $\langle m\rangle=N\gamma^{1/2}/2$ at $s=1$ should be compared with $\langle m\rangle_{random}=N/4$ predicted by a purely random placing of molecules on the N sites, (cf equation (9) with $\langle n\rangle=N/2$ at $s=1$). The low value of γ clearly favors aggregation of molecules on the surface resulting in larger aggregates and in fewer molecules, (i.e. lower $\langle m\rangle$), being adjacent to a bare surface site. Similarly $\langle n\rangle/\langle m\rangle_{random} =2$ as compared to $1+\gamma^{-1/2}$ for our cooperative model at $s=1$.

The higher value of number of molecules per aggregate, $\langle n\rangle/\langle m\rangle$, when $\gamma<<1$, is the key technical result which will be needed to explain the enhanced catalytic activity.

3) Kinetic Model Including Reactions

We now generalise the model of the previous section by allowing also processes leading to the changes of state $(n,m) = (n-1, m+1)$. Such changes conrrespond to the physical process

```
...A  A  A  A        ...A      A...
  1  1  1  1   ⇌      1        1      +A2
 -S'-S'-S'-S'        -S'-S-S-S'-
```

This is the only possible route whereby non-geminate recombination-desorption

can take place. It is of course the case that geminate recombination can also proceed in this manner. Since for real, two dimensional, surfaces, geminate recombination will be statistically unfavored as compared to non-geminate pairs, we shall refer to the rate of this desorption as the rate of catalytic activity.

The kinetic scheme (7) needs now to be augmented by allowing for the $(n,m) \rightleftharpoons (n-1, m+1)$ changes:

$$dX(m,n)/dt = (7) \; -k_2 X(n,m) + k_{-2} X(n-1, m+1) \qquad (16)$$

The notation k_2/k_{-2} refers to the mechanism where each dissociating/desorbing molecule has two near neighbors. k_2 is the rate constant of interest as it determines the rate of molecules desorbing after possibly non-geminate recombination. k_2 is, in our terminology, the rate constant for catalytic activity.

The central question is whether the catalytic reaction rate, $k_2X(n,m)$, be high even though the atoms are strongly chemisorbed on the surface.

From detailed balance, as in (10.0) and (10.1)

$$k_{-2}/k_2 = g(n,m)s/g(n-1,m+1) \qquad (10.2)$$

The new point in (10.2) is that m is increasing while n is decreasing. To see the quantitative implication we need an explicit form for g(n,m). That is not quite simple. The quantitative result is however clear: the process $(n,m) \rightarrow (n-1,m+1)$ creates one more disjoint region of dissociated molecules favored, by a factor of roughly $(n-m)/m$, as compared to desorption of a molecule isolated on a surface, (i.e. the process $(n,m) \rightarrow (n-1,m-1)$ or a molecule at the end of a region {the process $(n,m) \rightarrow (n-1,m)$}. The quantitative evaluation of the ratio $g(n,m)/g(n-1,m-1)$ is carried out in an appendix. The implications of the model are discussed in the next section.

4. Discussion

(a) The Physical Picture

The model here proposed provides the following physical picture: The surface strain created by the dissociation of an isolated molecule can be lowered by the dissociation of a neighboring second molecule. This favors the aggregation of dissociated molecules on the surface. The metal surface restructuring induced by dissociative chemisorption is then a cooperative effect and thus [9] has a sharp temperature dependence.

The non-geminate recombination of two atoms leading to desorption of a rearranged molecule requires that two molecules dissociate on neighboring sites as in the absence of surface diffusion (of the strongly bound atoms) an isolated chemisorbed molecule cannot lead to non-geminate recombination. Neither can molecules chemisorbed at the two edges of the aggregate. The formation of aggregates favors thus non-geminate recombination.

For a more realistic, two dimensional, model of the surface, aggregation implies a preference for non-geminate recombination given by the (mean) area to circumference ratio. It must be emphasized that the aggregation we are discussing is not due to interactions among the adsorbates but results from the cooperative nature of dissociative chemisorption-induced surface restructuring. The increase in catalytic activity that we demonstrate is thus a statistical (or thermodynamic) effect. Under optimal operating conditions (that is, in the temperature range where $s \simeq 1$) it becomes more favorable for a molecule to recombine/desorb from within an aggregate of dissociated molecules.

