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WORKSHOP ON
"SURFACE SCIENCE AND CATALYSIS"
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# DYNAMICS OF CHEMISORPTION AND SURFACE REACTION: NON-EQUILIBRIUM ENERGY DISTRIBUTION IN REACTANTS AND PRODUCTS

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# DYNAMICS OF CHEMISORPTION AND SURFACE REACTION: NON-EQUILIBRIM ENERGY DISTRIBUTION IN REACTANTS AND PRODUCTS

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## I. Introduction

Nozzle molecular beams, infrared emission, Fourier transform time resolved spectroscopy. J. B. Anderson and J. B. Fenn, **Phys. Fluids**, 8, 780, 1965.

## II. Effects of different kinds of energy on reactivity of molecules.

Translational energy effect on chemisorption of $H_2$, $O_2$, $N_2$, CO, $CO_2$, $CH_4$ and higher hydrocarbons on transition metals, rotational and vibrational energy effects on $CH_4$ chemisorption on W and Rh, vibrational energy effect on cyclopropane reaction on mica, G. Prada-Silva et al., **Surface Sci.**, 83, 453 (1979), D. J. Auerbach et al., **J. Chem. Phys.**, 81, 2515 (1984), C. T. Retter et al., **Phys. Rev. Lett.**, 54, 2716 (1985), H. J. Robota et al., **Surface Sci.**, 155, 101 (1985); S. L. Tang et al., **J. Chem. Phys.**, 84, 6488 (1986), C. T. Rettner et al., **J. Chem. Phys.** 84, 4163 (1986); C. T. Rettner et al., **J. Chem. Phys.**, 85, 1131 (1986); M. P. D'Evelyn et al., **Surface Sci.**, 167, 451 (1986); M. P. D'Evelyn, et al., **Surface Sci.**, 180, 47 (1987).

## III. CO oxidation on Pt and Pd

Translational energy of desorbed $CO_2$, angular distribution, rotational and vibrational energy excitation in desorbed $CO_2$, modeling of energy distribution. C. A. Becker et al., **J. Chem. Phys.**, 67, 3394 (1977), J. Segner et al., **Surface Sci.**, 138, 505 (1984), D. A. Mantell et al., **Surface Sci.**, 172 (1986).

## IV. Coverages effects on non-equilibrium energy distribution

Pulsed molecular beams, time resolved infrared emission, comparision of CO oxidation on Pt and Pd, D. A. Mantell et al., **Chem. Phys. Lett.**, 102, 37 (1983).

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# The Dynamics of Adsorption and Reaction on Surfaces

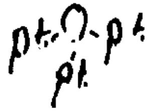
Sequence of elementary steps and overall kinetics

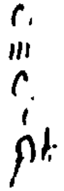
$$O_2 + 2* \rightarrow 2*O$$

$$CO + * \rightleftharpoons *CO$$

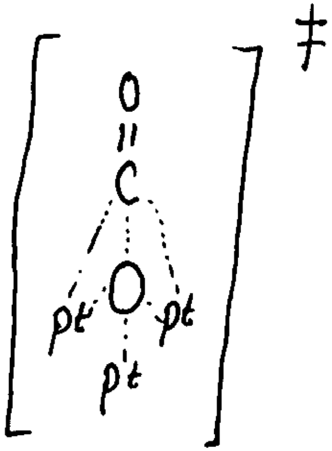
$$*CO + *O \rightarrow CO_2 + 2*$$

Complete structure of reactants, products and intermediates





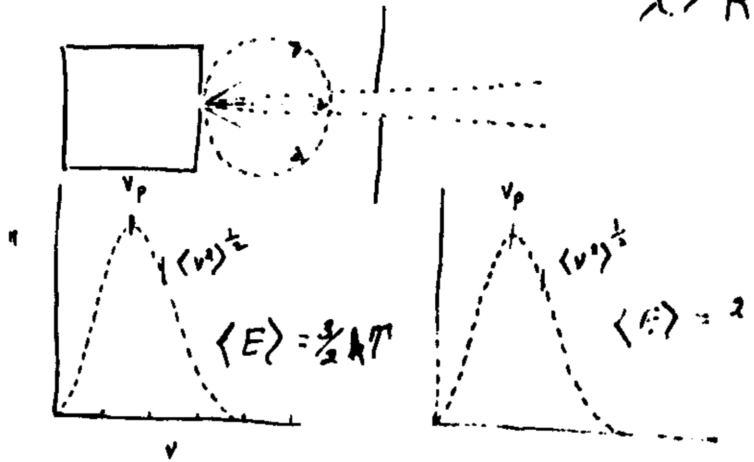
Dynamics – Structure and energetics along reaction path for each elementary reaction



