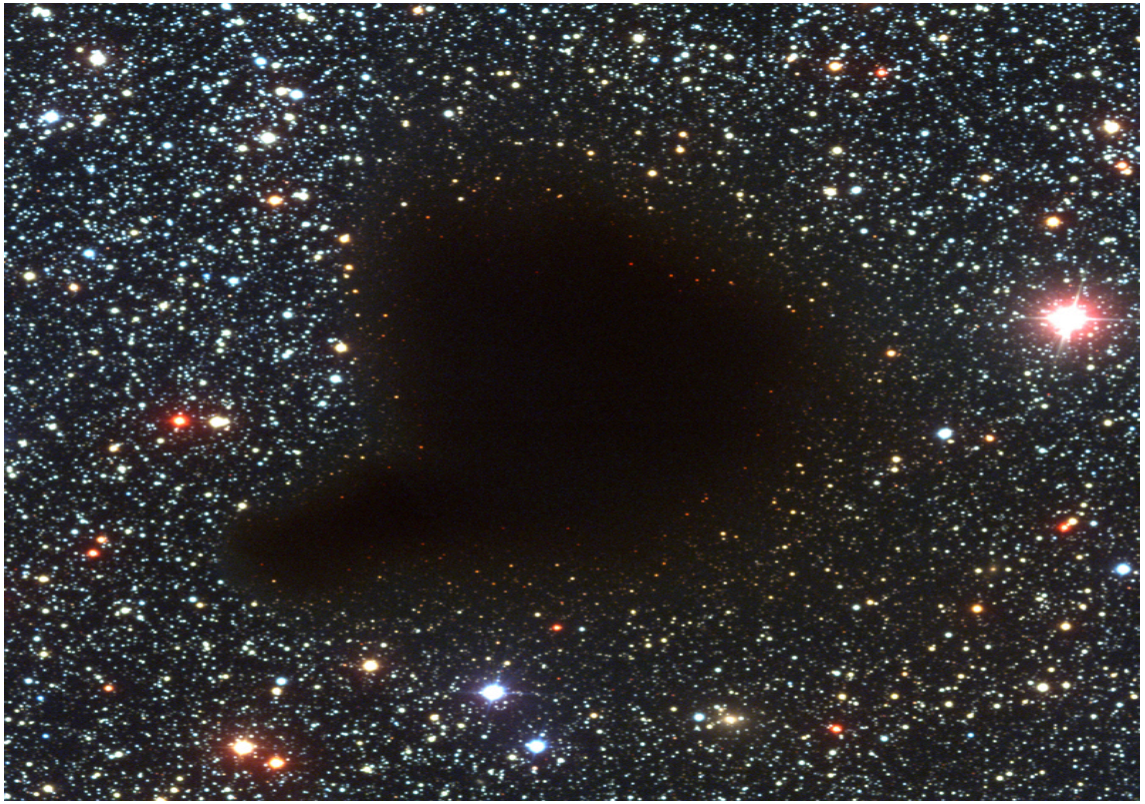
H trapping and sticking on graphite



Molecular Cloud Barnard 68

1. Formation of H_2 on (graphitic) interstellar dust grains
2. Etching of graphite-lined fusion reactor walls
3. Hydrogen storage in graphitic systems
4. Graphene
5. Dynamics of Eley-Rideal reactions on graphite

Outline

1. Some history
   - Eley Rideal reactions of H(g) with H/graphite

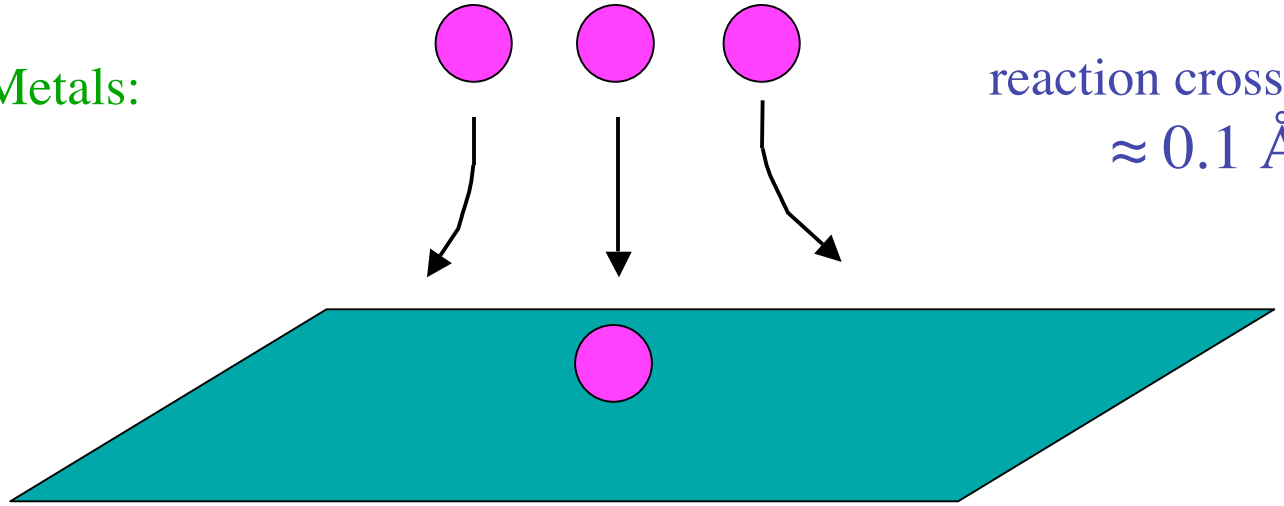
2. H chemisorption on graphite
   - Why so large?

3. H physisorption on graphite
   - Low energies and temperatures
   - Diffraction mediated trapping and sticking
   - H_2 : molecular precursors to dissociation on metals

What controls Eley-Rideal reactivity?

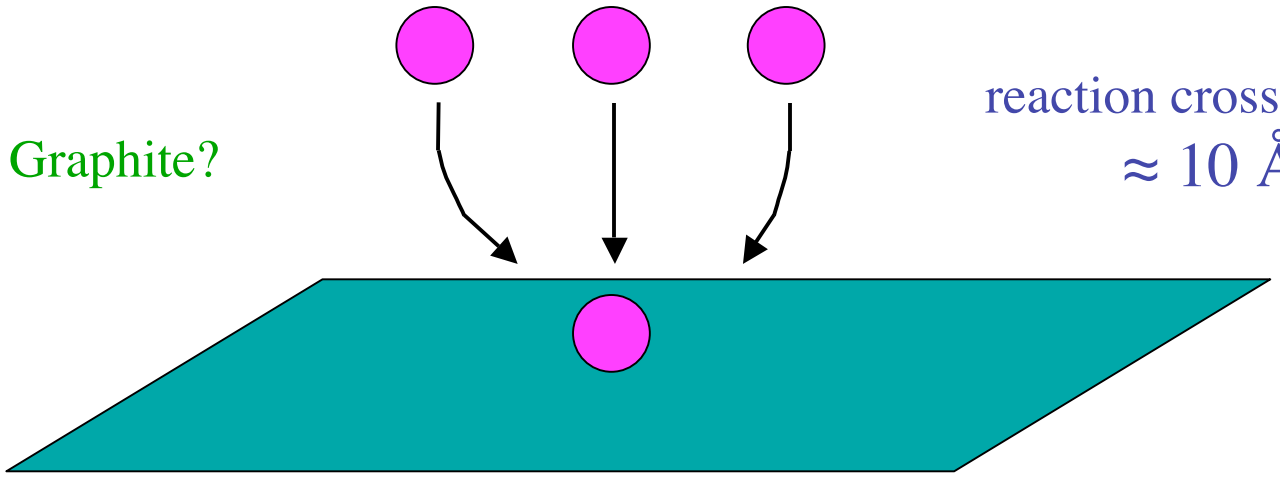
Competition between H-H and H-substrate attraction

Metals:



reaction cross section
≈ 0.1 Å^2

Graphite?



reaction cross section
≈ 10 Å^2

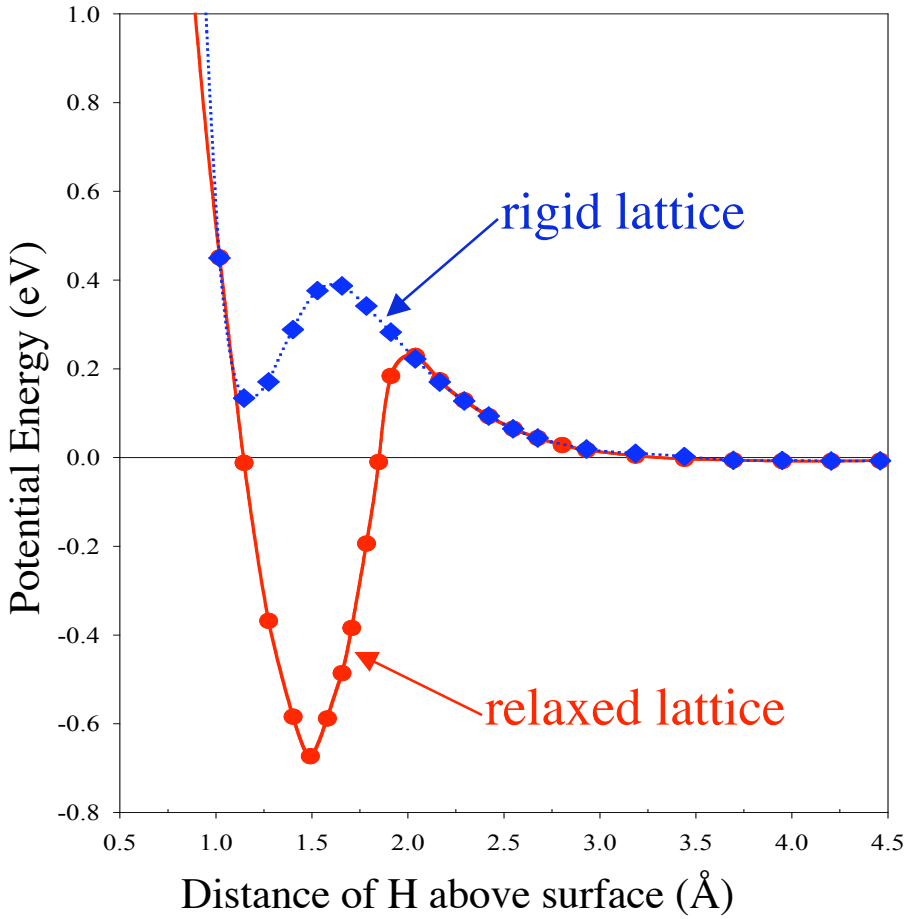
Jackson and Lemoine, *J. Chem. Phys* **114**, 474 (2001)

Lattice relaxation is required for H to chemisorb to a terrace carbons

Jeloaica and Sidis, *Chem Phys Lett* 300, 157 (1999)

Sha and Jackson, *Surf. Sci.* 496, 318 (2002)

Ferro, Marinelli and Allouche, *J Chem Phys* 116, 8124 (2002)



The bonding Carbon puckers by 0.36 Å

- drop in π-plasmon intensity

The barrier to adsorption is 0.25 eV

- $E_{act} = 0.2 \pm 0.1$ eV

H and D vibrational frequencies

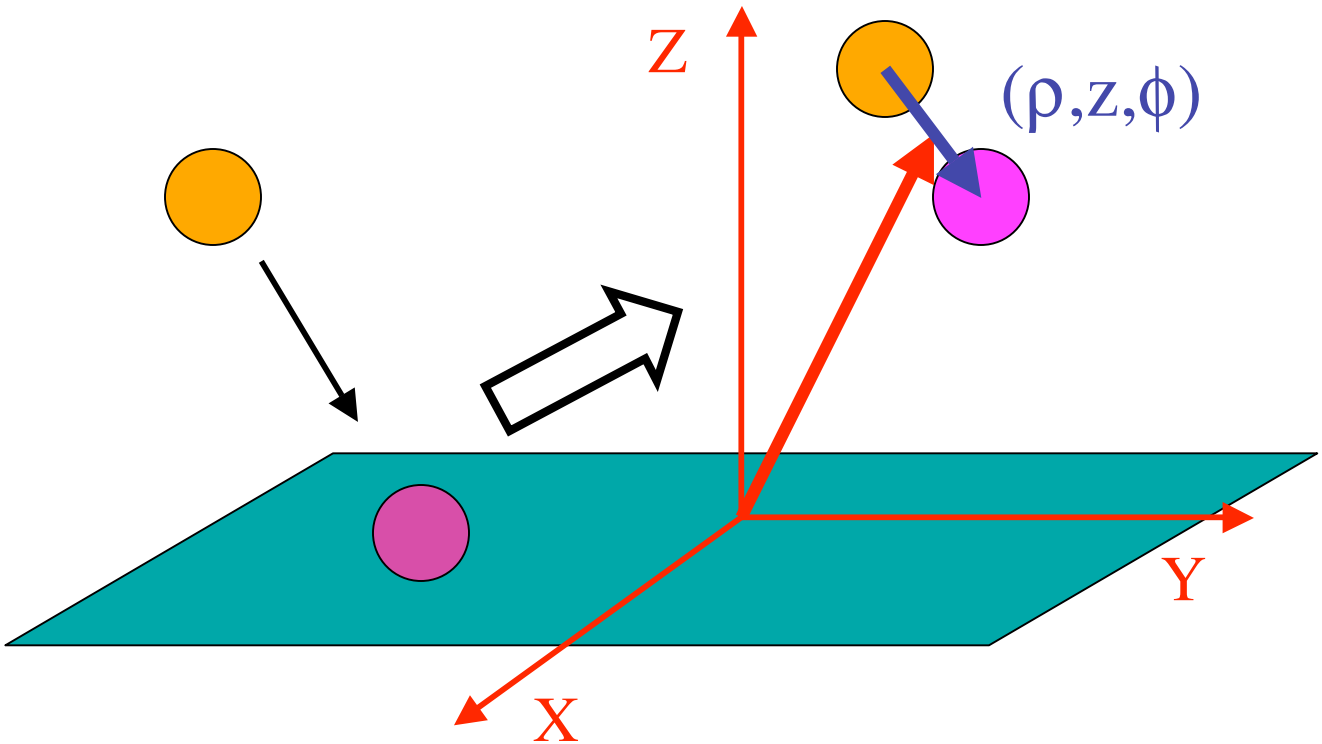
- consistent with HREELS

Zecho, Güttler, Sha, Jackson, Küppers, *J Chem Phys* 117, 8486 (2002)

