J. B. A. Dumas, 1800-1884

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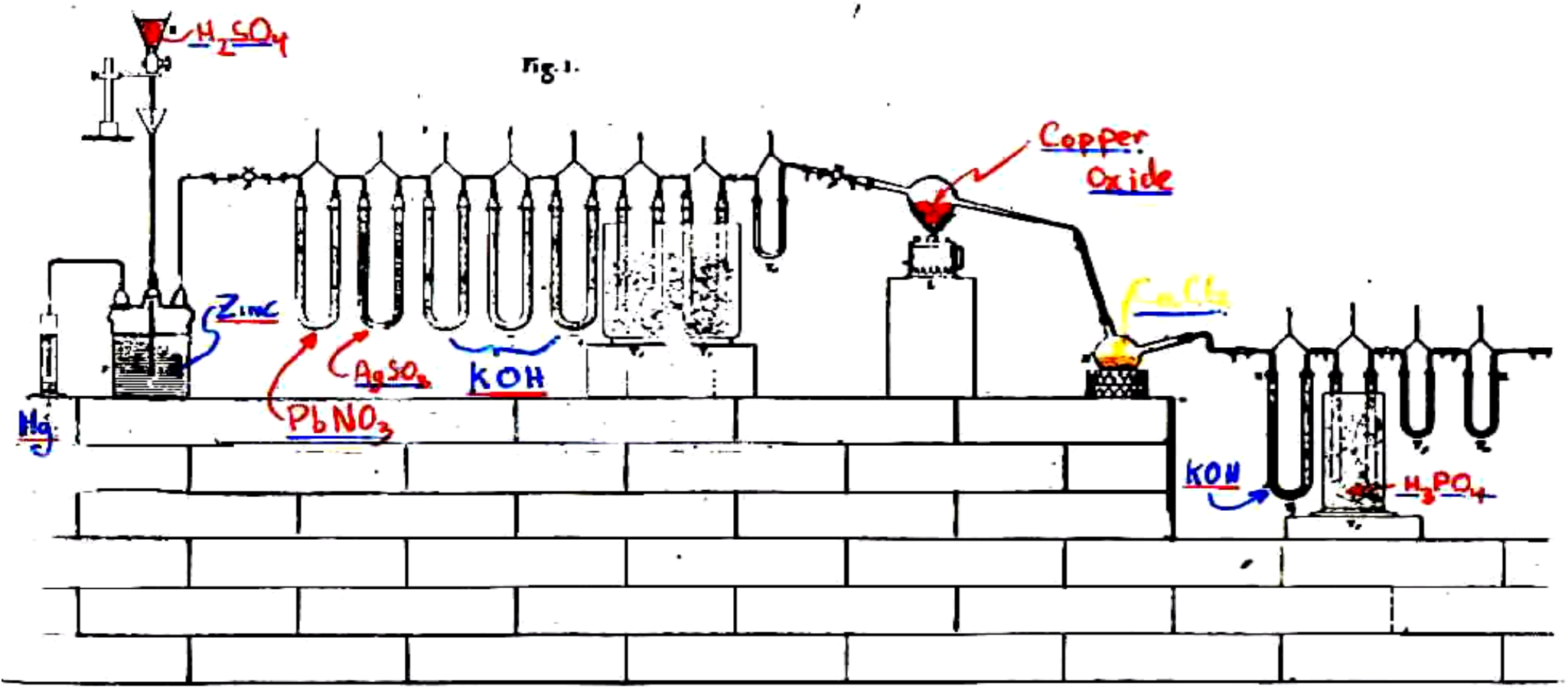
Early work on Hydrogen adsorption: I

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



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Early work on Hydrogen Adsorption II

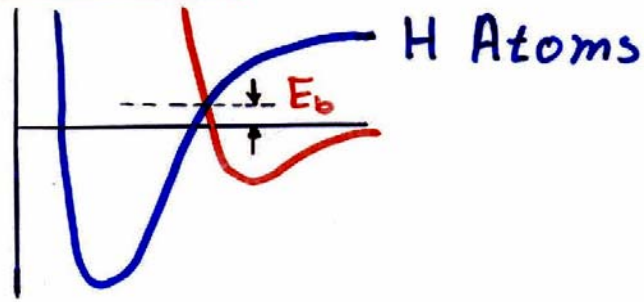
Measurements of The Barrier

1843	Melsens	Spontaneus Adsorption
1874	Hampe	No Adsorption
1910	Sieverts	No adsorption below 400°C
1921	Taylor, Burns	No adsorption below 218°C
1931	Ward	Spontaneous adsorption
1935	Beebe et. al.	Spontaneous adsorption
1948	Rienäcker, Sarry	$E_a = 0.5$ eV
1949	Kwan	$E_a = 0.9$ eV
1950	Allen, Mitchell	No adsorption below 320K
1950	Beeck	No adsorption
1953	Trapnell	No adsorption below 20°C
1953	Kington, Holms	Molecular adsorption at 78K
1954	Mikovsky, Boudart, Taylor	$E_a = 1$ eV
1956	Eley and Rossington	$E_a = 0.2$ eV
1971	Alexander and Pritchard	$E_a = 0.3$ eV

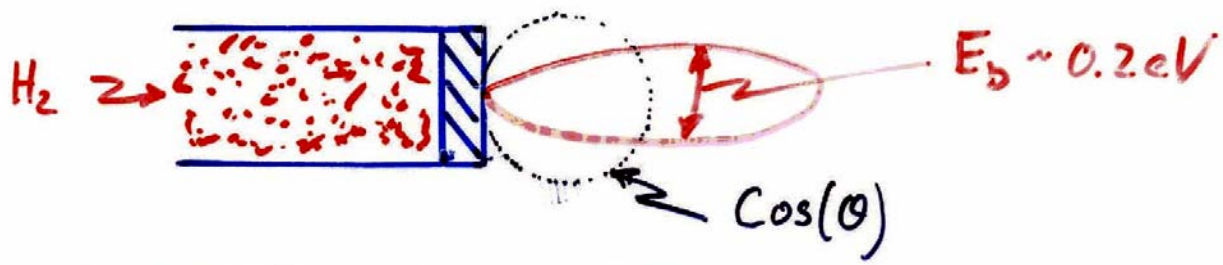
Early Work on Hydrogen on Cu: III

(1D Barrier Models)

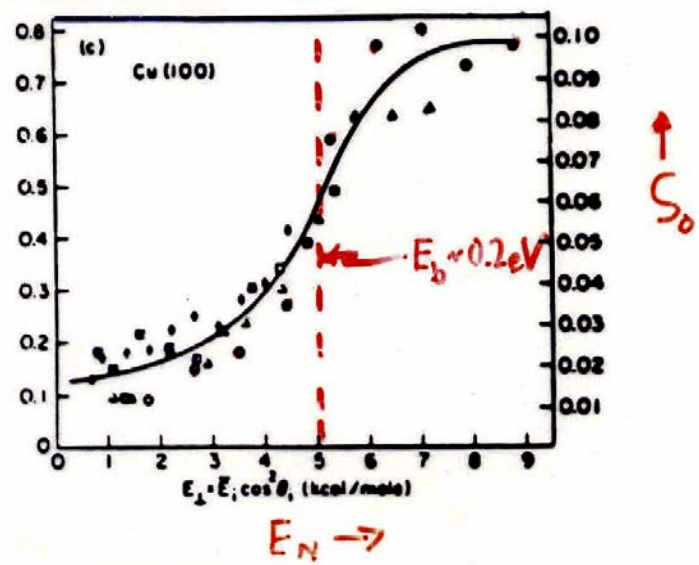
1. Lennard-Jones (1932)



2. Desorption Angular Distributions -Stickney et. al.(1971)



3. S(E,θ) - Balooch et. al (1974)



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History IV: Mysteries (c. 1990)

- **Many points were in dispute**
  - **Size of barrier**
    - ✓ *0.2 eV – Experiment:* Baloch, Cardillo and Stickney
    - ✓ *~ 1 eV – Theory:* Harris and Anderson (1985)
  - **Apparent violations of detailed balance**
    - ✓ *Energy and angular distributions of desorbing molecules* – Comsa and David
    - ✓ *Vibrational state distributions of desorbing molecules* – Kubiak, Sitz, and Zare (1985)
      - **P(V=1) = 50 f_{boltz} x T_S**
      - **But S(V=1) = 50 S(V=0) not consistent with adsorption data**
  - **Role of vibrational energy**
    - ✓ *"All sticking coming from V=0"* Anger, Winkler, and Rendulic (1989)
    - ✓ *"All sticking coming from V=1"* Hayden and Lamont (1989)

