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DI MILANO

## $H_2$ Dissociation on $Cu(111)$ : The Influence of Lattice Motion

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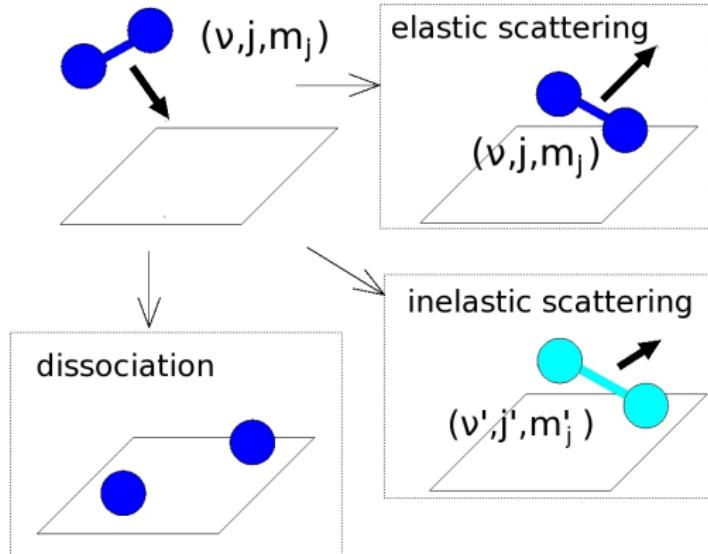
Thursday November 25th, 2010



# Outline



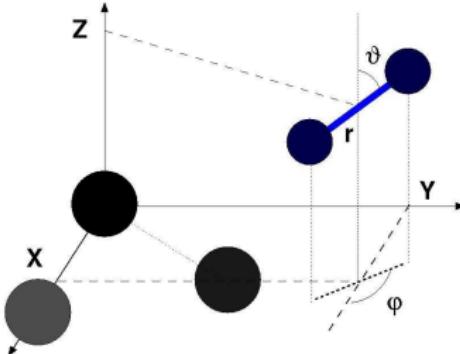
# Scattering of Molecules on Metal Surfaces



- Fundamental processes in surface chemistry and heterogeneous catalysis
- Direct comparison between theory and experiment is possible (UHV and molecular beam techniques)



# Theoretical Chemistry Group in Leiden

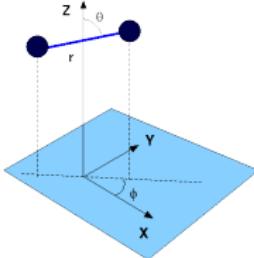


Previous work of the group of Prof. Geert-Jan Kroes on  $H_2$  dissociation

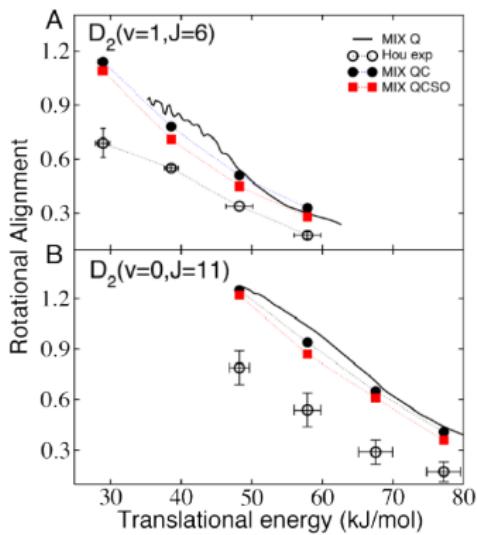
- Quantum effects (tunnelling)
- Full treatment of the  $H_2$  degrees of freedom



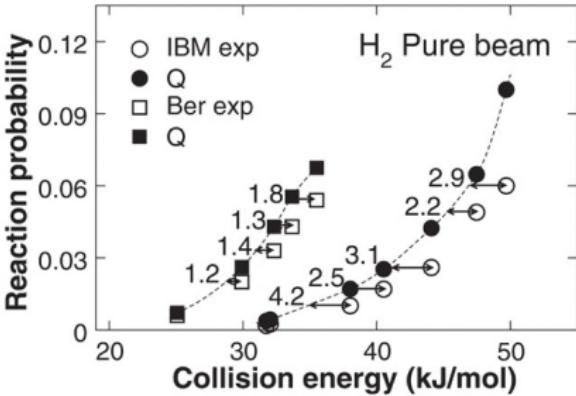
# $H_2/Cu(111)$ : previous results



C. Díaz et. Al., Science 326, 832-834, 2009  
"Chemically Accurate Simulation of a Prototypical Surface Reaction:  
 $H_2$  Dissociation on Cu(111)"

