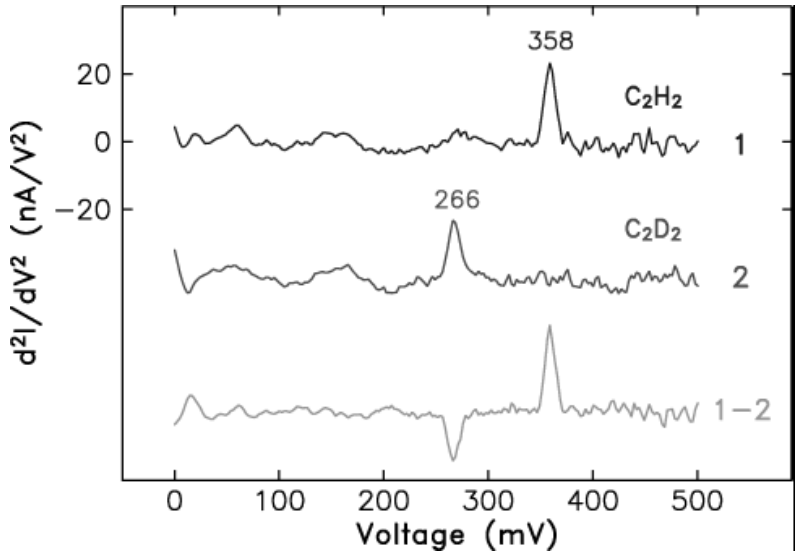
C_2H_2 on Cu(100): STM studies

Motivation:

Inelastic tunneling → vibrational excitation of molecule bonds.

→ atomic and molecular manipulations.

Single-molecule vibrational spectroscopy and microscopy,
Stipe, Rezai and Ho, Science 280, 1732 (1998).



Theory

Aim at:

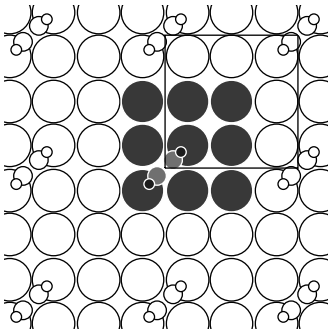
- Characterizing C_2H_2 chemisorption on Cu(100).
- Obtaining STM pictures of this system.
- Studying inelastic tunneling.

Planewave Pseudopotential *ab-initio* code.

- Total energies and forces.
- Ultrasoft pseudopotentials (ionic potentials).
- LDA-GGA (XC potential).
- Supercell geometry (periodicity)$\rightarrow$ slabs.

C_2H_2 on Cu(100): Supercell geometry 3×3

4-layer slab, 36-k points, 30 Ry cutoff.



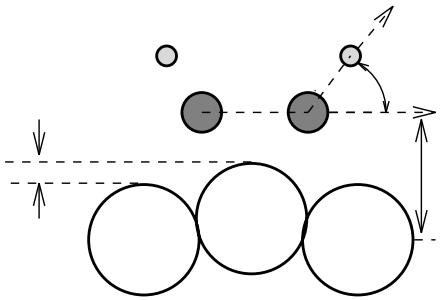
Chemisorption energy: **-1.31 eV**

Rotational barrier [010]→[110]: **85 meV**

Angle C-H with surface plane: **59.93°**

C-H distance: **1.10 Å** (Free C_2H_2: 1.07 Å)

C-C distance: **1.367 Å** (Free C_2H_2: 1.204 Å)



C-surface distance:**1.33 Å**

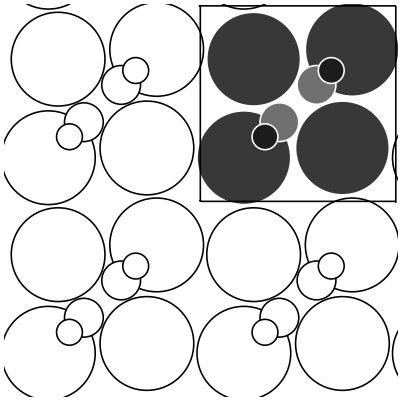
Δz Cu-Cu: **0.14 Å**

Tersoff & Hamann approach:

