Structure of matter, matter wave, atomic and molecular interactions. Atomic force microscopy.

Balázs Kiss, MD, PhD

kissb3@gmail.com

Nanobiotechnology and Single Molecule Research Group,

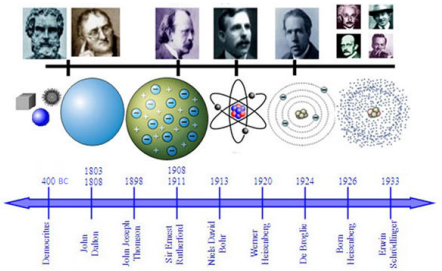
Department of Biophysics and Radiation Biology,

Semmelweis University

07. October 2020.

Textbook: pages 23-37

Atomic models

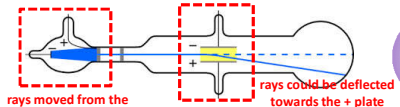


- **Democritus (~400 BC):** proposition of atomic structure („atomos": indivisible)
- **Dalton (1803):** stoichiometric law: elements consist of identical constituents
- **Thomson (1897):** discovery of electron (cathode rays)
- **Rutherford (1909-1911):** nucleus (nucleons: p^+ and n_0) and electrons
- **Bohr (1913):** discrete energy states

2

Thomson and Rutherford

Thomson: discovery of cathode rays

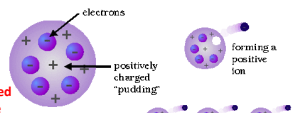


rays moved from the negative electrode to the positive electrode

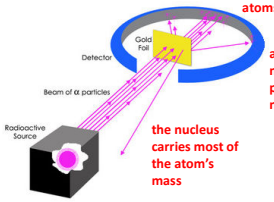
rays could be deflected towards the + plate

gas discharge tube

„plum pudding atom" or „blueberry muffin atom"



Rutherford: experiments with α-particles

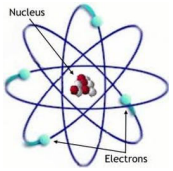


atoms are mostly empty space

atoms are made of a small positive nucleus

the nucleus carries most of the atom's mass

„planetary model"



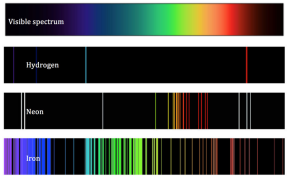
3

Bohr and Schrödinger

Bohr: describing the electron shells

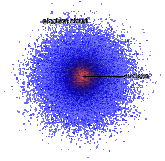
- electrons furthest from the nucleus have higher energy
- absorbing energy: jump from a lower orbit to a higher
- losing energy: emission of photons

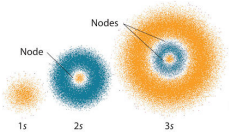
Emission spectra of certain elements



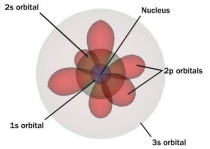
Schrödinger: quantum mechanical model of the electrons

- no exact path, rather predicts the odds of the location of the electron



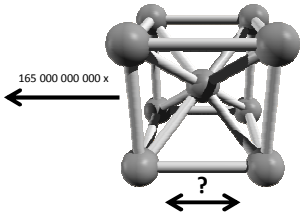


Complex shapes of orbitals: electron clouds



4

How are stable structures created/formed?



macroscopic scale: Atomium

nanoworld: face-centered cubic lattice of Fe

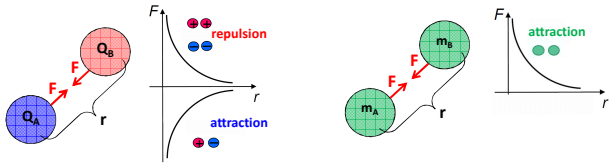
Governing principle:

consequence: DISORDER — repulsive interaction ⟷ attractive interaction — consequence: ORDER

Fundamental interactions in physics

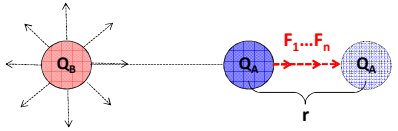
Interaction type	Binding particle	Range (m)	Relative strength
gravitation	every particle	infinite (~1/r²)	10^{-40}
electrostatic (Coulomb)	charged particles	infinite (~1/r²)	10^{-2}
strong nuclear	nucleons	10^{-15}	1
weak nuclear	every particle	10^{-18}	10^{-13}