# Molecular Beams

## "Oven" Source

$\lambda > R$

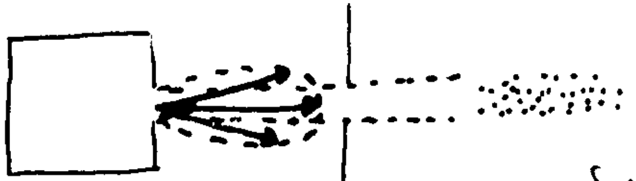


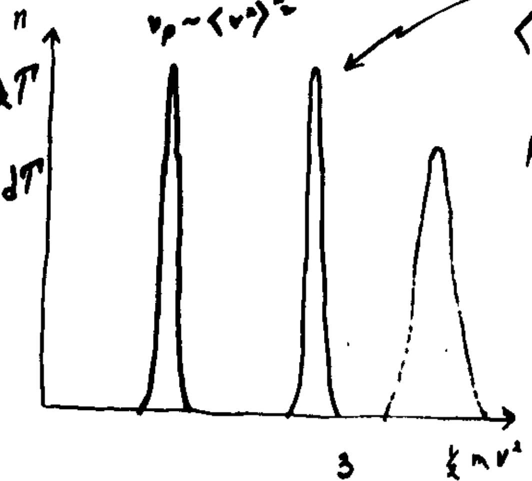
$\langle E\rangle = \frac{3}{2}kT$

$\langle E\rangle = 2kT$

## Nozzle Source

$\lambda << R$

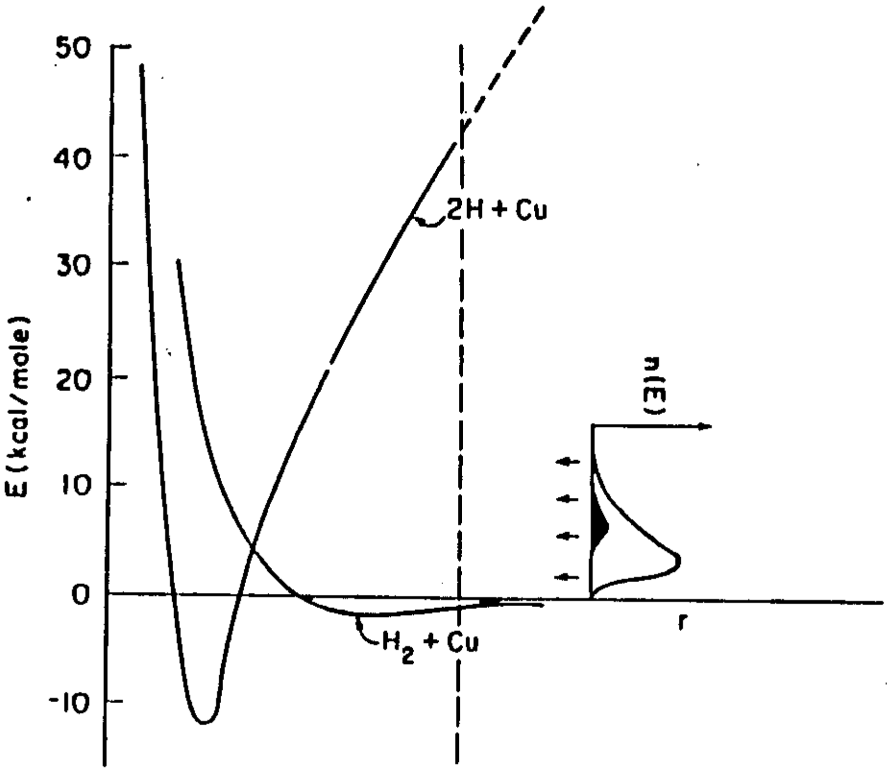




$\langle E\rangle = \frac{5}{2}kT = \int_0^T C_p\,dT$

Seed Nozzle
$\langle E\rangle \cong \frac{m}{m}\langle E\rangle$

Heated Nozzle
$T_{vib} \cong T_{nozzle}$



Schematic diagram of a one-dimensional potential diagram for hydrogen and copper showing the apparent barrier to dissociative adsorption. Also shown is a boundary drawn for convenience as a dashed line parallel to and a few Angstroms away from the surface. We also show crossing this boundary a Maxwell distribution at the crystal temperature normally incident upon the surface. The shaded region of this distribution represents those molecules which go on to dissociate while the remainder reflect. By detailed balancing this shaded distribution is also that of desorbing recombined hydrogen