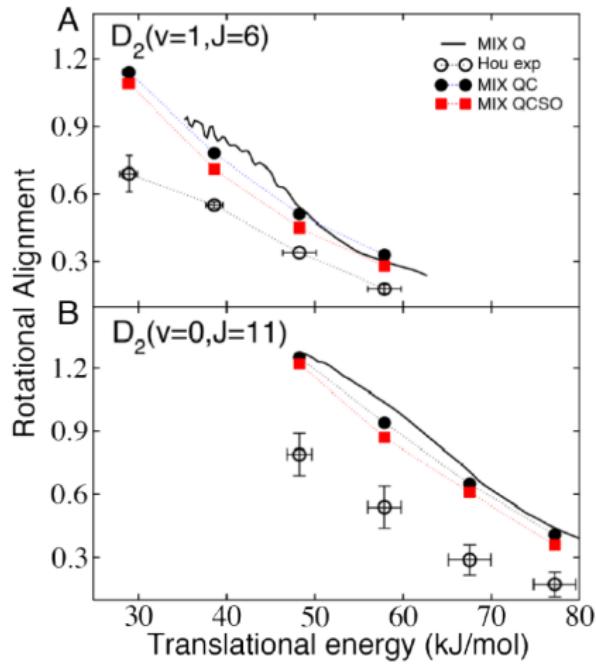


- Accurate results for **reaction probabilities**
- Still some improvements are needed, e.g. **rotational alignment**



# Lattice Motion: Surface Oscillator Model

$$V_{SO}(X, Y, Z, r, \vartheta, \varphi, Q) = V_{6D}(X, Y, Z - Q, r, \vartheta, \varphi) + \frac{1}{2}\mu\omega^2 Q^2$$



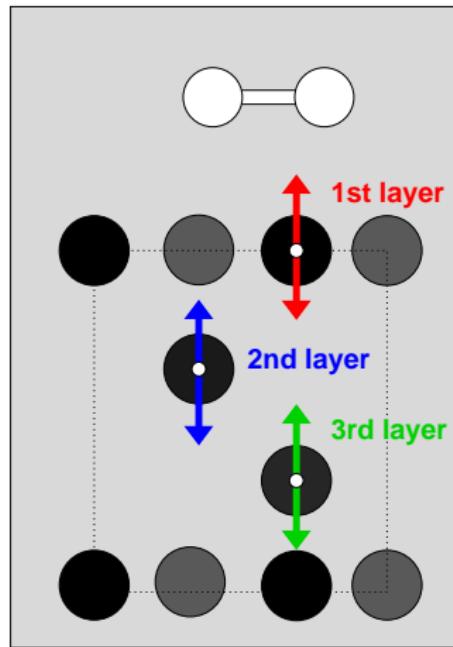
- $V_{6D}$  is shifted along  $Z$ , as if the whole surface move with  $Q$
- the potential for the surface vibration is quadratic



## Vibrational Degrees of Freedom of the surface

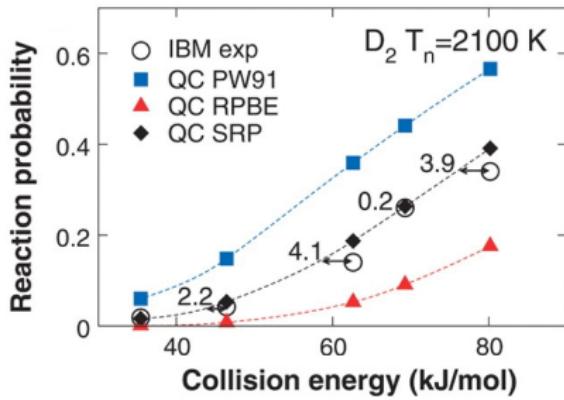
how does the Cu motion influence the dissociation barrier?