Coulomb-interaction ⟷ **Gravitation**



$$F_C = k \cdot \frac{Q_A \cdot Q_B}{r^2} \qquad F_g = G \cdot \frac{m_A \cdot m_B}{r^2}$$

Electric potential energy (E_{pot})

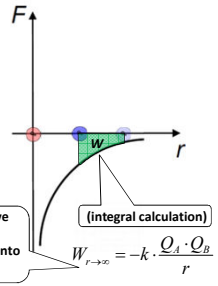


positive charge (fixed)

How much energy is needed to separate the - charge?

$W = F \cdot s = F \cdot \Delta r$

$F = ?$ (changes continuously!)



(integral calculation)

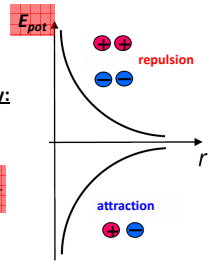
the negative charge is transported into infinite

$$W_{r \to \infty} = -k \cdot \frac{Q_A \cdot Q_B}{r}$$

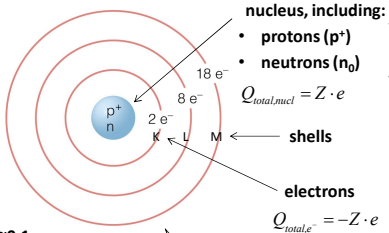
Electric potential energy:

$$E_{pot} = W_{\infty \to r}$$

$$E_{pot} = k \cdot \frac{Q_A \cdot Q_B}{r}$$



Structure of the Atom



nucleus, including:
- protons (p^+)
- neutrons (n_0)

nucleons

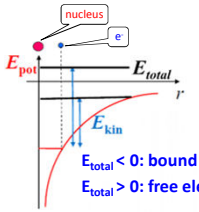
$Q_{total,nucl} = Z \cdot e$

$Q_{total,e^-} = -Z \cdot e$

$E_{kin} = \frac{1}{2} m v^2$

$E_{pot} = k \cdot \frac{Q_A \cdot Q_B}{r}$

$E_{total} = E_{pot} + E_{kin}$



$E_{total} < 0$: bound electron

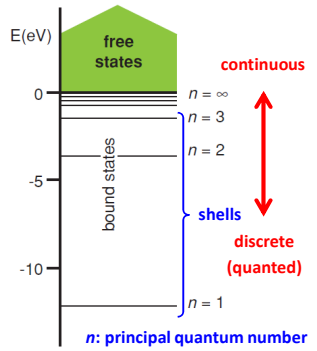
$E_{total} > 0$: free electron

Z: atomic number (number of protons)

N: neutron number

A: mass number (=Z+N)

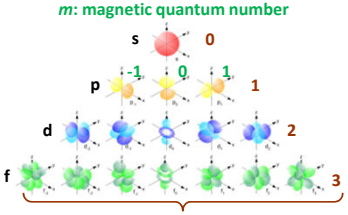
The energy states of the electron



an electron's possible energy levels in the hydrogen atom

l: azimuthal quantum number

m: magnetic quantum number



s: sharp;
p: principal;
d: diffuse;
f: fundamental.

subshells

see light emission measurement

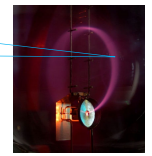
- Principle of minimum energy
- Pauli exclusion principle

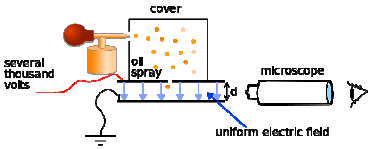
9

Particle-wave duality of the electron

cf. particle-wave duality of the photon

e⁻ beam is bent due to the presence of the magnetic field





particle

wave

mass

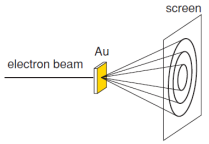
(Thomson, 1897; mass-to-charge ratio)