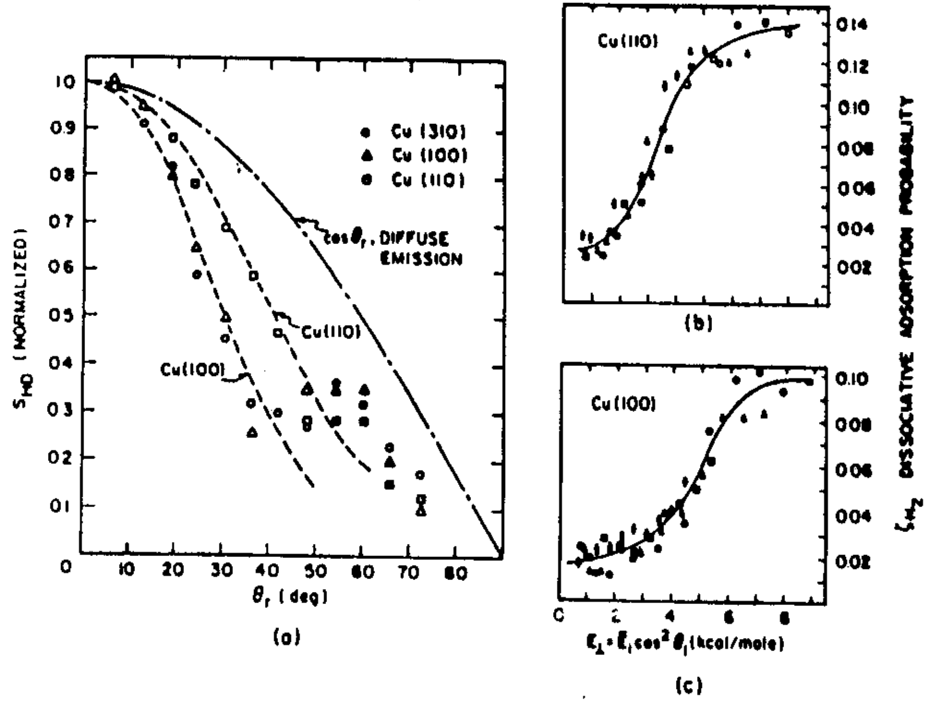


Fig. 2. Summary of results of the molecular beam study of the dissociative adsorption and desorption of hydrogen on copper [2]. (a) Angular distributions of hydrogen (HD) desorbing from three copper single crystal surfaces. The dashed lines are the results of permeation/desorption measurements for the same crystal faces. $\theta_r$ is the angle of inspection measured from the surface normal. (b) and (c) Energy dependence of the dissociative adsorption probability for $H_2$ on Cu (110) and Cu (100). The incident angle dependence ($\theta_i$ measured from the surface normal) which varied as $\cos^2\theta_i$ at constant incident energy, $E_i$, has been included by plotting the probabilities versus the correlating parameter, $E_\perp = E_i \cos^2 \theta_i$.

Balooch, Cardillo, Miller and Stickney, Surface Sci., 46, 358 (1974)