- **Localized** DOF, not collective
  - For each layer (up to the 3rd) motion of the **nearest Cu atoms**
  - Cu atoms displacement **perpendicular to the surface** (Z direction)

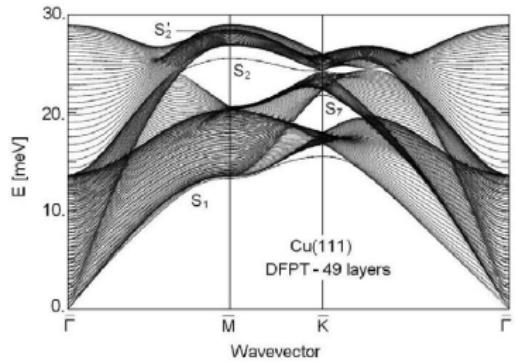
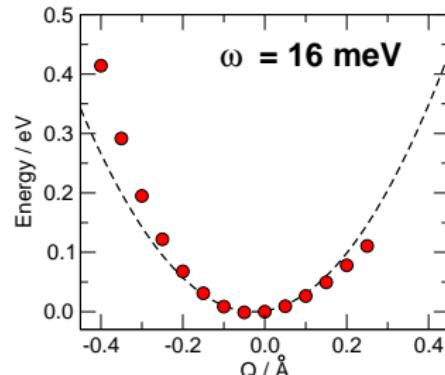
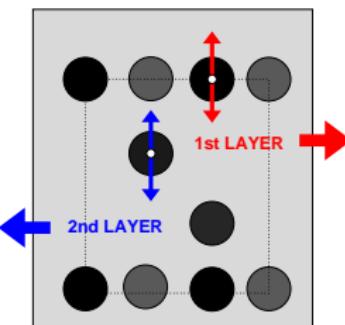
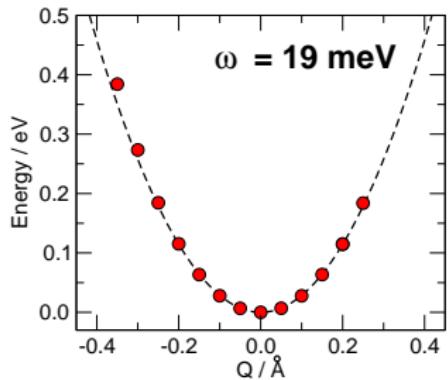


# DFT method

- **Supercell:** 2x2 unit cell, 4 Cu layers and 5 vacuum layers
- **Plane Waves:** cutoff 350 eV, 8x8x1  $\mathbf{k}$  points
- **Functional:** GGA mixed PW91/RPBE  
**Specific Reaction Parameter** (SRP) approach  
 $E^{MIX} = xE^{RPBE} + (1 - x)E^{PW91}$   $x = 0.43$
- Calculations with **DACAPO** code