H and H_2 readily add to edge carbons, but are not easily abstracted by H

Sha and Jackson, *J. Am. Chem. Soc.* 126, 13095 (2005)

Quantum flat-surface model



- The momenta conjugate to X, Y and ϕ are conserved

$$\Psi(t) = e^{iK_X X} e^{iK_Y Y} \sum_m \frac{1}{\sqrt{2\pi}} e^{im\phi} \psi_m(Z, z, \rho; t)$$

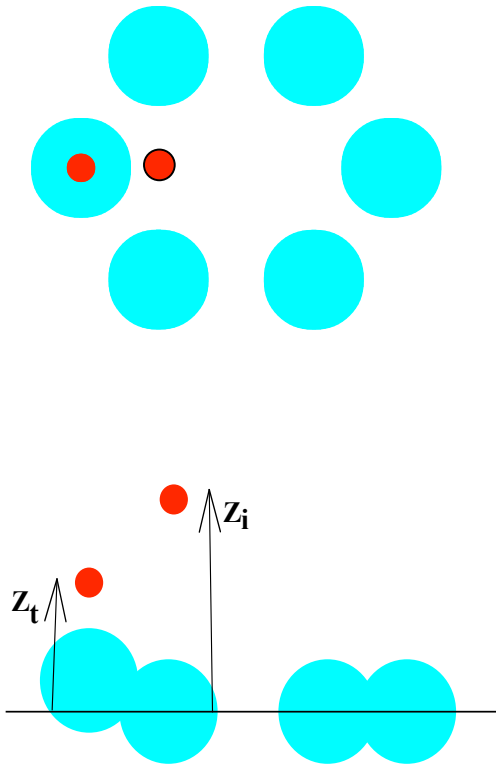
Persson and Jackson, *J. Chem. Phys.* **102**, 1078 (1995)

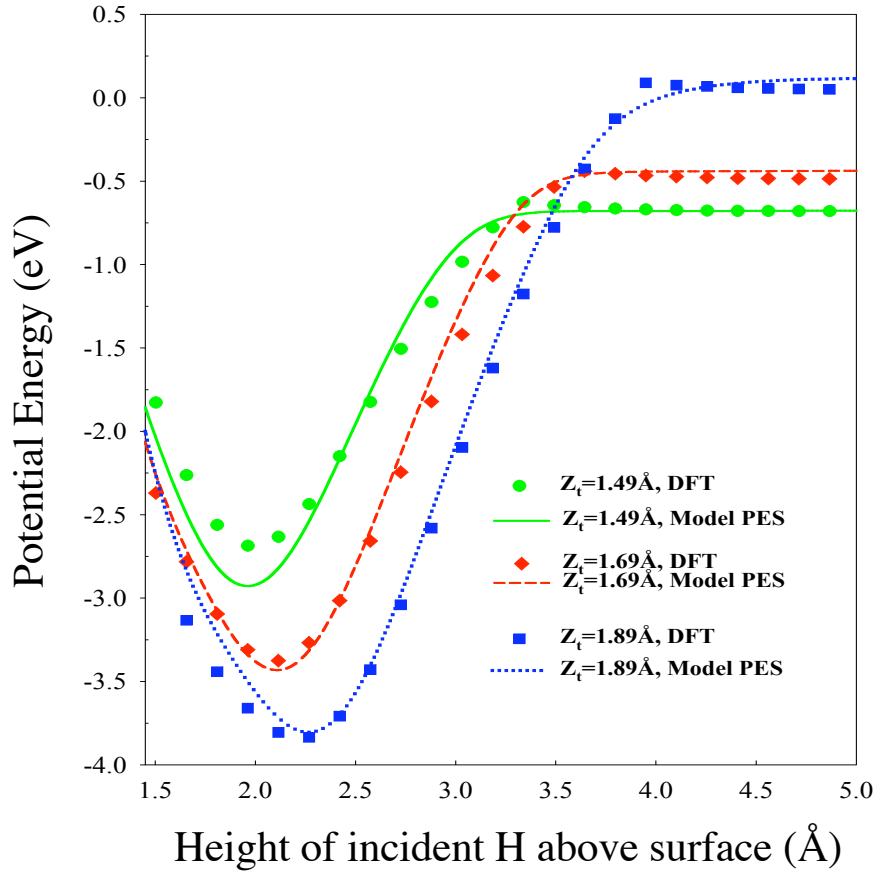
- FFT for z and Z, discrete Bessel transform for ρ

Lemoine and Jackson, *Comp Phys. Comm.* **137**, 415 (2001)

- Extract ro-vibrationally resolved cross sections

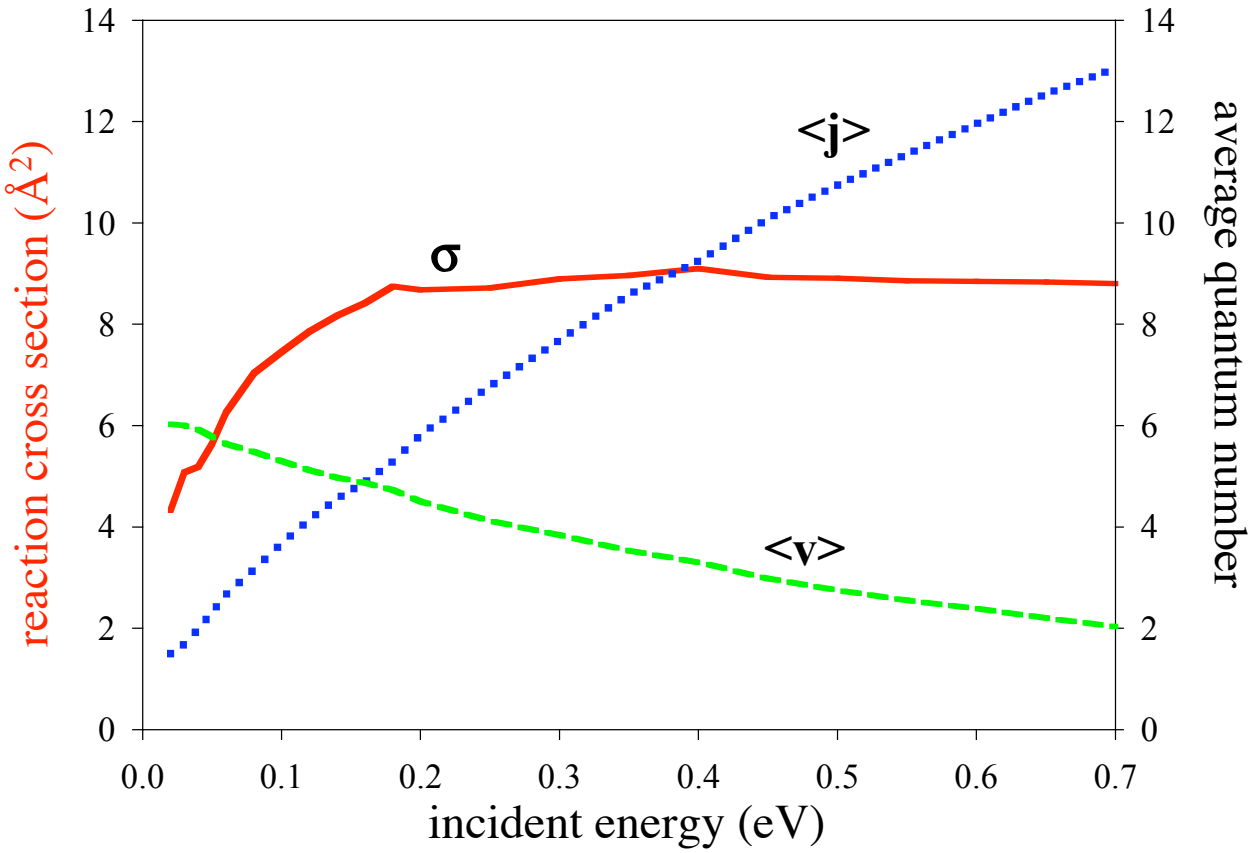
PES for H abstraction by H





- Strong H-H attraction dominates entrance channel
- The reaction to form H_2 is very exothermic
  - -4.0 eV for the adiabatic (relaxed lattice) case
  - -3.2 eV for the sudden (rigid lattice) case

H(g) + D-graphite ⟶ HD(g) + graphite



Internal energy ≥ 2 eV, Translational energy ≥ 1 eV

Experiment: $\sigma = 8$ Å^2 at 1/8 ML

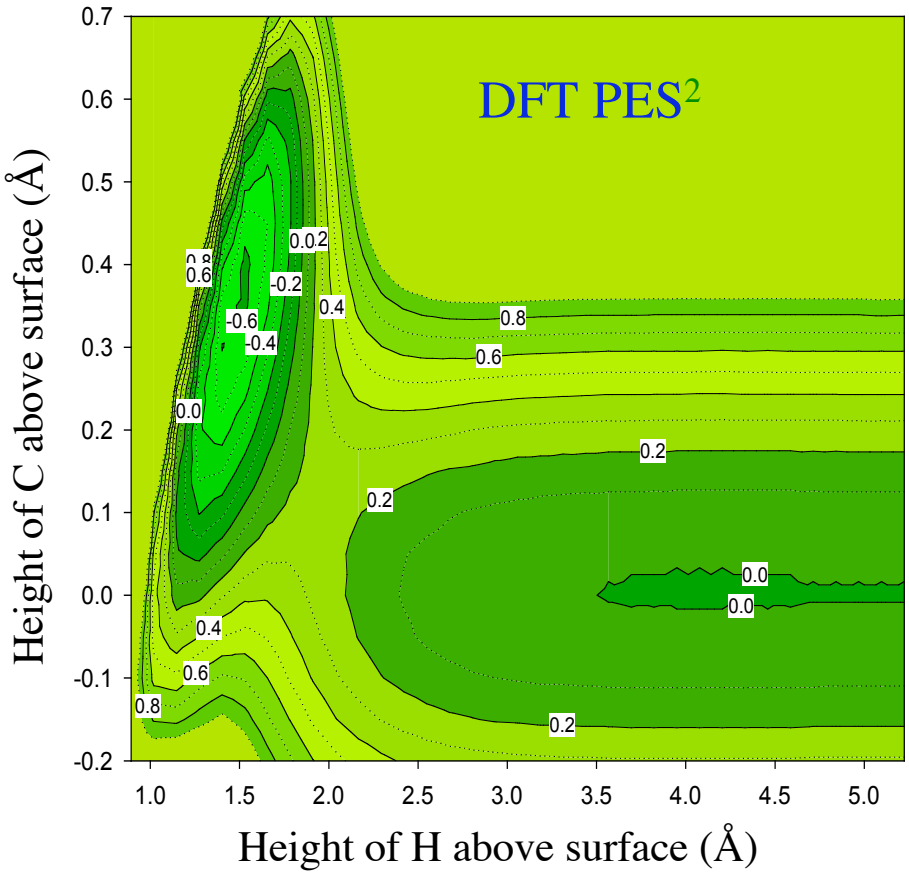
kinetics consistent with ER mechanism

Zecho, Güttler, Sha, Lemoine, Jackson, Küppers, *Chem Phys Lett* 366, 188 (2002)

Sha, Jackson , Lemoine, *J Chem Phys* 116, 7158 (2002)

Why is the H-graphite sticking probability so large?