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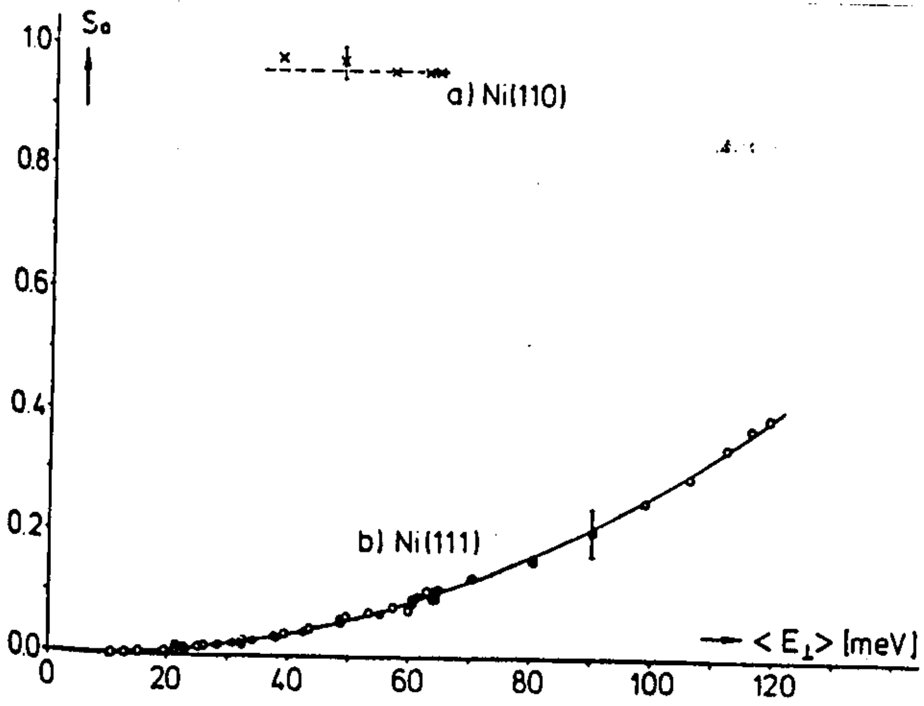
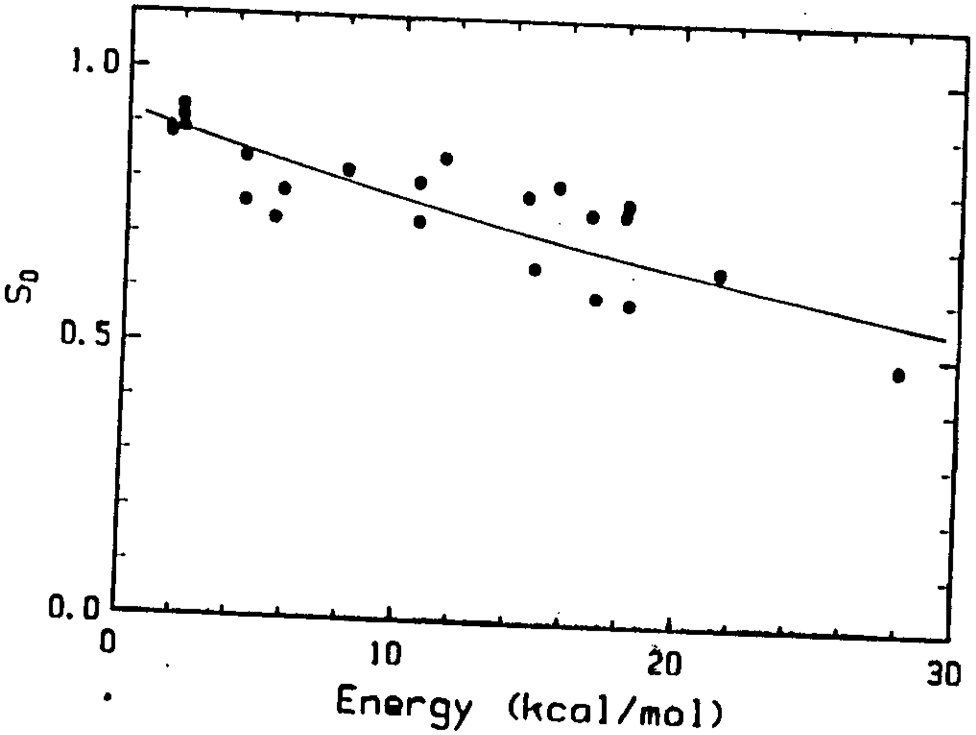


Robota, Vielhaber, Lin, Segner and Ertl,
Surface Sci, 155, 101 (1985)

## CO on Ni(100)



D'Evelyn, Steinbrück and Madix
Surface Sci., 180, 47 (1987).

