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CH$_4$ dissociation on Ni(100): Comparison of a direct dynamical model to molecular beam experiments

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This paper makes an extensive comparison of a dynamical model for a mechanism of direct dissociation to the detailed molecular beam experiments of CH$_4$ dissociation on a Ni(100) surface reported in the previous paper. When a PES incorporating a “exit channel” barrier is used in the model and steric (multidimensional) aspects are included approximately via a “hole” approximation, excellent agreement is achieved between the model and experiments. This strengthens the qualitative mechanistic conclusions of Holmblad, Wambach, and Chorkendorff [J. Chem. Phys. 102, 8255 (1995)]. © 1995 American Institute of Physics.

I. INTRODUCTION

A mechanistic discussion of the dissociation of small alkanes on metal surfaces has been an extremely active (and controversial) area within surface science over the past two decades because of its importance in industrial catalysis. No system is perhaps more important in this regard than the dissociation of CH$_4$ on Ni(100) since this is the best single crystal model for the rate limiting step in the commercial process of steam reforming of natural gas. The previous paper, hereafter referred to as I, presents detailed molecular beam experiments for the dissociation of CH$_4$ on a Ni(100) surface. These experiments show a very strong dependence of the bare surface dissociation probability $S_0$ on CH$_4$ incident normal energy $E_n$ and CH$_4$ vibrational (i.e., nozzle) temperature $T_v$. Moderate, but still significant dependences of $S_0$ on isotope and surface temperature $T_s$ are also observed. All dependencies on the various experimental parameters are strongly coupled; e.g., the dependence on $T_v$ depends on $E_n$, the dependence on $E_n$ depends on $T_s$, the dependence on $T_s$ depends on both $E_n$ and $T_v$, etc.

The authors of Paper I argue that many of their results are qualitatively consistent with a direct dissociation mechanism on a potential energy surface (PES) with an “exit channel” barrier, i.e., principally along a C–H vibrational coordinate. They fitted the observed dependence of $S_0$ on $E_n$ and $T_v$ to empirical “$S$”-shaped excitation functions, one for each of the three lowest vibrational states of a quasidiatomic R–H molecule. Although this provides a very good fit to the data and a reasonable rationale for the strong dependence on both $E_n$ and $T_v$, the empirical $S$ excitation functions are not fully consistent with two dimensional dynamics since the energy separation between the $S$ functions is more than the vibrational energy $\omega_{\text{vib}}$.

Luntz and Harris$^2$ have previously discussed in some detail a dynamical model for a mechanism of direct alkan dissociation on transition metal surfaces. This model is based on solving for the direct dissociation dynamics quantum mechanically on a reasonable reduced dimensionality PES for a quasidiatomic R–H interacting with a dynamic metal surface. With a PES where the barrier was largely entrance channel dominated, reasonable qualitative agreement was obtained between the model and molecular beam experiments for the dissociation of CH$_4$ on Pt(111), as well as with a variety of other molecular beam and thermal experiments.$^2$

In this paper, the reduced dimensionality dynamical model is developed for a PES with an exit channel barrier. In addition, steric factors (multidimensionality) are accounted for statically via the so-called “hole” approximation.$^3$ The resulting model shows excellent agreement with the molecular beam experiments of Paper I, and easily rationalizes the large separation between the empirical $S$ functions utilized to fit the data.

II. DYNAMICAL MODEL

In the dynamical model of Luntz and Harris,$^2$ quantum dynamics on an assumed PES $V(Z,D,Y)$ describes a mechanism of direct dissociative chemisorption of a quasidiatomic R–H on a metal surface. $Z$, $D$, and $Y$ are the translational, vibrational, and a surface phonon (cube) coordinate, respectively. The dependence of the dissociation reaction coordinate on all three then rationalizes in a simple way the dependence of $S_0$ on $E_n$, $T_v$, and $T_s$ and a strong coupling between the experimental dependences.