- Experimentally[1] $s_0 = 0.4 \pm 0.2$
- The Carbon must significantly distort before the H atom moves away



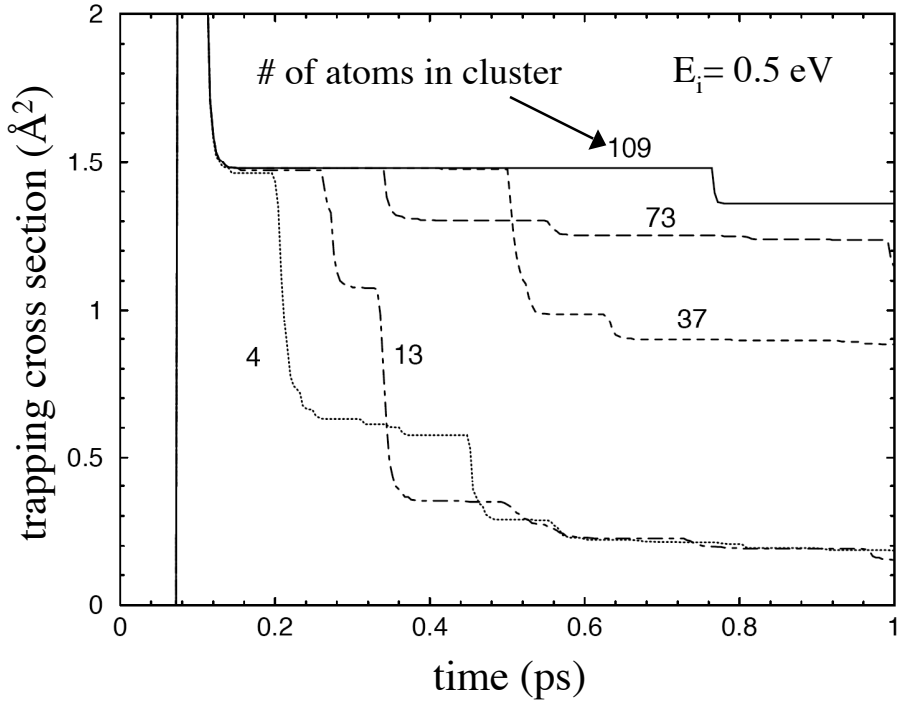
Collinear quantum model[2]

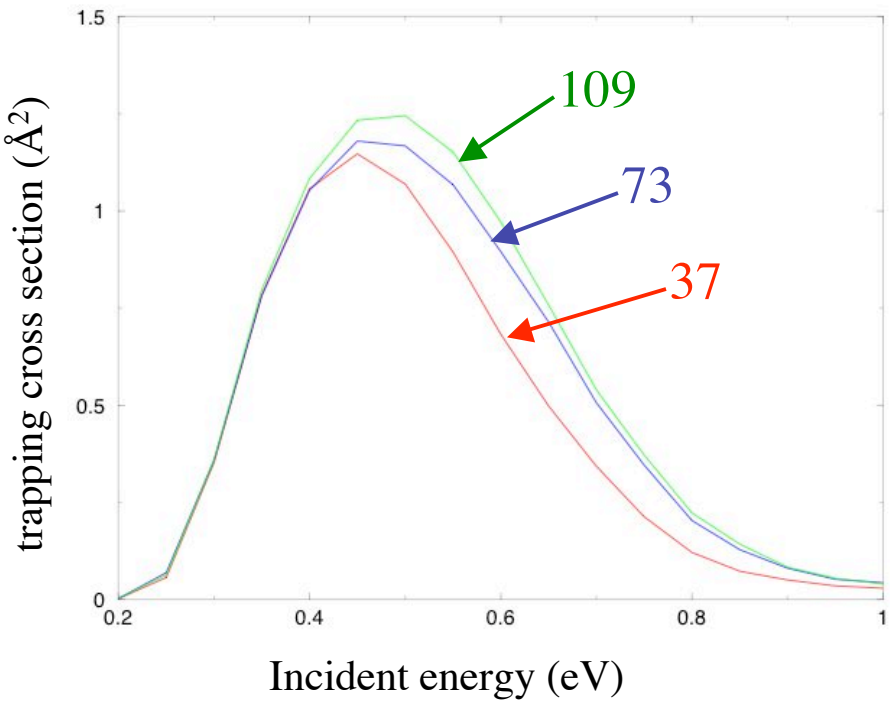
- The bonding carbon puckers in about 40 fs.
- There are several long-lived resonances.
- We (very) crudely estimated that $s_0 = 0.06$

1. Zecho, Güttler, Sha, Jackson, Küppers, *J Chem Phys* 117, 8486 (2002)
2. Sha, Jackson, Lemoine, Lepetit, *J Chem Phys* 122, 014709 (2005)

Quasiclassical cross sections

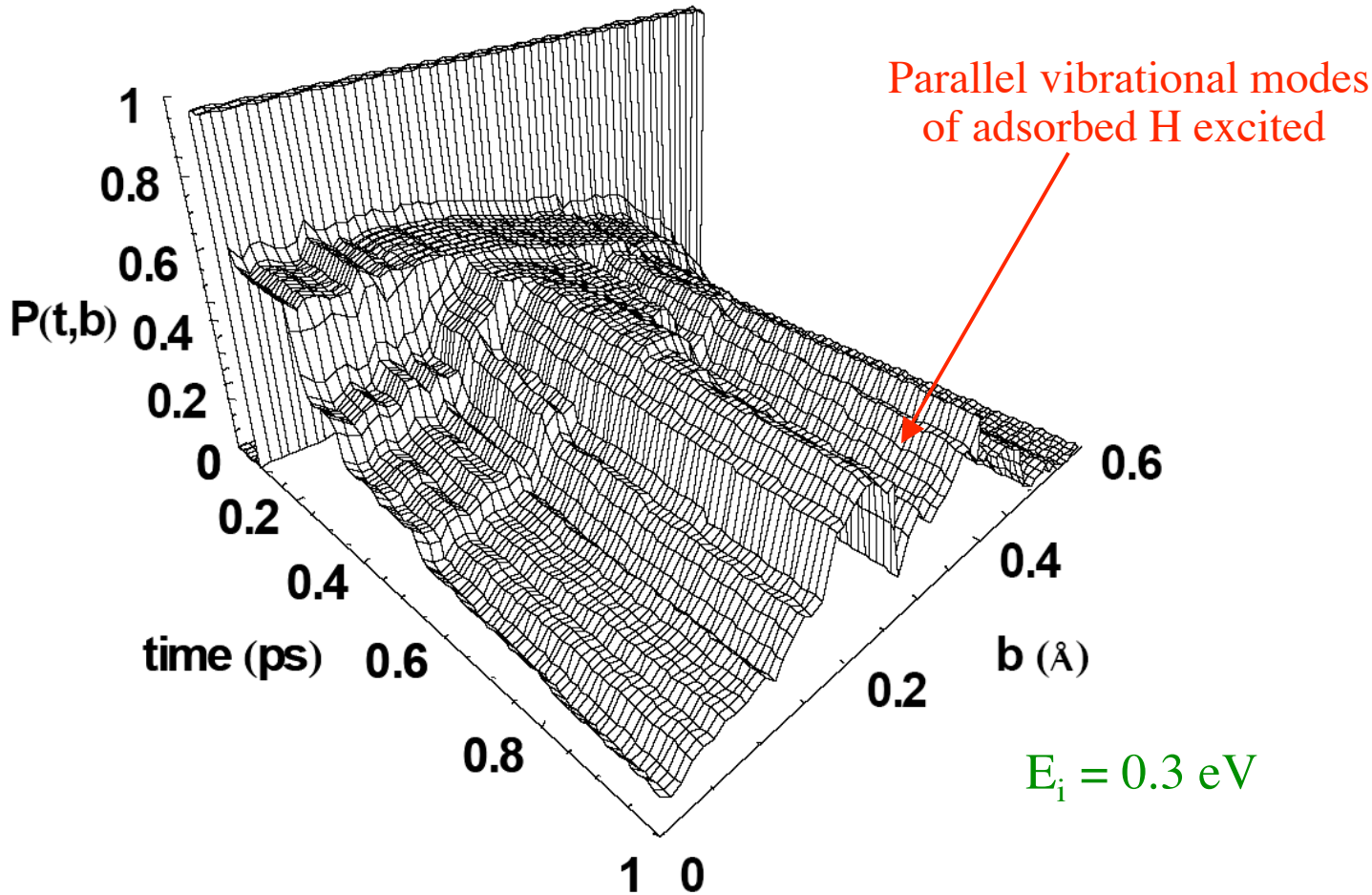
1. First try[1]: H, C, and another lattice mode Q
   - Run trajectories on 3D DFT-based potential energy surface
   - Compute trapping cross sections: $\sigma(E_i;t)$
   - Average over E_i for an H atom source at 2000K
     - s_0= 0.07 for D
   - Most of the incident atoms are below the barrier!
2. Second try[2]: increase graphite cluster size; same result (but erratum?)





1. J. Kerwin, X. Sha and B. Jackson, *J. Phys. Chem.* B 110, 18811-18817 (2006).
2. J. Kerwin and B. Jackson, *J. Chem. Phys.* 128, 084702 (2008).

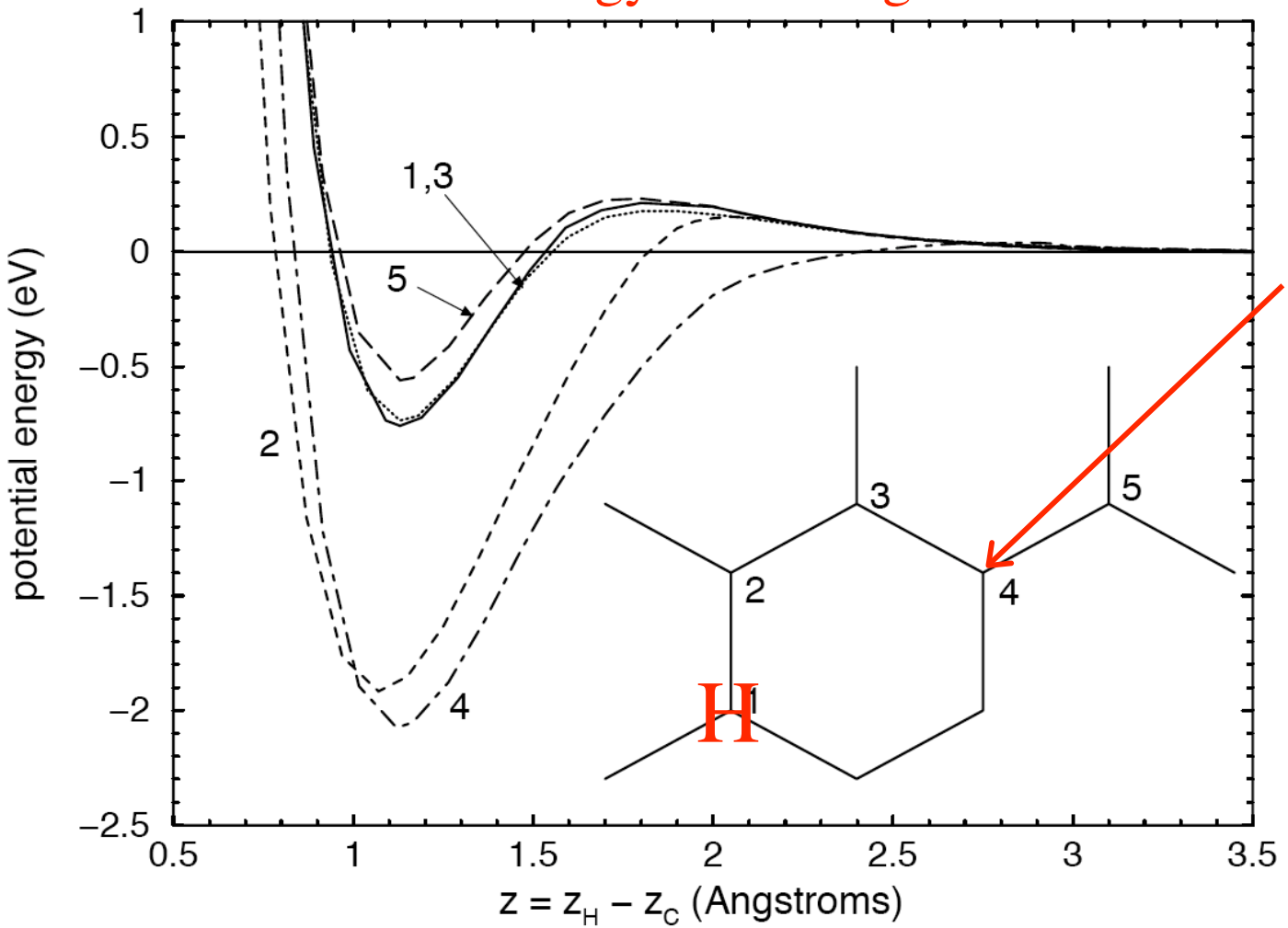
Classical trajectory calculations



Trapping probability vs time and impact parameter b

Cross section $\sigma(t) = \int_0^{2\pi} \int_0^{\infty} P(b;t)\, b\, db\, d\phi = 2\pi \int_0^{\infty} P(b;t)\, b\, db$

Potential energy for adding a second H



strong bond,
small barrier,
large cross section

Hornekaer, Rauls, Xu, Sljivancanin, Otero, Stensgaard, Laegsgaard, Hammer and Besenbacher, *Phys. Rev. Lett.* **97**, 186102 (2006).