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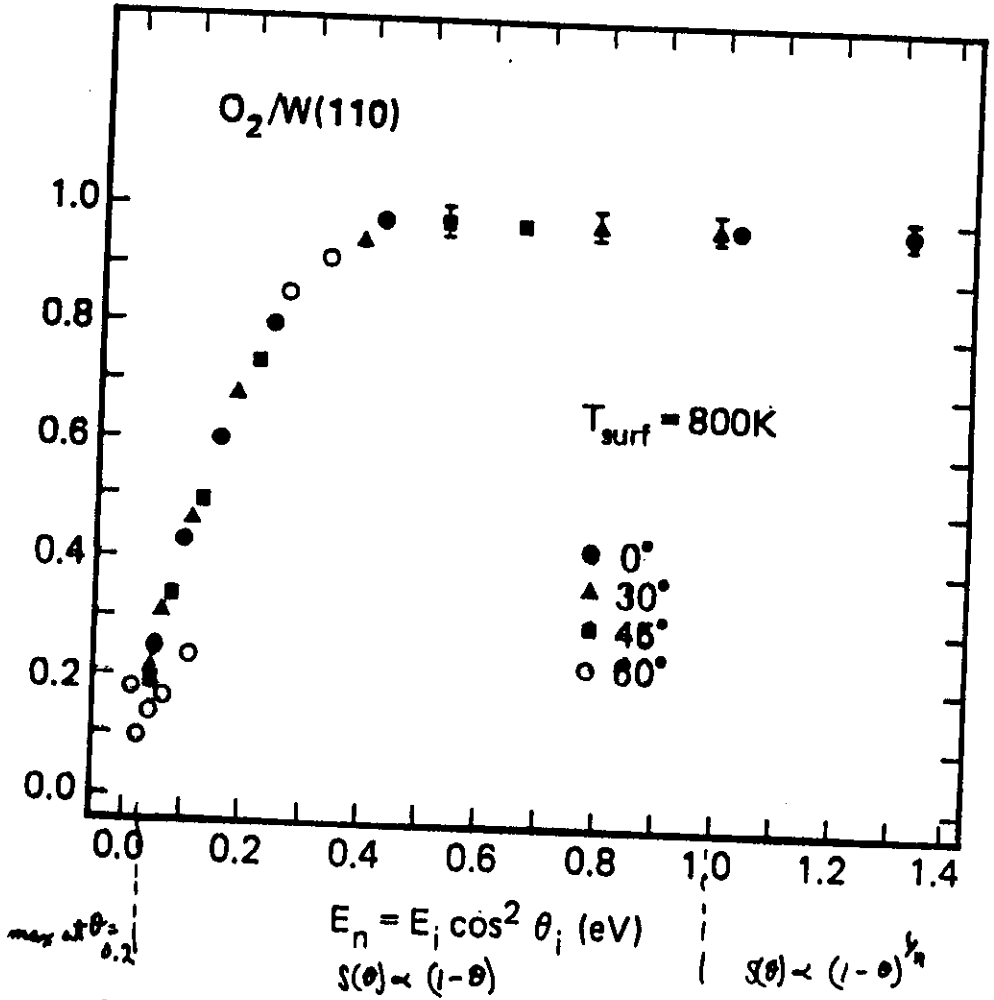
$\theta_{sat} \sim 0.5$ ML for $E_n \leq 0.25$ eV p(2x2)
$\sim 0.75$ ML $> 0.25$ p(2x1)
$\sim 1.0$ ML $> 0.75$ p(1x1)



Rettner, DeLouise and Auerbach, J. Vac. Sci. Tech.
~~to be published, 1986~~
A4, 1491 (1986).