In the original presentation of this model,$^2$ the importance of tunneling was emphasized by the authors. This has regrettably caused considerable confusion as to the essential aspect of the model, i.e., that it is a reduced dimensionality dynamical model for the mechanism of direct dissociation. Tunneling is in no way required by the mechanism nor for the model to be valid, and this has been pointed out briefly in subsequent discussions and applications of the model.$^5$ The dependence of the reaction dynamics on all three coordinates $Z$, $D$, and $Y$ occurs whether tunneling is important or not. The nuclear dynamics describing dissociation on the assumed PES is solved quantum mechanically so that if tunneling is important in the dynamics it is included automatically. However, the quantum solution of the dissociation dynamics in no way forces tunneling to be important. This is strictly a function of the assumed PES, e.g., the width of the barrier and the initial conditions, e.g., $E_n$. For the PES assumed here, tunneling is important in the reduced dimensionality approximation.
ality dynamical model under some initial conditions (low $E_n$ and $T_e$) and unimportant at others (high $E_n$ and $T_e$). While it is straightforward in the reduced dimensionality model to determine when tunneling is important, this is a considerably more subtle issue in full dimensionality dynamical models of dissociation (and hence in the experimental world). In this case, there is a wide distribution of barriers due to “steric” factors. A given incident energy can then be either above the barrier for some steric conditions (orientation, impact parameter, etc.) and below the barrier for other steric conditions. Since the dissociation probability also depends on the distribution of barriers, it is difficult to decide in a multidimensional world if tunneling is in fact dominant under many given experimental conditions. Since tunneling is not an essential aspect of the reduced dimensionality model used here, the role of tunneling is not discussed further in this paper. The relationship of this reduced dimensionality direct dynamical model to more traditional chemical theories, e.g., transition state theory, as well as a more detailed discussion of tunneling and the kinetic isotope effect will be presented elsewhere.\(^3\)

A. PES

The PES utilized previously\(^2\) has principally an entrance channel barrier and does not account for the very strong dependence of $S_0$ on $T_e$ observed in Paper I. (Calculations based on this PES have more than an order of magnitude smaller dependence on $T_e$ than is observed.) In addition, \textit{ab initio} cluster calculations for CH$_4$ dissociation on Ni(111)\(^9,10\) suggest that the transition state for that system occurs when a single C–H bond is extended by ca. 1 a.u., considerably more than in the original PES of Luntz and Harris. In order for the dynamical calculations to be qualitatively consistent with the cluster calculations for dissociation on a Ni surface, we have therefore constructed a two dimensional stiff lattice PES $V(Z,D)$ where the barrier is principally in the exit channel:

$$V(Z,D) = \frac{1}{2}[V_A + V_M - \sqrt{(V_A - V_M)^2 + \chi^2}],$$

(1)

where $\chi=0.5$ eV is a mixing parameter, $V_A$ and $V_M$ are atomic and molecular potentials, respectively. $V_A$ is almost identical to that used previously,

$$V_A = M[W_{H1}.D_{H1}.\lambda_{H1}(Z-0.5D)] + M[W_{R2}.D_{R2}.\lambda_{R2}.Z] + V_{RH}e^{-\lambda_{RH}D},$$

(2)

where the Morse function $M$ is given as

$$M[W_{X1}.X1.\lambda.X] = W[1 + F(F-2)]; \quad F = e^{-\lambda(X-X_0)}.$$ 

(3)

Specific parameters for $V_A$ are $W_{H1}=2.76$ eV, $\lambda_{H1}=0.53$ a.u.$^{-1}$, $D_{H1}=1.1$ a.u., $W_{R2}=2.17$ eV, $\lambda_{R2}=0.7$ a.u.$^{-1}$, $D_{R2}=3.4$ a.u., $V_{RH}=100$ eV, and $\lambda_{RH}=1.6$ a.u.$^{-1}$. However, $V_M$ is modified from before and is given as

$$V_M = W_m[F - \gamma(Z)] - V_{min}(Z) + V_0e^{-\lambda_0z},$$

(4)

with $F = e^{-\lambda(z-D_m)}$ and the attractive term $\gamma(Z)$ given as

$$\gamma(Z) = (2 - \eta) + \eta \tanh((Z-Z_c)/W_Z).$$

(5)

