Molecular Beam Scattering as a Probe of Surface Chemical Dynamics: part 1

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Chemical Dynamics at Surfaces

Principle Goal

- To develop an understanding of the detailed mechanisms by which surface chemical reactions occur in terms of
 - Potential Energy Surfaces
 - How systems evolve on these surfaces

Approach

- Measure molecular scattering and sticking with as complete control and characterization of initial final states
 - Angle
 - Kinetic Energy
 - Rotational, Vibrational, Electronic States
 - Alignment and Orientation

- Compare measurements and theory to develop understanding

Outline

- **1.** Early history
- 2. The Revolution of the 1920s and 30s
 - ✓ Development of Key Paradigms
- 3. Advent of Molecular Beams, UHV Surface Science, and Power Computers
 - ✓ Approach to unraveling the complex sequence of events
 - ✓ Methods and examples: momentum resolved measurements
- 4. Advent of laser based methods for quantum state-specific beam preparation and measurements
 - ✓ Methods and examples: state resolved measurements

5. Case Studies

- Activated Adsorption of Hydrogen on Cu
- Nonadiabatic effects in interactions on metal surfaces

Davy – Explosion Proof Lamp





Early Work on Surface Chemical Reactions

- Davy (1817)
 - explosion proof lamp for miners
 - Pt gauze glowed when exposed to gasses from coal mines

Döbereiner(1823)

- Pt gauze glowed on exposure to hydrogen and oxygen
- Increased with porosity of gauze
 - "cold fusion" of 1823
 - used to make "lighter"
 - generally regarded as 1st example of catalysis
- Henry (1824)
 - Davy lamp reactions
 - $2 H_2 + O_2 H_2O$
 - $-2 \text{ CO} + \text{O}_2 \text{>} \text{CO}_2$

- Faraday (1834)
 - reacting gasses held on Pt by electrical forces
- Berzelius (1836)
 - reacting gasses held on Pt by a "catalytic force ... not independent of the affinities of matter, but only a new manifestation of the same".
 - Origin of term catalysis
- Dumas (1843)
 - Quantitative study of adsorption of H_2 on Cu



FIG. 85.-J. B. A. DUMAS, 1800-1884

Early Work on Hydrogen Adsorption: I

J.B.A. Dumas, Recherches sur la Composition De L'Eau Annales de Chemie et de Physiques 111 8 (1843)



Early Work on Hydrogen Adsorption: II

Is there a barrier to adsorption or does Hydrogen adsorb spontaneously?

• 1843	Melsens	Spontaneous adsorption
• 1874	Hampe	No adsorption
• 1910	Sieverts	No adsorption below 400° C
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Lennard Jones Picture of Activated Adsorption

PROCESSES OF ADSORPTION AND DIFFUSION ON SOLID SURFACES.

BY J. E. LENNARD. JONES (Bristol).

Received 4th January, 1932.





FIG. 3 .- The interactic 1 of a molecule and a metal.

2) 10 Irving Langmuir LANGMUIR ADSORPTION Adsorption on lattice sites Blocks Further Adsorption Direct Adsorption (1-0) S Θ $(1-0)^2$ Dissociation PRECURSOR MEDIATED ADSORPTION (1929) · Cs/W and O2/W · Evidence from Sticking Probabilities vs. Coverage Precursor S Ð

Langmuir

Irving Langmuir looked into blackened light bulbs and created modern surface chemistry.



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Surface Reactions: Complex Sequence

Initial Interaction

- Direct: bounces back
 - Elastic diffraction
 - Inelastic
 - Direct (ER) reaction
- Adsorption
 - Direct, precursor mediated
 - Dissociation, activation barriers
- Diffusion
- Reaction
 - Langmuir-Hinshelwood
 - Eley-Rideal
- Desorption
 - Activation barriers
 - Mirrors initial interaction



Approach

Step 1 – work with non-reactive atoms

- Translational energy flow with surface modes

Step 2 – work with non-reactive molecules

- Rotational modes
- Vibrational modes

Step 3 – study reactions

Atom – Surface Interaction Potential



Molecule – Surface Interaction Potentials



Reactive Channels



Molecule – Surface Interaction Potentials



Atom – Surface Interaction Potential



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Effusive Molecular Beam

- L. Dunoyer, 1911
 - First Molecular Beam



L. Dunoyer, Le Radium 8, 142 (1911)

- Otto Stern, 1919 …
 - 1921 Stern-Gerlach Experiment
 - 1943, Noble Prize "for contribution to the development of the molecular ray method and discovery of the magnetic moment of the proton"



Fig. 1. Arrangement for producing molecular rays.