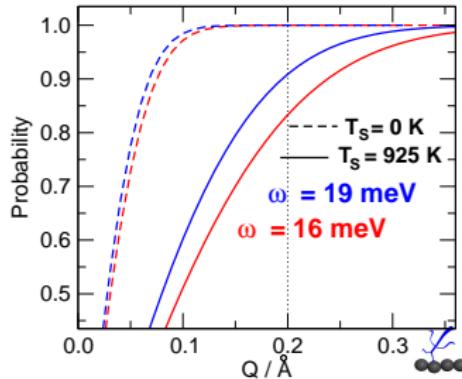
# Vibrations of Cu atoms



$$P = \sum_n \omega_n p_n$$

$$\omega_n = \frac{e^{-\beta E_n}}{Z}$$

$$p_n = \int_{-x_0}^{x_0} |\psi_n|^2 dx$$



## $H_2/Cu(111)$ : sites and barriers

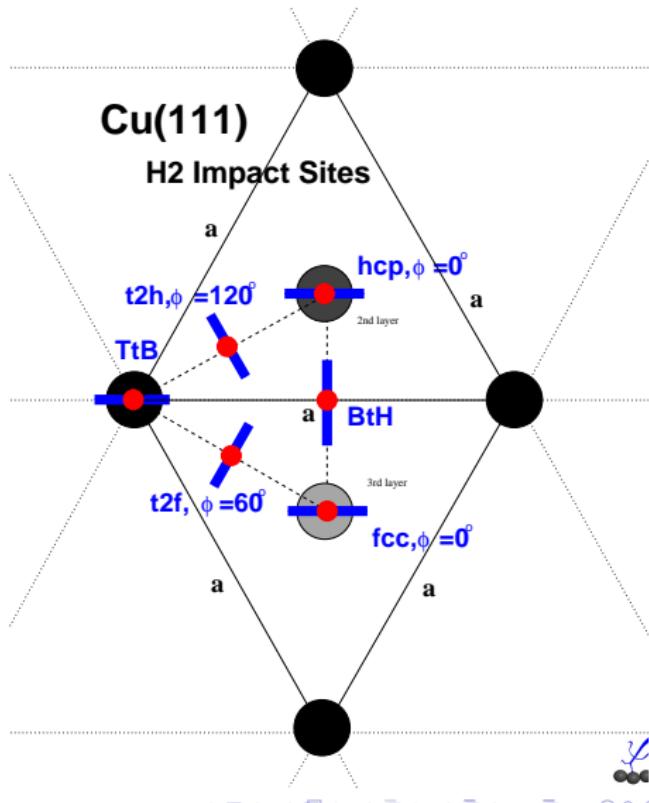
For each **impact site**:

- new barrier geometry  
 $(r, Z, \theta)$
  - new barrier height  
 $E_{\text{barrier}}$

For small  $Q$  these effects are approximately linear:

$$\Delta E_{\text{barrier}} \approx -\beta Q$$

$$\Delta Z_{\text{barrier}} \approx \alpha Q$$

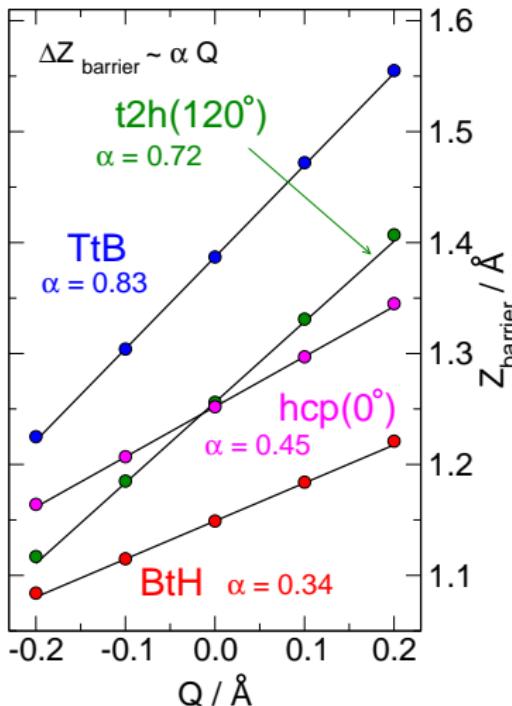


# Barrier Displacement - 1<sup>st</sup> Layer Cu motion

Barrier	Q (Å)	$\theta$ (°)	Geometry	
			$\Delta r$ (Å)	$\Delta Z$ (Å)
BtH	-0.2	90.	0.01	-0.06
	0.2	90.	0.01	0.07
t2h	-0.2	90.	-0.04	-0.14
	0.2	90.	0.06	0.15
TtB	-0.2	90.	-0.04	-0.16
	0.2	90.	0.06	0.17
hcp	-0.2	83.	-0.04	-0.09
	0.2	96.	0.06	0.09

- Bigger  $\Delta Z$  than  $\Delta r$
- $\Delta Z$  similar to  $Q$  near the TOP Cu atom
- Tilting angle for hcp barrier, mostly geometrical effect