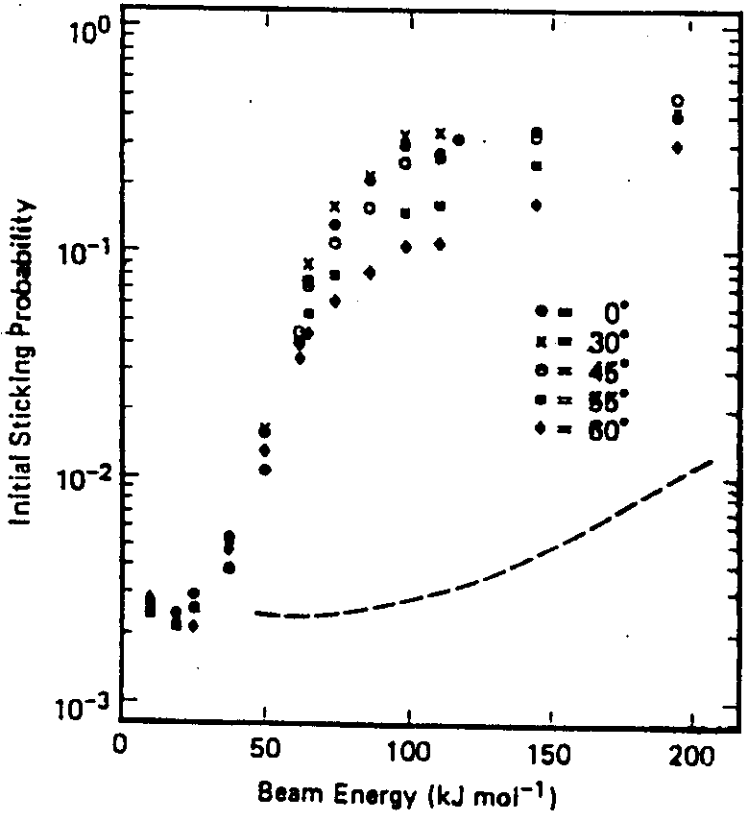


FIG. 1. Initial sticking probability for $N_2$ on W(110) as a function of beam energy at various angles of incidence for a sample temperature of 800 K. It is seen that the data are insensitive to incidence angle for 0° ≲ θ ≲ 45°. The dashed line indicates the sticking probabilities predicted for θ = 60° obtained by assuming normal energy scaling for the θ = 0° data. Clearly the actual 60° results fall much closer to the uncorrected 0° data. Error bars (~ ± 25%) have been omitted for clarity of presentation.

Auerbach et al., J. Chem. Phys., 81, 2515 (1984).

$S_0 = \alpha \chi \exp[\beta \times E_{trans} + E_{vib}]$

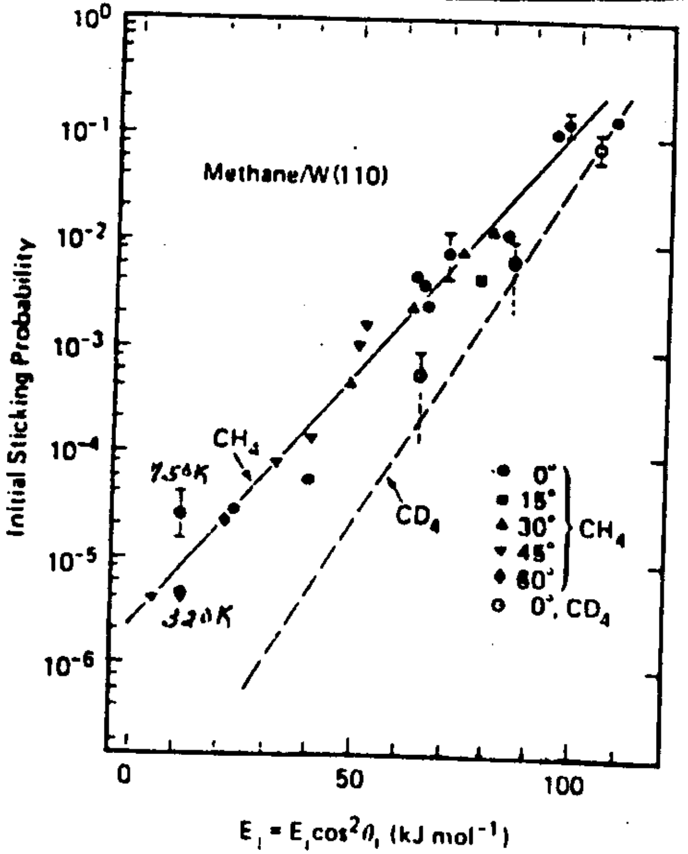
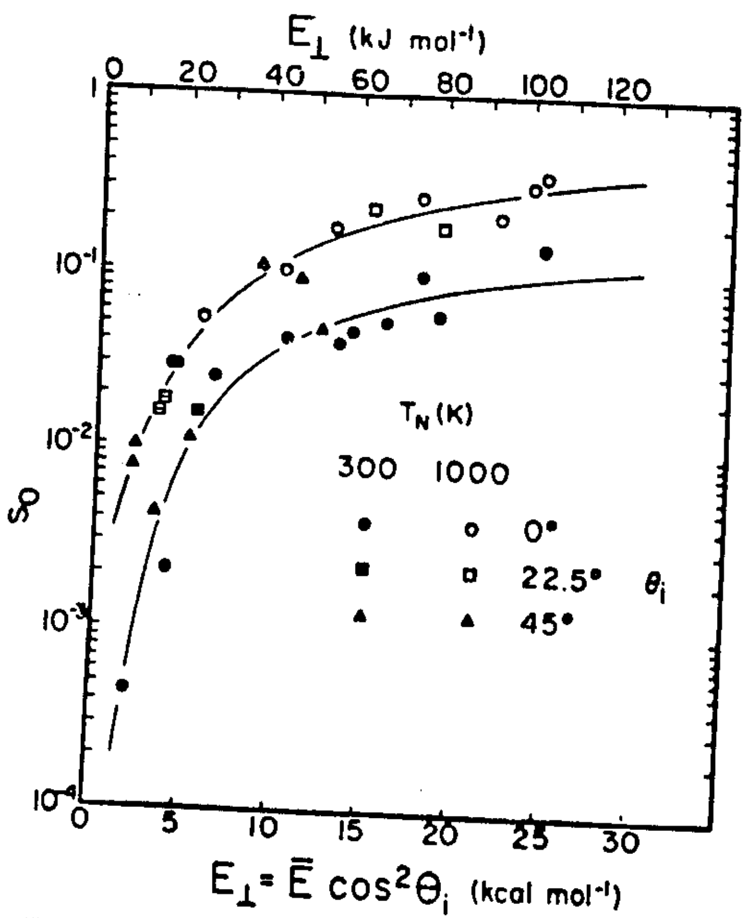