$m_e = 9.1*10^{-31}$ kg

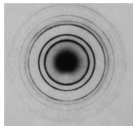
charge

(Millikan, 1910)

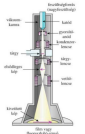
$e = -1.6*10^{-19}$ C



Davisson and Germer, 1927



diffraction of fast electrons through a gold foil

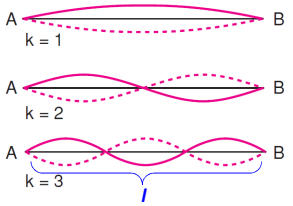


electron microscope

10

The electron as a wave

Analogy: stationary waves of a stretched string



$l = k\frac{\lambda_k}{2} \quad k = 1,2,...$

only discrete values are allowed!

λ: wavelength of the matter wave

$\lambda = \frac{h}{p} = \frac{h}{m_e \cdot v}$

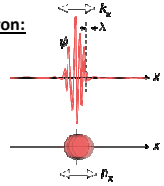
De Broglie, 1923

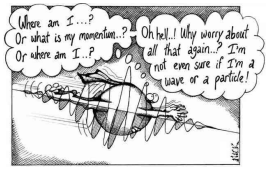
The state function of the electron:

ψ(x,t)

(Schrödinger)

- location (x): where ψ(x,t)=1
- momentum (p): "shape" of ψ(x,t)

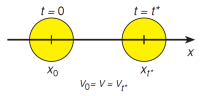


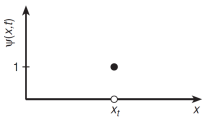


11

The propagation law of free electrons

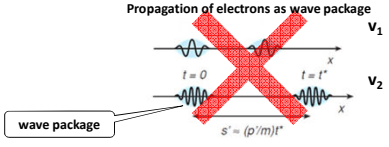
Classical mechanics: state of motion

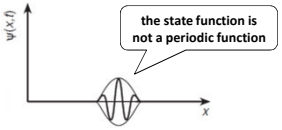




position of a classical object can be determined exactly

Propagation of electrons as wave package



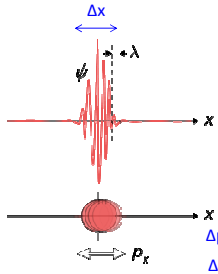


the state function of the electron

ψ(x,t) will disperse while propagating

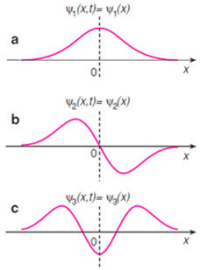
12

The electron bound in an atom



in the electric field of the atomic nucleus (or proton)

deformed state function



Δp~Δ(1/λ)

Δ(1/λ) ≥ 1/Δx

The Heisenberg uncertainty relation

the uncertainty of the momentum (Δp) in the case of a free electron:

$$\Delta x \cdot \Delta p \geq h$$

$$\Delta E \cdot \Delta t \geq h$$

"one-dimensional H-atom"

Δt: uncertain, so E can be certain:

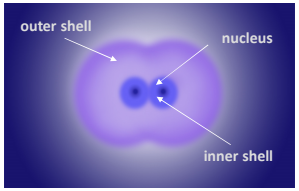
discrete energy levels

13

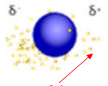
Textbook page 44-51

Atomic interactions

short range interaction: repulsion between nuclei (electron cloud overlap)

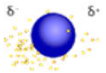


long range interaction: coulombic attraction

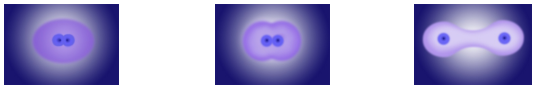


repulsion (inner shells and nuclei)

equilibrium attraction = repulsion

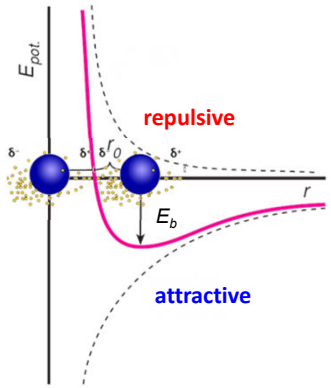


attraction (outer shells)