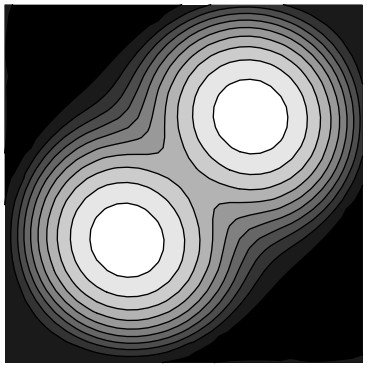
$$\frac{\partial I}{\partial V} \propto \sum_\nu |\psi_\nu(\mathbf{r}_0)|^2 \delta(E_\nu - E_F) = \rho_{\text{surface}}(\mathbf{r}_0, E_F)$$

Where $\mathbf{r}_0$ is the center of the tip.

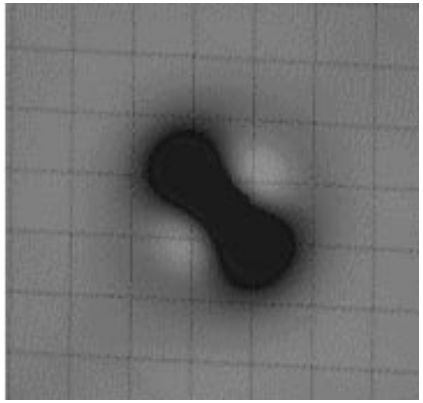
Unit cell.



LDOS map.



Stipe et al.



Change in the I-V slope at **phonon** threshold:

$$\frac{\partial I}{\partial V}_+ - \frac{\partial I}{\partial V}_- \propto \Delta\rho_{\rm surface}(\mathbf{r}_0, E_F)$$

Net change in the normalized conductance: $\eta = \frac{\Delta\rho_{\rm surface}}{\rho_{\rm surface}}$

where $\Delta\rho_{\rm surface} = \frac{1}{2i\pi}{\rm tr}\Delta G^>$

separable in elastic and inelastic contributions:

$$\Delta G^> = \underbrace{G_0^> \Sigma^a G_0^a + G_0^r \Sigma^r G_0^>}_{\rm elastic} + \overbrace{G_0^r \Sigma^> G_0^a}^{\rm inelastic}$$

