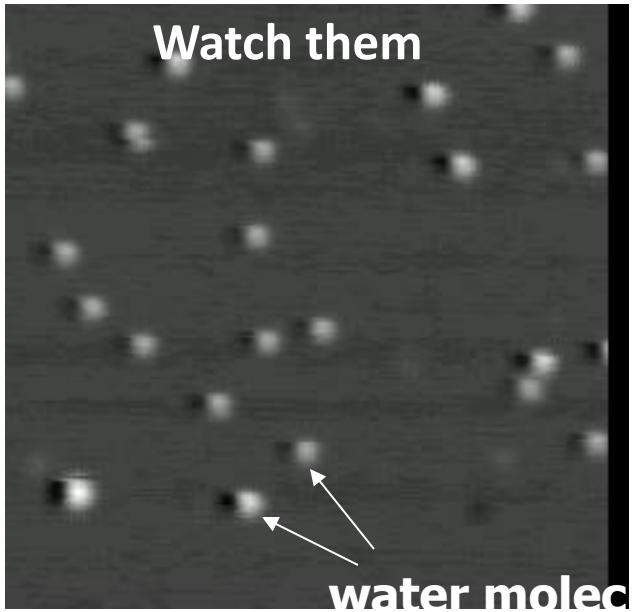
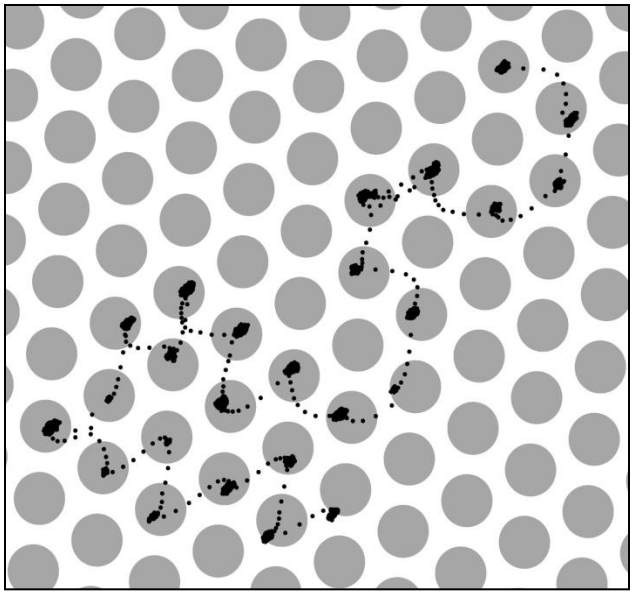
STM application to studies of diffusion and reactions of adsorbed species

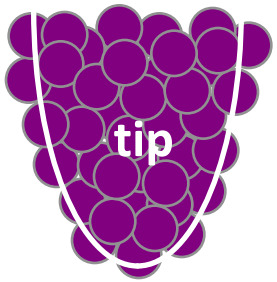
Diffusion of water molecules on a Palladium (111) surface