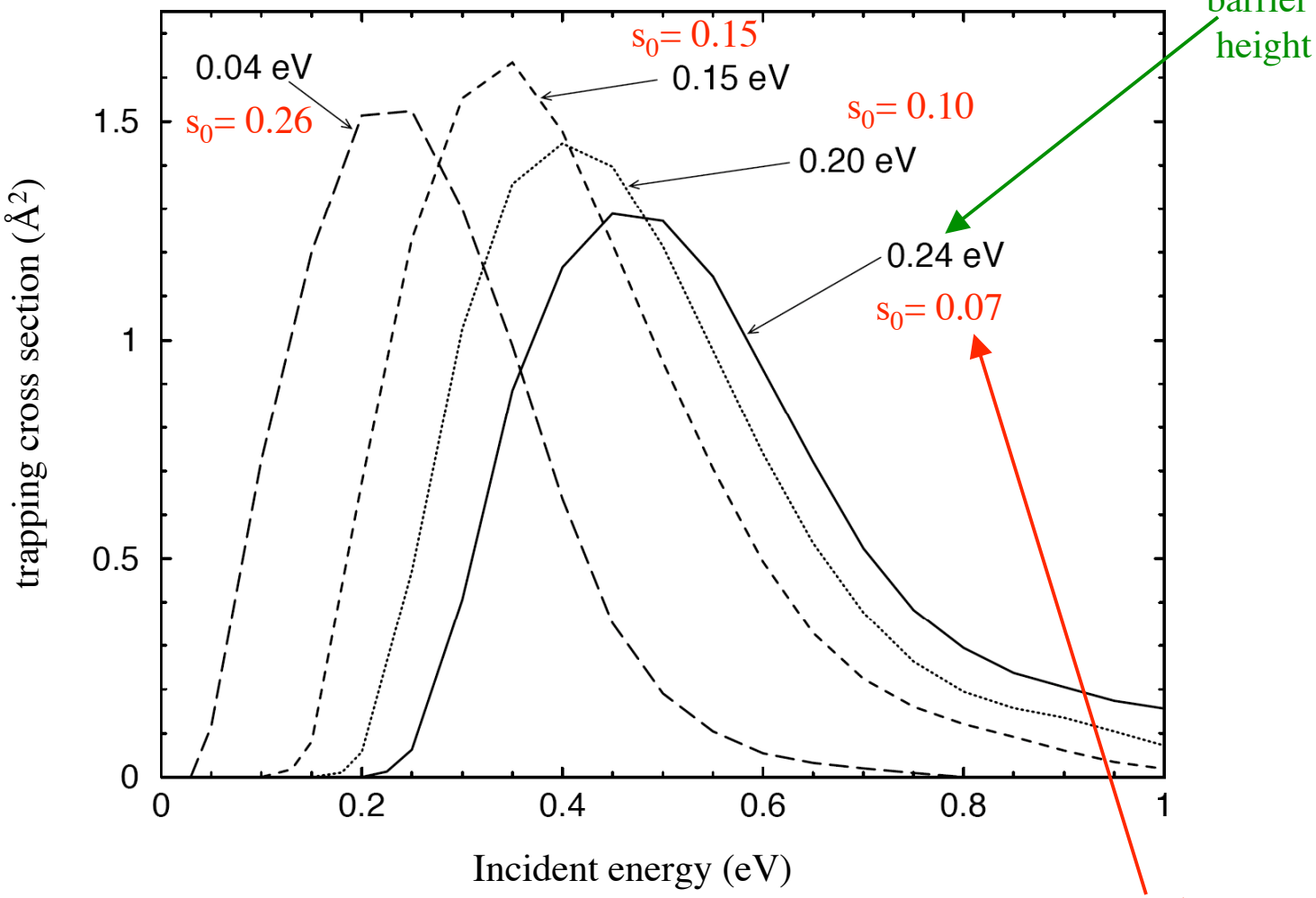
Rougeau, Teillet-Billy and Sidis, *Chem. Phys. Lett.* 431, 135 (2006).

Casolo, Lovvik, Martinazzo and Tantardini, *J. Chem. Phys.* 130, 054704 (2009)

Quasiclassical cross sections

D chemisorption cross section for different barrier heights

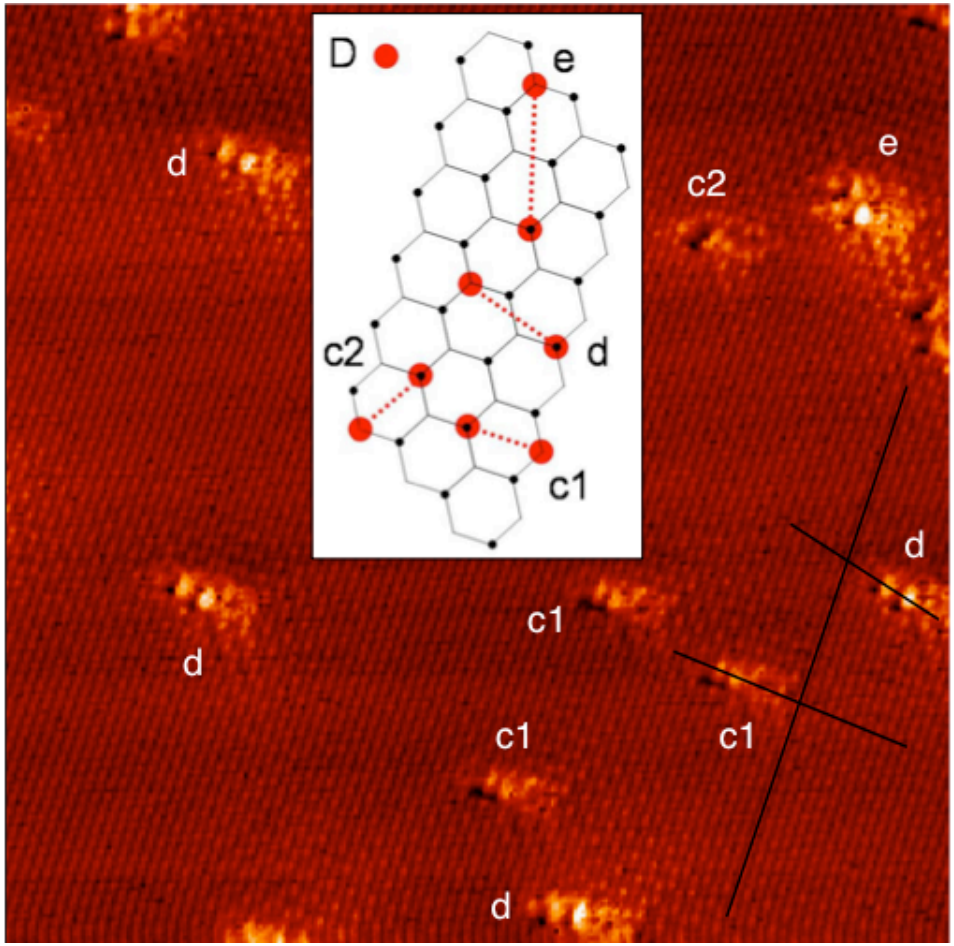
150K, 109 atom cluster



averaged over energies for an H atom source at 2000K

J. Kerwin and B. Jackson, *J. Chem. Phys.* 128, 084702 (2008).

H “pairing” on graphite



A. Andree, M. L. Lay, T. Zecho, J. Küppers *Chem. Phys. Lett.* **425**, 99 (2006)

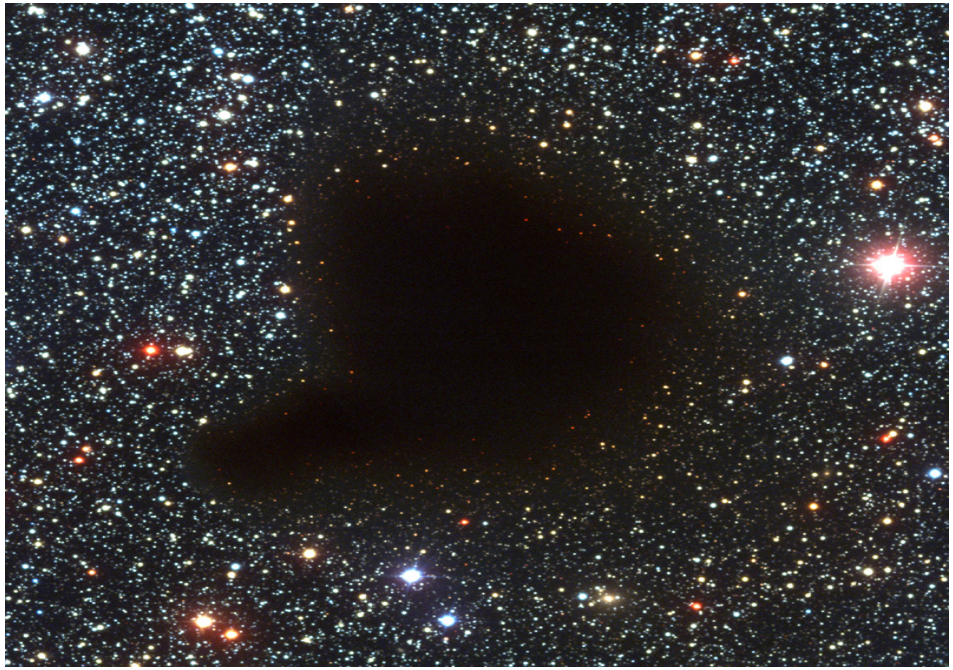
Hornekaer, Sljivancanin, Xu, Otero, Rauls, Stensgaard, Laegsgaard, Hammer, Besenbacher, *Phys. Rev. Lett.* **96**, 156104 (2006)

Conclusions

1. The graphite lattice must pucker in order for H to chemisorb on the terrace
   - there is a barrier
   - the zero coverage sticking probability is small
     - for a 2000K source
   - interesting trapping resonances

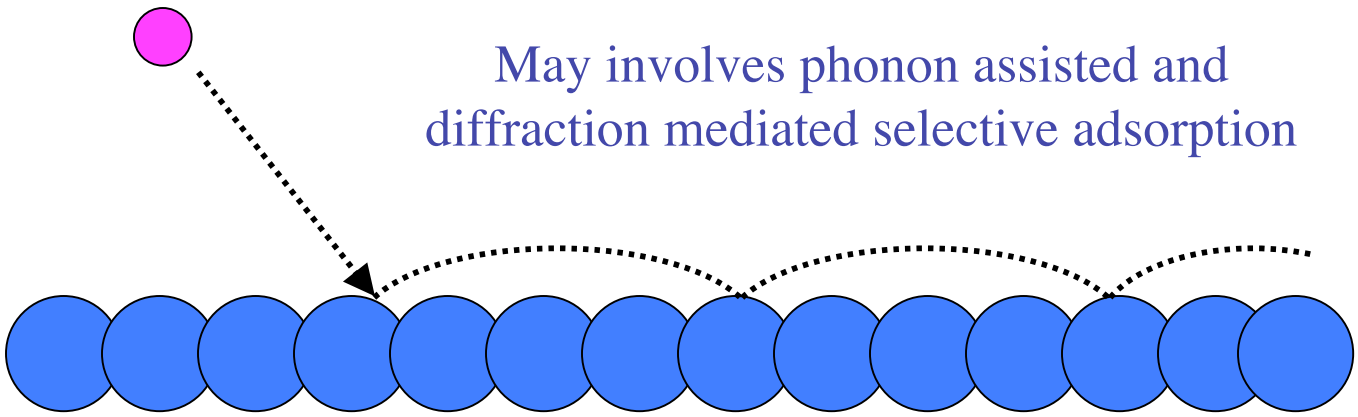
2. The probability for addition of a second H is strongly site dependent, involving additional lattice relaxation
   - Some sites have negligible barriers
   - The sticking probability at higher coverage can be large, but only for specific sties

Physisorption of H on graphite



At low T, chemisorption is unlikely.

Adsorption and Eley-Rideal abstraction may proceed via H physisorption.