O. Stern *Z. Phys* 7, 249 (1921)
W. Gerlach and O. Stern *Z. Phys* 8, 110 (1921)
O. Stern *Z. Phys* 39, 761 (1926)

Supersonic Molecular Beam

Cooling via Isentropic Expansion

- Narrow velocity distribution



Beam Velocity Distributions



M: Mach Number

Seeded Supersonic Beam



Properties of Molecular Beam Sources

Effusive Beam

- Low Pressure, molecular free flow
- Broad velocity distribution
- Temperature of internal states = temperature of source

Supersonic Beam

- High pressure hydrodynamic flow
- High intensity, narrow velocity spread
- Separate control of translation, vibration, and rotation

Supersonic Beam

Mode	Nozzle Temp	Gas Mixture
Translation	Yes	Yes
Rotation	weak	weak
Vibration	Yes	weak

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Early Molecular Beam Experiments

Cube Models Angular Distributions



Rudnicki and Wachman Surface Science 34, 679 (1973)

"Law of Parallel Momentum Conservation"

°⊆fn

<u>Cft=Cit</u>

potential

well, W

Ωc

Surface scattering instrument

- Time-of-flight distribution
 - information on velocity after scattering and residence times
- $I(\Delta t) = f(t_1 + t_2 + t_3)$
- t1: arrival time (known from initial velocity)
- ✓ t2: residence time
- ✓ t3: final velocity



Conservation of Parallel Momentum ?





Stochastic Trajectory Simulations

Generalized Langevin Methods

- Numerically solve classical equations of motion for "*primary* zone".
- Energy exchange to rest via *friction and random forces*



References:

- ✓ R. Zwanzig, Ann. Rev. Phys. Chem. 16, 67 (1965)
- ✓ J.D. Doll and D.R. Dion JCP 65, 3762 (1976)
- S.A. Adelman and B.J. Garrison JCP 65, 3751 (1976)
- ✓ J.C. Tully, JCP **73**, 1975 (1980)

Figure: NO dissociation on Pt(111) J.C. Tully, Surface Science **299/300**, 667 (1994)



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Scattering from Liquids



Nathanson et. al. *J. Phys. Chem.* **100**, 13007 (1996) Klassen and Nathanson, Science **273**, 333 (1996)

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Rotational Excitation



 Seeded supersonic beam of NO incident on clean Ag(111)

- Few rotational states

Facile rotational excitation

- Direct T \rightarrow R transfer
- Unexpected peak in population vs. rotational state

→ "Rotational Rainbow

Kleyn, Luntz, Auerbach, PRL 47 1169 (1981)

Optical Rainbows









Simulations of Scattering of NO + Ag(111)

- Analysis:
 - Rotational Rainbow results from strong orientation dependence to energy transfer

Prediction:

 There will be a strong orientation dependence to the trapping (adsorption) probability



J.C. Tully and M.J. Cardillo, *Science*, **223**, 445 (1984) Muhlhausen, Williams, Tully, *J. Chem. Phys.* **83**, 2594 (1985)



Molecular adsorption of alkanes on platinum surfaces: A predictive theoretical model

James A. Stinnett and Robert J. Madixa)

Department of Chemical Engineering, Stanford University, Stanford, California 94305

(Received 22 January 1996; accepted 18 April 1996)



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Summary – Inelastic Scattering and Trapping

- Smooth Potentials
- Nearly impulsive scattering
- Sufficient energy loss → trapping
 - Phonons, rotation important
 - Vibration, eh pairs usually small
- Scattering divides into two channels:
 - Direct inelastic
 - Trapping possibly followed by desorption

Predictive theory is available



End of part 1a

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Adsorption and Reactions

- Can we find more direct evidence to support reaction paradigms ?
 - Precursor mediated dissociative adsorption
 - Direct "Eley-Rideal" reactions

Can we overcome activations barriers to dissociative adsorption ?

- Kinetic Energy
- Vibrational Energy

Adsorption Mechanisms and Adsorption Probability vs. Coverage



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Molecular Beam Instrument for Adsorption Studies



FIGURE 5. The molecular beam apparatus, constructed in Pyrex glass.