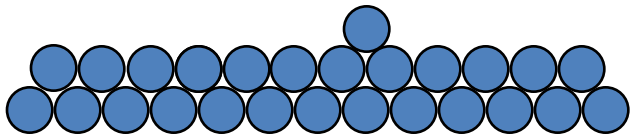
Movies



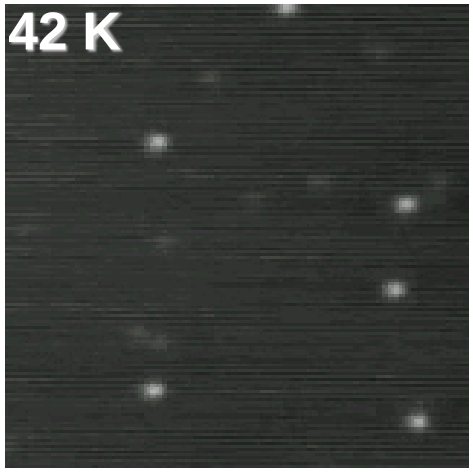


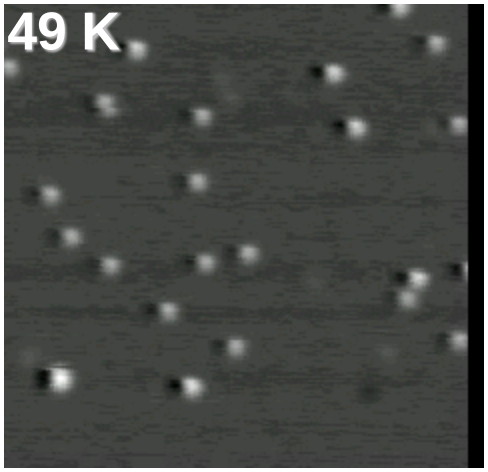
… or ride them

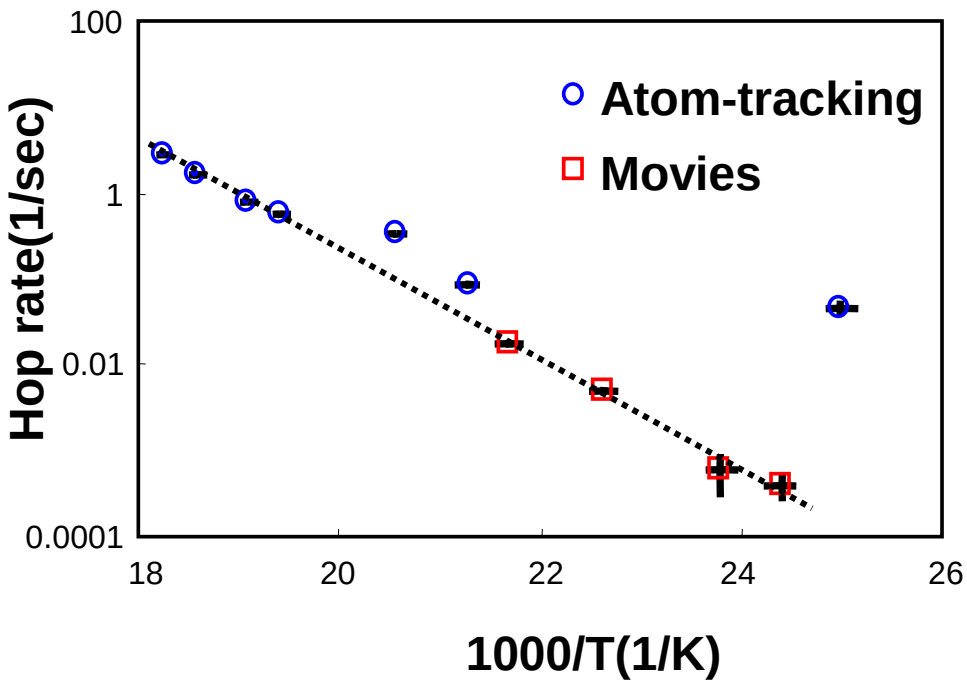




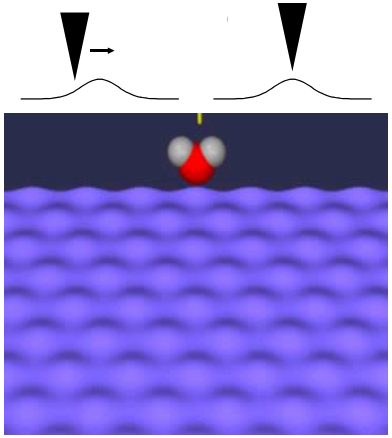
Water monomers

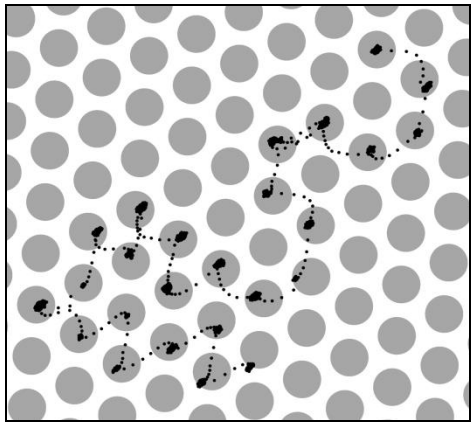






Atom-tracking





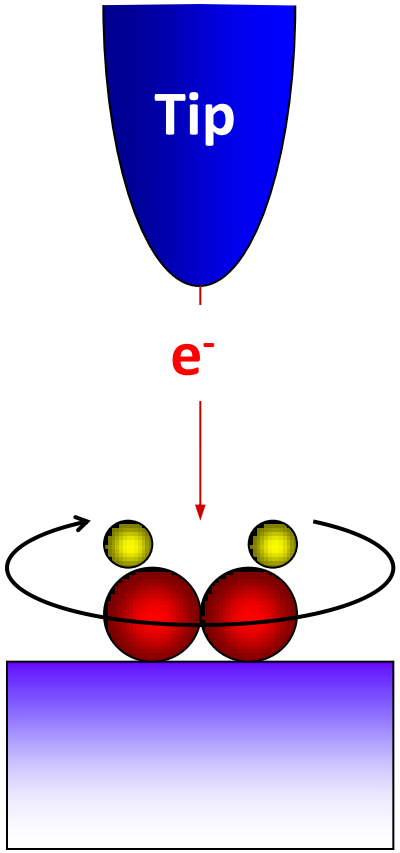
Hoping rate, $r = \nu \cdot \exp(-E/kT)$

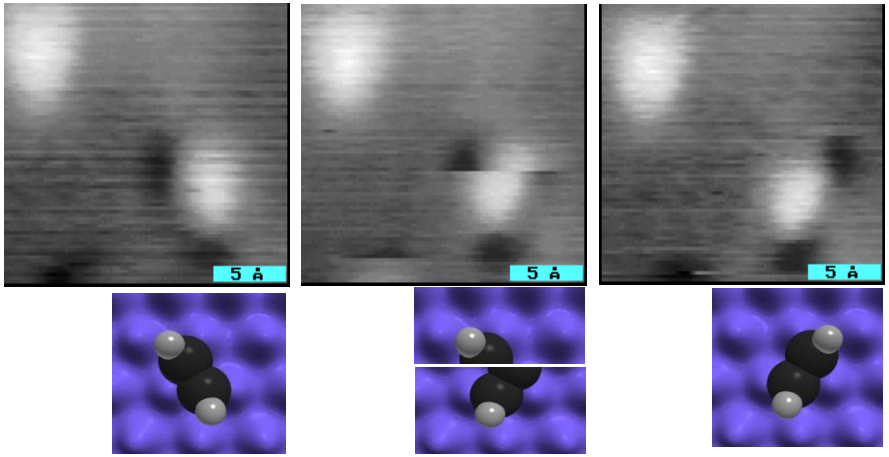
Energy barrier, $E = 126 \pm 7$ meV

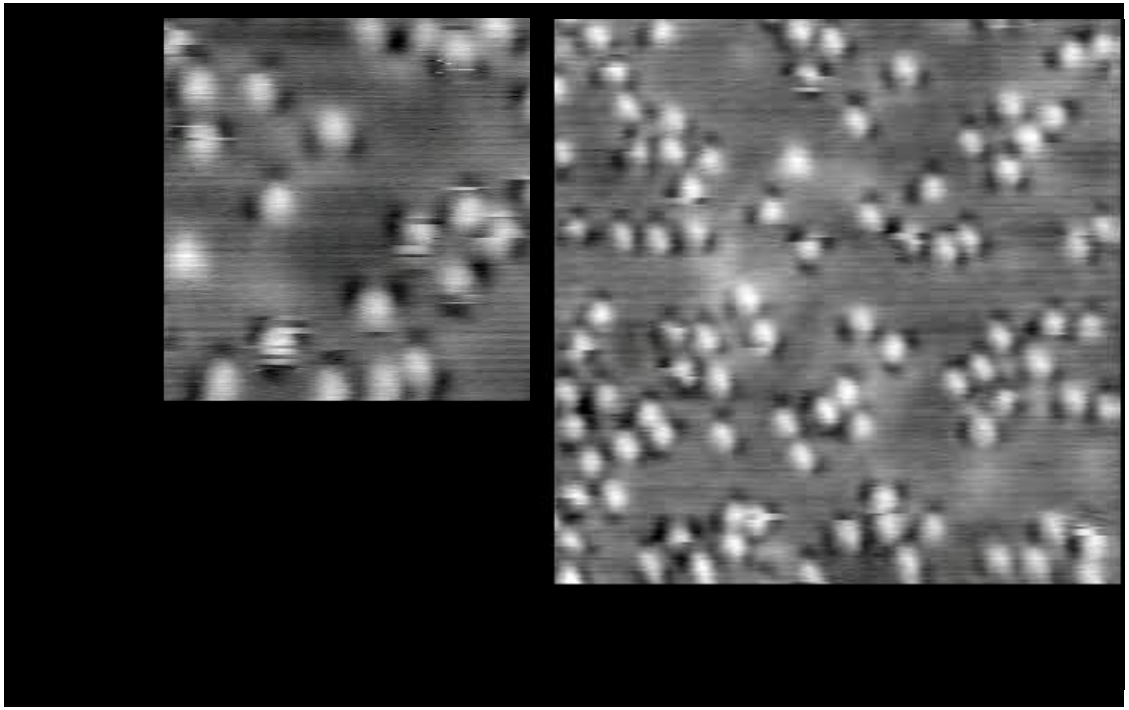
(2.9 kcal/mol)