Weak but persistent coupling

$m_{part}/M_{lattice} < 1$ and/or low incident energy, moderate T

The lattice is not significantly perturbed from equilibrium

$$V(\vec{r},\{\vec{u}_\alpha\}) \approx V(\vec{r},\{\vec{u}_\alpha = 0\}) + \sum_\alpha \left(\frac{\partial \vec{V}}{\partial u_\alpha}\right)_{\vec{u}_\alpha = 0} \bullet \vec{u}_\alpha$$

particle DOF

displacement of lattice atom α from equilibrium

$$V(\vec{r},\{\vec{u}_\alpha\}) \approx V_0(\vec{r}) + \frac{1}{\sqrt{N}} \sum_{\vec{q}} g_{\vec{q}}(r)\left(a_{\vec{q}} + a^+_{-\vec{q}}\right)$$

The coupling is "one-phonon", but needs to be treated to infinite order

- the particle can interact with the bath for a long time

Use a density matrix approach

$$\rho = \sum_{\mathbf{n}} \frac{1}{Z} e^{-E_{\mathbf{n}}/kT} \left| \Psi_{\mathbf{n}}(t) \right\rangle\!\left\langle \Psi_{\mathbf{n}}(t) \right|$$

particle-bath wave function for initial bath state **n**

$$\frac{\partial \rho}{\partial t} = -\frac{i}{\hbar}[H, \rho]$$

Derive a short time propagator for reduced density matrix σ:

$$\sigma(r, r'; t) = tr_b \langle r | \rho(t) | r' \rangle$$

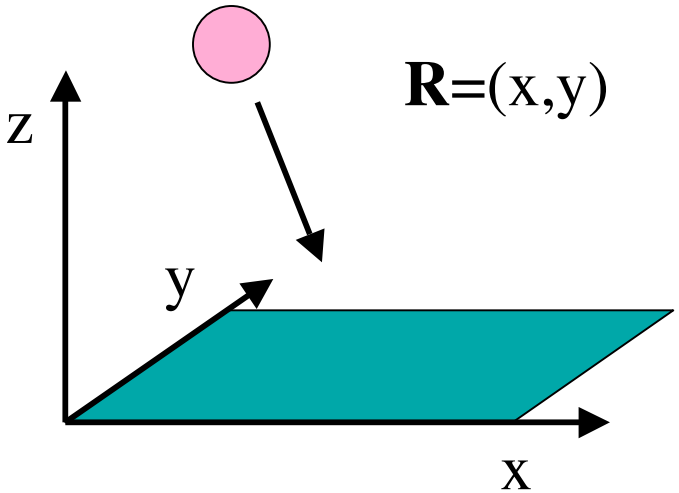
Assume that the lattice is not significantly perturbed from equilibrium

$$\rho(t) \approx \sigma(t)\, s(0)$$

equilibrium bath density matrix

Wangsness and Bloch (1953); Redfield (1957)

H-graphite(0001) scattering



R=(x,y)

$$V(\vec{r},\{\vec{u}_\alpha\}) = De^{-2\alpha\left[z - W(\mathbf{R},\{\mathbf{u}_\alpha\})\right]} - V_{att}(z)$$

displacement of lattice atom at site α

$W(R,\{u_\alpha=0\})$ = static surface corrugation

$$V(\vec{r},\{\vec{u}_\alpha\}) \approx V(\vec{r},\{\vec{u}_\alpha = 0\}) + \sum_\alpha \left(\frac{\partial V}{\partial u_\alpha}\right)_{\vec{u}_\alpha = 0} \bullet \vec{u}_\alpha$$

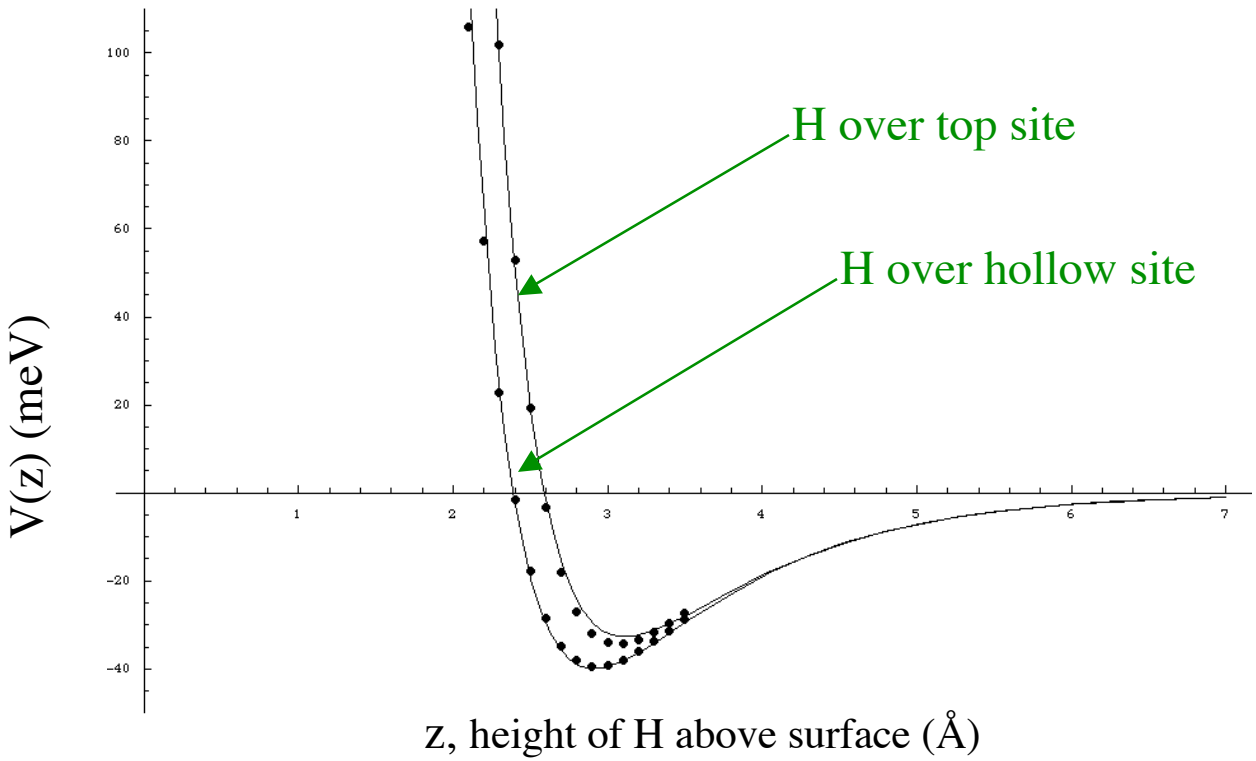
Phonon coupling: $$\frac{dW}{du_{iz}} = A_z\, e^{-\frac{1}{2}Q_c^2 (\mathbf{R}-\mathbf{R}_i)^2}$$

Bortolani, Franchini, Garcia, Nizzoli, Santoro, *Phys. Rev. B 28, 7358 (1983)*

We compute (using DFT): $A_z = 0.44$

Compute, or use analytical models for phonons

H - graphite(0001) PES



….. MP2 calculations of Bonfanti, Martinazzo, Tantardini and Ponti, J. Phys. Chem. C 111, 5825 (2007)

____ model PES

Equation of motion

Choose a basis:

$$\left(\overline{H}_p + V_{wall}\right)\phi_\alpha(z) = E_\alpha\ \phi_\alpha(z)$$

$$K_R\ |i\rangle = \varepsilon_i\ |i\rangle$$

diffraction states i = (n,m)

$$\sigma_{\alpha i,\beta j}(t+\Delta t) = \sigma_{\alpha i,\beta j}(t) - \frac{i\Delta t}{\hbar}\left(E_\alpha + \varepsilon_i - E_\beta - \varepsilon_j\right)\sigma_{\alpha i,\beta j}(t)$$

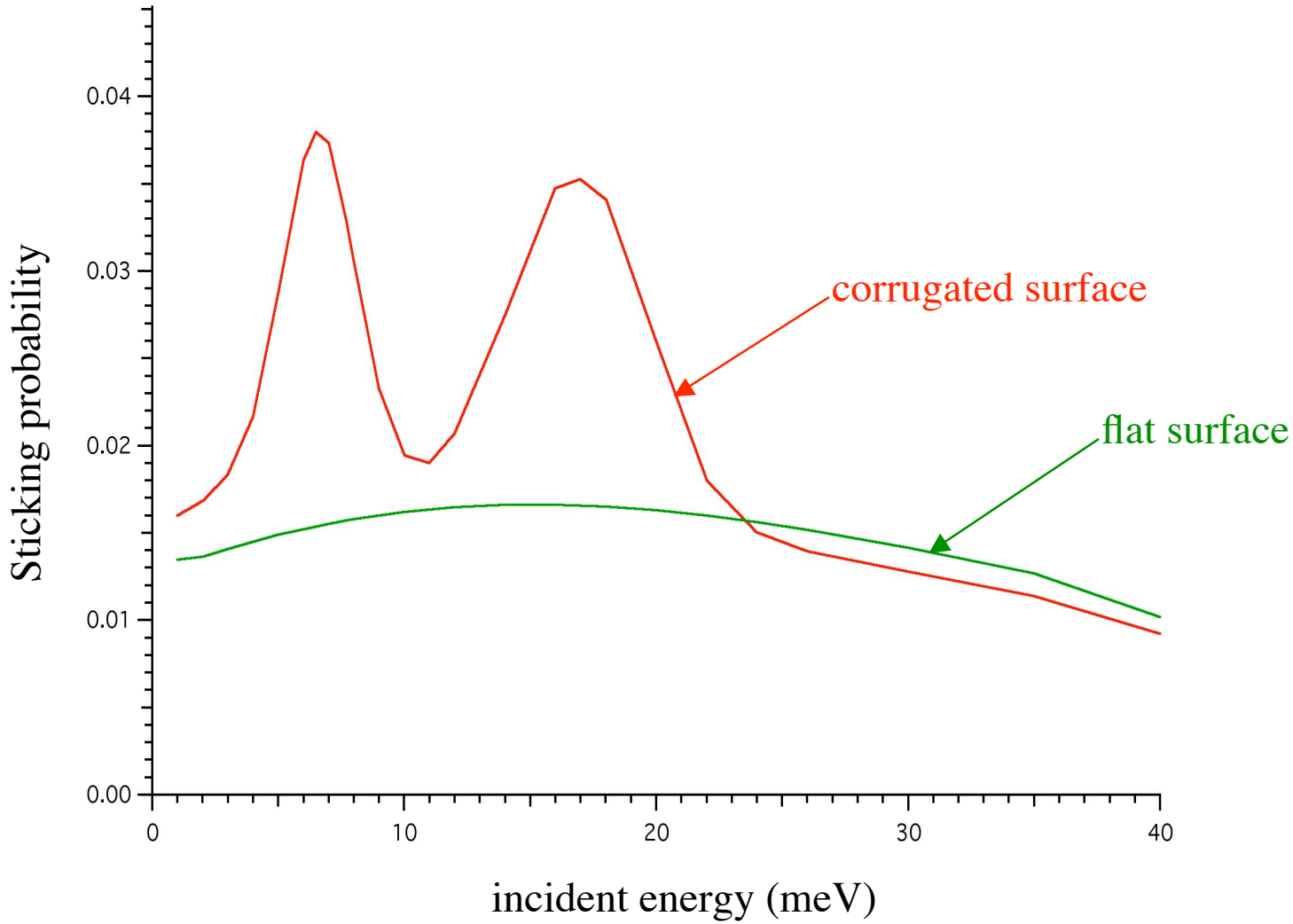
$$-\frac{i\Delta t}{\hbar}\sum_k\sum_\gamma\left[U_{\alpha\gamma}Q_{ik}\sigma_{\gamma k,\beta j}(t) - \sigma_{\alpha i,\gamma k}(t)U_{\gamma\beta}Q_{kj}\right] - \frac{\Delta t}{\hbar^2}\sum_\gamma\sum_\delta\left[A_{\alpha\gamma}\Delta_{\alpha\gamma}\Delta_{\gamma\delta}\sigma_{\delta i,\beta j}(t) + \ldots\right]$$

Corrugation part of PES = U(z) Q(x,y)

phonon part of PES = Δ(z) f({a_q,a_q^+})