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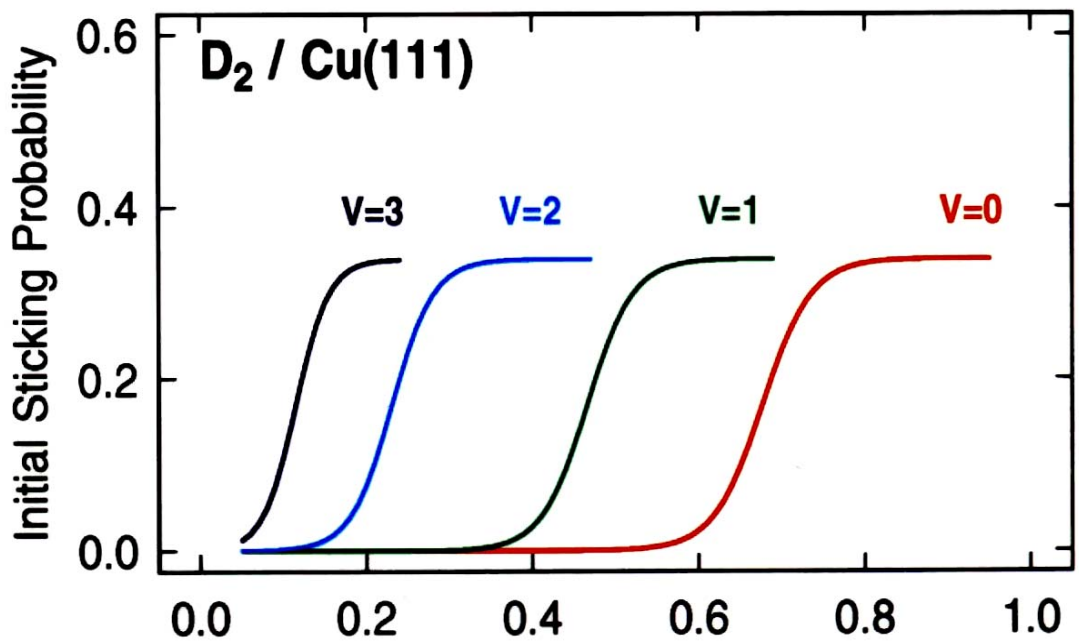
A simple idea

- **Many of the "mysteries" came from two assumptions**
  - **$S(V, E_i) = f(V) \times g(E_i)$**
  - **$g(E_i)$ = step function**

- **A more realistic view**



H. A. Michelsen and D. J. Auerbach

J. Chem. Phys., **94, 7502-7520 (1991).**

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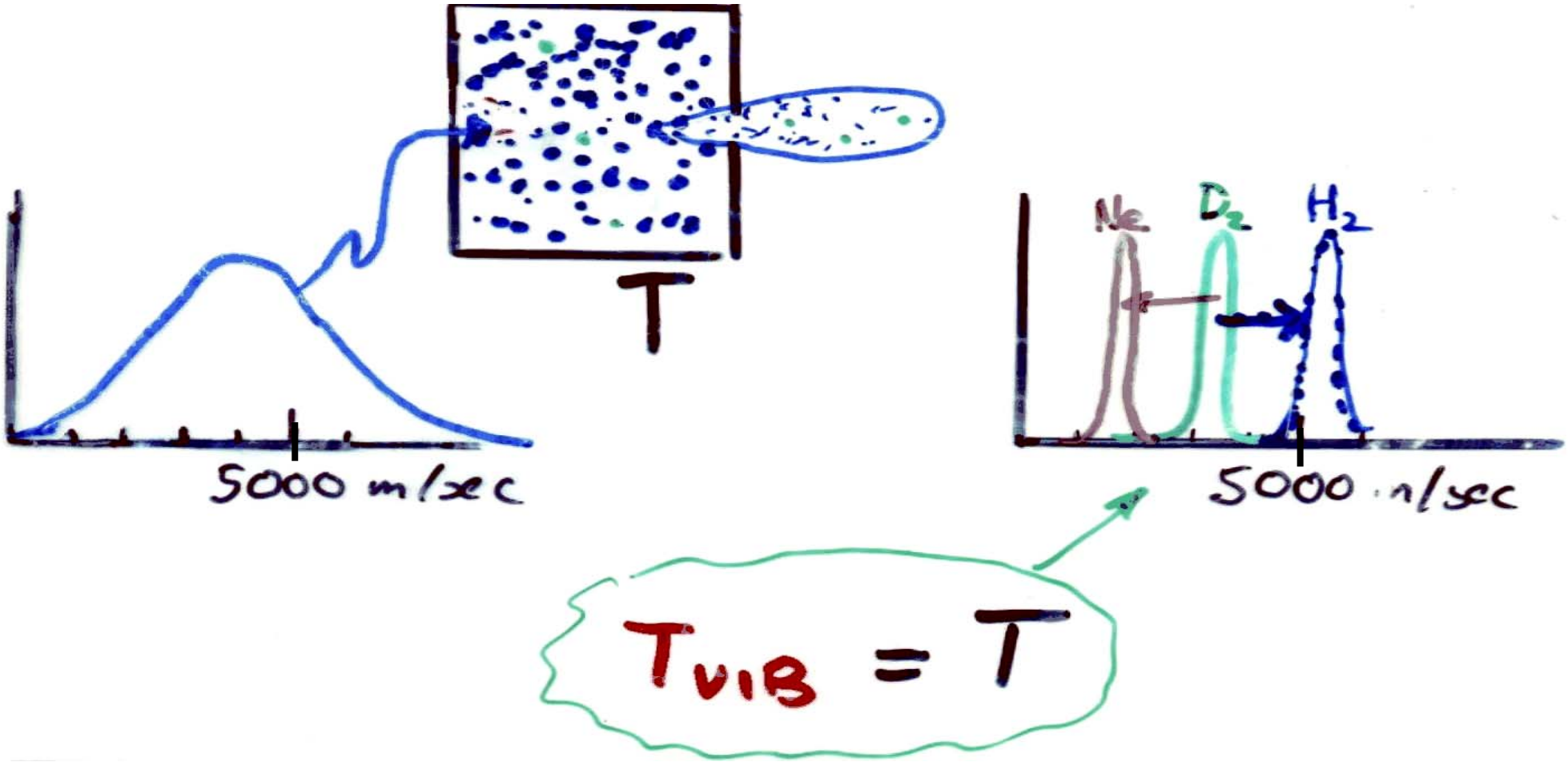
Seeded Supersonic Beams



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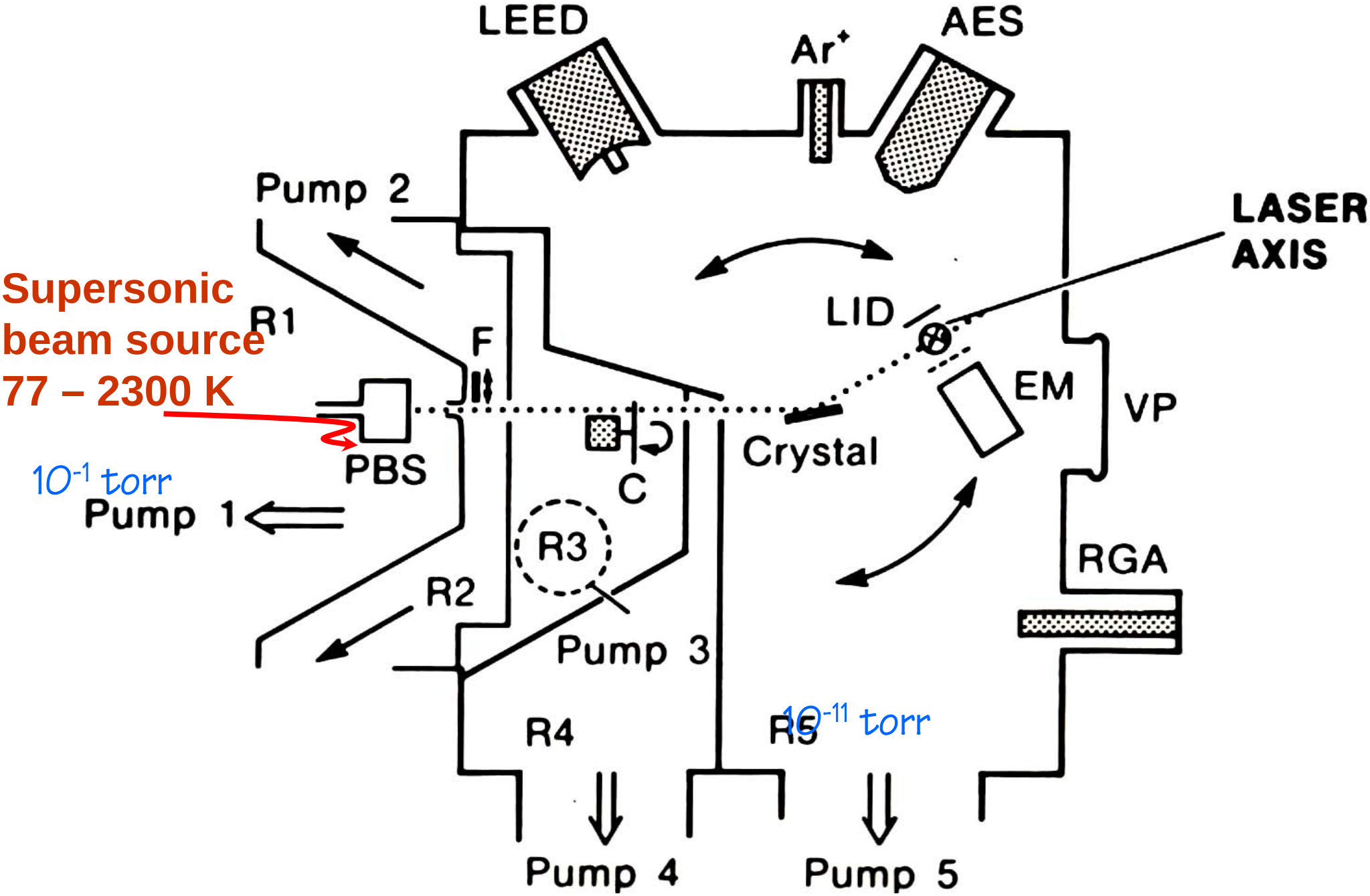
Schematic of Molecular Beam Instrument