14

Atomic interactions



$$E_{pot} = E_{attraction} + E_{repulsion}$$

$$E_{pot} = -\frac{A}{r^n} + \frac{B}{r^m}$$

A, B: interaction-specific constants (atom-dependent)

n (attraction) < m (repulsion)

r_0: binding distance

E_b: binding energy

15

Primary bonds

intramolecular
strong
primary

⟷

intermolecular
weak
secondary

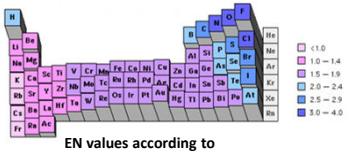
„tendency of an atom to attract electrons"

- **covalent:** common electron state around the participating nuclei, strong: E_b > 1eV
- **metallic bond:** multi-atomic system, E_b > 1eV
- **ionic bond:** Coulomb-forces between ions, E_b > 1eV

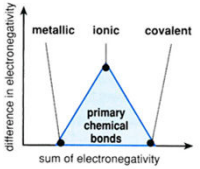
type depends from **electronegativity (EN)**

$EN = |E_i| + |E_{ea}|$

ionization energy | electron-affinity



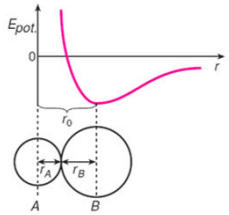
EN values according to Pauling

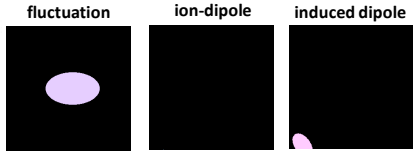


16

Secondary bonds 1

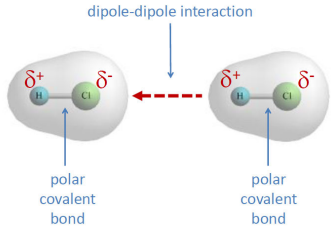
- **Van der Waals:** between two apolar atoms (without permanent dipole moment) where a temporarily created dipole interacts with an apolar molecule or atom thus converting it into a dipole **(induced dipole)**
  - **Van der Waals radius:** $r_0=r_A+r_B$
  - **Intermolecular or intramolecular**
  - **Important biological role: formation of organic structures**
  - **Weak: (E_b ~ 0,02 eV)**





Secondary bonds 2

- **Dipole-dipole interaction:**
  - constant charge distribution is present in a (given part of a) molecule
  - partially (+) and (-) segments are held together by electrostatic interactions (Coulomb-forces)
  - intra-/intermolecular
  - weak interaction (E_b = 0.003-0.02 eV)



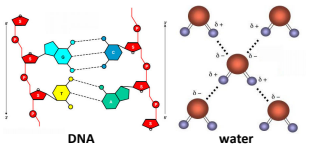
$$E_{attraction} = p * E$$

p: dipole momentum (p=Q*d)

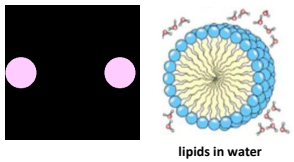
E: electric field strength generated by the surrounding partners

Secondary bonds 3

- **H-bond**: the H-atom interbridges two other atoms (F, O, N) of high electronegativity
  - **r ~ 0.23 - 0.35 nm**
  - **E ~ 0.2 eV**

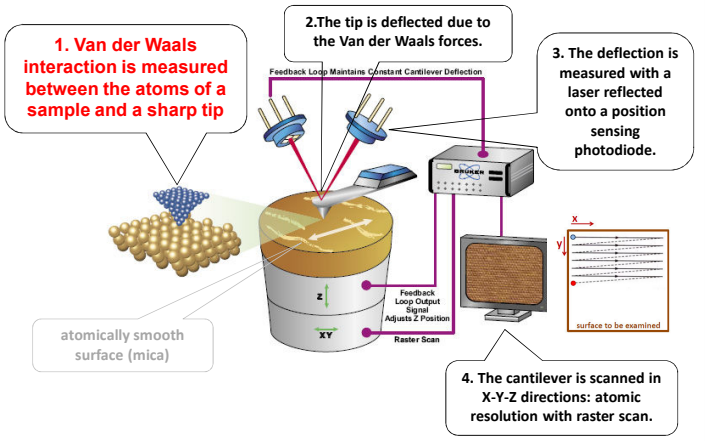


- **Hydrophobic interaction:** weak Van der Waals interaction (E_b = 0.003 - 0.02 eV), thermal motion (kT ~ 0.025 eV) could disrupt the system
  - ordered water molecules exclude the apolar structures (contact surface can be minimized)