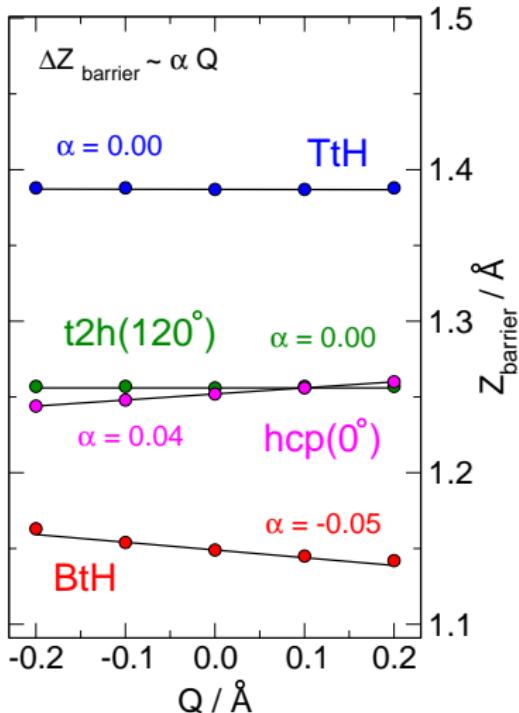
$$\Delta\theta_{geom} = 4.4^\circ$$



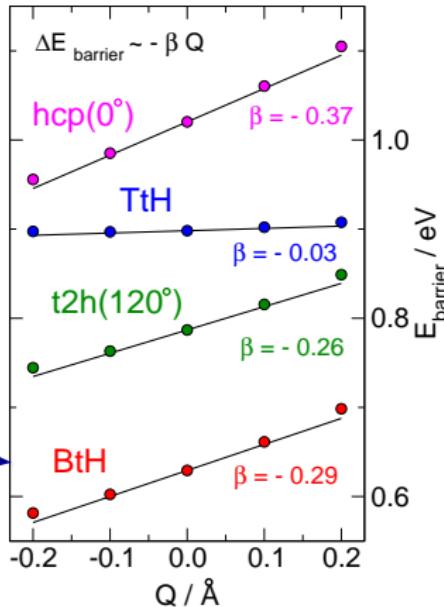
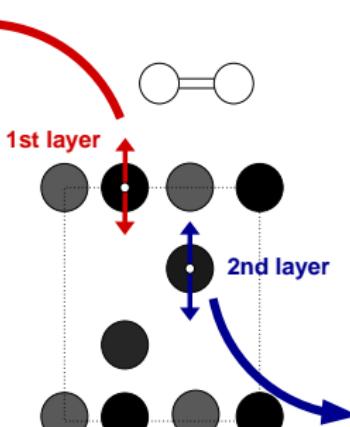
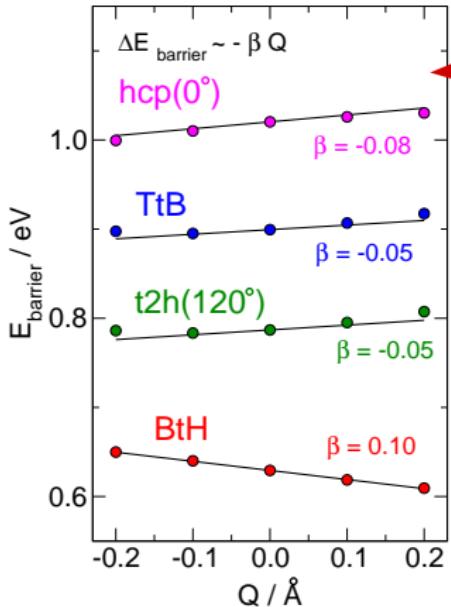
# Barrier Displacement - 2<sup>nd</sup> Layer Cu motion

Barrier	Q (Å)	$\theta$ (°)	Geometry	
			$\Delta r$ (Å)	$\Delta Z$ (Å)
BtH	-0.2	90.	-0.03	0.01
	0.2	90.	0.03	-0.01
t2h	-0.2	90.	-0.02	0.00
	0.2	90.	0.02	0.00
TtH	-0.2	90.	-0.01	0.00
	0.2	90.	0.00	0.00
hcp	-0.2	90.	-0.01	-0.01
	0.2	90.	0.00	0.01