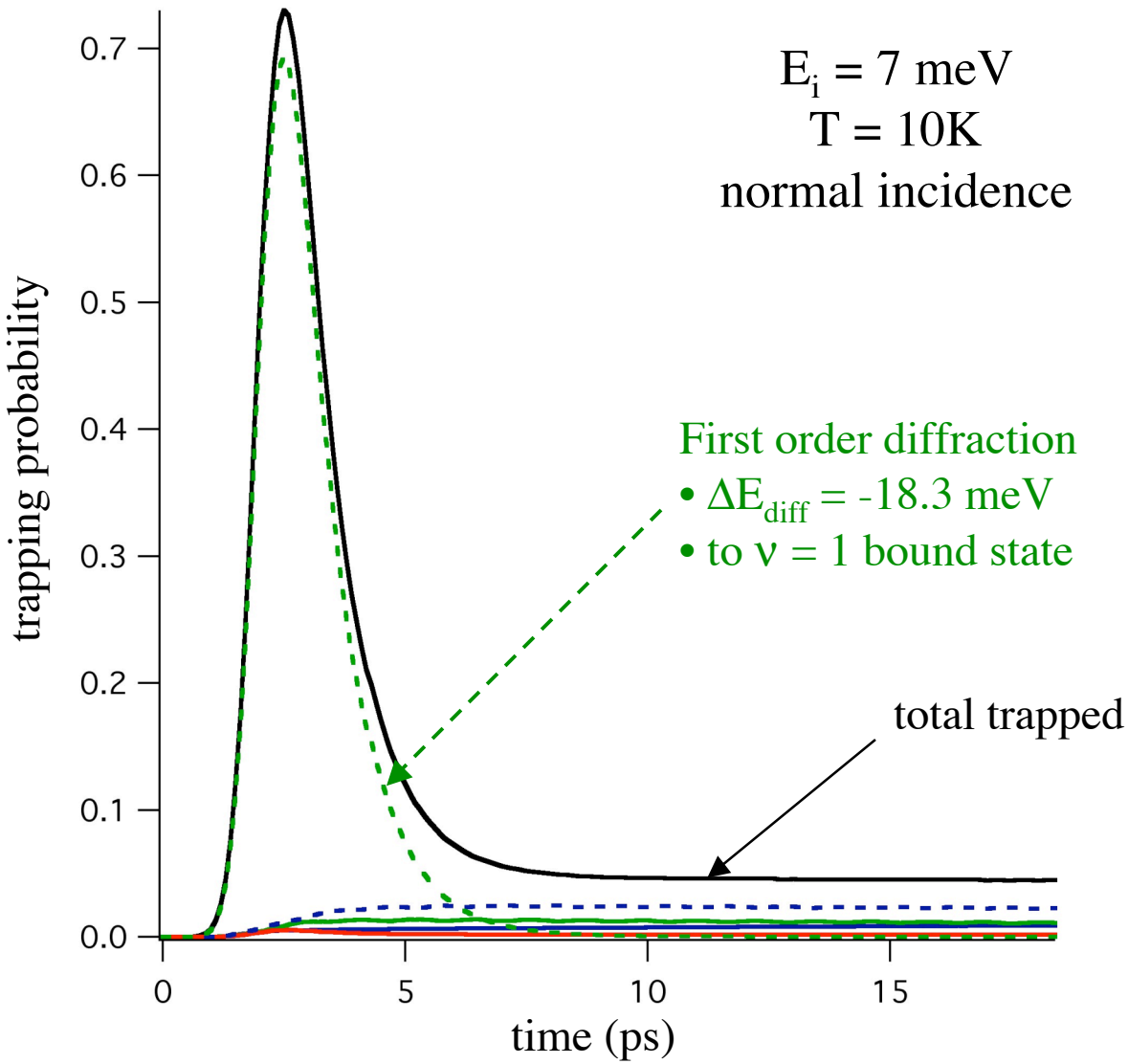
$$cpu \propto N_z^3\ N_{diff}^2$$

H sticking on graphite(0001); T = 10K



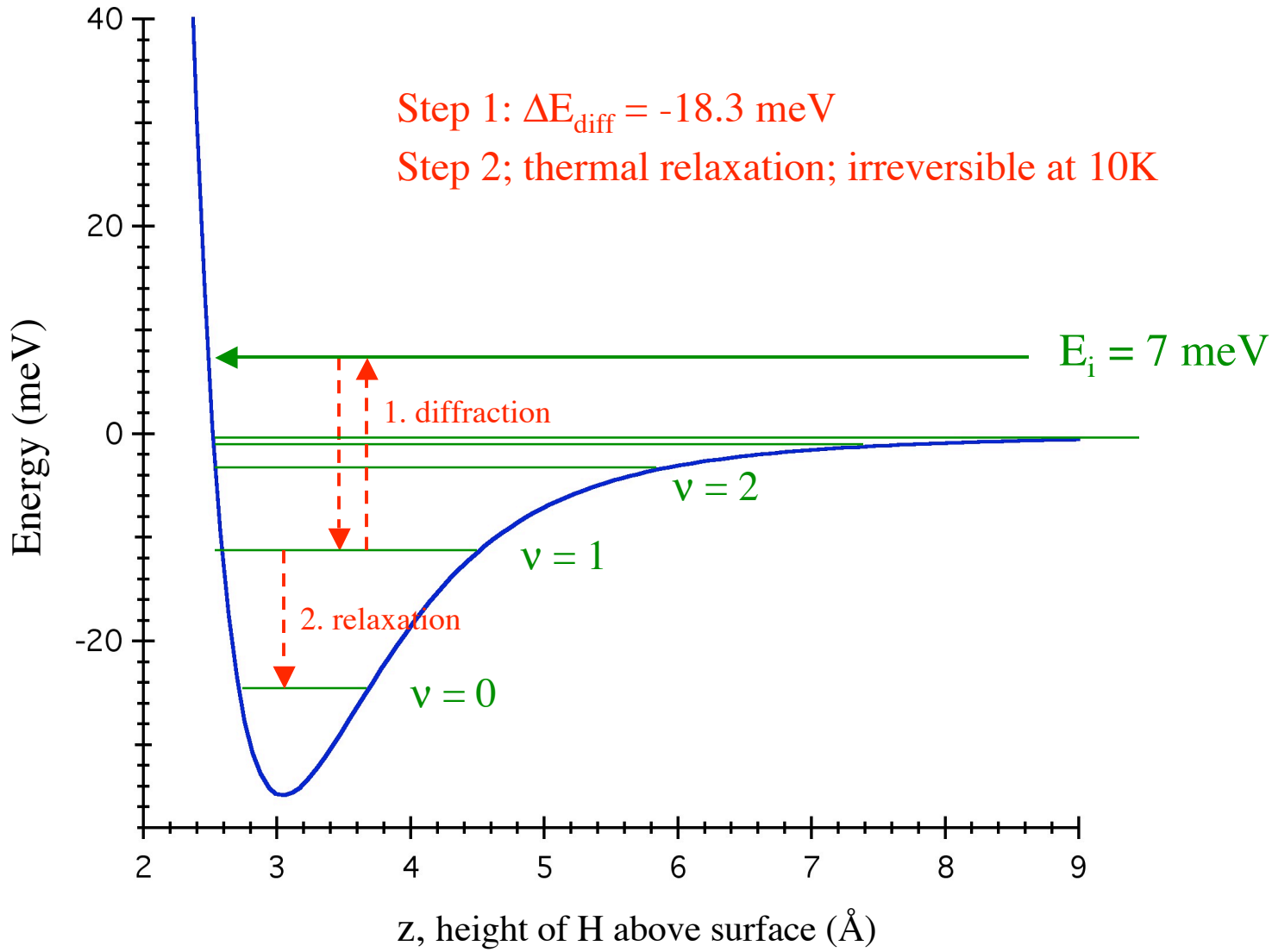
Medina and Jackson, *J. Chem Phys 128*, 114704 (2008)

State-resolved trapping of H on graphite(0001)

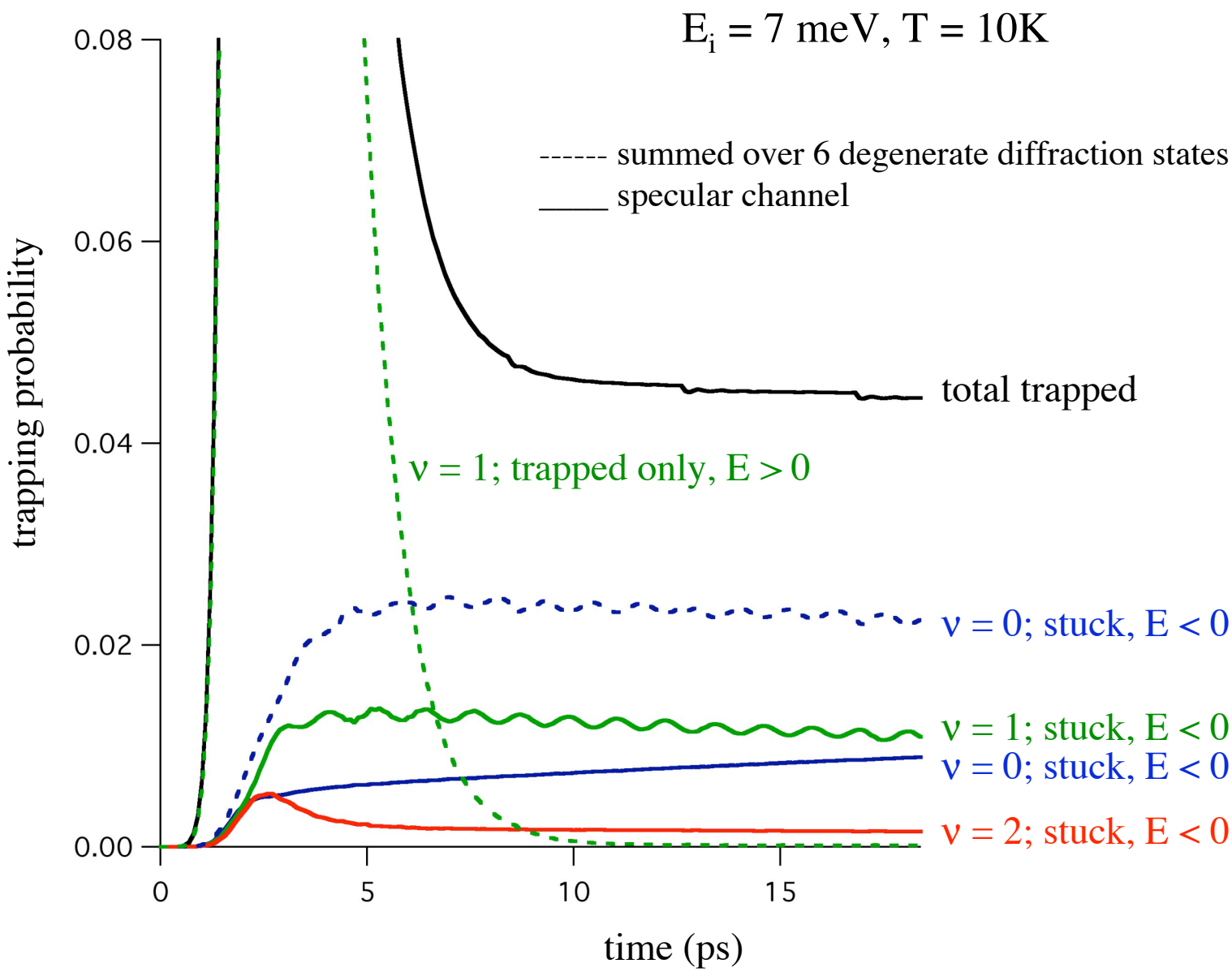


Medina and Jackson, *J. Chem Phys 128*, 114704 (2008)

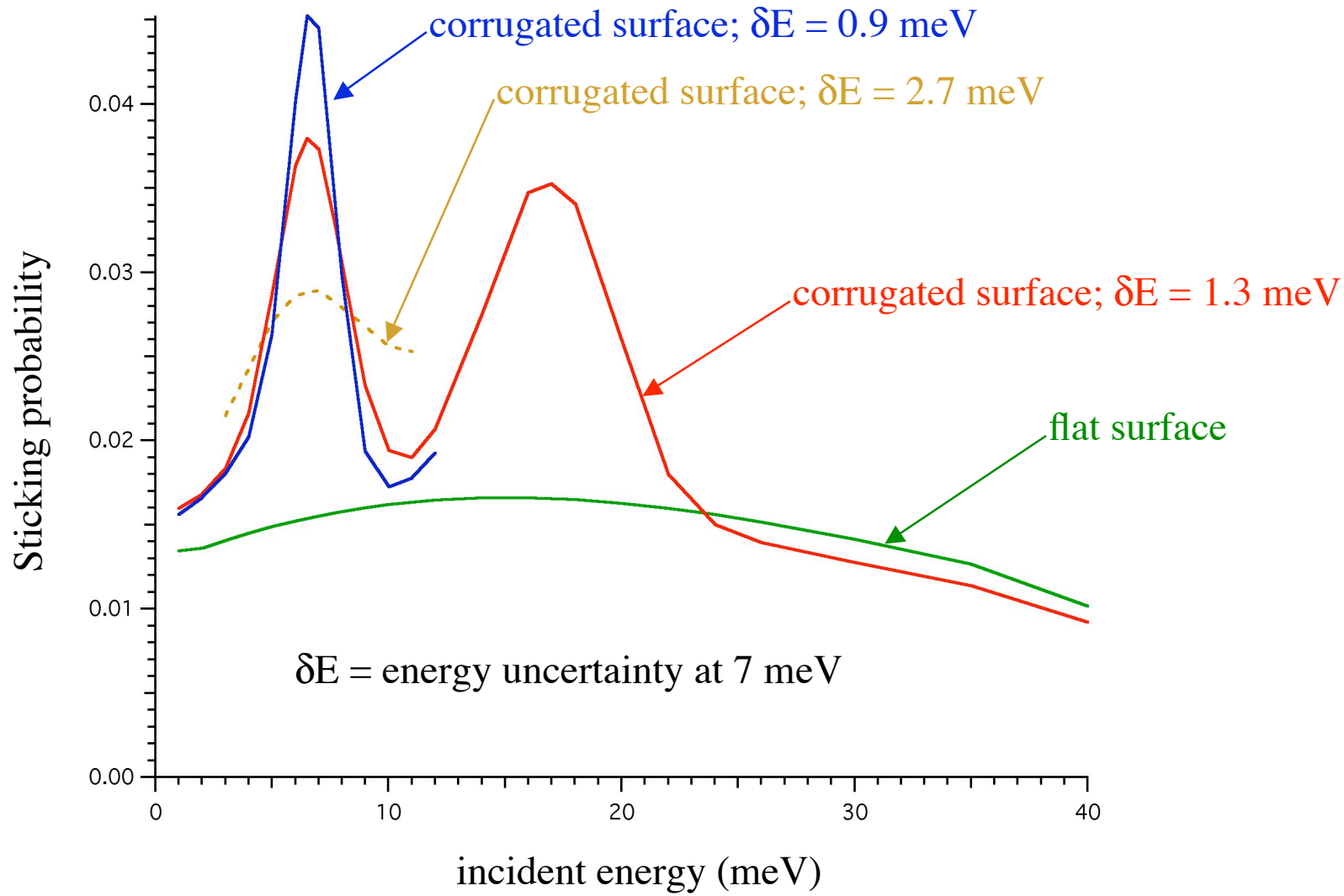
State-resolved trapping of H on graphite(0001)