The model we employ and, in particular, the formation of a large number ($\langle m \rangle$, cf equation (14)) of aggregates for $s \simeq 1$, is based on one critical assumption: that on an ideal, defect-free, bare surface, the dissociative

chemisorption of a physisorbed molecule or of a molecule impinging on the surface with thermal kinetic energy occurs with a low probability. By low we mean small as compared to the probability at finite coverage (i.e. on a locally strain-free restructured surface). It would clearly be useful to have additional experimental and/or computational support for this assumption.

(b) Quantitative Implications

The three questions we addressed in this paper can be conveniently made into one by taking as the variable not the temperature T but s. s is the value of the equilibrium constant for dissociative chemisorption on a restructured surface. It is the temperature dependence of s that is measured by the heat of dissociative chemisorption (or of recombinative desorption) for a finitely covered surface.

γ is the equilibrium constant (per surface site) between the bare surface and its restructured form. γ depends on the temperature as in equation (6). Since in our physical considerations the strain free energy is large compared to RT in the temperature range of interest, we take $\gamma \ll 1$ and, in the zeroth approximation to be independent of the temperature.

The first result of our model is the ratio k_2/k_{-2} of rate constants for recombination/dissociation of molecules with near neighbors, cf the kinetic scheme (16). We compute this ratio vs. s, Figure 3, using equations (10.2), (A.1), (13) and (14). It is clearly evident that there is an enhanced rate of recombinative desorption.

The onset of the temperature range for catalytic activity is where there is a fairly rapid onset of dissociative adsorption and of the number, $\langle m \rangle$ of islands of dissociated molecules, Figure 4. This demonstrates that when $\gamma \ll 1$ so that cooperative behavior is necessary, the catalytic activation occurs over a narrower temperature range then when $\gamma \simeq 1$. Finally, the range (17)

when $s \simeq 1$, will occur at a lower temperature, the more exothermic is the dissociation process on the surface. This is our third point.

In future publications we intend to present the results of solving the kinetic scheme (16) using realistic values for the parameters s and gamma so as to show both temporal and thermal dependences.

It is our hope that improvement of this model permits understanding the behavior of real systems. These may include the physisorption to dissociative chemisorption transition of dinitrogen on iron surfaces, the sequential decomposition of hydrocarbons adsorbed on transition metals as a function of temperature. We shall attempt to elucidate why ethylene decomposes below 150K on a stepped rough nickel crystal surface while only around 230K on a (111) orientation flat surface. We hope to predict the coverage dependence of the dissociative adsorption probability that is so well demonstrated in reference 4. Perhaps, the unique chemical activity of bimetallic systems and oxide-metal interfaces could also be related to adsorbate induced restructuring.

Appendix: The Counting of Configurations

A configuration of the one dimensional model is a particular assignment of the n molecules to the N possible lattice sites. Since $N > n$, this can be done in more then one way. For our purpose, we need the number of configurations for a given number m where m is the number of unbroken succession of A_2 molecules on the (one dimensional) lattice. Our counting is fashioned after Ising [18] in his original work on the Ising model of ferromagnetism.

For a given N, n and m the division of A_2 molecules into the aggregates on the lattice is specified by choosing the m A_2 molecules which are left most in the aggregate (of course, an aggregate here can also be just one model). This can be done in $\binom{n}{m}$ ways. There are N-n empty lattice sites.

There are m such empty sites that immediately precede an occupied sites. The empty sites can then be chosen in $\binom{N-n}{m}$ ways. The total number of possible configurations is

$$g(n,m) = \binom{n}{m}\binom{N-n}{m} \qquad (A.1)$$

For the ratio k_{-2}/k_2, equation (10.2), which is of particular interest, we find

$$\frac{g(n,m)}{g(n-1,m+1)} = \frac{n(m+1)^2}{(N-n+1)(n-m)(n-m-1)} \to \gamma(1-\gamma^{1/2})^{-2} \simeq \gamma \ll 1 \quad N\to\infty \quad s=1 \qquad (A.2)$$

Here we replaced, in the $N\to\infty$ limit, the values of m and n by their means as given by equations (13) and (14).

It follows that $k_{-2} = \gamma k_2$ at s=1 or

$$k_{-2} \ll k_2, \; s=1. \qquad (A.3)$$

The catalytic rate, given by k_2 X (m,n), cf equation (16) is thus particularly high.

Similar computations give

$$k_{-0}/k_0 \to (1-\gamma^{1/2})^2, \; s=1, \; N\gamma\to\infty \qquad (A.4)$$

so that at s=1, k_{-0} and k_0 are comparable and

$$k_{-1}/k_1 \to 1 \quad , \; s=1, \; N\to\infty \qquad (A.5)$$

ACKNOWLEDGEMENT

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Science Division, of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098. The Fritz Haber Research Center is supported by the MINERVA Gesselschaft.