The $Z$ dependent well depth $V_{min}(Z)$ is given by

$$V_{min}(Z) = W_mF_2(Z)[F_2(Z) - \gamma(Z)],$$

(6)

where $F_2(Z) = e^{-\lambda_a|D_{min}(Z)-D_m|}$ and the $Z$ dependent equilibrium bond length $D_{min}$ is given as

$$D_{min} = \ln[2\phi_{D_m}/\gamma(Z)]/\lambda_m.$$ 

(7)

Other parameters in $V_M$ are $W_m=4.87$ eV, $\lambda_m=0.97$ a.u.$^{-1}$, $D_m=2.06$ a.u., $V_0=90$ eV, and $\lambda_0=1.5$ a.u.$^{-1}$.

This PES is similar in spirit to that originally presented by Luntz and Harris, e.g., the PES is constructed from a Landau–Zener mixing of an atomic potential $V_A$ and molecular potential $V_M$. The chief difference to the PES used previously is that the well depth in $V_M$ is weakened and the equilibrium bond length stretched in a smooth fashion as the molecule approaches the surface. Both effects are appropriate to describe the filling of a molecular antibonding resonance as the molecule approaches the surface, which is the essential physics underlying an exit channel barrier. Parameters were chosen to position the barrier at $D=3$ a.u., in agreement with the cluster calculations, and to reproduce the barrier height $V^*$ used previously by Luntz and Harris. The latter is strictly for convenience in comparing to dynamical calculations on the previous (entrance channel) PES\(^2\) but is certainly qualitatively consistent with estimates of $V^*$\(^9,10\).

Other than these initial considerations, no further attempt was made to adjust the PES to optimize agreement of the dynamical calculation with experiment. A contour diagram of the PES $V(Z,D)$ is shown in Fig. 1.

![Fig. 1. Contour plot of the stiff lattice PES $V(Z,D)$ used in the model. $Z$ and $D$ are given in a.u. and the energy contour interval is 0.1 eV.](image)

The fundamental reason that the barrier in the PES for dissociation on Ni may be further towards the exit channel relative to that for Pt cannot be answered unequivocally until electron structure calculations are performed for CH$_4$ interacting with Pt (clusters or supercell). One possibility, however, is the suggestion that dissociation on Pt is slightly endothermic.\(^7\) Such endothermicity usually pushes the barrier towards the entrance channel. Another possibility is that
the same manner as before from the two dimensional
ods were presented earlier. Values of
semiclassically. Details of the model and calculational meth-
quantum mechanically but treats the phonon coordinate
model treats the molecular dissociation coordinates fully
so-called surface mass model of Luntz and Harris. This

\[ V_{nd}^* = V_{3d}^* + \Delta V^*. \]

where \( V_{3d}^* \) is the barrier height along the minimum energy path in Fig. 1 and \( \Delta V^* \) represents the increase in barrier from steric hindering due to less than optimal impact param-
eters or orientational angles. For lack of any more definitive
information, we simply assume that \( \Delta V^* \) is distributed
according to a Gaussian,

\[ f(\Delta V^*) = e^{-(\Delta V^* - \Delta_0)^2/2\sigma^2}. \]