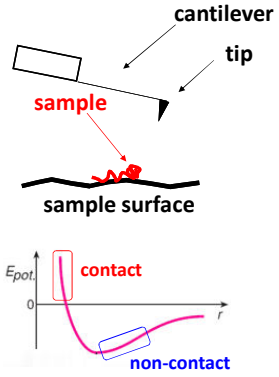


Textbook page 573

Atomic force microscope (AFM)



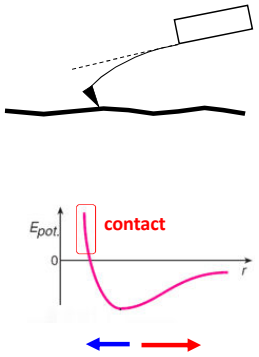
AFM operating modes

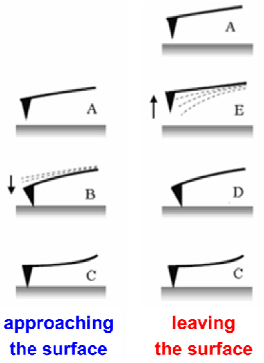


- **Contact:** the tip touches the surface, the **deflection of the cantilever** (i.e. the force exerted on the sample by the tip) is held **constant**.
  - **Z-feedback** system: deflection is maintained at a constant value (setpoint) by lifting or lowering the cantilever.
  - **topography data** (i.e.: height) in each x;y point is calculated from these Z movements
- **Non-contact:** the **cantilever is oscillated without contact** with the surface: resonant frequency (f_0) and the amplitude of the oscillation changes with surface topography.
  - **Z-feedback:** maintains the amplitude by lifting or lowering the oscillating cantilever.

21

Contact mode AFM

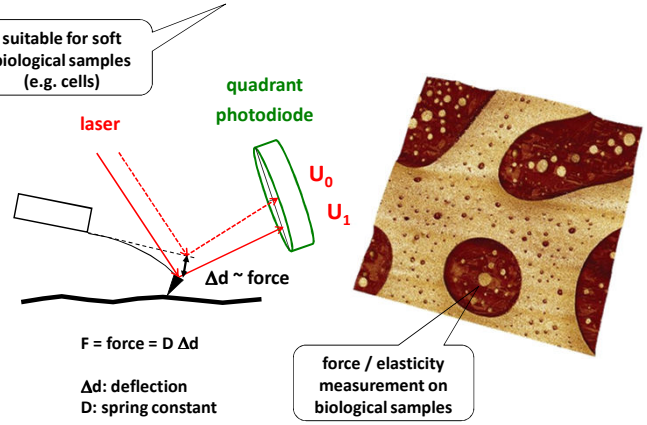




22

Contact mode AFM

suitable for soft biological samples (e.g. cells)



F = force = D Δd

Δd: deflection
D: spring constant

force / elasticity measurement on biological samples

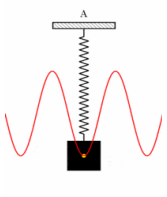
23

Practice: Resonance

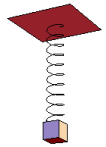
Resonance

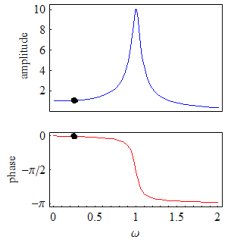
Resonance: a driven oscillation occurring when the oscillatory system is exposed to a driving force with a frequency close to its eigenfrequency (f_0). Amplitudes may become extremely large.