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FIGURE CAPTIONS

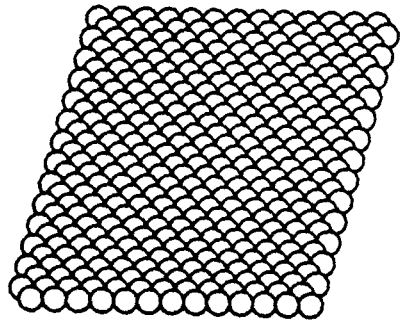
Figure 1a Models of the flat (111), stepped and kinked crystal faces of platinum.

Figure 1b Thermal desorption spectra from the flat (111), stepped and kinked crystal faces of platinum.

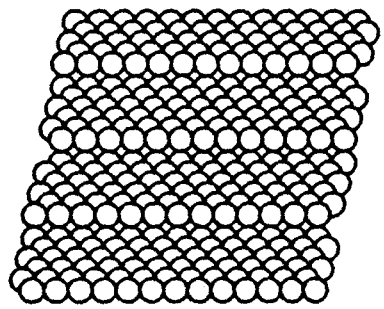
Figure 2 Thermally activated sequential decomposition of light alkenes chemisorbed on the Pt(111) crystal face.

Figure 3 The rate constant ratio $f=k_2/k_{-2}$ of rate constants for recombinative desorption/dissociation chemisorption of molecules with near neighbors vs. s, the equilibrium constant (K_2) for process (II) .$-RT\ln K_2$ is the free energy for dissociative chemisorption on a finitely covered surface i.e. without the strain caused by an initial local surface restructuring which is concomitant with the dissociation. The three plots are for three values of γ, $\gamma=0.1$, 0.01 and 0.0001 respectively. $-RT\ln\gamma$ is the strain free energy due to dissociation of an isolated molecule. Note the higher values of f for the lower values of γ.

Figure 4 The fraction $\langle n\rangle/N$ of surface sites covered by dissociated molecules and the number, $\langle m\rangle$, of 'islands' of dissociated molecules vs. s. Other details as in Figure 3. Note the steep rise in $\langle n\rangle$ and the high values of $\langle m\rangle$ near $s=1$ when γ is low.



fcc (111)



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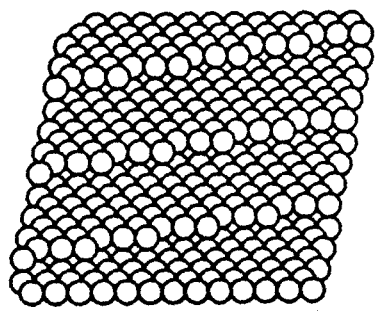