Attempt frequency, $\nu = 10^{12.0 \pm 0.6}\ s^{-1}$

Excitation of frustrated rotational modes in acetylene molecules on Pd(111) at T = 30 K

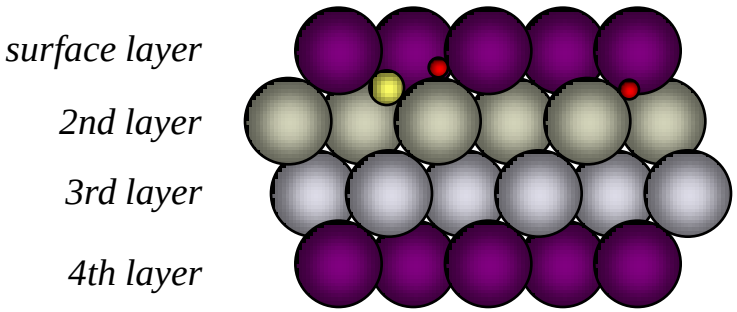




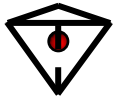


Sub-surface impurities (O, C, ...)

Interstitial sites in Pd

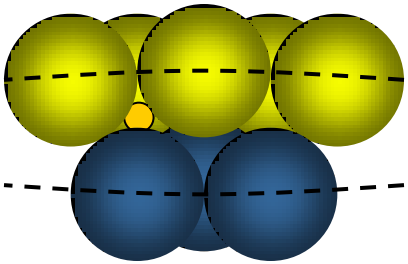


octahedral site

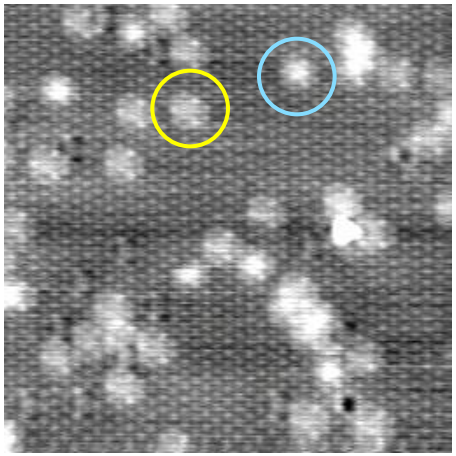


tetrahedral site

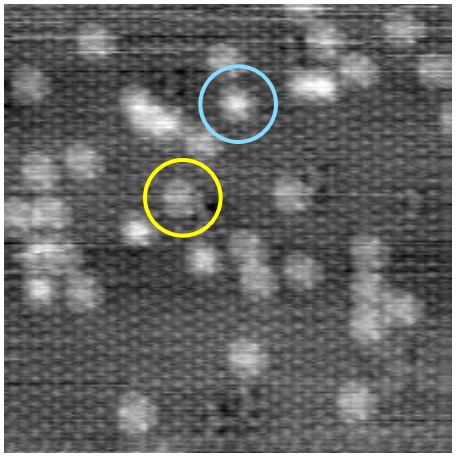
Diffusion:



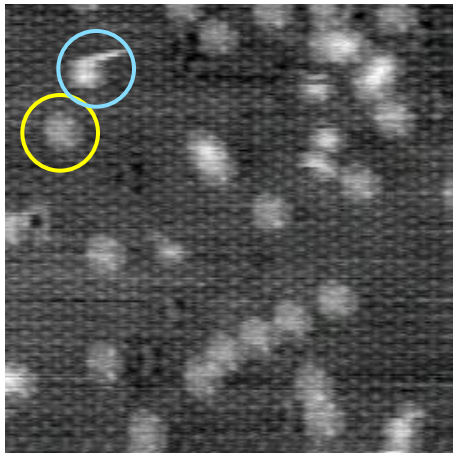
Concentration of impurities = 1-2 % monolayer