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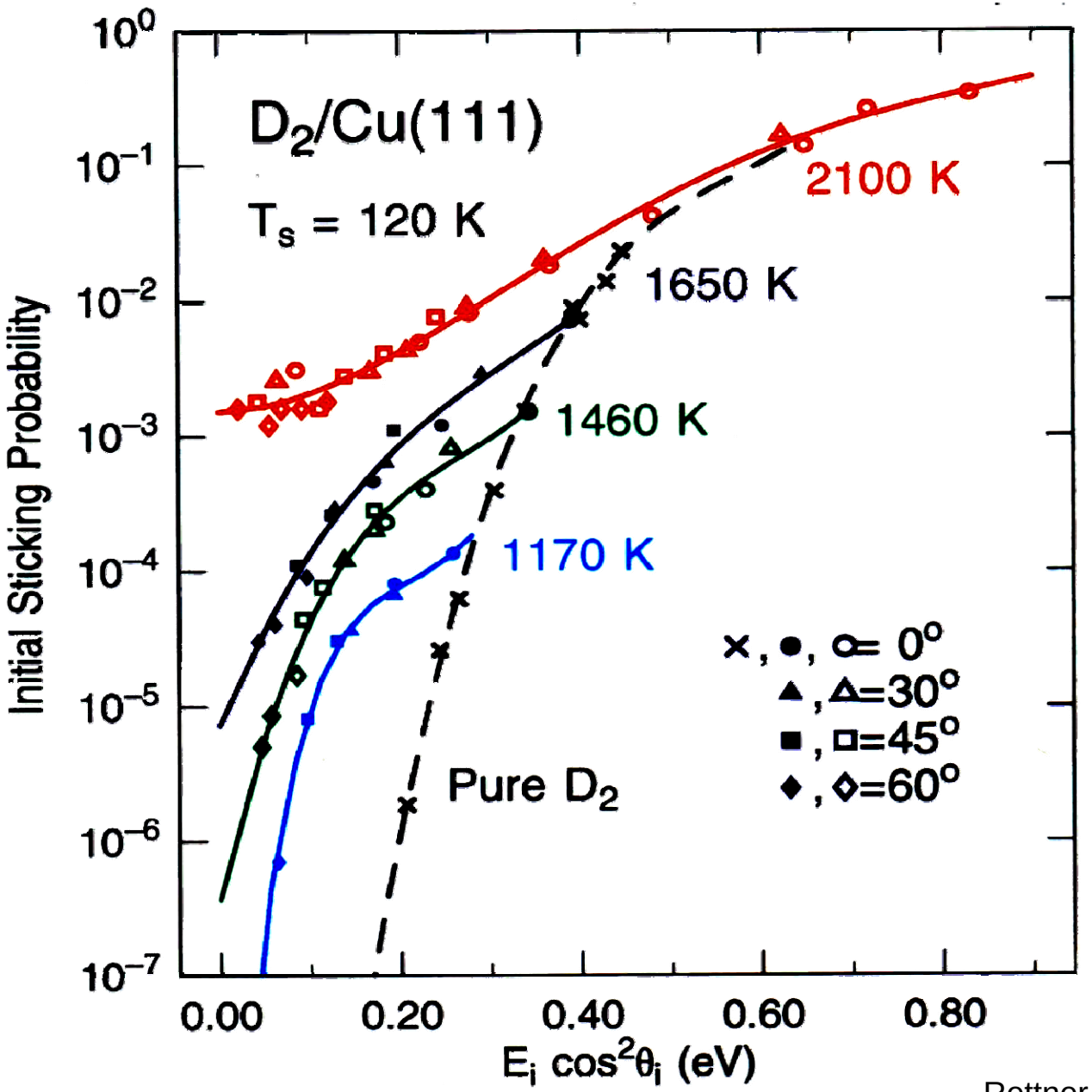
Adsorption Probability vs. Energy

for several vibrational temperatures



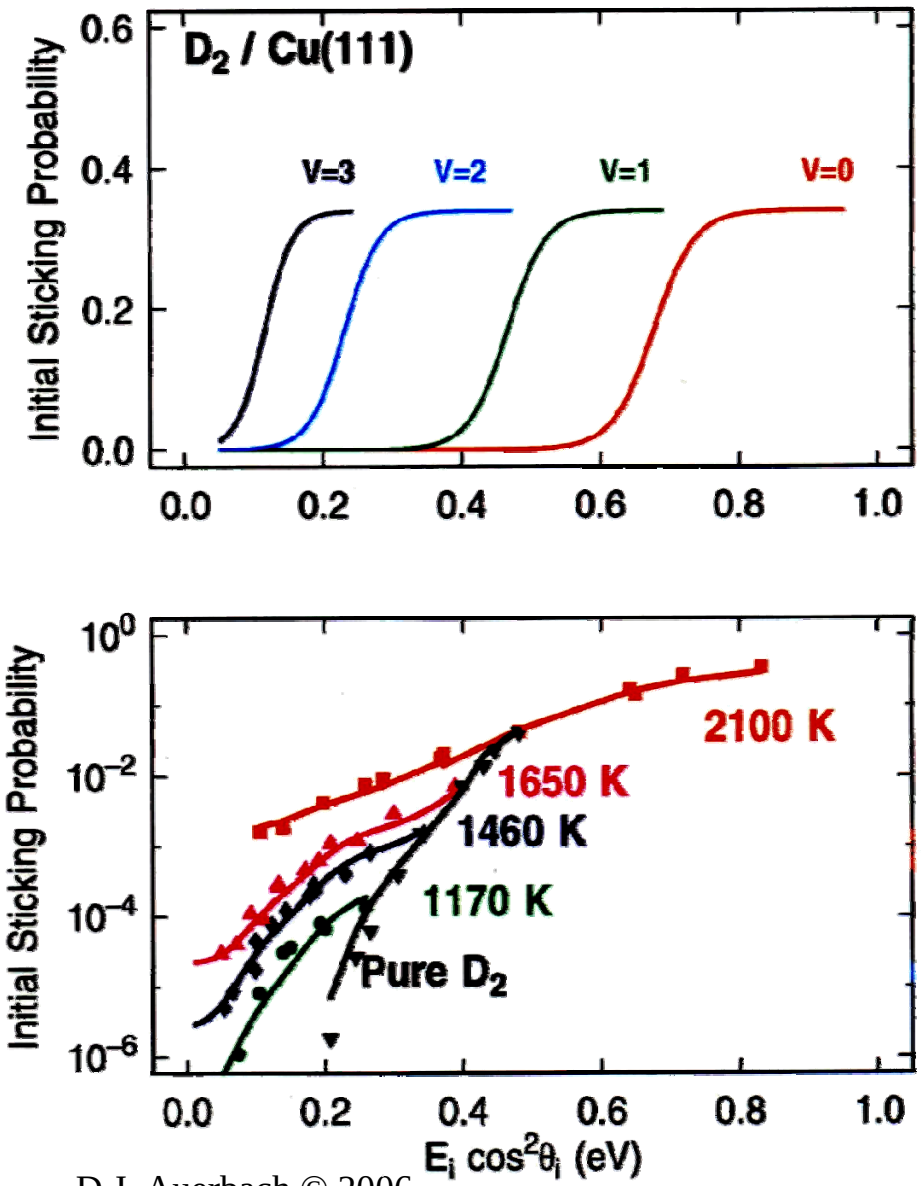
D.J. Auerbach © 2006

Rettner, Auerbach, and Michelsen
Phys. Rev. Lett. **68**, 1164 (1992)