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Figure 1a

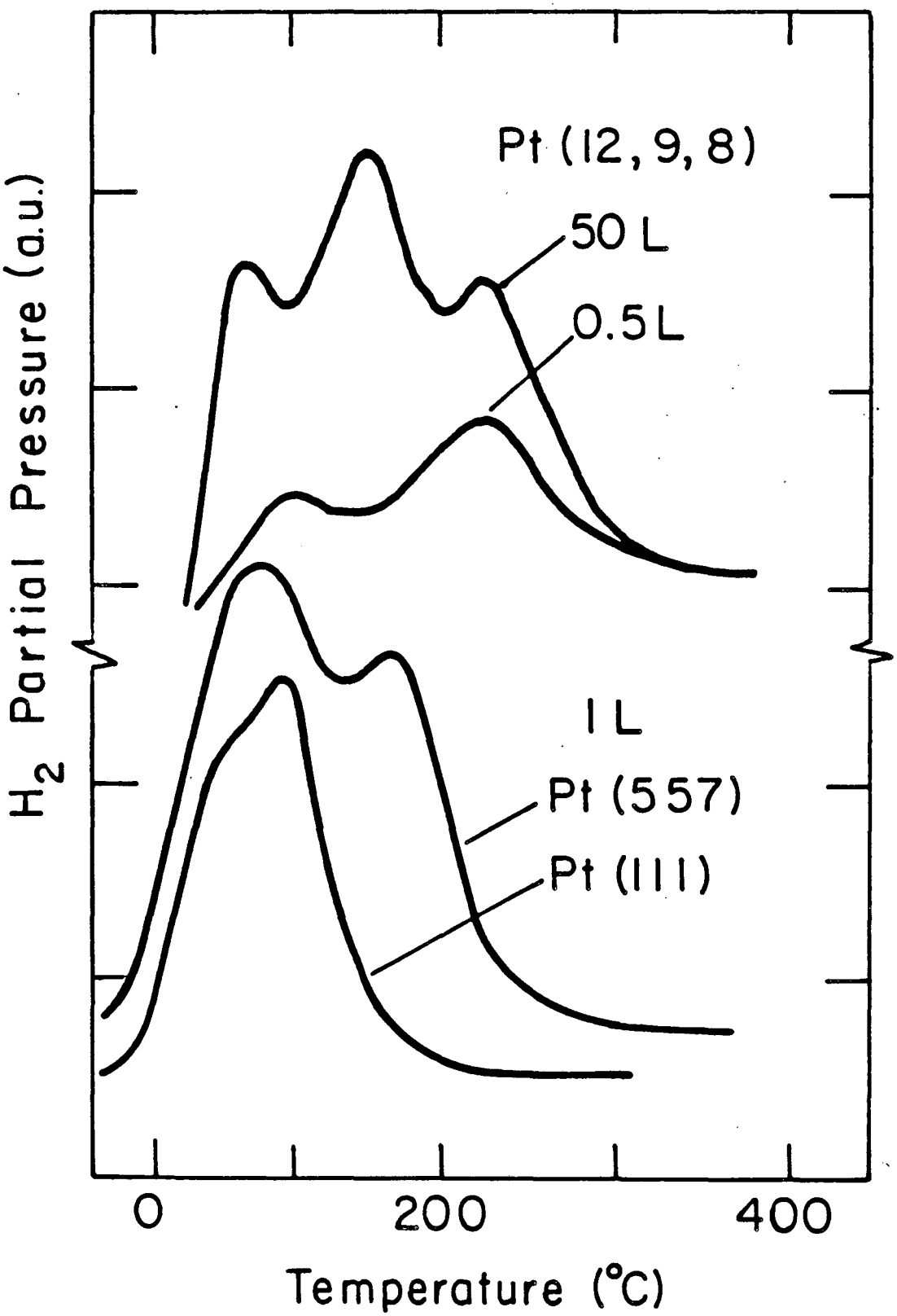