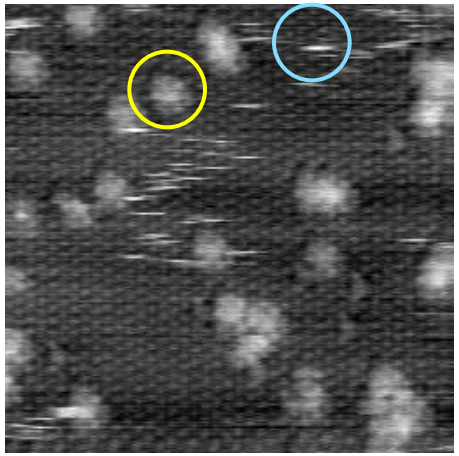
215K



225K



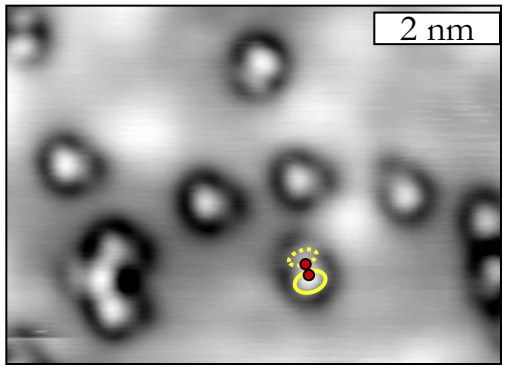
240K

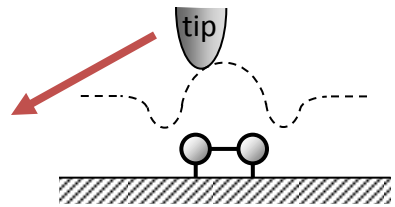


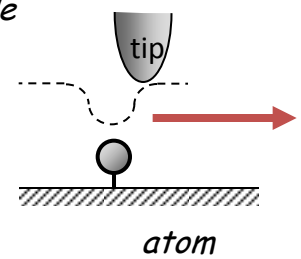
260K

Thermal and tip-induced dissociation of O_2

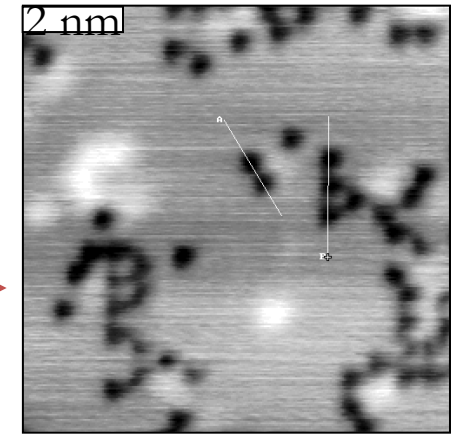
Molecular oxygen at 30K

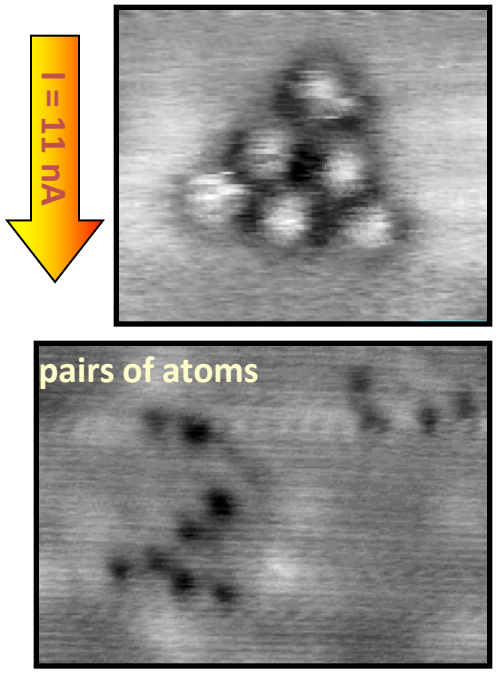


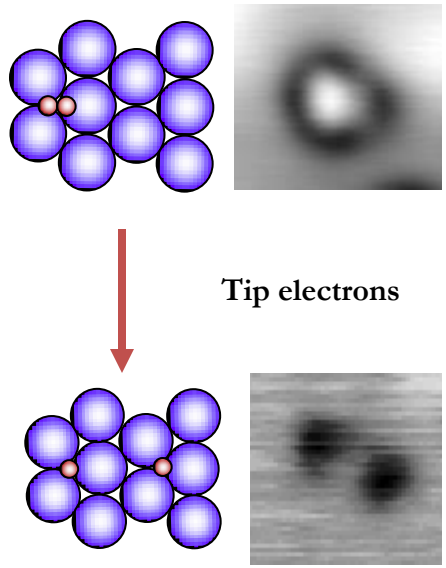


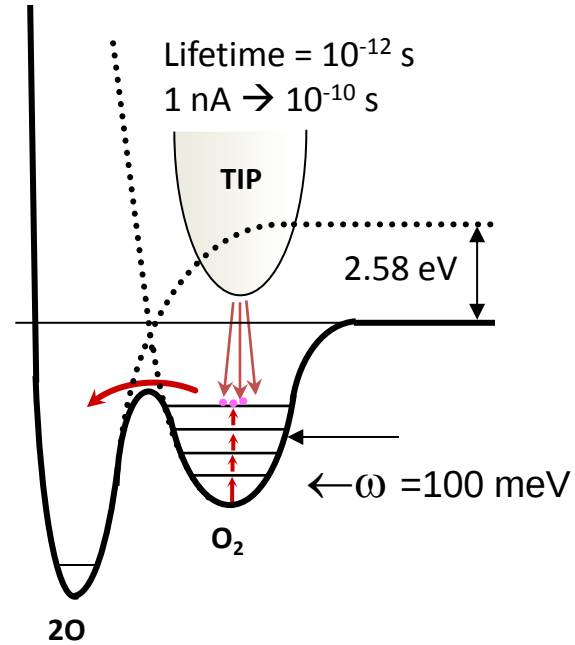


Atomic oxygen after heating to 210 K



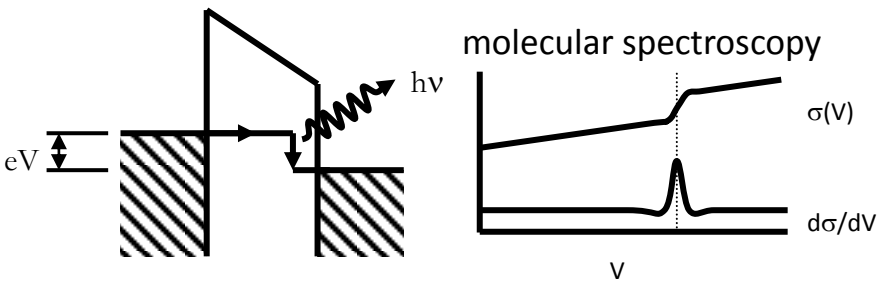






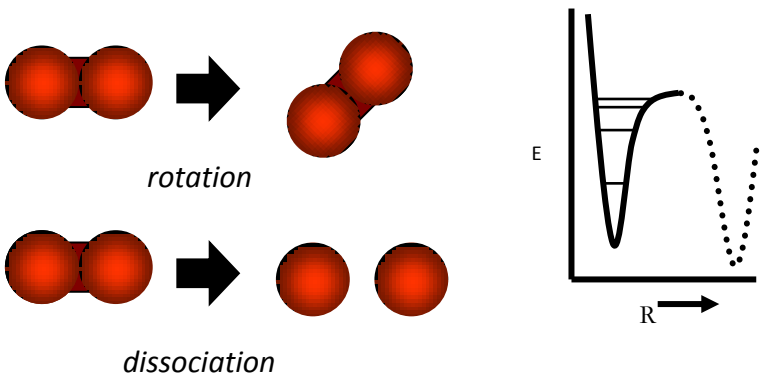
A unique capability of STM:
Single molecule vibration spectroscopy