We choose \( \Delta_0 = 0.4 \text{ eV} \) and \( \sigma = 0.2 \text{ eV} \) to insure a gradual turn
on of barriers generally consistent with the experimental
widths observed in Paper I, as well as many other experi-
mental systems. We do not, however, try to vary these pa-
rameters to achieve any specific fit to the data. Given this
distribution of barriers, then the \( n \)-dimensional sticking
\( S_0^{nd}(E_v,v,T) \) is given according to the hole model as

\[ S_0^{nd}(E_v,v,T) = \frac{\int S_0^{3d}(E_v - \alpha_v \Delta V^*,v,T) f(\Delta V^*) d(\Delta V^*)}{\int f(\Delta V^*) d(\Delta V^*)}. \]

where \( \alpha_v \) represents the rigid shift of the sticking curve in the \( \nu \)-th vibrational state with barrier shift \( \Delta V^* \). A reasonable approximation is

\[ \alpha_v = [\epsilon_v(u,v)]/d(\Delta V^*), \]

with \( \epsilon_v(u,v) \) the classical threshold for the given vibrational state obtained via
two dimensional classical dynamics on the given PES. Val-
ues of \( \alpha_v \) for the PES in Fig. 1 were determined by varying
slightly one of the parameters \( (V_{RIH}) \) which strongly affects
principally the barrier height and then calculating the shift in
the sharp classical thresholds for each vibrational state on the
modified PES. \( \alpha_v = 1, 0.5, \) and \( 0.1 \) for \( v = 0, 1, \) and \( 2, \)
respectively, on the PES of Fig. 1. \( S_0^{nd}(E_v,v,T) \) for \( T_s = 500 \text{ K} \) is shown in Fig. 2(b). Comparison with \( S_0^{3d}(E_v,v,T) \) of Fig. 2(a) shows that the multidimensionality broadens and
lowers the sticking curves for each vibrational state, and that
this effect is much more pronounced for the lower vibrational
states due to the larger values of \( \alpha_v \). Because of this,
a fit of these \( S_0^{nd} \) curves to simple S-shaped functions then
produces vibrationally dependent thresholds which are separ-
ated by more than \( \omega_{ vib } \). Thus the “inconsistency” in the fit
of experimental S curves that is observed in Paper I is in fact
a natural and necessary consequence of interpreting a multi-
dimensional dissociation in terms of 2d (or 3d) dynamical
models.

Sticking curves representing the various experiments in
Paper I are then calculated via appropriate averages, i.e.,

since the Pt \( 5s \) orbital tails much further into the vacuum
than the Ni \( 4s \) orbital (relative to the respective \( d \) orbitals), this
should result in stronger Pauli repulsion for Pt (at large
Z) and could shift the barrier towards the entrance channel.

The three dimensional PES \( V_{3d}(Z,D,Y) \) is constructed
in the same manner as before from the two dimensional
PES, i.e., \( V_{3d}(Z,D,Y) = V(Z - Y,D) + (1/2) \kappa Y^2 \). This
describes the coupling of the barrier to the lattice and the bare
phonon potential.

B. Three dimensional dynamics

The dynamics on the PES \( V_{3d} \) was calculated using the
so-called surface mass model of Luntz and Harris. This
model treats the molecular dissociation coordinates fully
quantum mechanically but treats the phonon coordinate
semiclassically. Details of the model and calculational meth-
ods were presented earlier. Values of \( S_0^{3d}(E_v,v,T) \) are calcu-
lated for the three dimensional PES, where \( v \) is the R–H
vibrational quantum number. An example is shown in Fig.
2(a) for \( T_s = 500 \text{ K} \).

C. Multidimensionality: “Hole” model

The experimental results represent sticking in a multi-di-
dimensional world and reflect much steric hindering. In Luntz
and Harris this multidimensionality was not specifically in-
cluded in the calculations, and its neglect was cited as the
prime reason that the calculated increase in \( S_0 \) with incident
energy was much faster than that of experiments; i.e., that
the energy scale for all theoretical plots was roughly half that
of the experimental plots. In this section, we approximately
include the multidimensionality through the so-called hole
model. This model accounts qualitatively for the multi-
dimensionality by relating the sticking to the (normalized) vol-
ume of phase space for which the incident energy is above
the classical threshold. This represents a classical sudden ap-
proximation for the remaining \( n - 3 \) dimensional coordi-
nates, and accounts in an approximate way for the static
distribution of barrier heights representing steric hindering.
This neglects entirely, however, any dynamic coupling of
these \( n - 3 \) dimensional coordinates to the reaction path.