Vibrationally State Resolved S_0

D_2 / Cu(111) – 120 K

Fit to Adsorption Data



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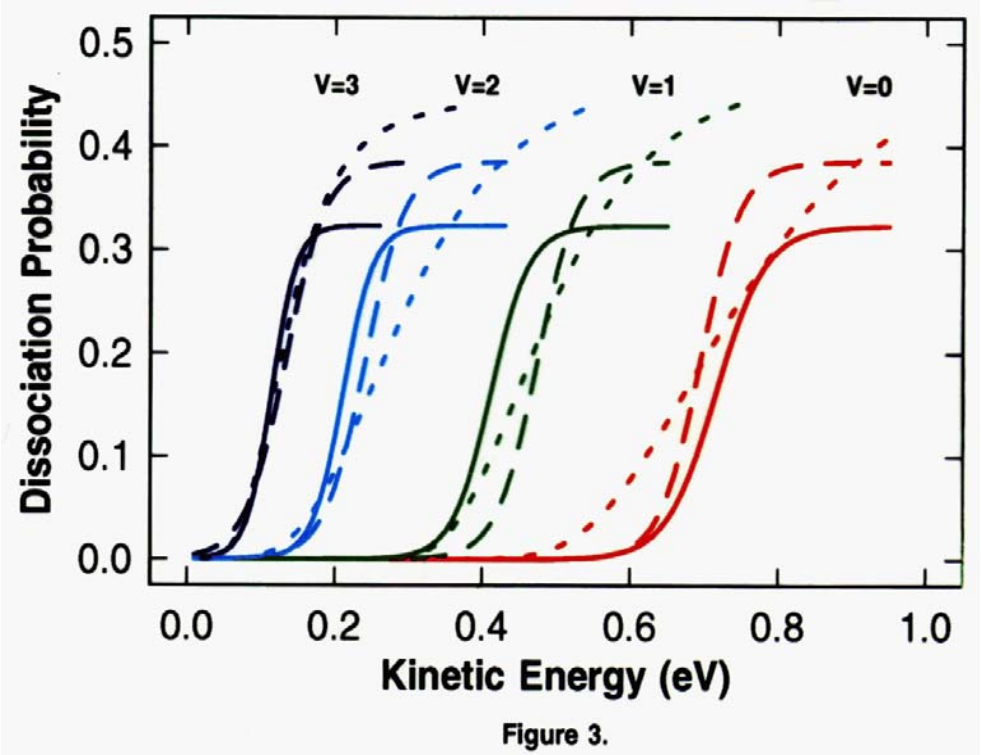
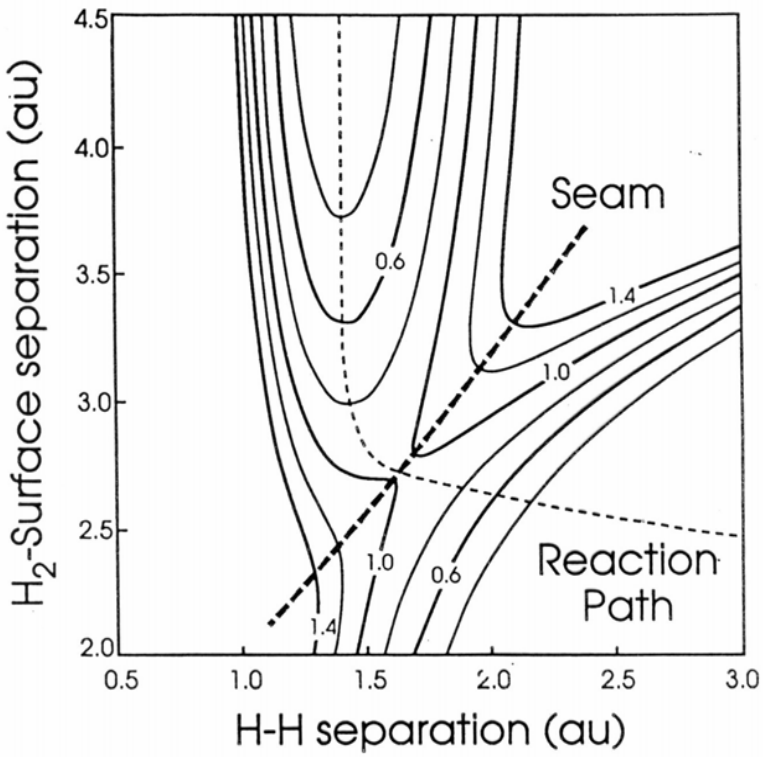
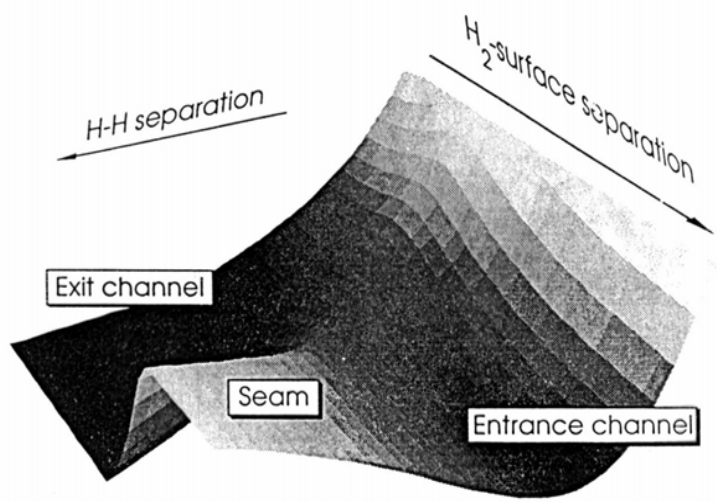
Fits with different functional forms demonstrates robustness



Rettner, Michelsen, and Auerbach
Phys. Rev. Lett. **68**, 1164 (1992)

H_2 / Cu Potentials





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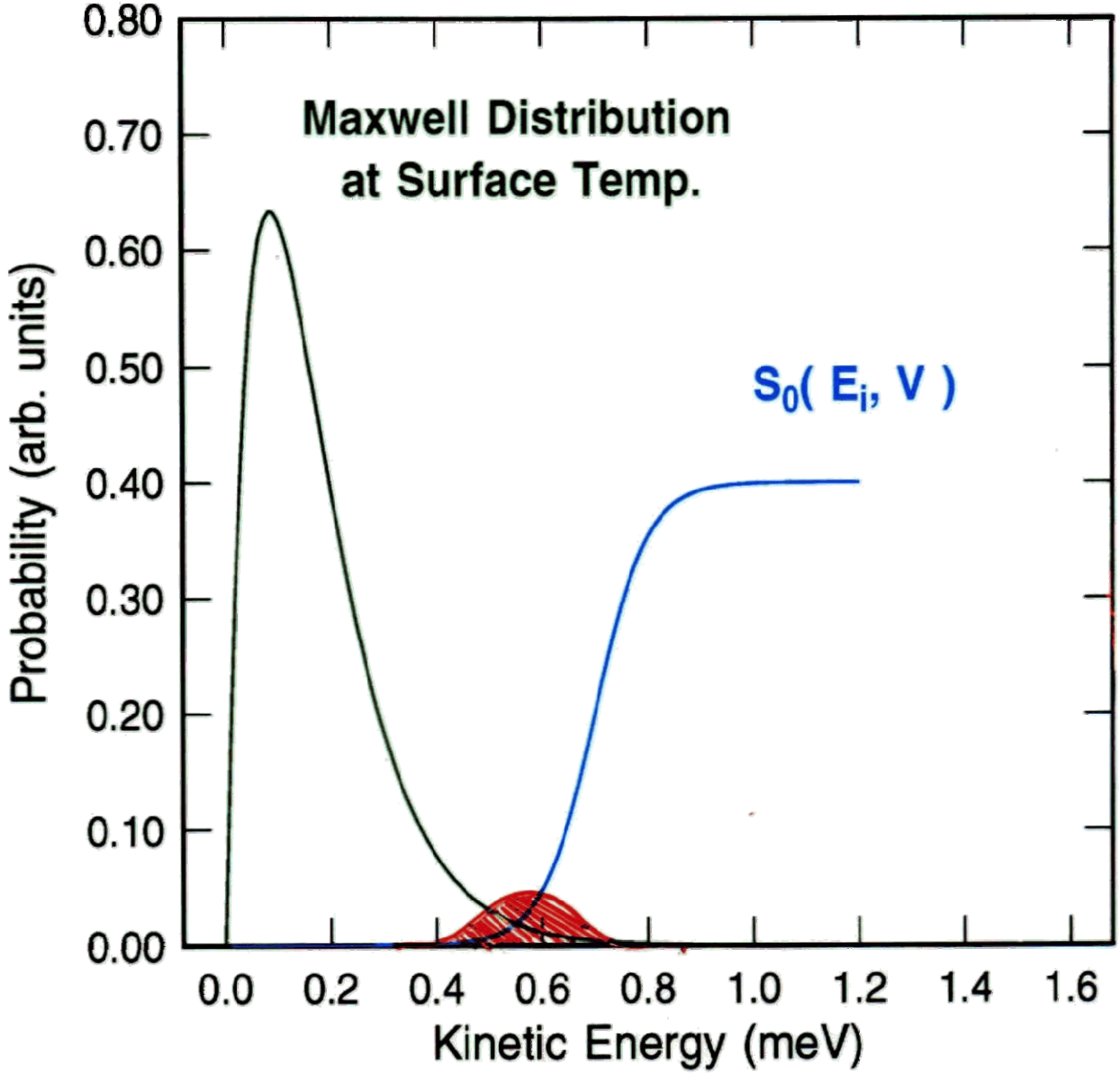
Principle of Detailed Balance

flux that adsorbs = flux that desorbs



DET-BAL1 EXG * 07/02/93

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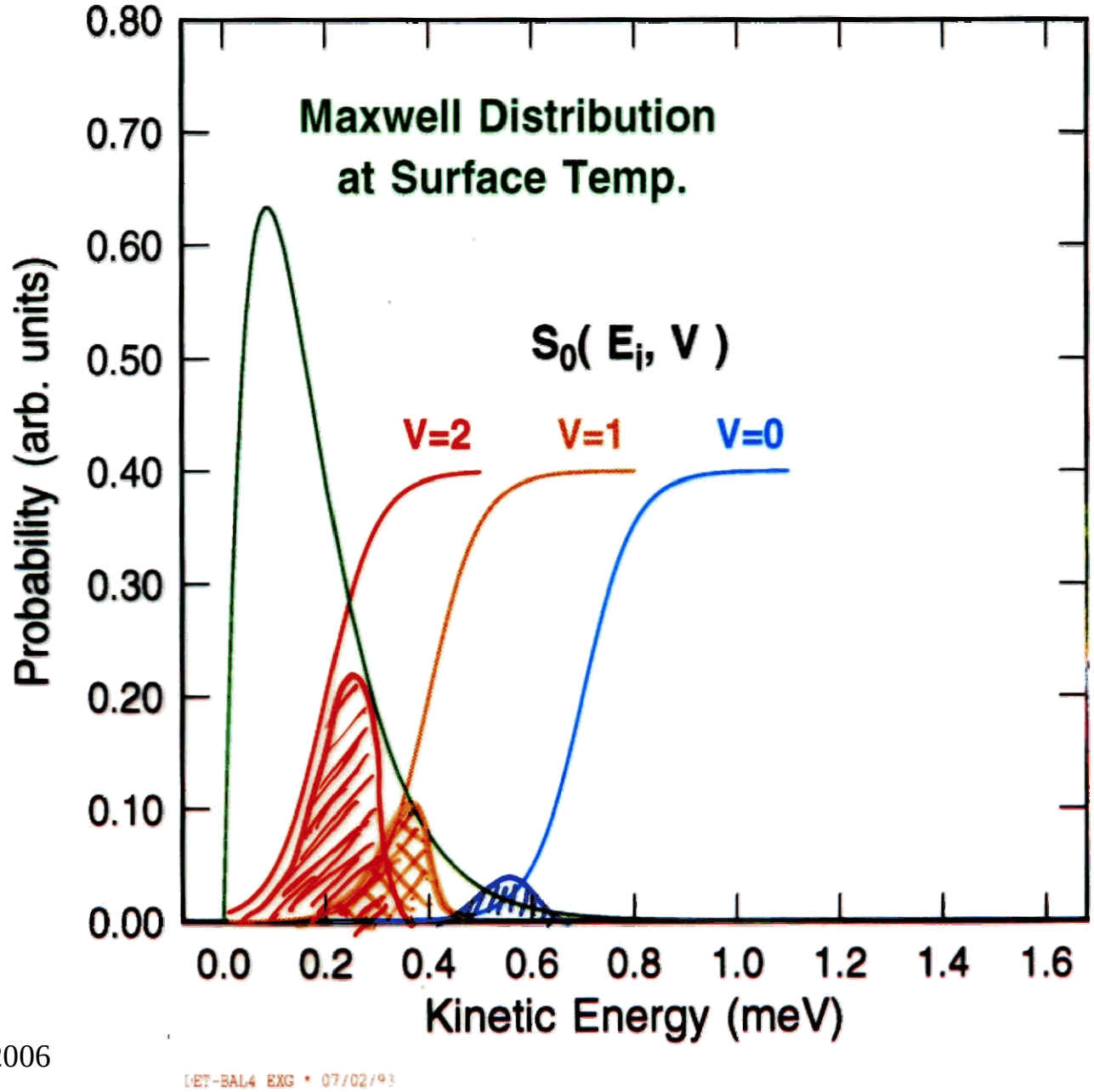
Principle of Detailed Balance II