Spectroscopy on single atoms and molecules

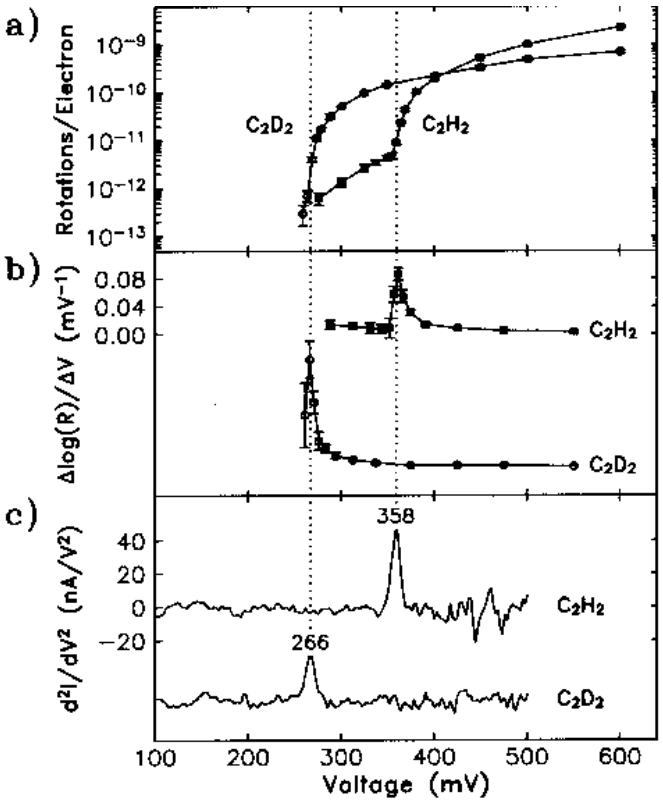


$\Delta\sigma/\sigma \sim 0.01 - 0.1$

Manipulation of molecules



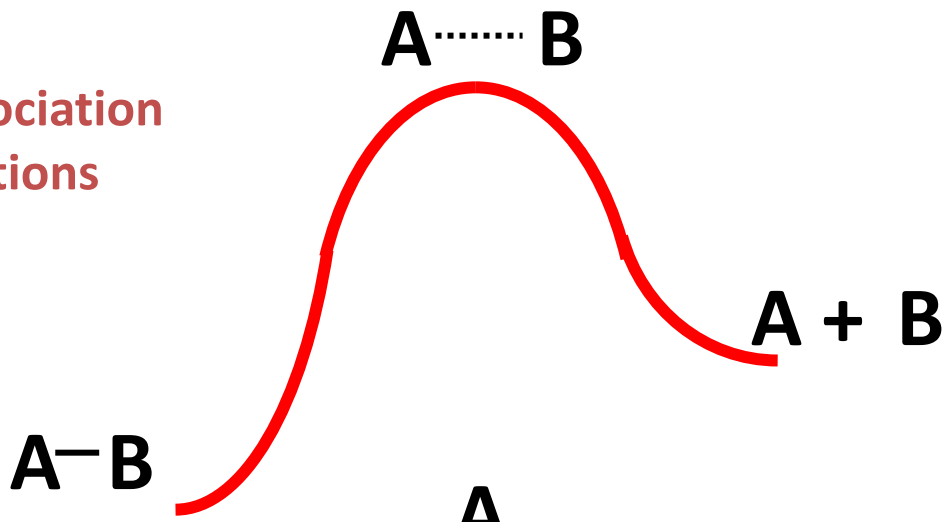
IETS Vibrational spectra of C_2H_2 on Cu(100). From Wilson Ho



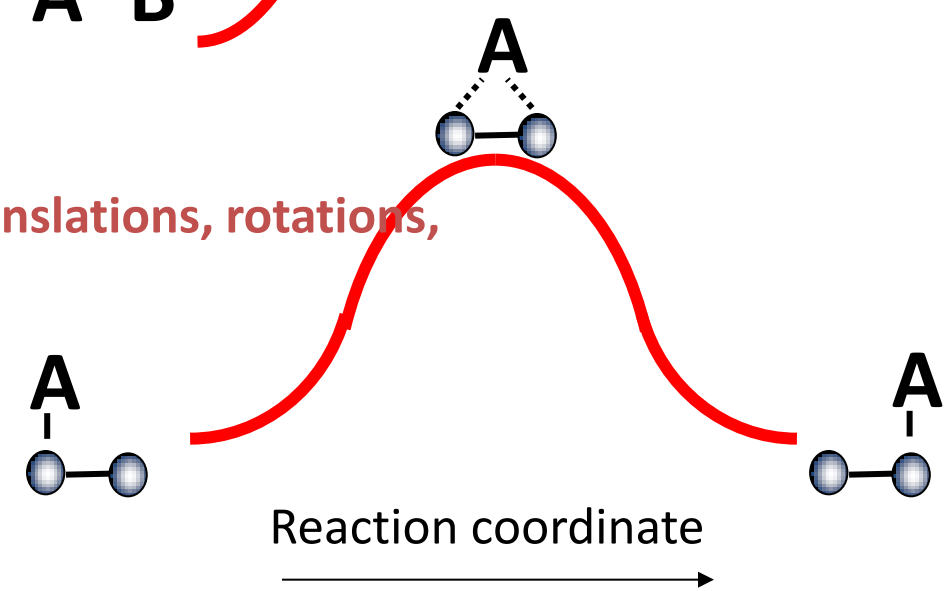
Single molecule reactions initiated by tunneling electrons

What is the nature of the elementary excitations that give rise to a chemical or physical modification?