- Negligible change in barrier geometry
- Displacement mainly in  $r$



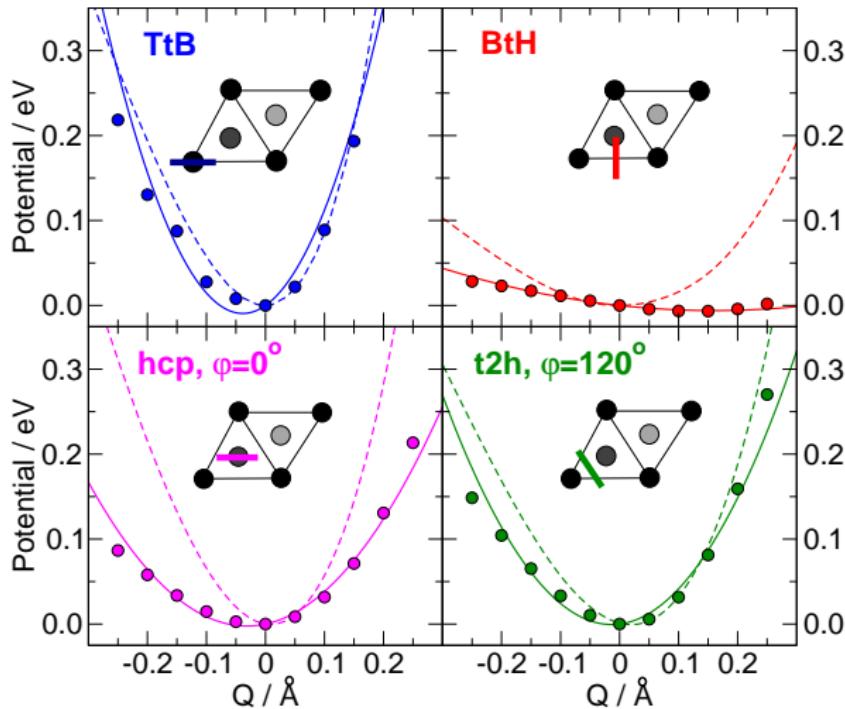
# Barrier Height - 1<sup>st</sup> Layer vs 2<sup>nd</sup> Layer Cu motion



$E_{\text{barrier}}$  more sensitive to 2<sup>nd</sup> Layer motion!



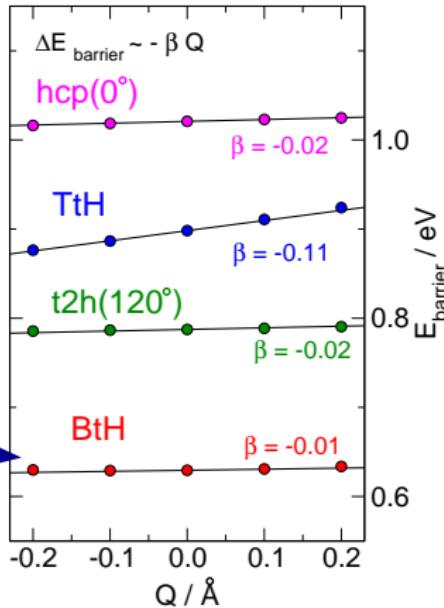
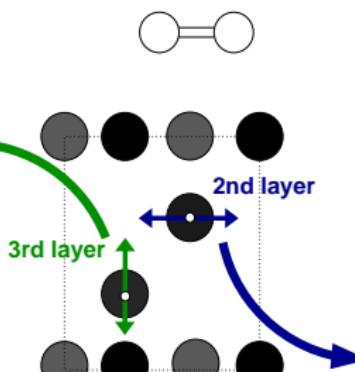
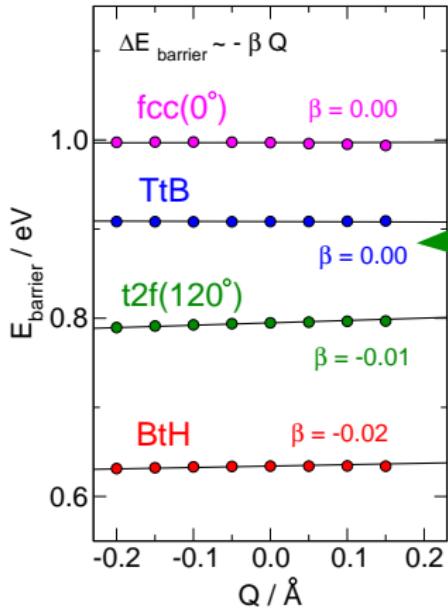
# 1<sup>st</sup> Layer vs SO Model