FIG. 1. Initial sticking probability for $CH_4$ (solid symbols) and $CD_4$ (open symbols) on W(110) as a function of beam energy at various angles of incidence. The surface temperature for these measurements was 800 K. The solid and dashed lines correspond to the predictions of a model based on tunneling through a one-dimensional parabolic barrier (see text).

Rettner, Pfnür and Auerbach, J. Chem. Phys., submitted.

Gdowski and Madix, Surface Sci., 167, 451 (1986).

Summary of the dependence of $s_0$ at $T_s = 407$ K on translational energy ($\bar{E}$), incident angle ($\theta_i$), and nozzle temperature ($T_N$). Solid symbols: supersonic beams with $T_N = 300$ K. Open symbols: supersonic beams with $T_N = 1000$ K. Open symbols with horizontal bar: quasi-effusive beams with $T_N = 1000\ \mathrm{K} = T_{rot}$. Smooth curves are least-squares fits to the data by the empirical function $s_0(E_\perp) = s^* \exp[-E^*/(E_\perp + D)]$. Values of $s^*$, $E^*$, and $D$ are 0.21, 83 kJ mol$^{-1}$ and 5.7 kJ mol$^{-1}$, respectively, for the $T_N = 300$ K data and 0.82, 116 kJ mol$^{-1}$ and 16.4 kJ mol$^{-1}$ for the $T_N = 1000$ K data.

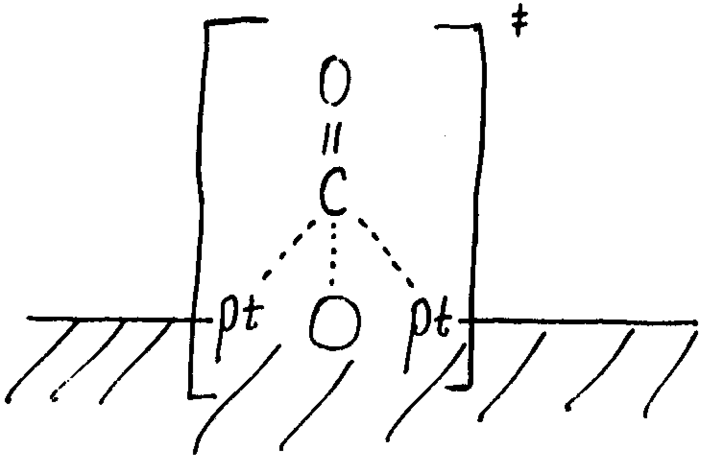


Comparison of sticking probabilities at $\theta_i = 0°$ and two nozzle temperatures with estimates (see section 4.2) of the total populations of excited vibrational states of the incident $CO_2$ molecules.

| | | $T_N = 300$ K | $T_N = 1000$ K |
|---|---|---|---|
| | $s_0(\bar{E} = 17$ kJ mol$^{-1})$ | 0.002 | 0.03 |
| | $s_0(\bar{E} = 43$ kJ mol$^{-1})$ | 0.04 | 0.10 |
| | $s_0(\bar{E} = 72$ kJ mol$^{-1})$ | 0.10 | 0.27 |
| | $s_0(\bar{E} = 103$ kJ mol$^{-1})$ | 0.15 | 0.35 |
| Total populations of excited vibrational states (estimated) | Sym. stretch | 0.0002 | 0.12 |
| | Bend | 0.04 | 0.58 |
| | Asym. stretch | $1 \times 10^{-5}$ | 0.02–0.03 |