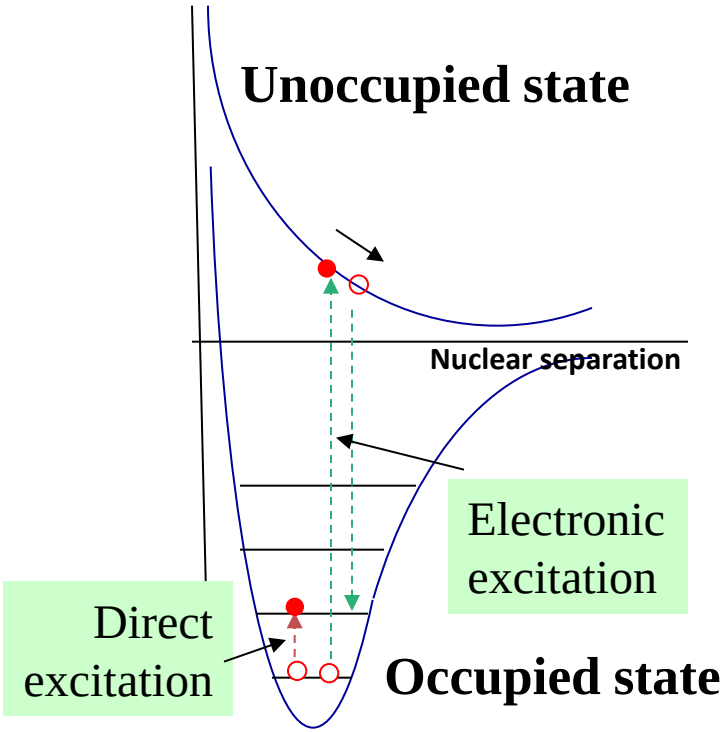
Dissociation reactions



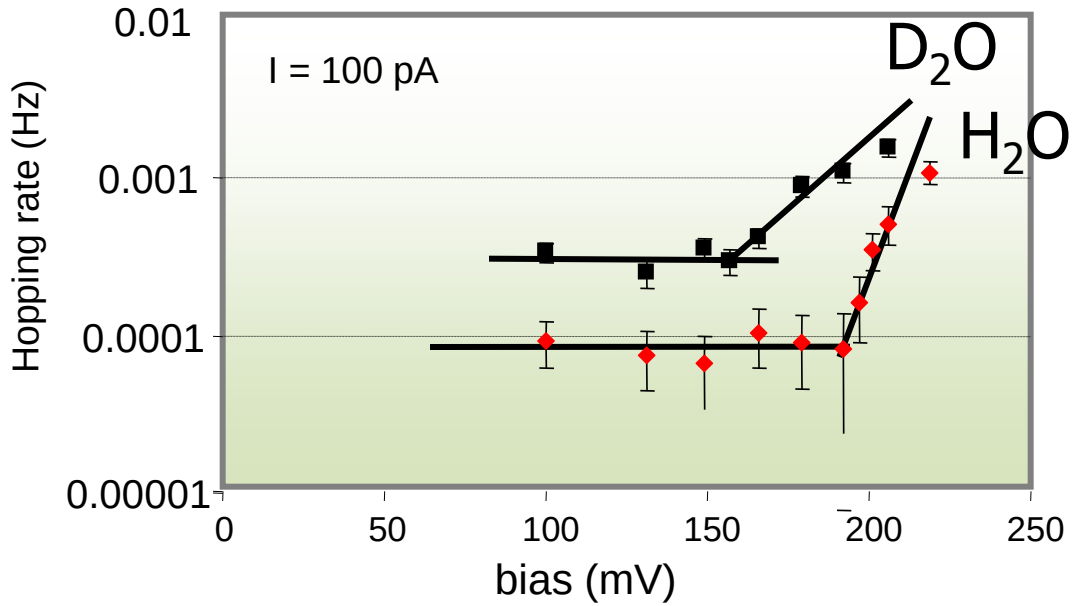
Translations, rotations, …



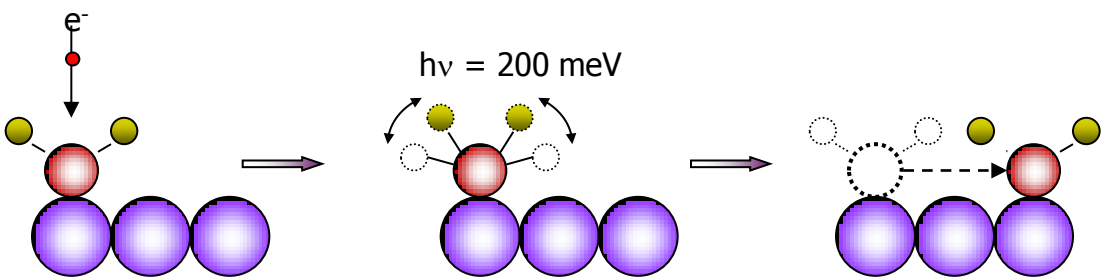
Frank-Condon effect



Tip-induced water hoping on Pd(111)

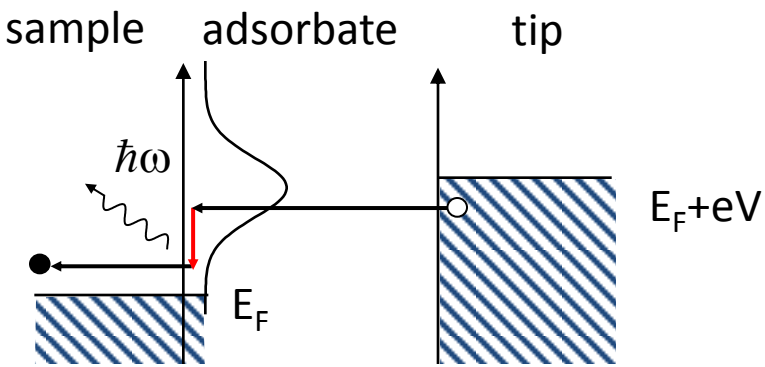


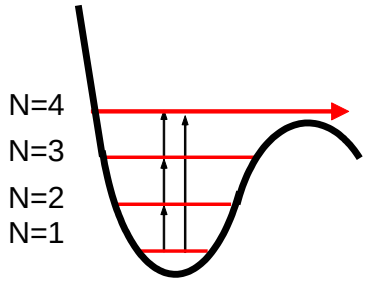
Coupling of scissor and frustrated translation vibration modes



E. Fomin, M. Tatarkhanov, T. Mitsui, M. Rose, D.F. Ogletree and Miquel Salmeron. Surf. Sci. 600, (3) 542-546 (2006)

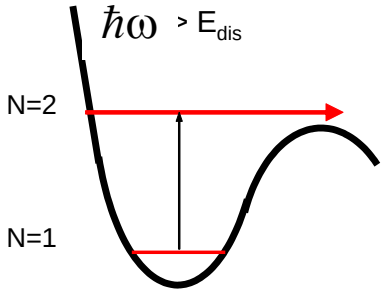
Energy transfer to water molecules: excitation of vibrations