Free oscillation



Driven oscillation

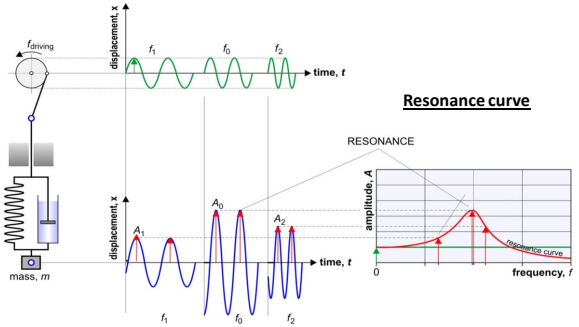




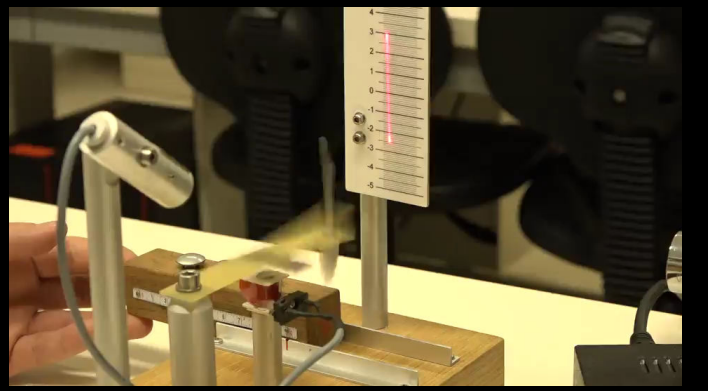
24

Non-contact/oscillating mode AFM

Resonance: a driven oscillation occurring when the oscillatory system is exposed to a driving force with a frequency close to its eigenfrequency (f_0). Amplitudes may become extremely large.

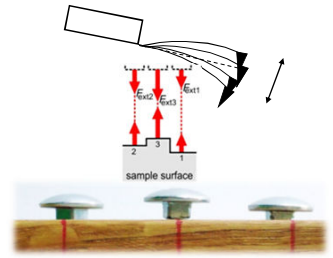


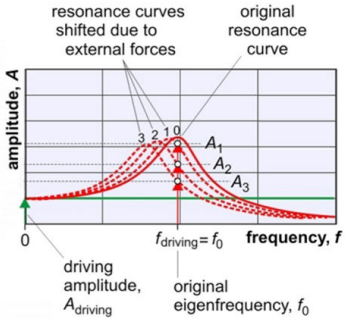
Non-contact/oscillating mode AFM model

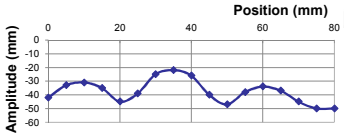


N.B.: magnetic interaction models the Van der Waals forces

Non-contact/oscillating mode AFM



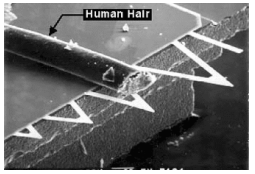


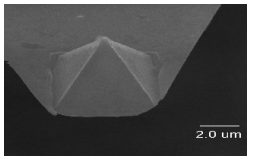


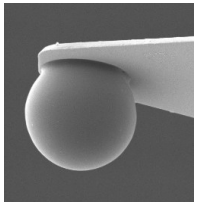
$$f_0 = \frac{1}{2\pi}\sqrt{\frac{D}{m}}$$

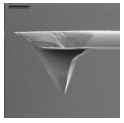
Cantilevers

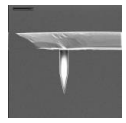
- **Material: mainly silicon nitride**
- **Tip radius: 0.1 nm - 100 µm**
- **Spring constant ~ 0.1 - 10 N/m**
- **f_o ~ 50-500 kHz**



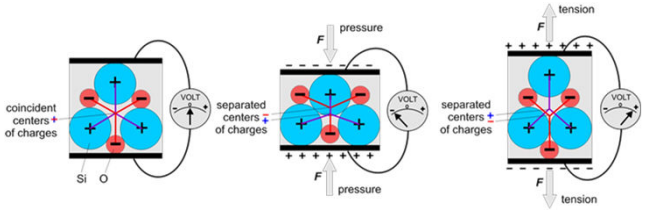






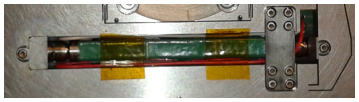


Principle of X-Y-Z raster scanning: piezoelectricity



- **direct piezoelectric effect: deformation → voltage**
- **inverse piezoelectric effect: voltage → deformation**
- **X, Y, Z axis piezo: e.g. 150 V → 40 µm**