flux (V) that adsorbs = flux (V) that desorbs



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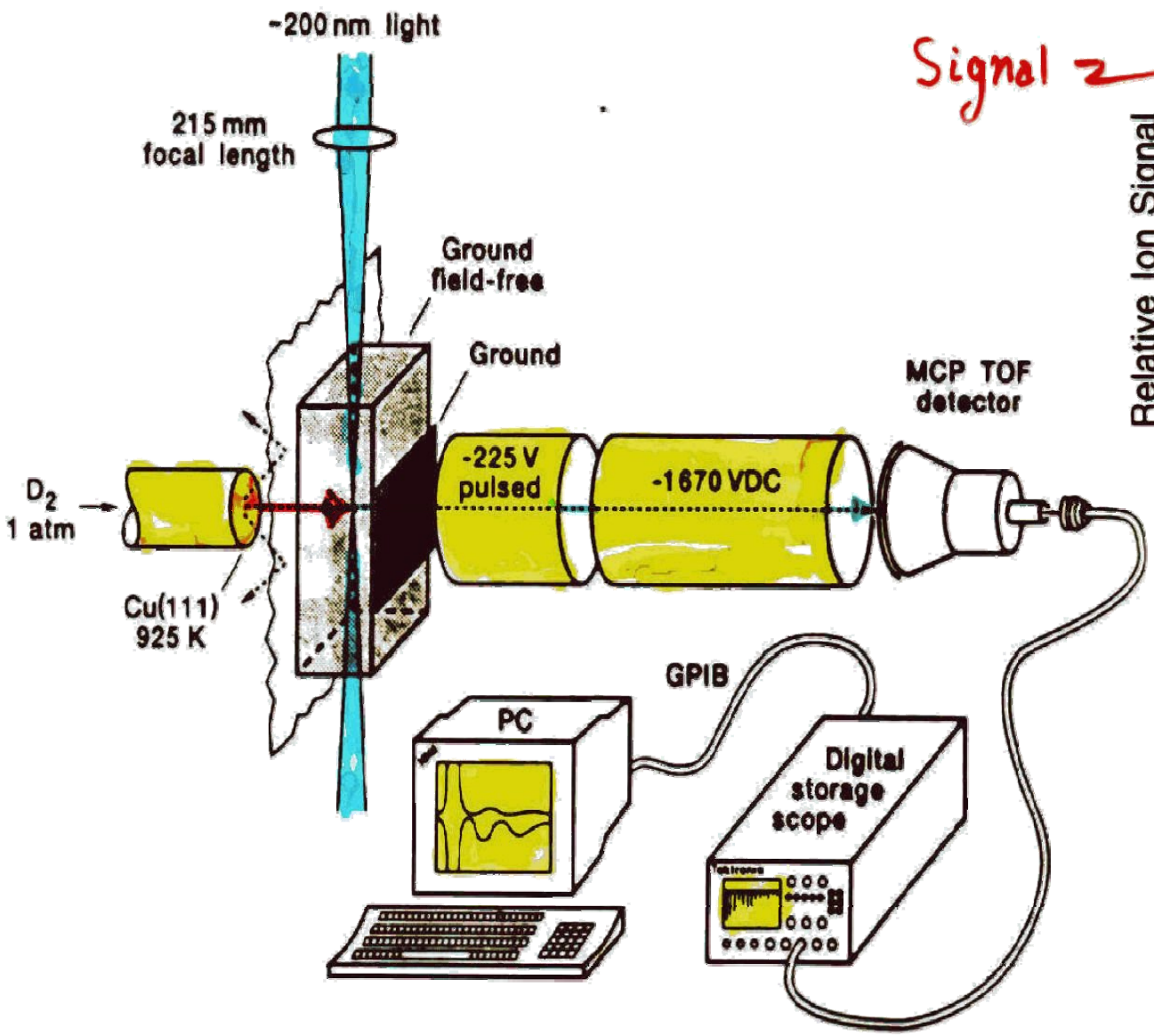
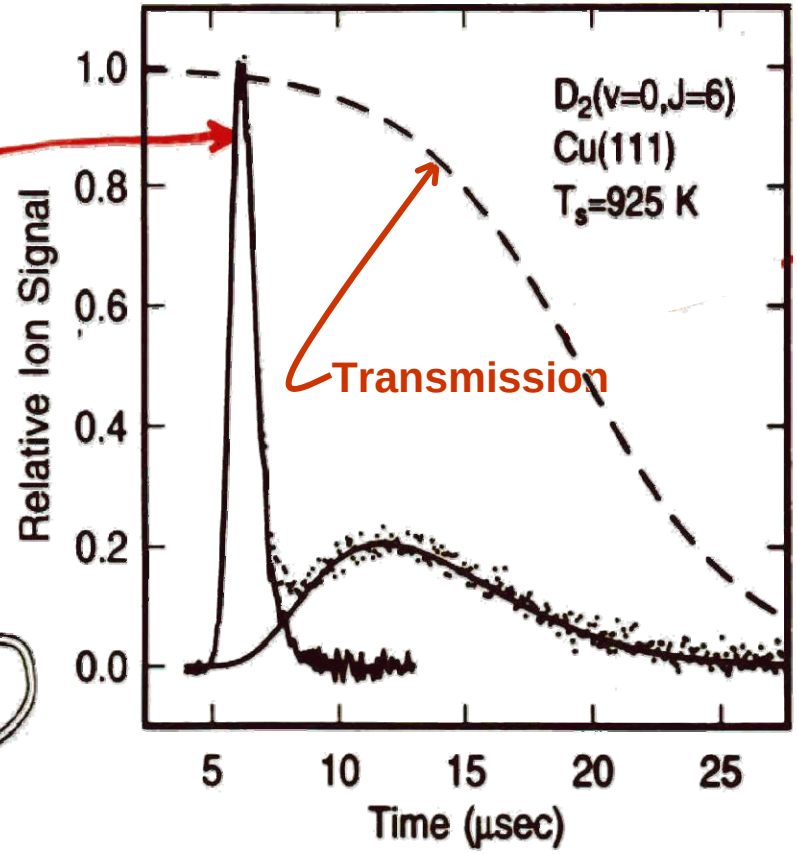
Post permeation Desorption TOF experiment