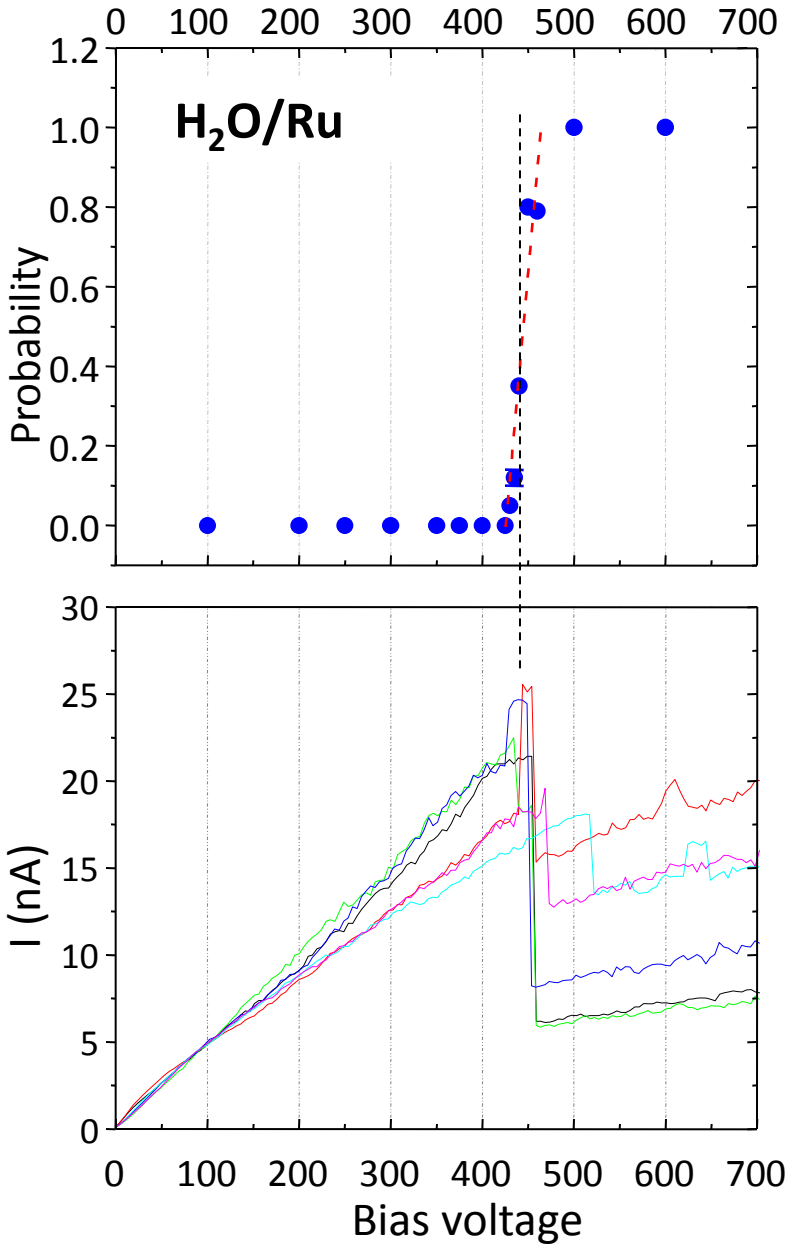


•single level, multi-electron excitation

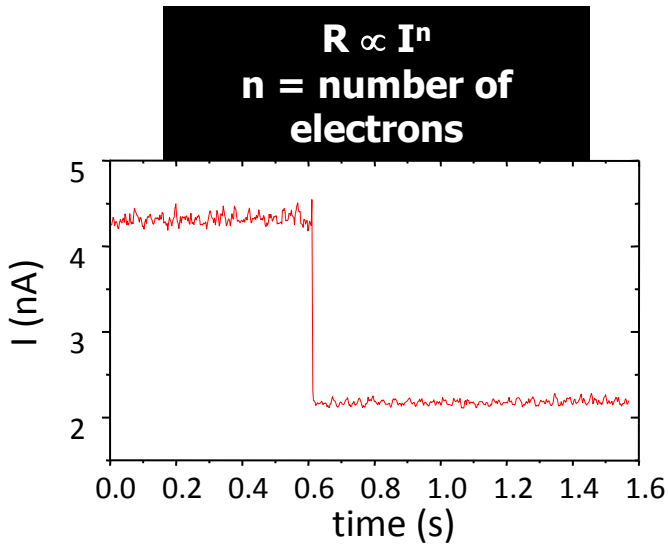
•multi-level, single electron excitation

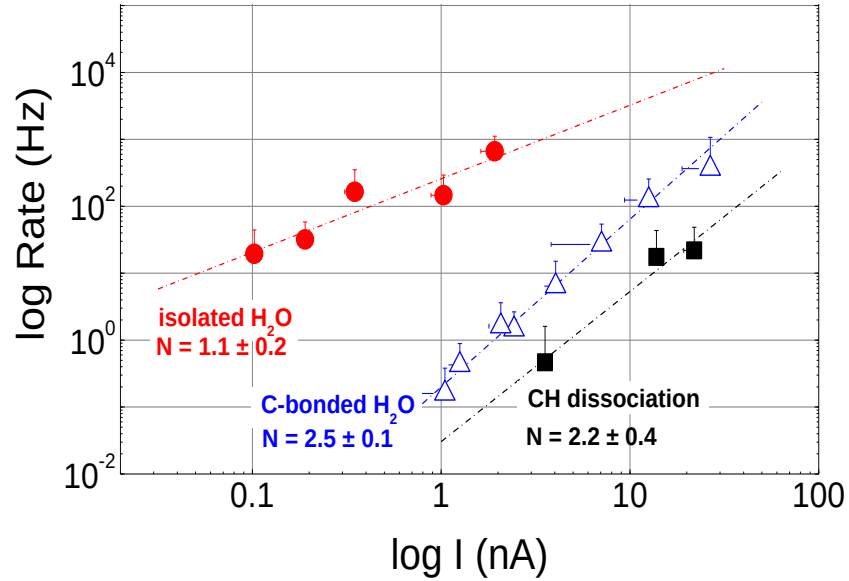


•single level, single electron excitation



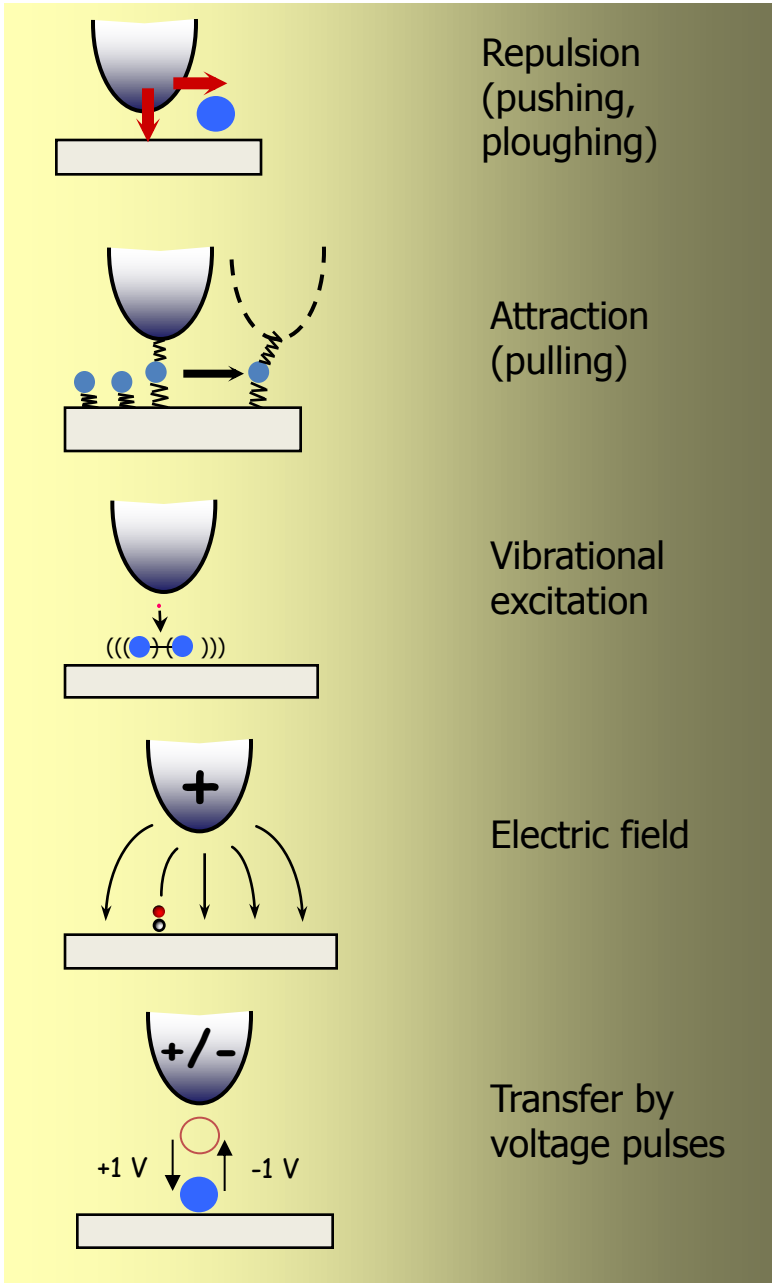
How many quanta need be excited for a chemical reaction ?