0.1-nm-accuracy possible



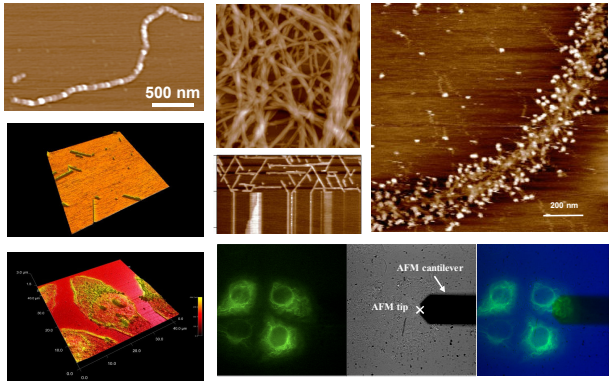
29

AFM - properties

- **Main advantages:**
  - 3D surface profile.
  - Images are collected with ~10 pm vertical and somewhat worse horizontal resolution.
  - Any surfaces (conductors, insulators and semiconductors) can be imaged.
  - Works in ambient air, special gas or in fluid environment as well.
  - Usually does not require fixation or staining of the sample.
  - Biological samples can be examined in their native state and physiological environment.
- **Main disadvantages:**
  - Samples must adhere to a substrate. Surface adhesion may lead to distortion.
  - Slow scan speed.
  - Scan height limited to few microns („the flatter the better").
  - Scan size limited to few tens of microns.
  - High cost.

30

Images recorded in our lab at the Department



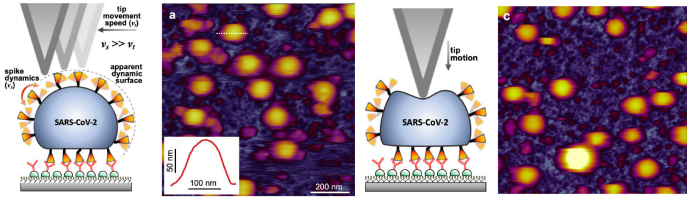
31

Native SARS-CoV-2 imaged in our lab

Topography, spike dynamics and nanomechanics of individual native SARS-CoV-2 virions

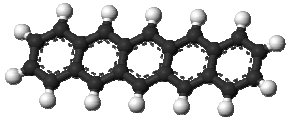
Bálint Kiss[1#], Zoltán Kis[2,3#], Bernadett Pályi[2], Miklós S.Z. Kellermayer[1*]

bioRxiv preprint doi: https://doi.org/10.1101/2020.09.17.302380



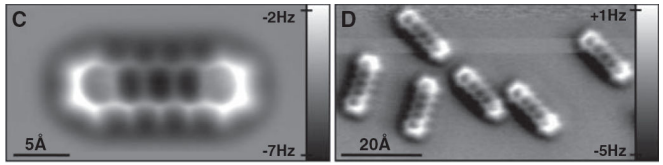
32

Pentacene molecule



electron current through the tip (STM)

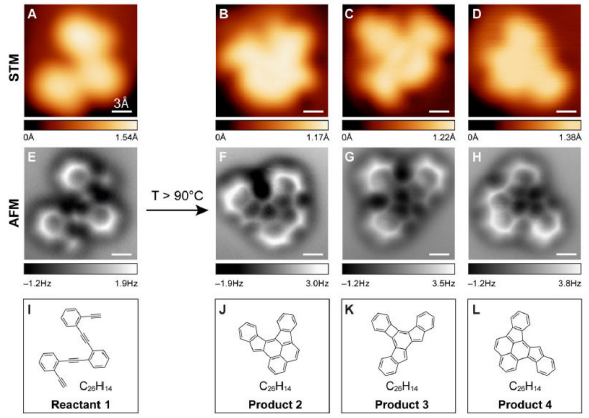
AFM images (tip covered with CO)



Nature Chemistry 1, 597 - 598 (2009)

33

Visualizing chemical reactions



34

Thank you for your attention!