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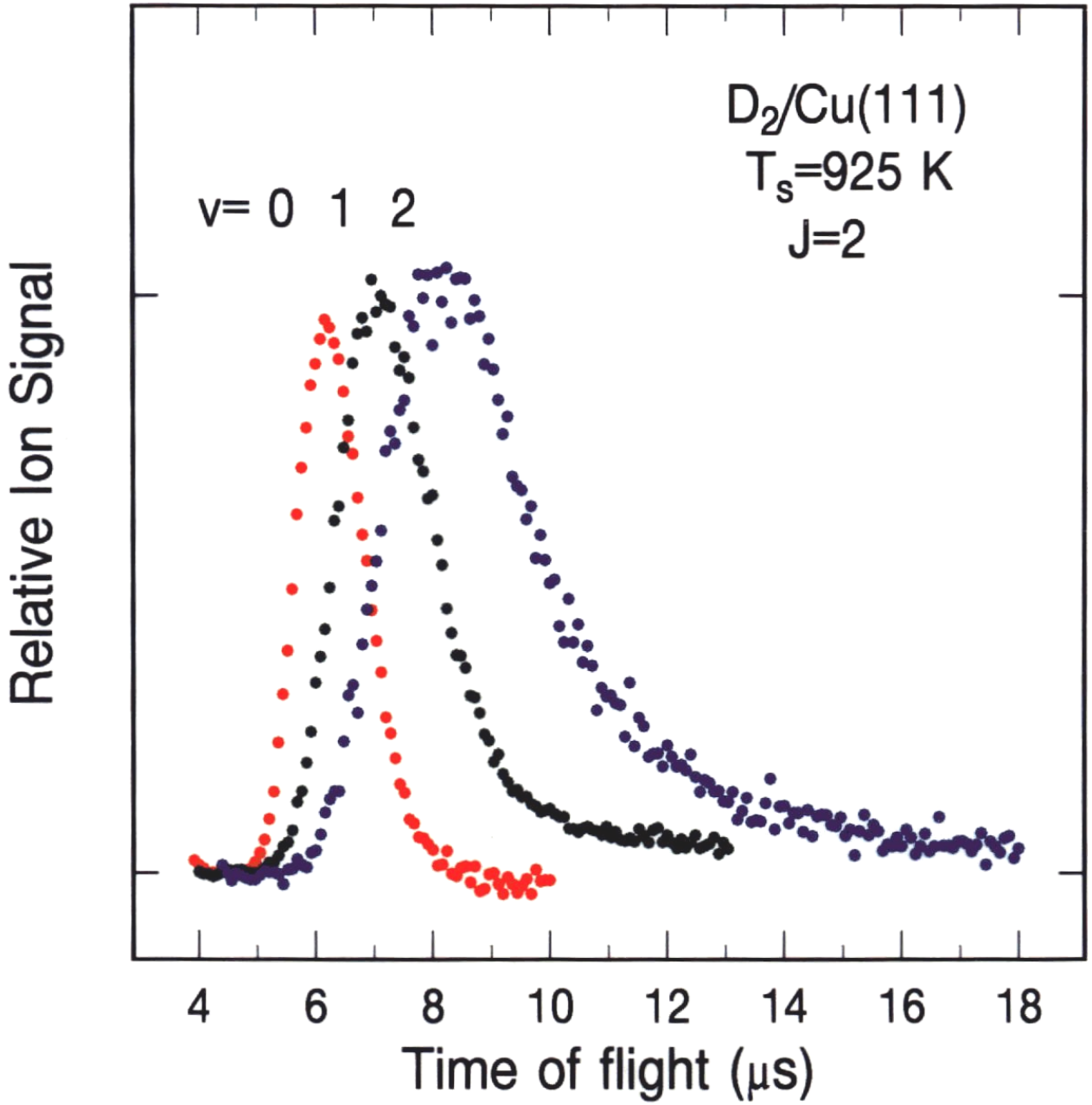
Time of Flight for Desorbing D_2 vs. V

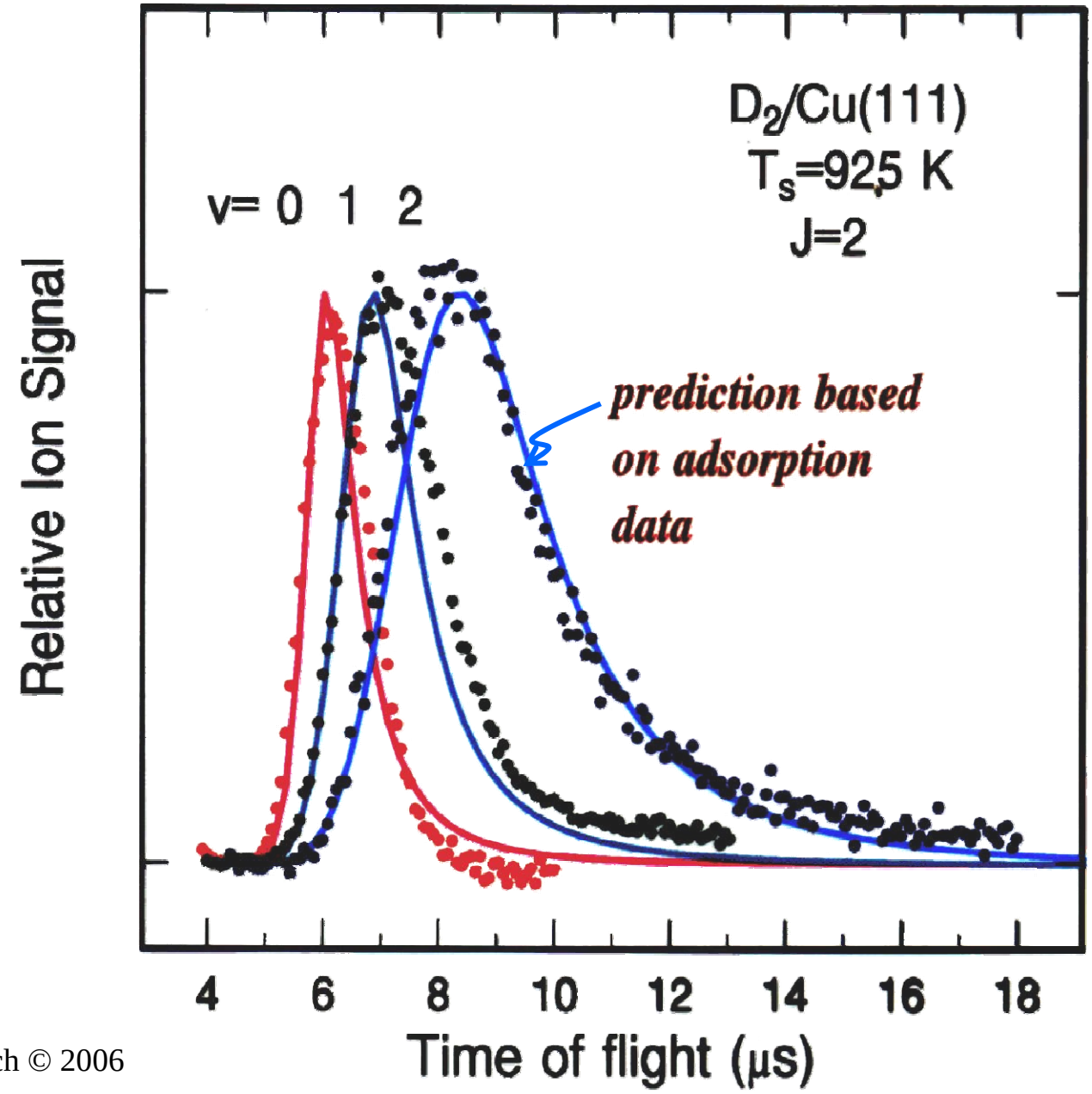


Michelsen, Rettner, Auerbach PRL **68**, 1164(1992)

D.J. Auerbach © 2006

Time of Flight for Desorbing D_2 vs. V:

prediction from adsorption data



Michelsen, Rettner, Auerbach PRL **68**, 1164(1992)

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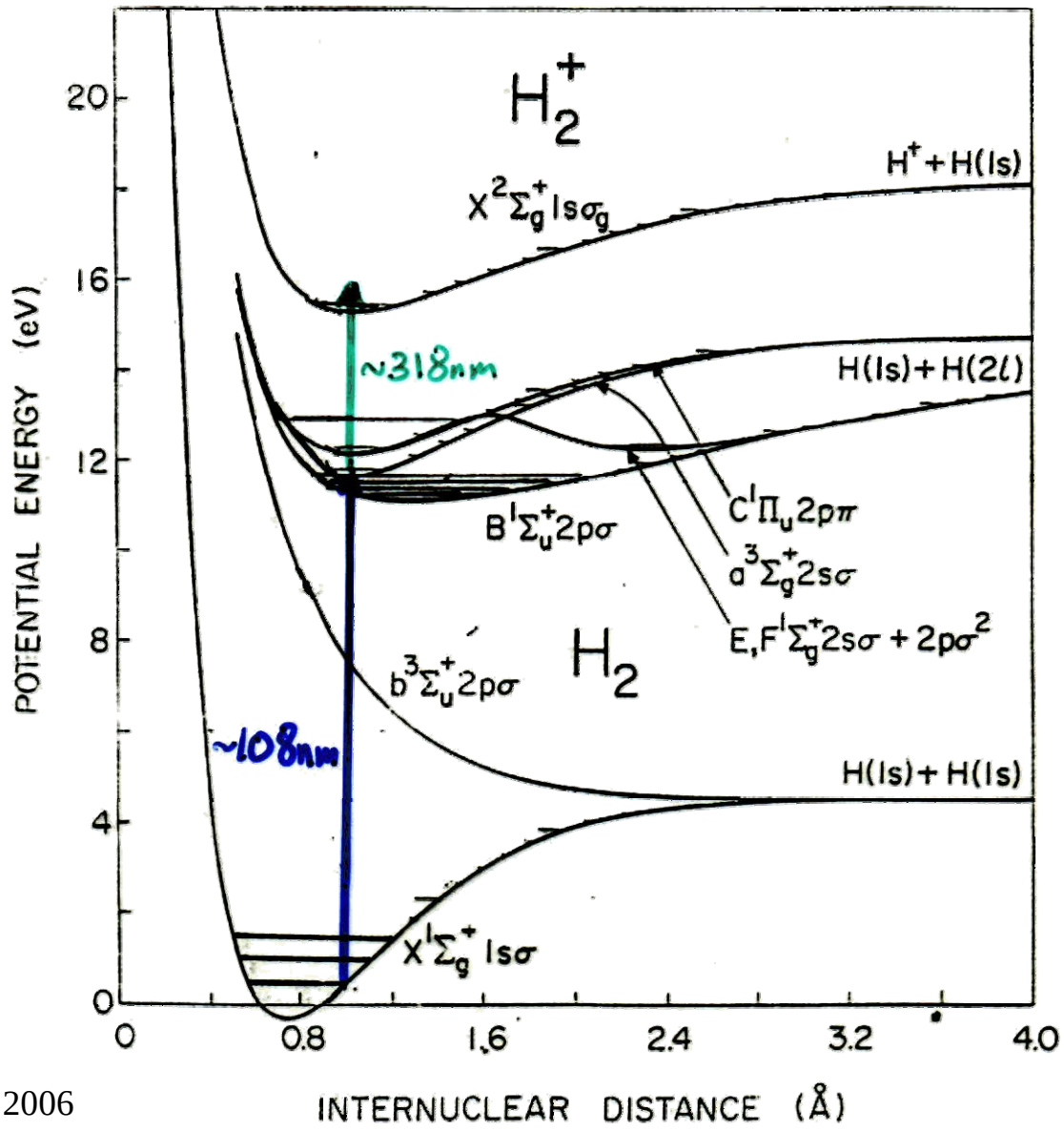
Two Color REMPI - H_2