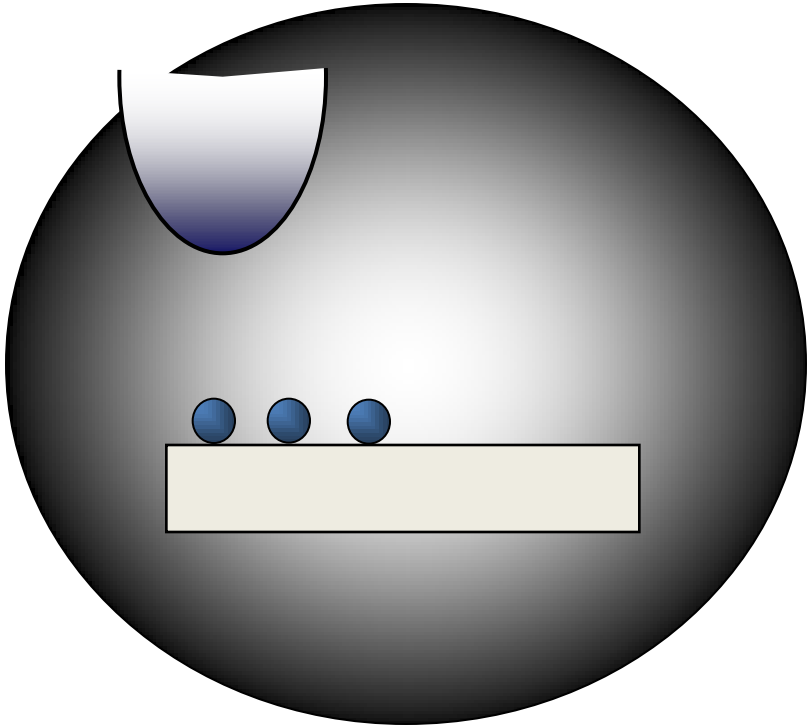
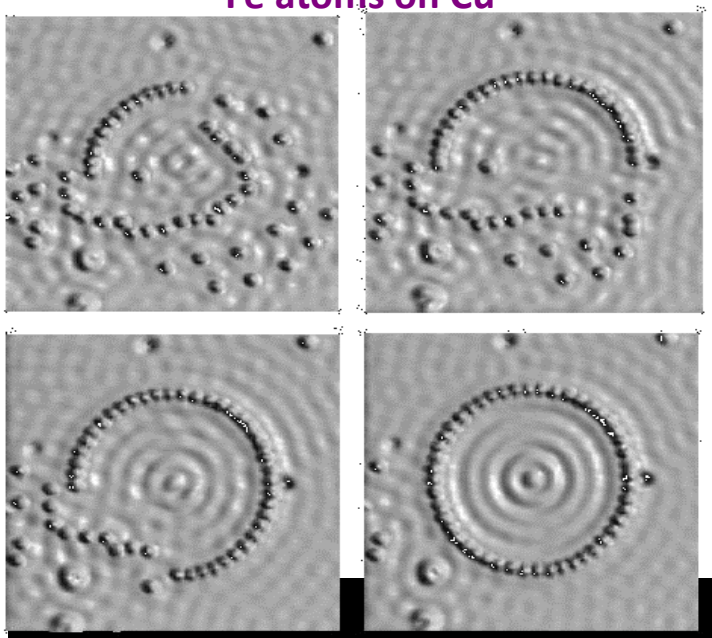
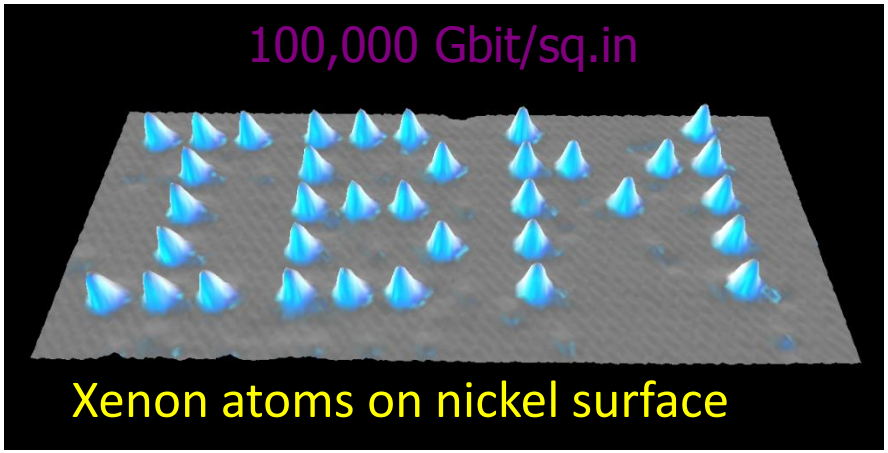
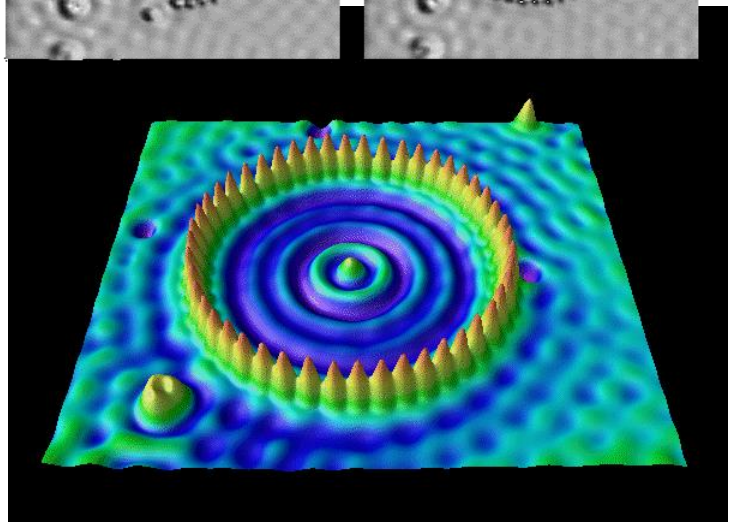




• Diffusion of monomers on Pd(111)	(N= 1)	hv = 200 meV
• Diffusion of isolated monomer on Ru:	(N=1)	hv = 450 meV
• Diffusion of monomer bonded to C on Ru: (N=2)	hv = 450 meV	
• Diffusion of OH on Ru		hv < 250 meV
• Dissociation of isolated OH, H_2O on Ru	(N > 1)	hv = 450 meV
• Dissociation of H2O in a cluster on Ru	(N = 1)	hv = 450 meV

The STM as a tool for atomic scale manipulation





Building of a quantum "corral" with Fe atoms on Cu