To incorporate these effects, we take the \( n \)-dimensional
barrier height \( V_{nd}^* \) as

\[ V_{nd}^* = V_{3d}^* + \Delta V^*. \]

FIG. 2. Comparison of \( S_0^{nd}(E_v,v,T) \) for \( T_s = 500 \text{ K} \) calculated using the
reduced dimensionality 3d model (a) with calculations using a multidimen-
sional \( (nd) \) model (b).
using stretches the energy scale and translational excitation ($T_v$) relative to that of a 3d model using the same PES. The latter occurs due to the much larger suppression of sticking in the lower vibrational states relative to the higher ones with the inclusion of steric hindering.

III. COMPARISON OF MODEL TO EXPERIMENTAL RESULTS

Figure 4 compares calculated values of $S_{0}(E_n,T_v,T_s)$ with the measurements in Paper I. It is evident that there is excellent qualitative agreement, although the calculated dependence of $S_0$ on $T_n$ is slightly less than that observed. No attempt was made to either vary the PES of Fig. 1 or the parameters defining $f(\Delta V^*)$ to improve the agreement since it is felt that this level of agreement is already beyond the limits of validity of approximations in the model.

Figure 5 compares the calculated isotope effect with that measured in Paper I. Again, excellent qualitative agreement is obtained. This isotope effect is principally determined by the shift in vibrational zero point of R–D relative to R–H. The fact that the calculated isotope dependence is slightly less than that observed is in complete accord with the slightly smaller role of $T_v$ in $S_0$ exhibited in Fig. 4.

Figure 6 compares the calculated $T_s$ dependence with that observed in Paper I. Again, good qualitative agreement is obtained. For the experimental conditions prevailing in Paper I, the observed $T_s$ dependence is rather modest in Fig. 6(a). This $T_s$ dependence does, however, become stronger as $E_n$ and/or $T_n$ are lowered. Both effects are apparent in model calculations. In fact, at both low $T_n$ (≤450 K) and $E_n$, the $T_s$ dependence is predicted to be quite strong. This region is unfortunately not experimentally accessible since $S_0$ is too low to measure for these conditions. The reason the $T_s$ dependence is so small at $T_n$=850 K is that the $S_0$ is then dominated by sticking of the higher vibrational states where the sticking is large and the center of mass energy dependence due to surface thermal motion is slight. It should be pointed out that the model calculations for the increase in the $T_s$ dependence at lower $T_n$ preceded the experiments, so that this represented a prediction of the model.

Figure 7 compares the calculated isothermal “bulb” dissociation probability with both experiment[11] and $S_0$ calculated using extrapolations of the experimentally derived $S$.
curves of Paper I. As stressed in Paper I, there is excellent agreement between the thermal rates and predictions based purely on the molecular beam experiments (experimentally derived $S$ curves). This was taken as partial evidence that the same direct dissociation mechanism that dominates the beam experiments is also dominant in the bulb experiments. We see that there is also excellent agreement of the thermal rates with the direct dynamical model as well, further confirming this conclusion. Both the molecular beam experiments and the model predict some curvature in a plot of $\log (S_0)$ vs $1/T$ over an extended temperature range, e.g., non-Arrhenius behavior. This arises principally from the varying dominance of different (quasidiatomic) vibrational states in the temperature range and their different overall dependence on $T$. The model predicts a somewhat higher $T$ (750 K) than the experimental $S$ curves (300 K) for the dominance of vibrationally excited states in the isothermal rate, in general agreement with the somewhat smaller effects of $T_v$ in the model (Fig. 4). Nevertheless, the curvature in both results imply that there should also be some experimental curvature well if measurements were possible over such an extended temperature range. This suggests that there is some additional uncertainty in estimating the rate in the catalytically important temperature range of ca. 1000 K from a pure Arrhenius extrapolation of rates measured at lower $T$. In addition, calculated apparent activation energies, i.e., slopes in the plot of $\log (S_0)$ vs $1/T$, vary considerably over the range of $T$ and only at very high $T$ ($\gg$1000 K) become equivalent to the potential barrier height of 0.76 eV assumed in the model. The fact that such Arrhenius plots often do not measure true barrier heights has been stressed previously.\textsuperscript{2,6} At isothermal conditions ($T_s = T_v$) and at sufficiently high $T$ (or wide barriers) so that tunneling is completely unimportant, then traditional transition state theory may provide an approximation to the isothermal rate of reaction for this mechanism of direct dissociation. Naturally transition state theory can say nothing about the molecular beam experiments under nonequilibrium initial conditions.