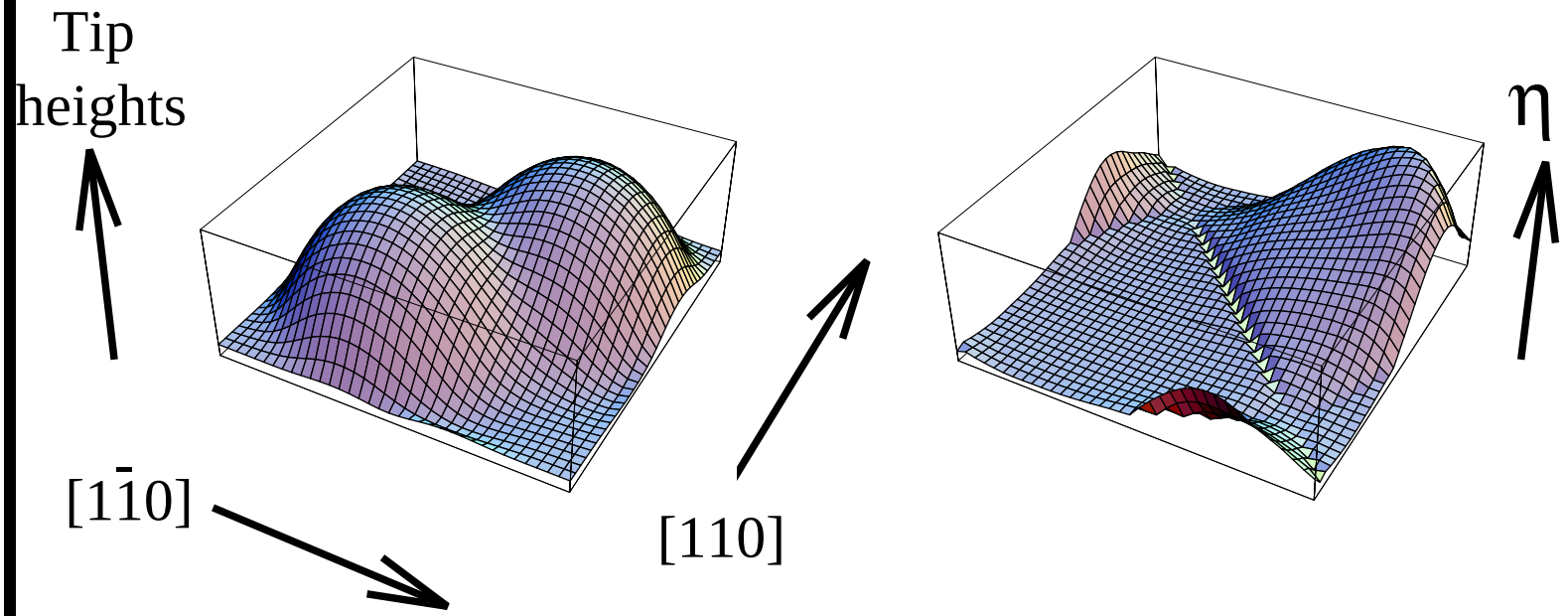
evaluated with *ab-initio* wave functions.

Results:

C-H stretching mode: $\Omega_{\text{theory}} = 348$ meV ($\Omega_{\text{exp}} = 358$ meV)

$\eta \approx \eta_{\text{inelastic}} \approx 6\%$ (Stipe et al. $\sim 9 - 12\%$)

STM image (theory) Inelastic image (theory)

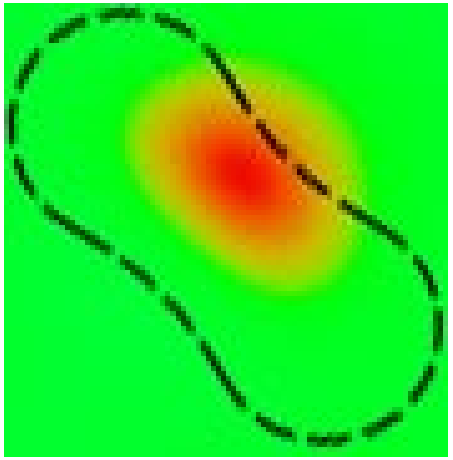


Comparison with experimental pictures:

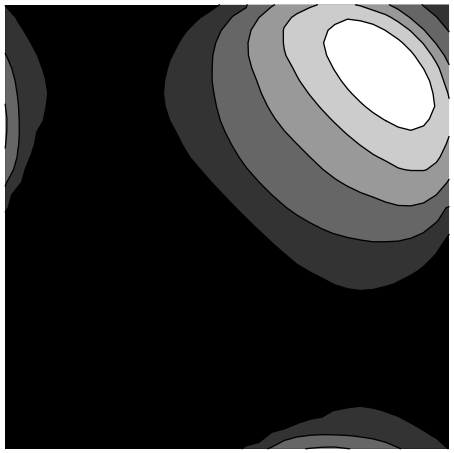
Experiments from

Stipe, Rezai, and Ho, *Phys. Rev. Lett.* **82**, 1724 (1999)

Inelastic image (experiment)



Inelastic image (theory)



Conclusions

- Planewave pseudopotential GGA calculations are useful and accurate.
- C_2H_2 chemisorbs on Cu (100): center site along [100].
- LDOS maps give an approximate STM picture.
- The phonon perturbation of the LDOS gives the inelastic picture. Overall agreement with experiment in:
  - change in the conductance
  - local sensitivity