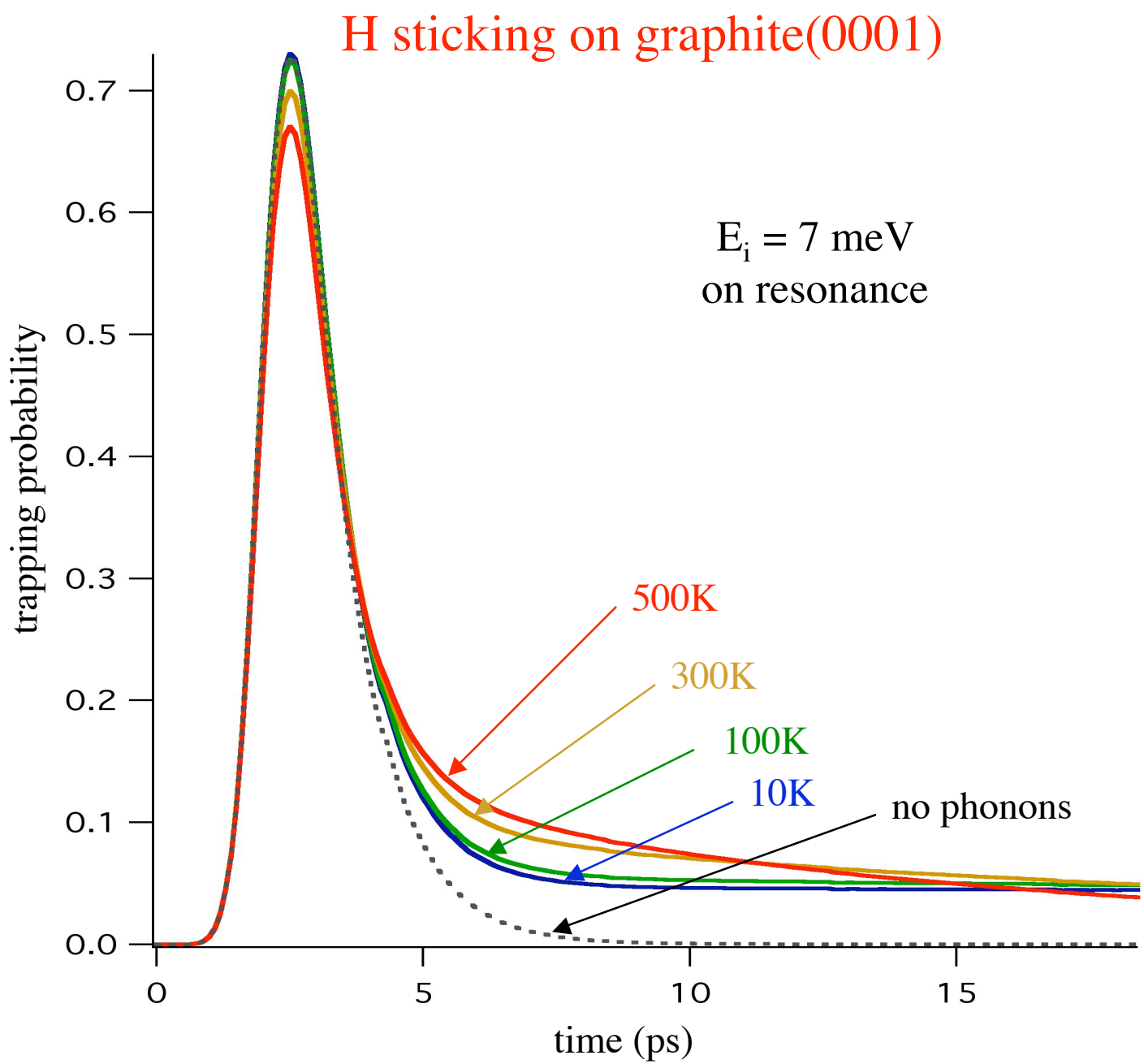


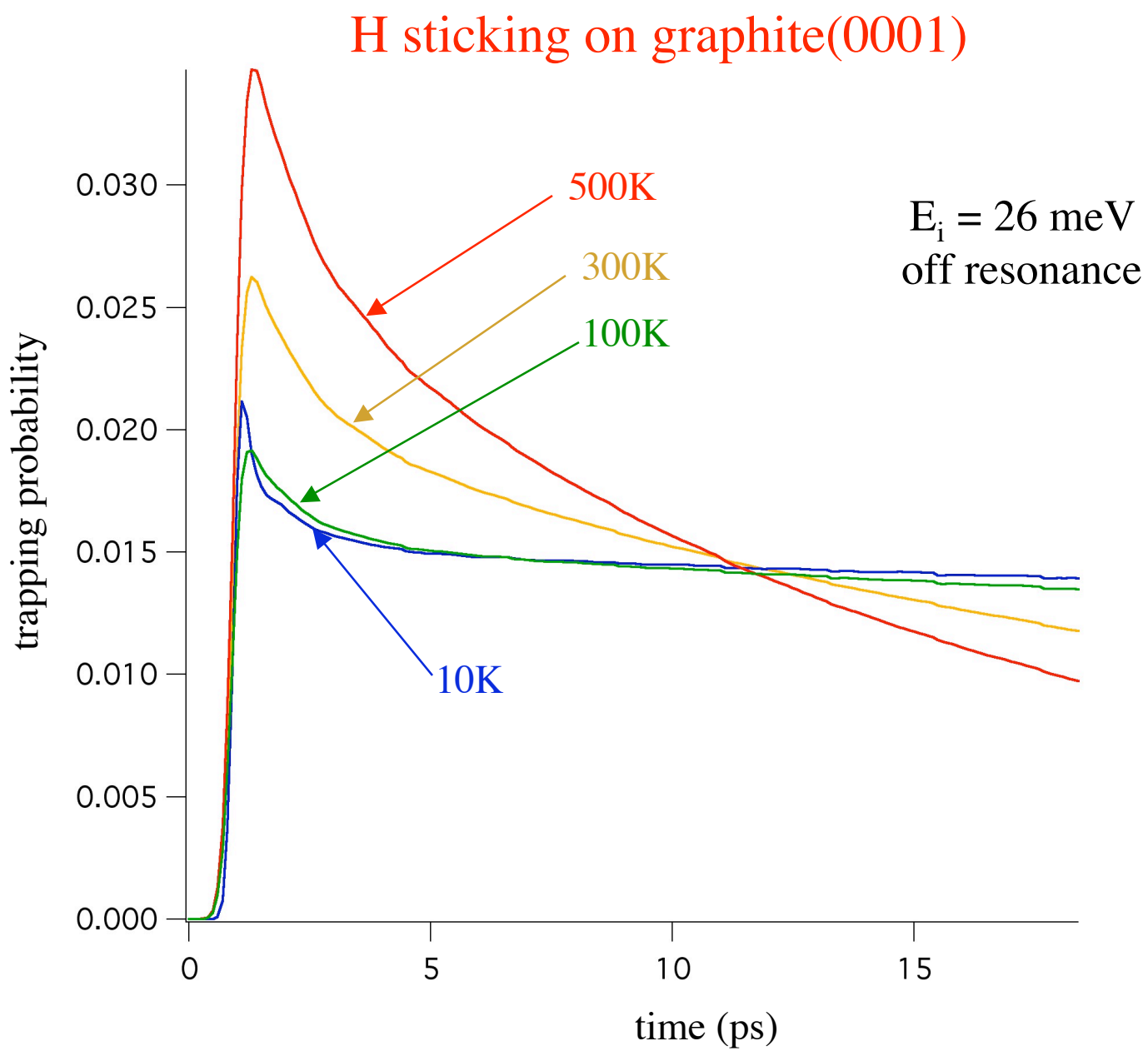
State-resolved trapping of H on graphite(0001)



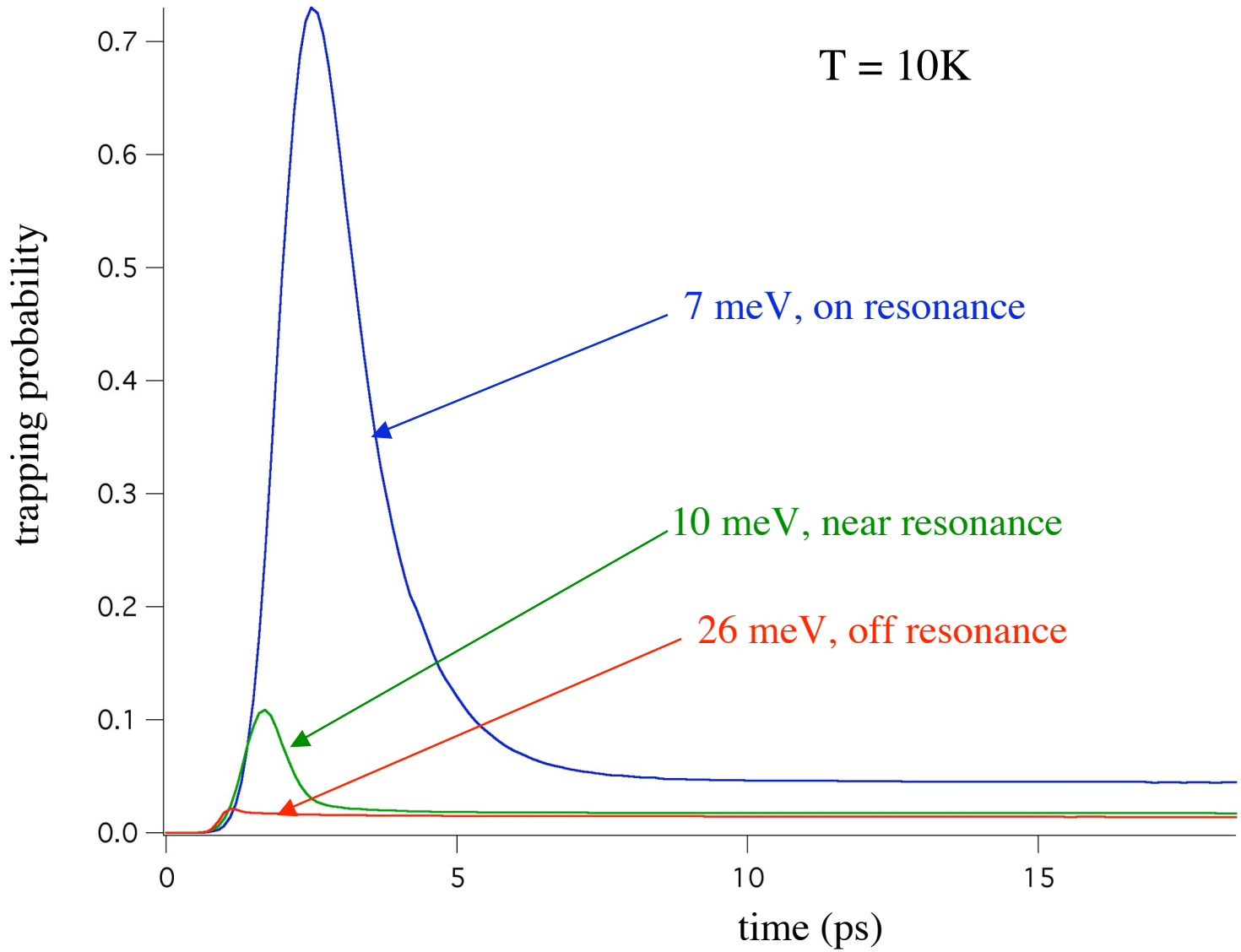
H sticking on graphite(0001); T = 10K




H sticking on graphite(0001)
E_i = 7 meV
on resonance
500K
300K
100K
10K
no phonons
trapping probability
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0
5
10
15
time (ps)


H sticking on graphite(0001)
500K
300K
100K
10K
E_i = 26 meV
off resonance
trapping probability
0.030
0.025
0.020
0.015
0.010
0.005
0.000
0
5
10
15
time (ps)

H sticking on graphite(0001)