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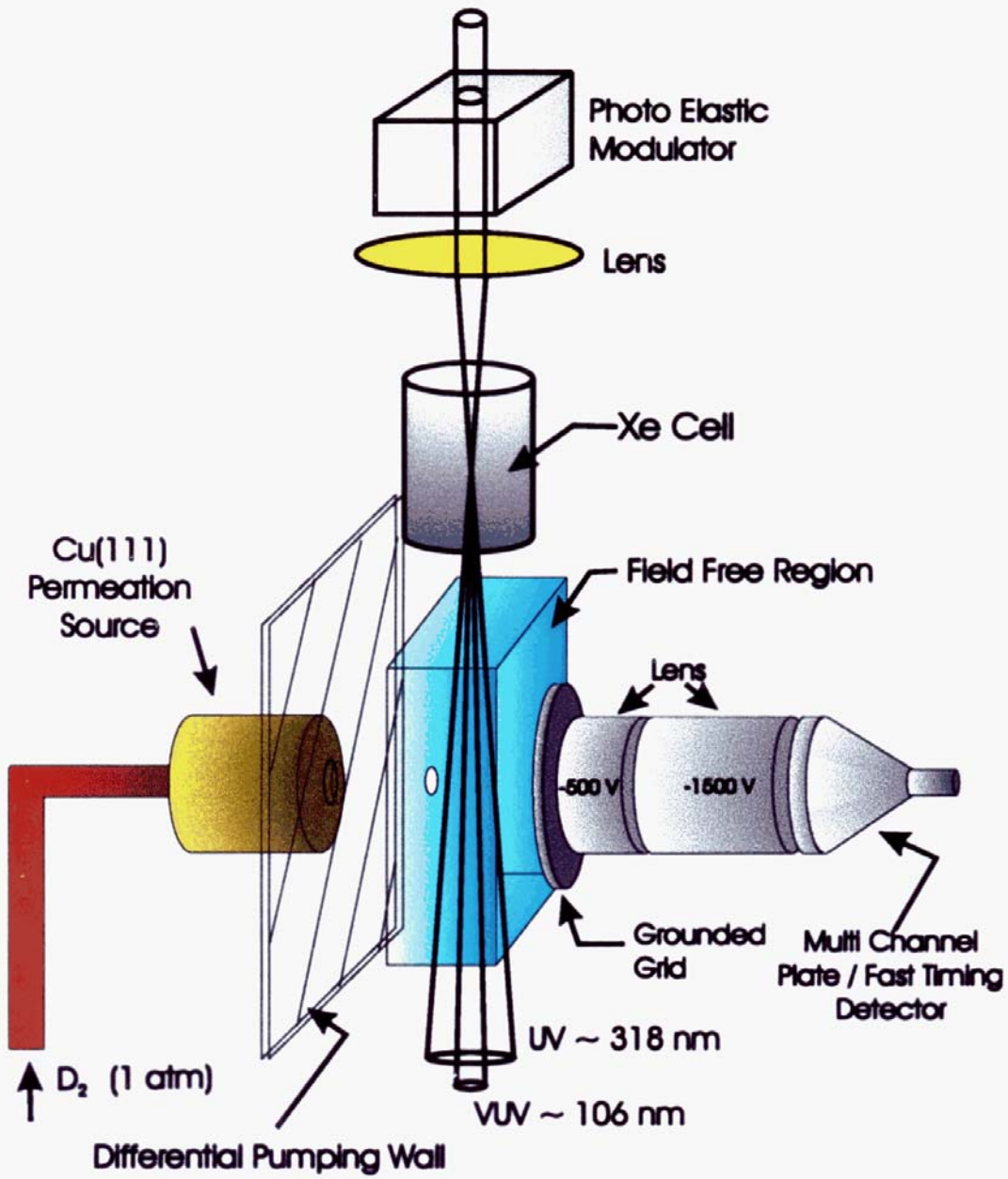
Measurement of Rotational Polarization (With Energy Resolution)



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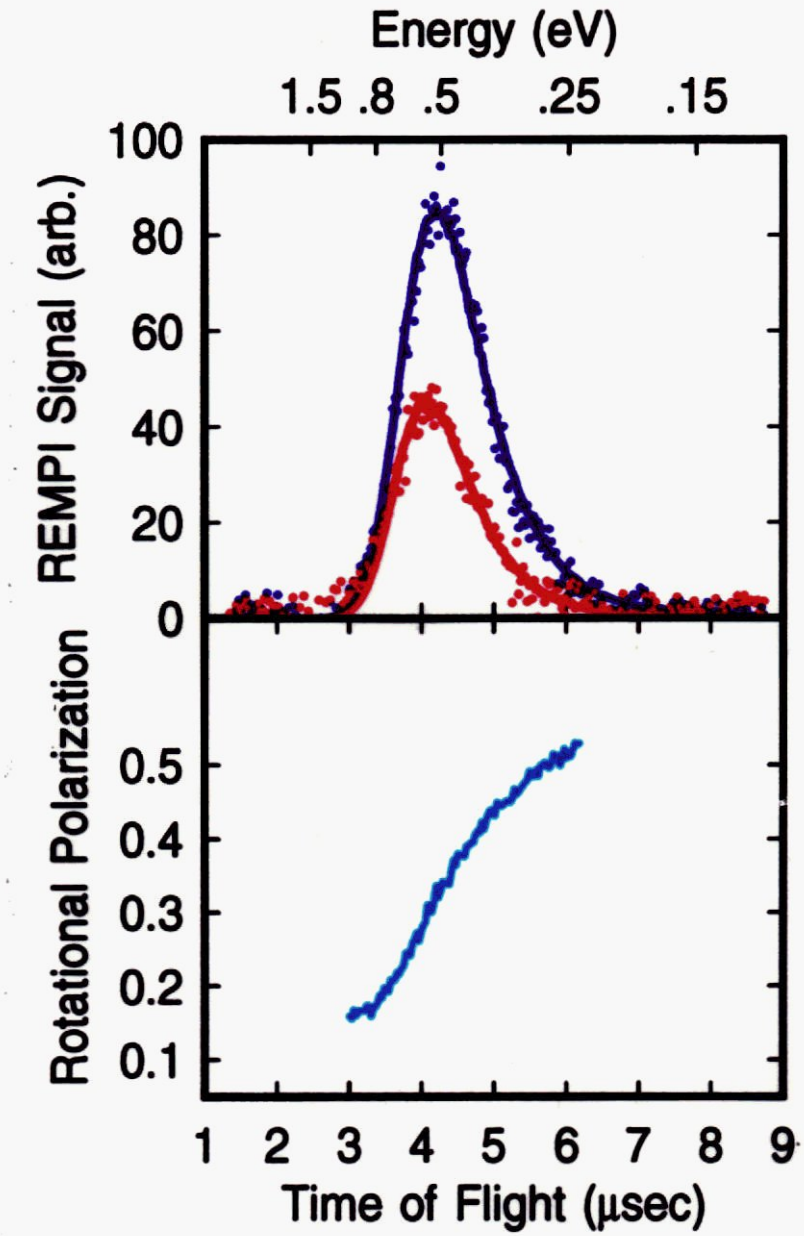
Energy Dependence of Steric Effect