Figure 1b XBL 792-5816

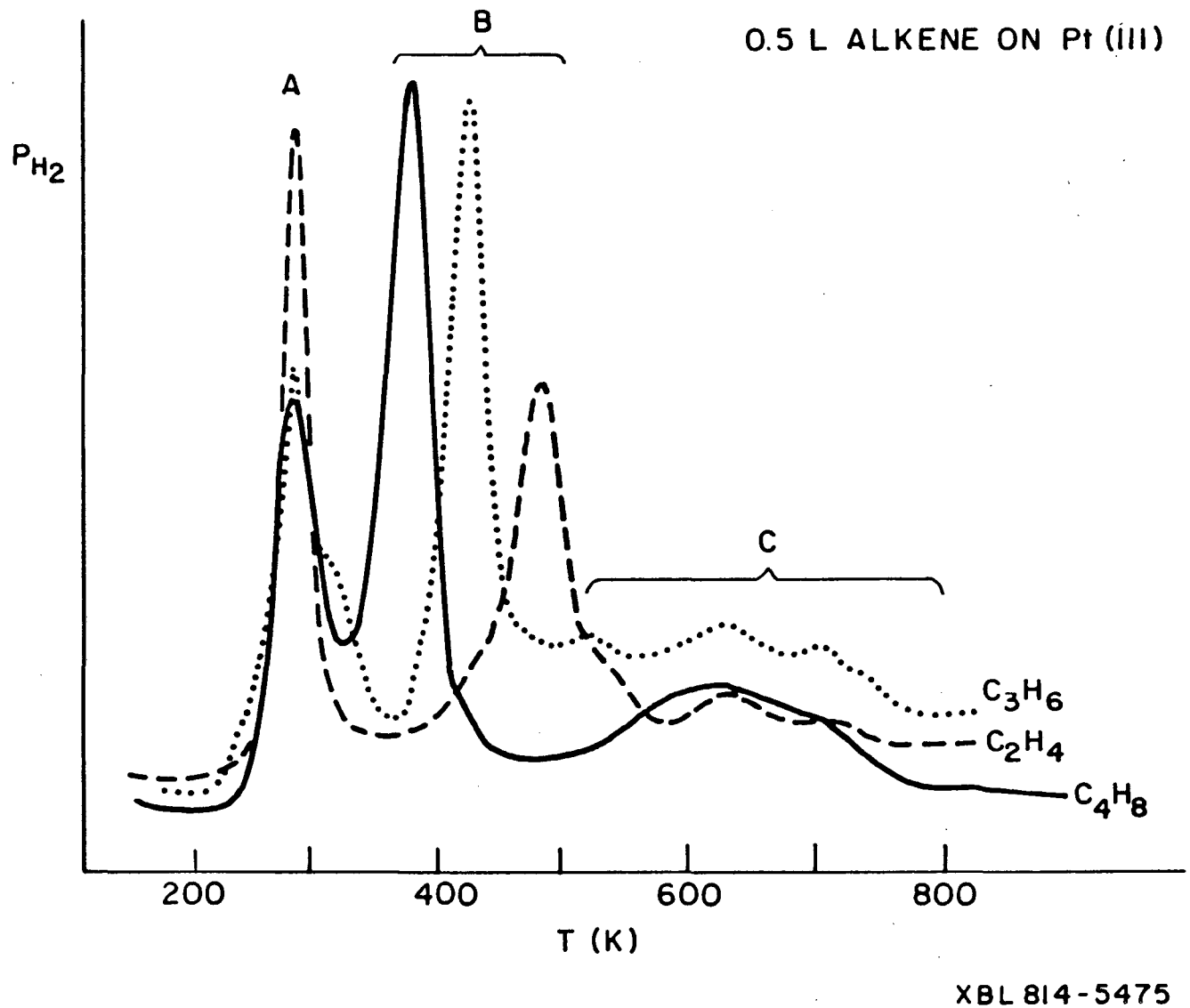
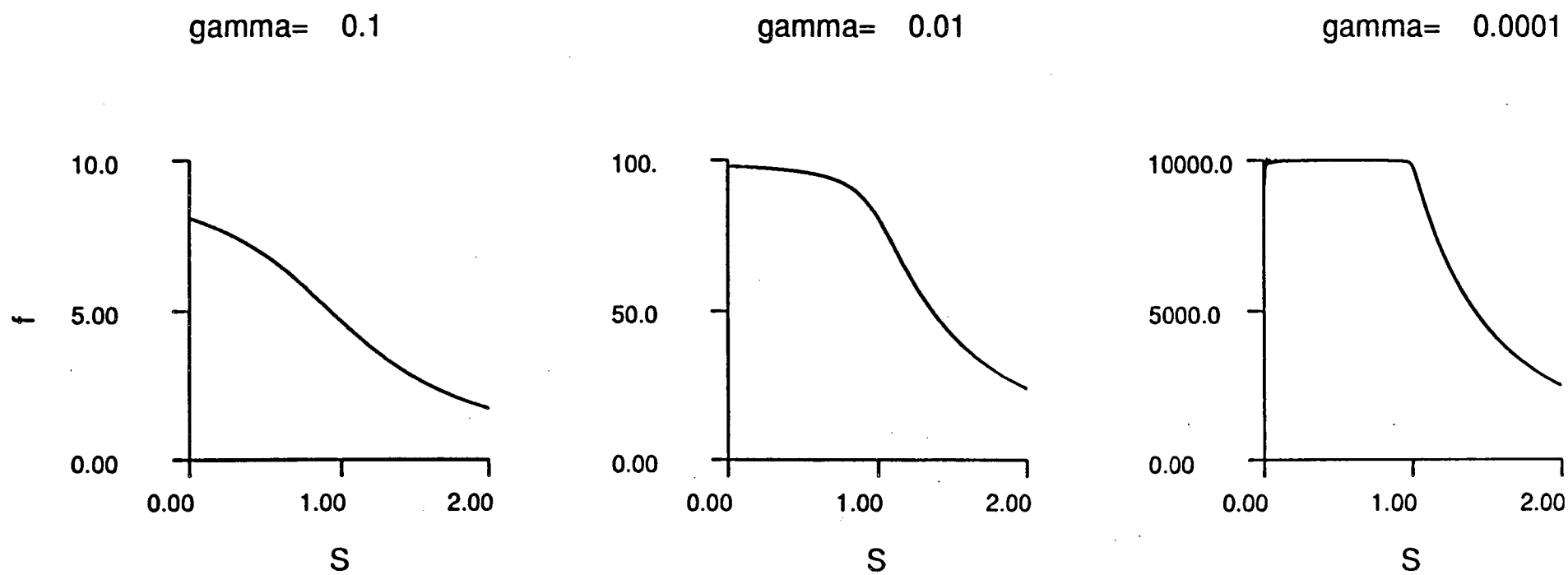