D.A. King and M.G. Wells Proc R. Soc. Lond. A. **339**, 245-269 (1974)

Measurements of Adsorption Probability



D.A. King and M.G. Wells Proc R. Soc. Lond. A. **339**, 245-269 (1974)

Results and Kinetic Model



- As surface temperature is increased Adsorption probability decreases.
 - Effect arises from competition between migration and desorption
 - Higher temperatures \rightarrow desorption wins

Predictions

- At high T_s molecules desorb after trapping before they can chemisorb.
 Therefore the **observed trapping fraction should increase**
- Raising the kinetic energy should decrease trapping → adsorption probability should decrease

Direct Inelastic and Trapping Components



Rettner et al. PRL 61, 986(1988)

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Effect of E_i (precursor mediated adsorption)

- Decrease in adsorption probability with kinetic energy provides direct dynamical evidence for precursor states
- Unexpected increase at higher energy \rightarrow direct mechanism



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Dynamical Evidence for ER reactions

- For Langmuir-Hinshelwood reactions, reactants first equilibrate with the surface.
 - Therefore the product retains no "memory" of the incidence conditions
- Hallmark of a direct process
 - the product momentum retains "memory" of the incidence momentum



C.T. Rettner and D.J. Auerbach Science 263(5145), p. 365-367, 1994

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Can we overcome activation barriers to dissociative adsorption ?

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Activated Adsorption: $N_2 + W(110)$



- Dissociative adsorption probability shows a dramatic increase with E_i
- Results do not scale with normal momentum
 - one dimensional picture is not adequate



Lee, Madix, Schlaegel, Auerbach Surface Science **143**, 626 (1984)

Activated Adsorption: $CH_4 + W(110)$

- Exponential increase in adsorption probability
 - Not an S shaped curve
- Large isotope
- Results suggest tunneling mechanism





Activated Adsorption: Examples



Adsorption and Reactions

Can we find more direct evidence to support reaction paradigms ?

- Precursor mediated dissociative adsorption
- Direct "Eley-Rideal" reactions

Can we overcome activation barriers to dissociative adsorption ?

- Kinetic Energy
- Vibrational Energy

Method

Measure adsorption probability at low nozzle temperature

- Low vibrational temperature
- Vary energy by seeding technique \rightarrow change gas mixture

Repeat measurement at high nozzle temperature

- High vibrational temperature

Compare results and same kinetic energy



C.T. Rettner et al. PRL 54, 2716, 1985; JCP 83 4163 (1986);

Summary – Adsorption Probabilities

- Molecular beam methods provide direct dynamical evidence for important paradigms
 - precursor mediated adsorption
 - Direct Eley-Rideal reactions
 - Activated adsorption
- Many surprising and unexpected results
- Both translational and vibrational energy are effective in overcoming activation barriers
- Heated beam technique is not adequate to address the role of vibrational motion
 - Not mode specific
 - Available energy it too limited

End of Part 1b

Extra Slides





FIG. 9. Initial sticking probability of N_2 on W(110) as a function of incidence kinetic energy for normal incidence. The dashed curve represents a Gaussian barrier height distribution corresponding to the relative probability of a molecule dissociating at a given incidence energy. This has been fitted to the sticking probability data with the Gaussian shape imposed as a constraint to the fit, as described in the text.

Dissociative Chemisorption of CH₄ on W(110): Dramatic Activation by Initial Kinetic Energy

C. T. Rettner, H. E. Pfnür, ^(a) and D. J. Auerbach *IBM Research Laboratory, San Jose, California 95193* (Received 29 October 1984)

The initial dissociative chemisorption probability of CH₄ on a W(110) surface is found to increase by $\sim 10^5$ on raising of the CH₄ incident translational energy, reaching a value of ~ 0.2 at 100 kJ/mole. This is by far the largest such effect (by $\sim 10^3$) reported to date and is consistent with a mechanism dominated by quantum tunneling, a conclusion further supported by measurements for CD₄.

PACS numbers: 82.65.Jv, 35.20.Gs, 79.20.Rf, 82.65.My



FIG. 1. Initial sticking probability for CH₄ (solid symbols) and CD₄ (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).

Surface Science 130 (1983) 395-409 North-Holland Publishing Company

DIRECT-INELASTIC AND TRAPPING-DESORPTION SCATTERING OF N₂ AND CH₄ FROM Pt(111)

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Received 14 December 1982: accepted for publication 15 April 1983

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Explosion Proof Lamps





Early Work on Hydrogen Adsorption: II

Is there a barrier to adsorption or does Hydrogen adsorb spontaneously?

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• 1921	Taylor, Burn	No adsorption below 218° C
• 1931	Ward	Spontaneous Adsorption
• 1935	Beebe et al.	Spontaneous Adsorption
• 1948	Rienaecker, Sarry	E _a ~ 0.5 eV
Kinetic Model



(ii) Vibrational excitation of NH3 on Au(111)



Fig. 4. Effect of kinetic energy on the vibrational excitation probability of NH₃ in collisions with a Au(111) surface (ref. 9). The energies of the various r_2 quanta are indicated by the arrows (10 kcal/mole=0.433 eV).