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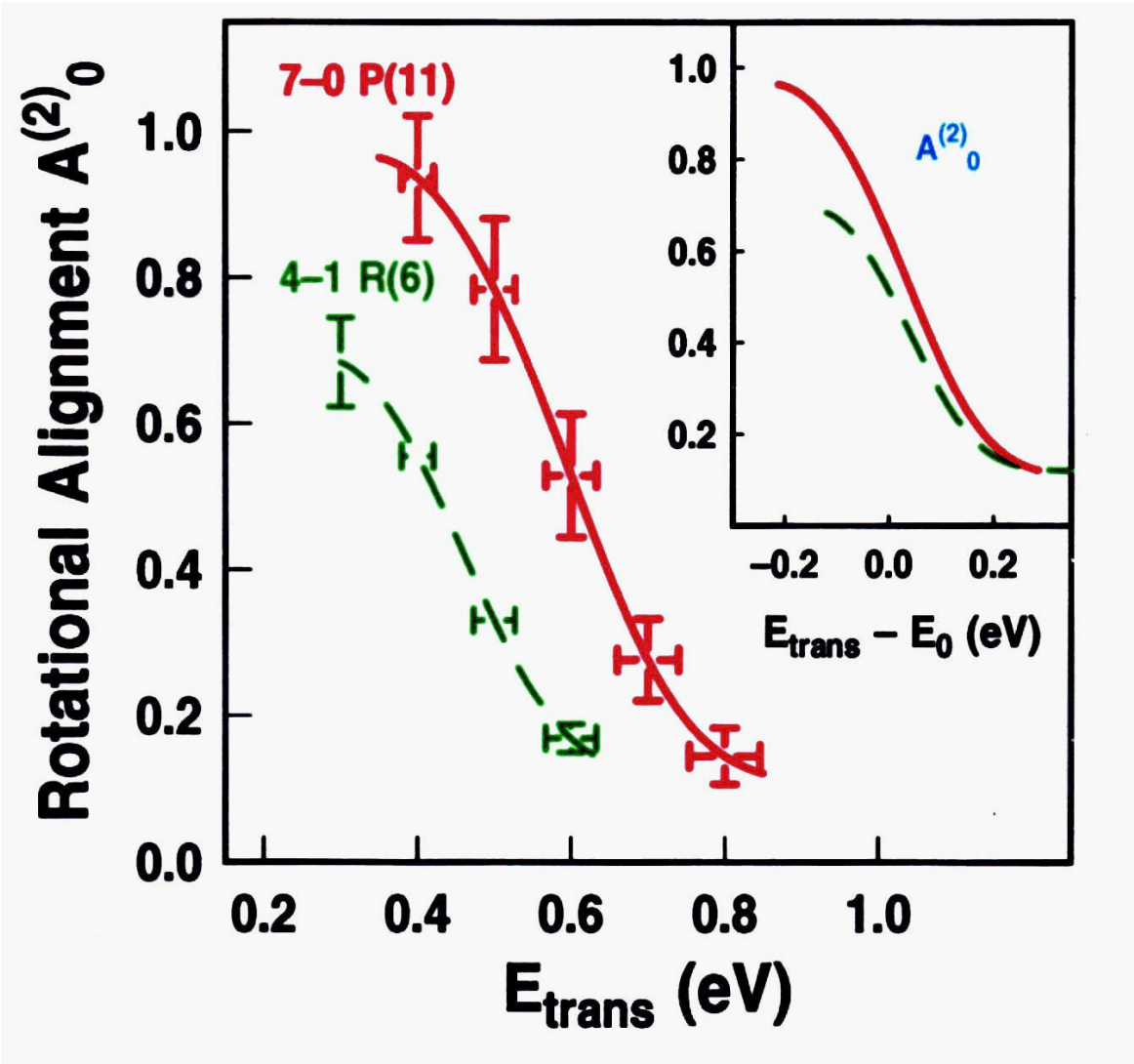
Energy Dependence of Rotational Alignment:

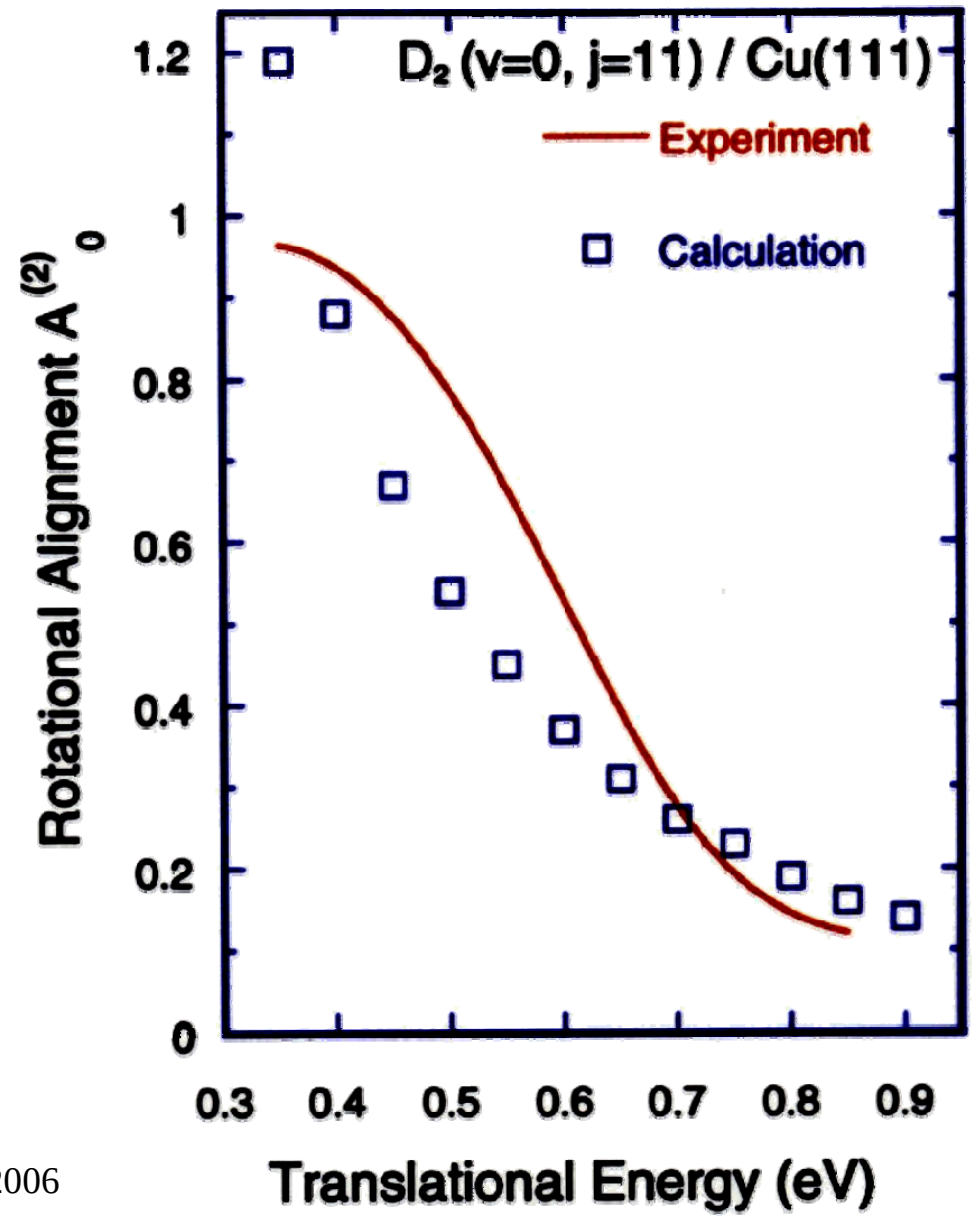
D_2 Desorption from Cu(111)



D.J. Auerbach © 2006

Hou, Gulding, Rettner, Wodtke, and Auerbach
Science 277, 5322, 1997

Comparison of Measured and Calculated Rotational Alignment vs. Energy



Calculation:
Jiqiong Dai and John Light
JCP 1998

Experiment:
H. Hou, S. Gulding, C.T. Rettner, A.M. Wodtke, and D.J. Auerbach
Science **277**,5322 (1997)

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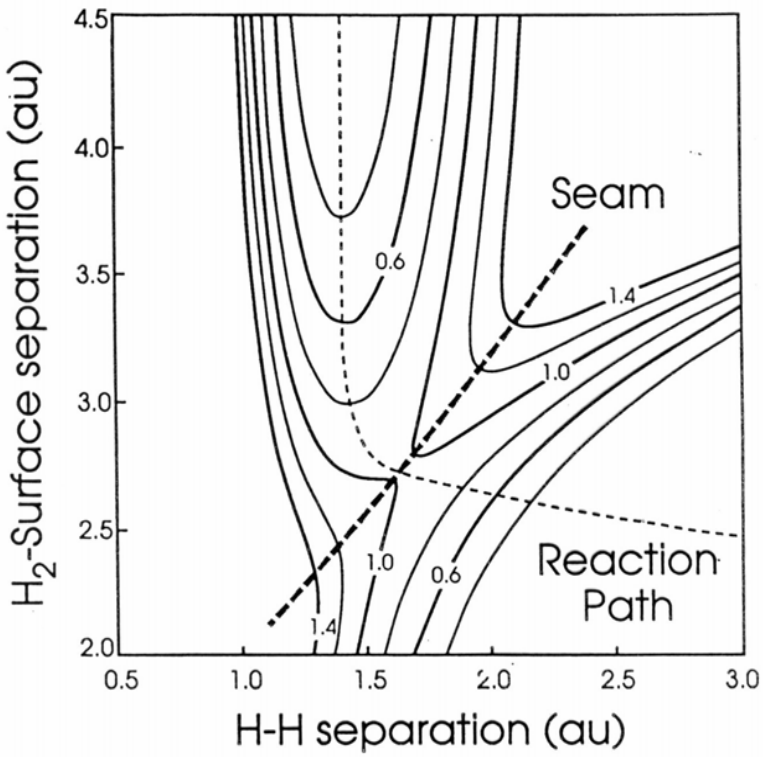
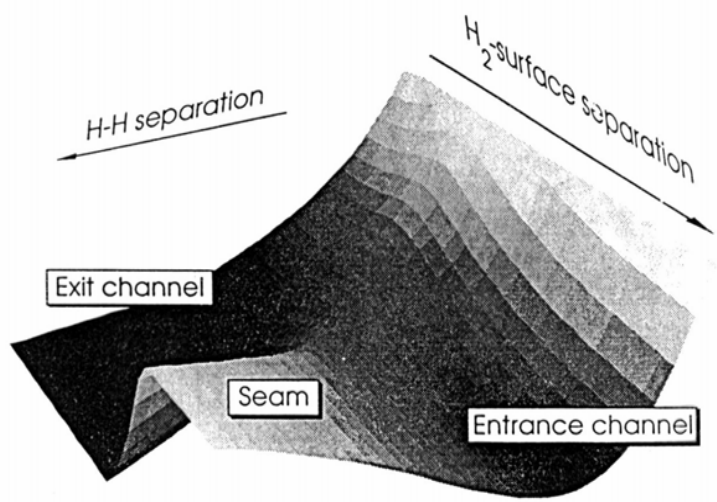
H_2 / Cu Potentials





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Thanks

- ✓ H.A. Michelsen, H. Hou, C.T. Rettner, IBM
- ✓ R.N. Zare, H.A. Michelsen, Stanford
- ✓ A. M. Wodtke, S.J. Gulding, UCSB

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