Agreement between SO Model and 1<sup>st</sup> layer atom motion



# Other lattice coordinates

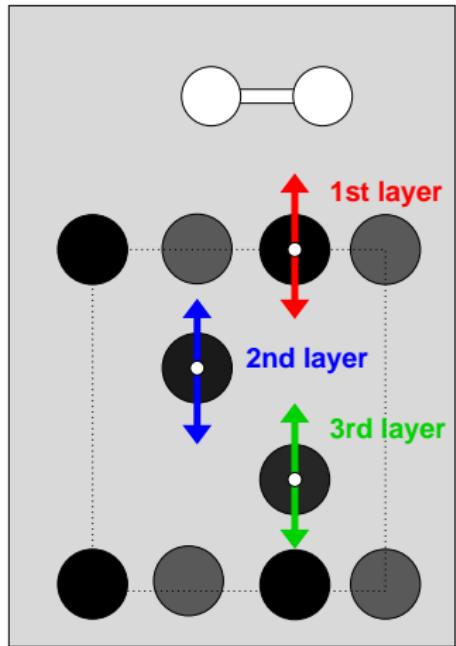


$E_{\text{barrier}}$  mostly independent of other lattice coordinates



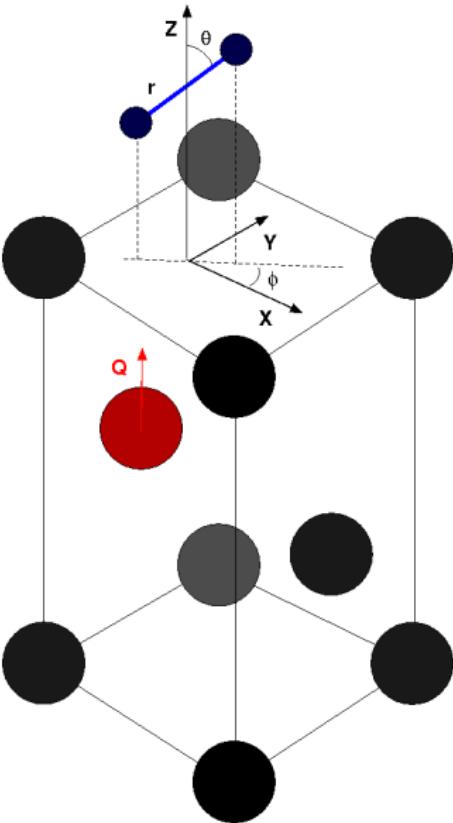
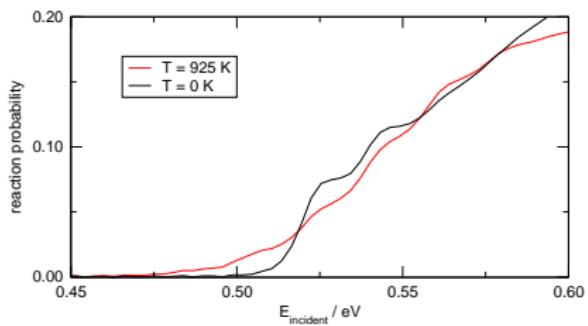
# Conclusions

- 1<sup>st</sup> layer Cu  $\perp$  motion
  - Shift along Z of the barrier position
  - Small changes in barrier height
- 2<sup>nd</sup> layer Cu  $\perp$  motion
  - Small displacement of the barriers
  - Linear dependence of barrier height on Q
- SO Model reproduce the 1<sup>st</sup> Layer Cu motion
- dynamical effect of 2<sup>nd</sup> layer Cu  $\perp$  motion?



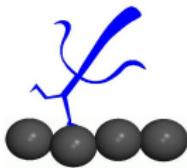
# Further developments

- Investigate the effect of the 2<sup>nd</sup> layer Cu motion in  $H_2$  dissociation with dynamics
  - Extend the SRP **Potential Energy Surface** including another DOF
  - Compute dynamical properties with **7D Quantum Dynamics**



# Acknowledgments

- Prof. Gian Franco Tantardini, Dr. Rocco Martinazzo



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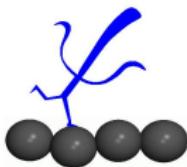


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... and you, for your attention!