0.5 L ALKENE ON Pt (111)
A
B
C
P_{H_2}
C_3H_6
C_2H_4
C_4H_8
200
400
600
800
T (K)
XBL 814-5475

Figure 2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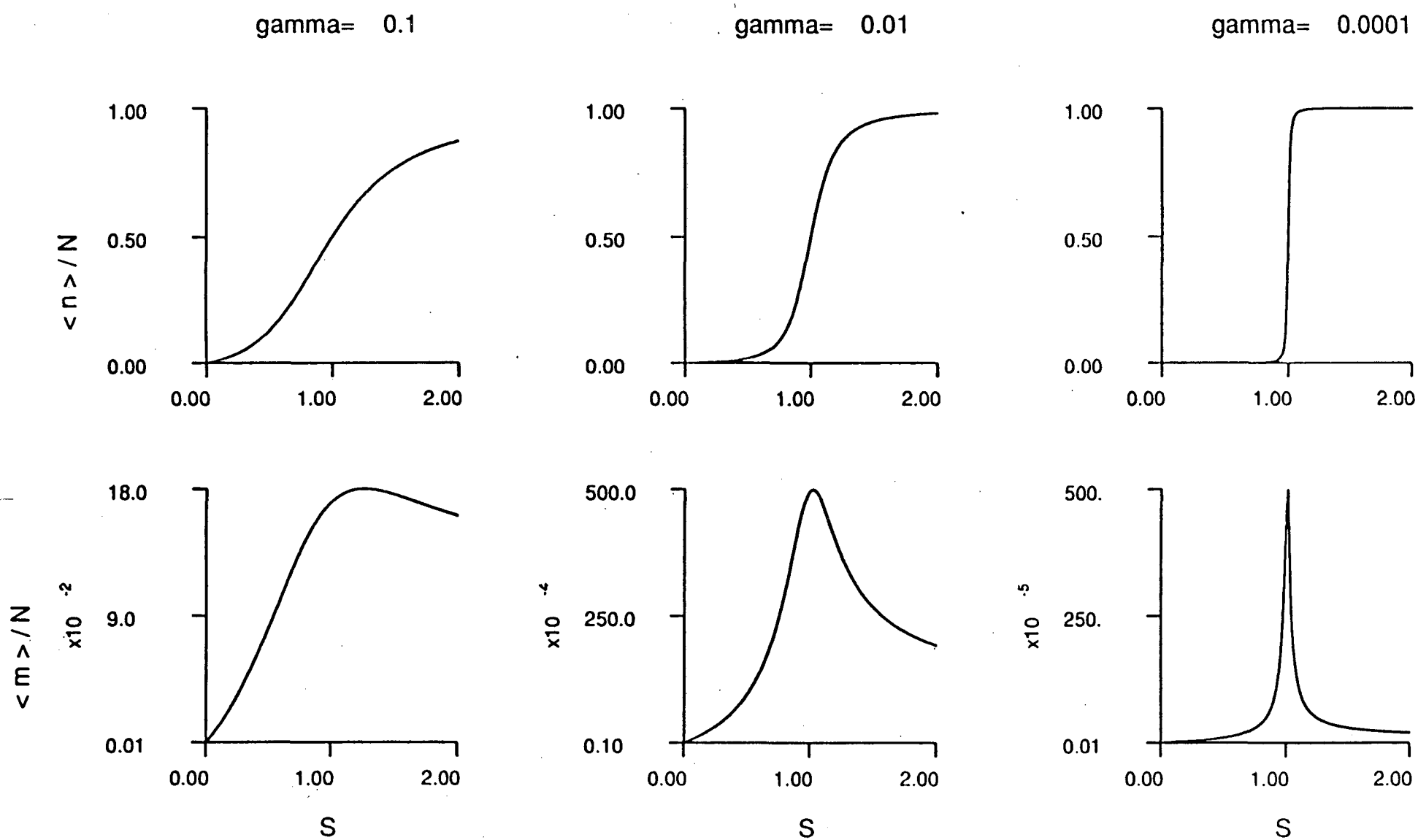
0.00
10000.0
5000.0
0.00
0.00
1.00
2.00
S

Figure 3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x10 -5
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0.50
0.00
18.0
9.0
0.01
500.0
250.0
0.10
500.
250.
0.00
1.00
2.00
S

Figure 4

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