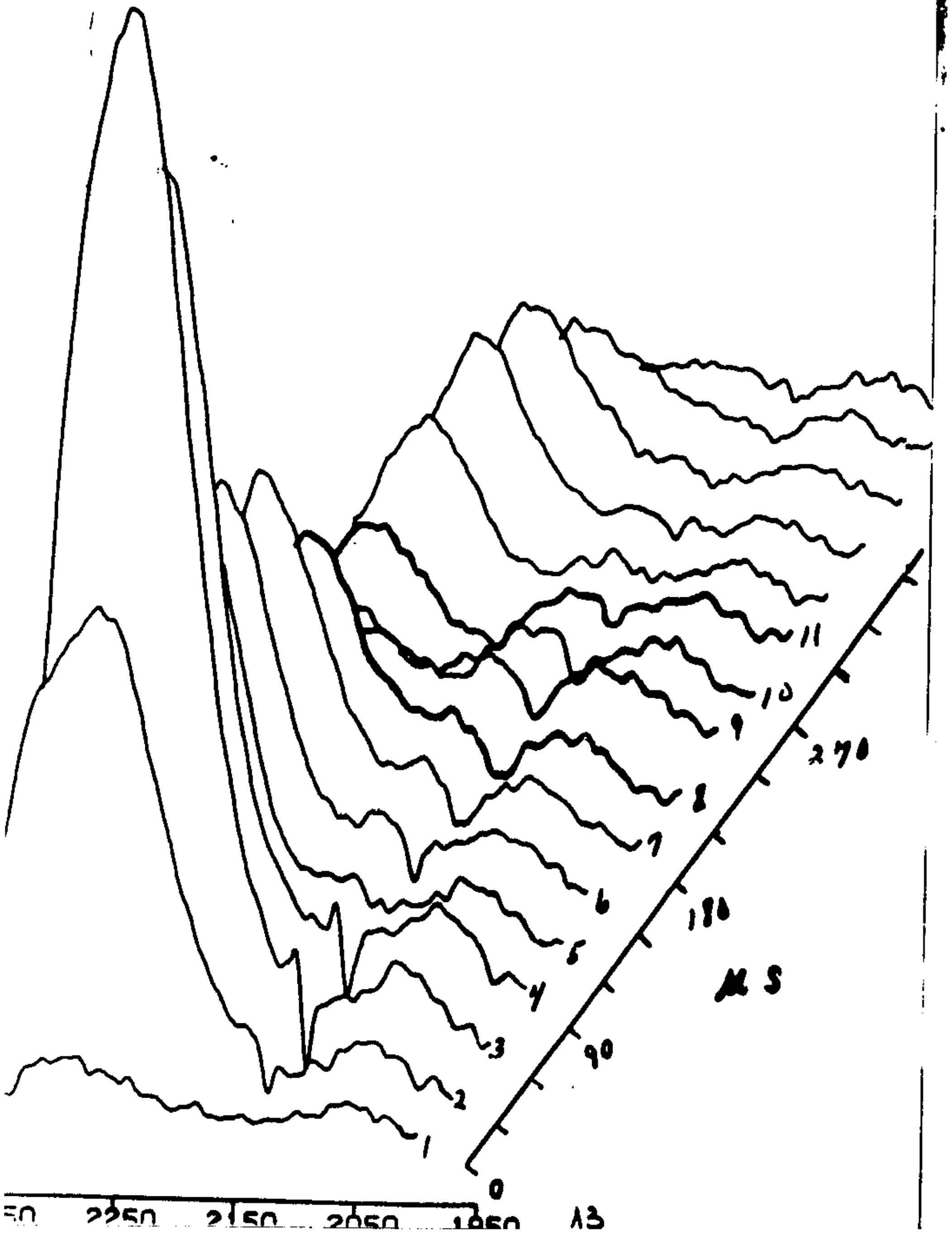
| $T_{sur}$ | $T_{SS}$ | $T_B$ | $T_{AS}$ | $T_R$ |
|---|---|---|---|---|
| 730K | 1300 | 1600 | 1500 | 1050 |
| 900K | 1700 | 1750 | 1600 | 1200 |

## Proposed Structure of Activated Complex



See Mantell et al., Surface Sci., (1986) 172, 281

High Pressure
" Temp



# Conclusions

1. Fourier transform emission stoboscopy can follow transients on a 10's of μS time scale.

2. C.O oxidation on Pt is very coverage dependent even at extremely low coverage and Pd is not.

3. Comparison suggests Pt dynamics not just a result of defect.

4. Interpretation will require single crystal work and theoretical developments.