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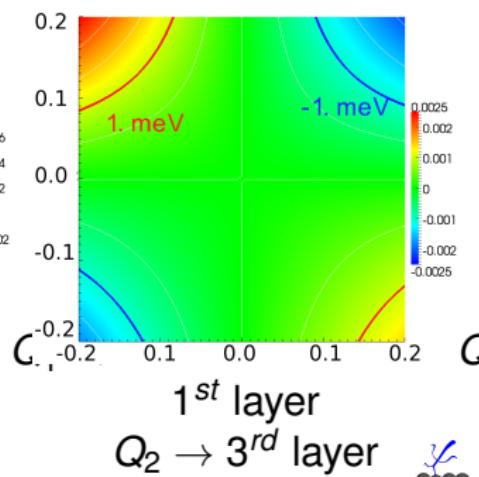
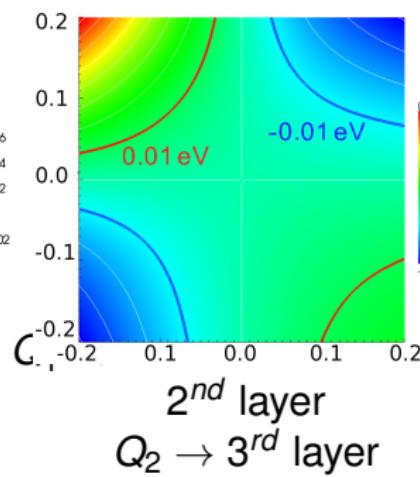
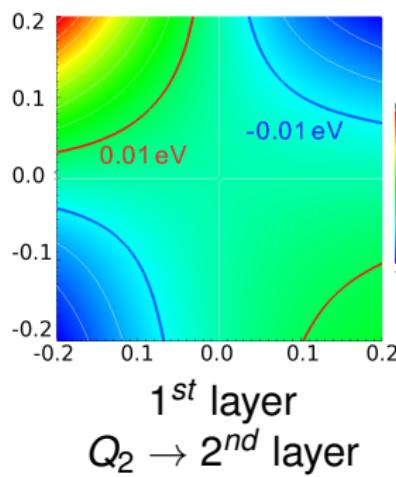
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# Surface DOF: Potential Energy Coupling

$$V_{2D}(Q_1, Q_2) = V_{1D}(Q_1) + V_{1D}(Q_2) + V_{coupling}(Q_1, Q_2)$$

Contour plots of  $V_{coupling}$



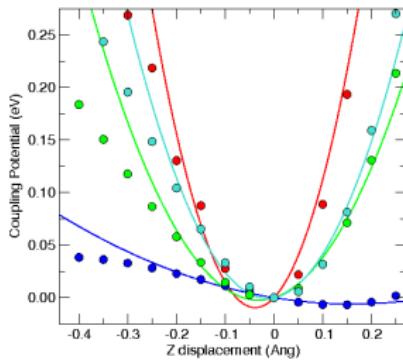
# $H_2$ - Surface Coupling Potential

$$V_{7D}(\xi, Q) = V_{H2@Cu}(\xi) + V_{phonon}(Q) + V_{coupling}(\xi, Q)$$

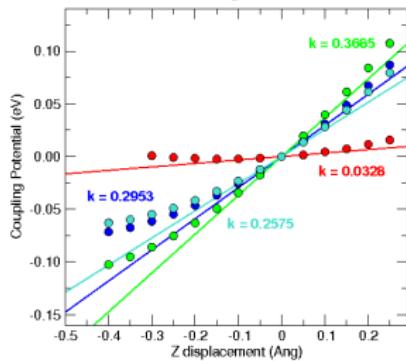
$$\xi = (X, Y, Z, r, \vartheta, \varphi)$$

compare different surface DOF by comparing  
 $V_{coupling}(\xi_{barrier}, Q)$  vs  $Q$        $\xi_{barrier} \rightarrow$  lowest barrier geometry

1<sup>st</sup> Layer Cu



2<sup>nd</sup> Layer Cu



3<sup>rd</sup> Layer Cu