Dissociative adsorption on stepped metal surfaces

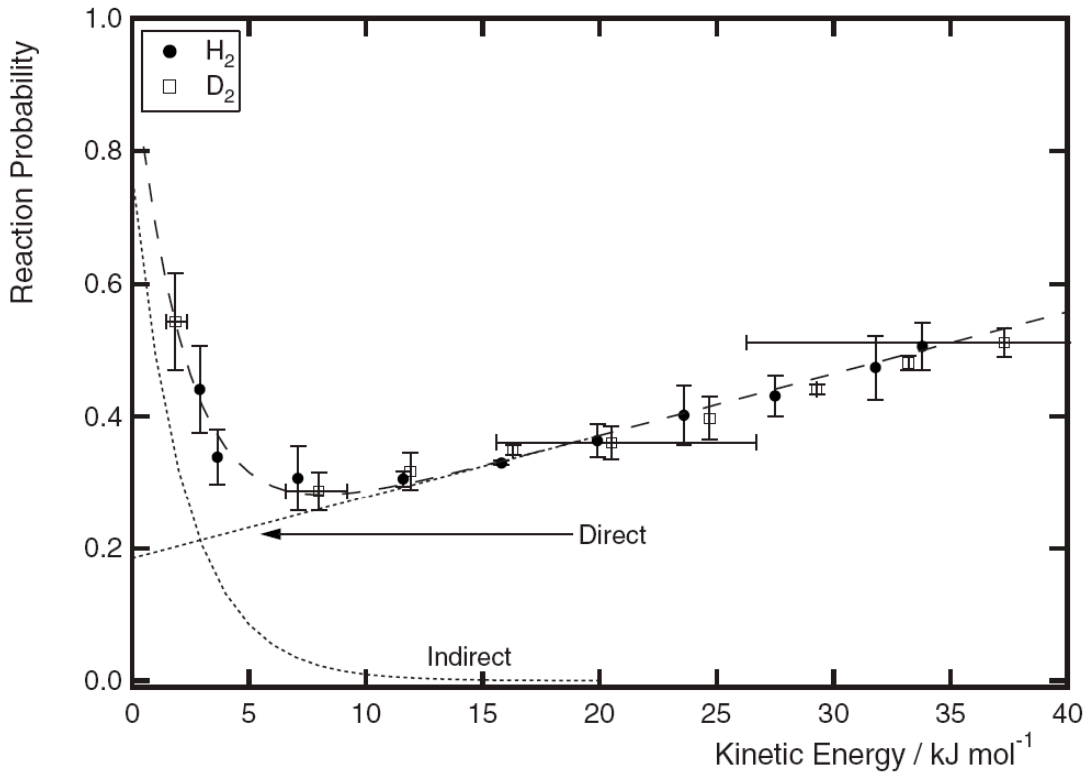
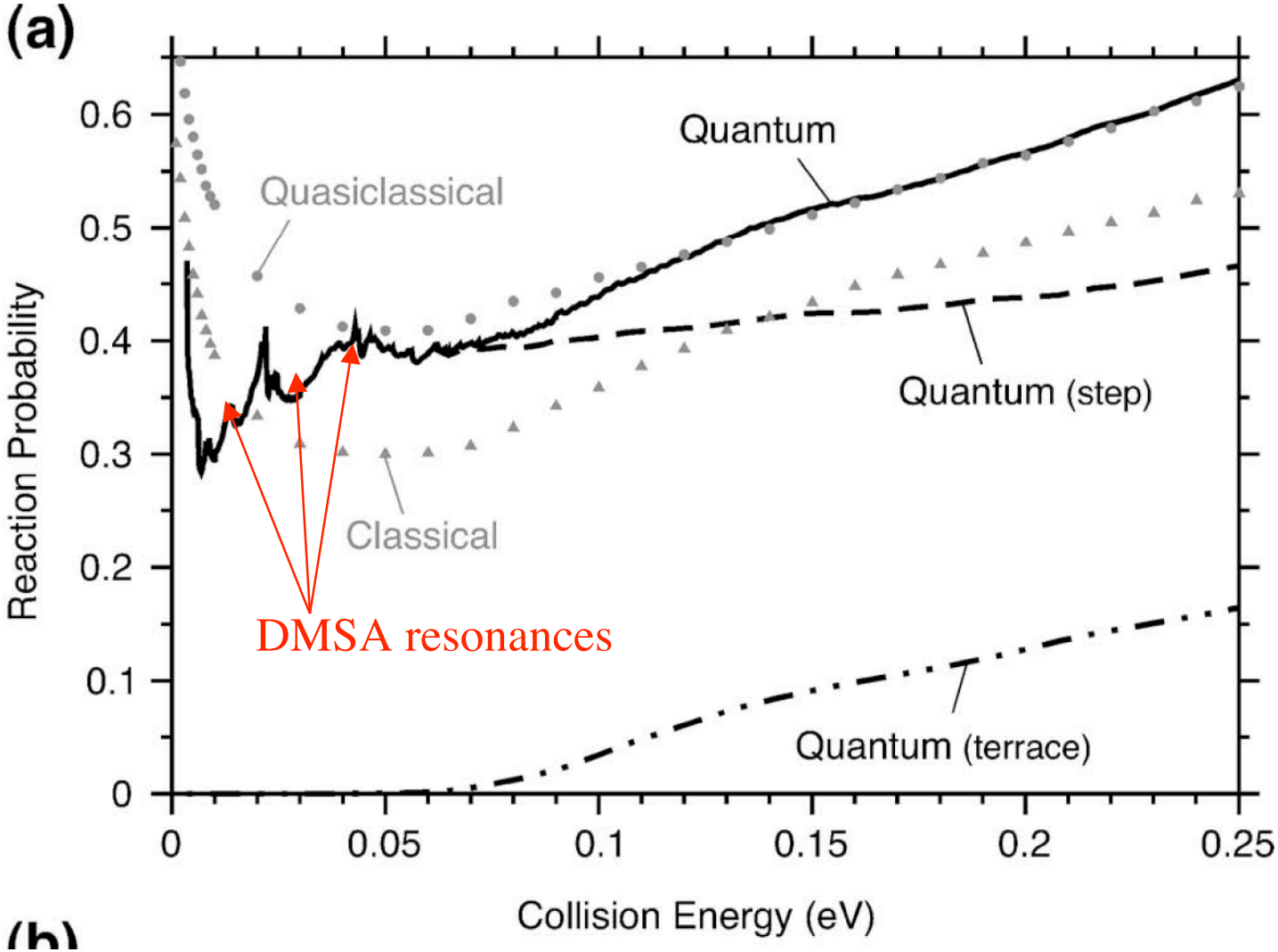


FIG. 1. The reaction probability of H_2 and D_2 on Pt(211). Below 7 kJ mol^{-1}, the data are obtained by seeding in N_2, all other data are obtained by heating the nozzle. The data are fitted with an exponential decay and a linear dependence (dashed line). See text for details.

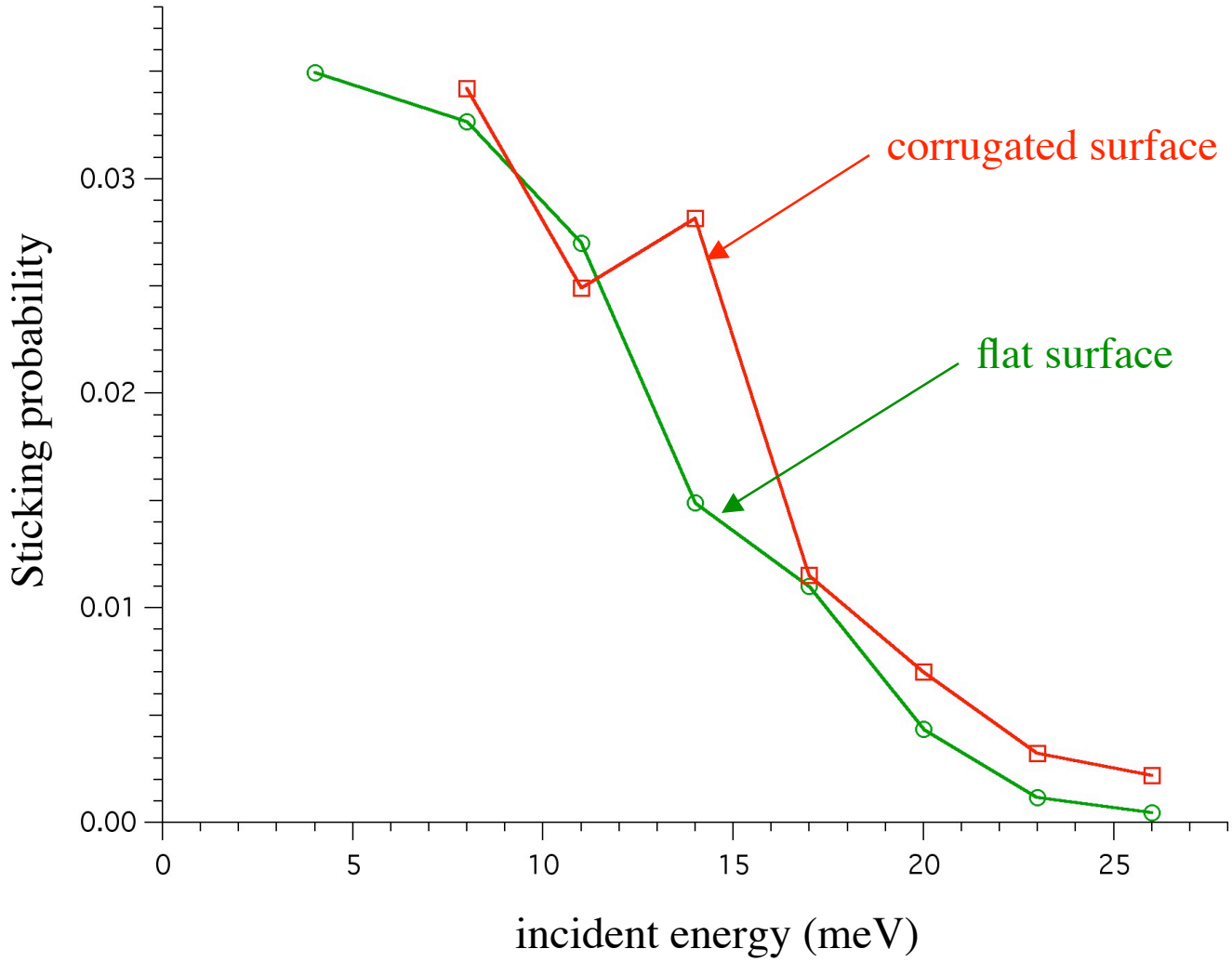
Groot, Schouten, Kleyn and Juurlink, *J. Chem. Phys.* 129, 224707 (2008).

Dissociative adsorption on Pt(211)

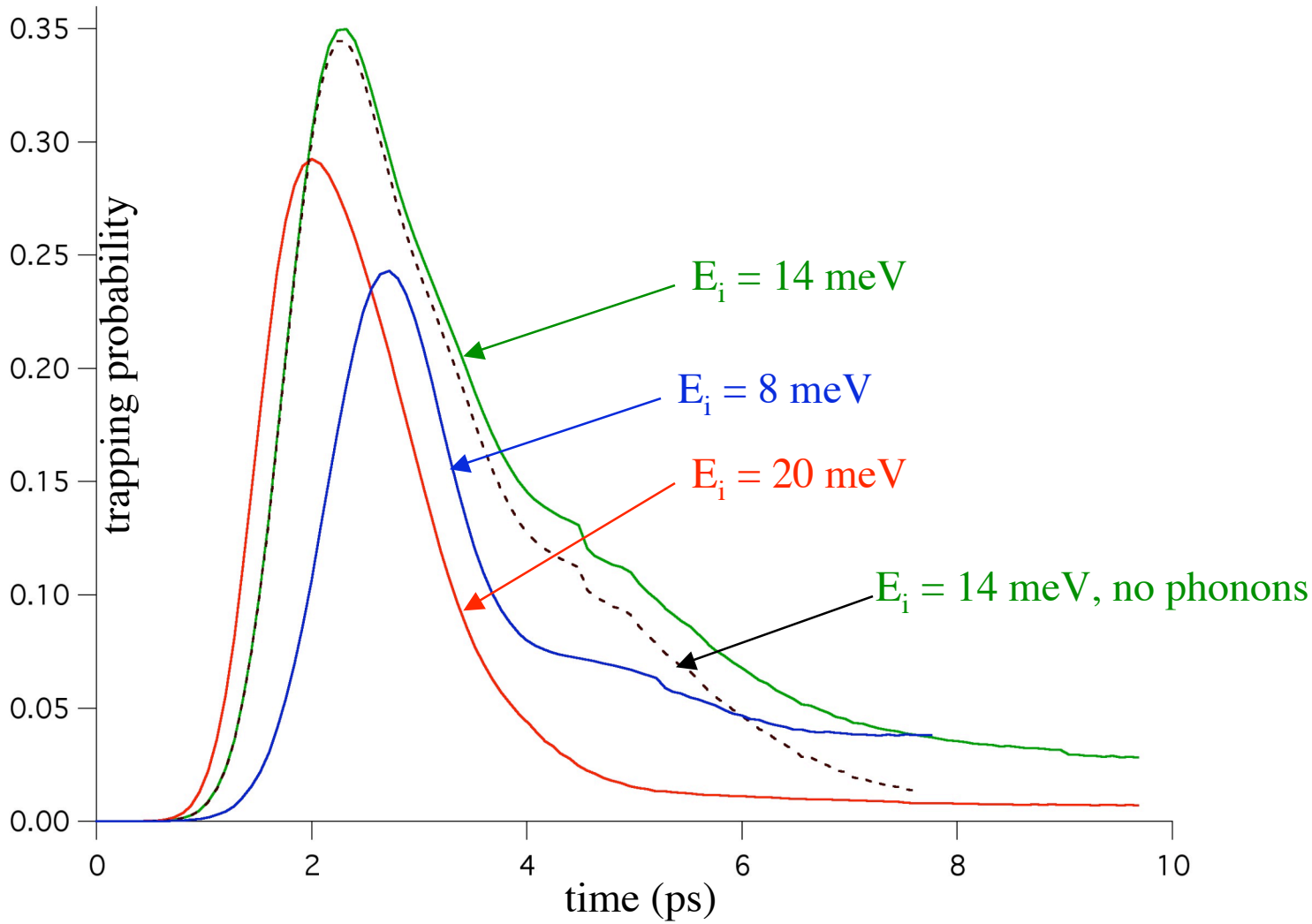


Olsen, McCormack, Luppi and Baerends, *J. Chem. Phys.* 128, 194715(2008).

H_2 sticking on "Pt(211)"; T = 10K



H_2 trapping on "Pt(211)"; T = 10K



Conclusions (physisorption)

1. The sticking probability of H on graphite at very low energies is a few %
   - Slow variation with incident energy (at low energy)
   - Strongly enhanced by diffraction mediated selective adsorption
     - Relaxation time ≈ resonance lifetime
     - Well depth > ΔE_{diff}

2. Similar dynamics play a role in molecular precursors to dissociative adsorption

Acknowledgements

1. H(g) + H/graphite Eley-Rideal reactions
   - Xianwei Sha[a], Didier Lemoine[b]
2. H-graphite chemisorption
   - Xianwei Sha[a], Jay Kerwin[c]
3. H-graphite physisorption
   - Zuleika Medina[d]

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[d]*Department of Physics, Penn State*

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