In addition to the direct mechanism discussed here, other authors have suggested that the dissociation of CH\textsubscript{4} on metals is dominated by completely different mechanisms. For example, Ukraintsev and Harrison\textsuperscript{12} have proposed a statistical mechanism for dissociation where the CH\textsubscript{4} is strongly coupled to a local cluster of surface atoms. This strongly coupled collision complex subsequently decays via RRKM unimolecular decay. With several adjustable parameters, a model of this mechanism has produced reasonable fits to molecular beam experiments on another system [Pt(111)]. A fit of this statistical model to the experiments reported in Paper I may also be possible. However, “fits” of a model to experiments should not be taken as irrefutable proof of the mechanism. Hence, the detailed agreement obtained by fits of either the direct dynamical model or the statistical model with experimental results should be viewed quite cautiously. However, the direct dynamics mechanism and the RRKM unimolecular decay mechanism are based on completely different physics so that they should predict quite different be-

![Figure 5](image5.png)  
**FIG. 5.** Comparison of the measured isotope effect in Paper I (a) with that calculated using the nd model (b). $T_s = 475$ K for all measurements, but various $T_v$ were utilized (see Paper I). Conditions were duplicated for all calculations in (b).

![Figure 6](image6.png)  
**FIG. 6.** Comparison of the experimental dependence of $S_0(E_n, T_v, T_s)$ on $T_s$ for different $E_n$ and $T_v$ from Paper I (a) with that calculated using the nd model under identical conditions (b).
behaviors for future experiments that are specifically designed to distinguish between mechanisms. Naturally, this author feels that the direct mechanism provides the most reasonable physical basis for a description of the dissociation process.

IV. CONCLUSIONS

It is suggested in Paper I that the experimental molecular beam results are consistent with a mechanism of direct dissociation on a PES with an exit channel barrier. In this paper, a detailed comparison is presented for the predictions of a quantum dynamical model for such a mechanism with the experimental results of Paper I. The experimental results are only partially consistent with a reduced dimensionality (3d) model since the experiment requires vibrationally dependent $S$ curves which are separated by more than $\omega_{vib}$. Inclusion of multidimensionality (stereic hindering) via the hole model, however, produces excellent agreement with the experiments and removes any inconsistencies. The overall good agreement between the model and the experiment demonstrates that the mechanistic conclusions of Paper I are at least justifiable and reasonable.

There has been no attempt in the model to fit the experimental data. A reasonable PES and barrier distribution have been simply assumed at the outset without any reference to the experimental data of the previous paper. Even better agreement between the model and experiment could be easily achieved by “adjusting” the width of the barrier distribution in the hole model (and perhaps the PES). However, the level of agreement between the model calculations and experiment is already felt to be better than the limitations imposed by the approximations in the model, so that “fitting” the data by adjusting such parameters would be misleading as to the accuracy of such a model.

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FIG. 7. Comparison of the isothermal rate measured previously and as predicted from the experimentally derived $S$ curves of Paper I (a) with $S_0(T_e - T_e, T_e)$ calculated using the $n\sigma$ model (b). The solid line is the total rate and the various dashed curves are the contributions of individual vibrational states to the overall thermal rate.