École polytechnique fédérale de Lausanne

CHEMINA
Laboratory of Chemical Nanotechnology

Surfaces in the Real World - Adsorption
Lesson 2

MSE 304

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September 19th 2025

Plan of the Course: Fundamentals, Characterization, and Applications

1: Intro to Surfaces & Interfaces

2: Surfaces in the Real World - Adsorption

3: Surface Fundamentals – Energy & Structure

4: Solid-Solid Interfaces

5: Characterization of Real Surfaces

6: Solid-Liquid Interfaces + Techniques

7: Interfacial Phenomena

8: Charged Solid-Liquid Interfaces

9: Surface Chemistry

10: Biological Processes at Surfaces

11: Electronic Properties of Surfaces

12: Thin Film Technologies

13: Biosensor Fundamentals

14: Biosensing applications

Things may be adapted in real time – thank you for your patience!
Midterm feedback (Week 5) – Recap session Week 7?

Recap from Lesson 1

- Surface science is *not* a mature field
- Why study surfaces and interfaces?
- Challenges of studying surfaces and interfaces
- Keeping surfaces clean is very challenging – UHV can help

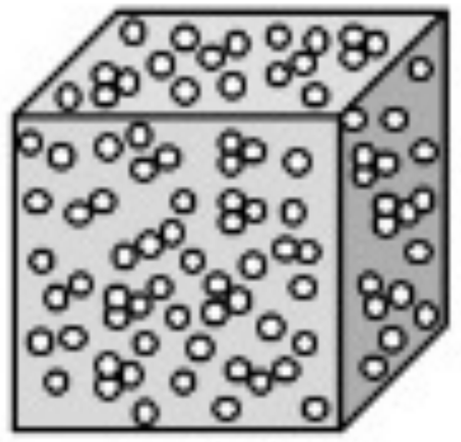
What’s really on a surface and how do we deal with it?

Outline of Lesson 2

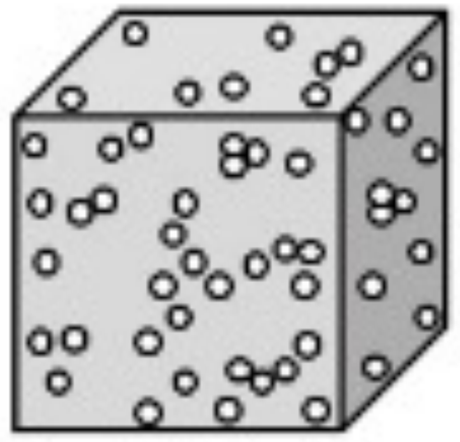
- Basics of physisorption and chemisorption
- Short recap of crystal structures
- Visualizing surfaces at the atomic level – scanning tunneling microscopy (STM)
- Surface contamination sources & problems
- How to obtain clean surfaces – cleaning hierarchy

Instantaneous Contamination on Surfaces

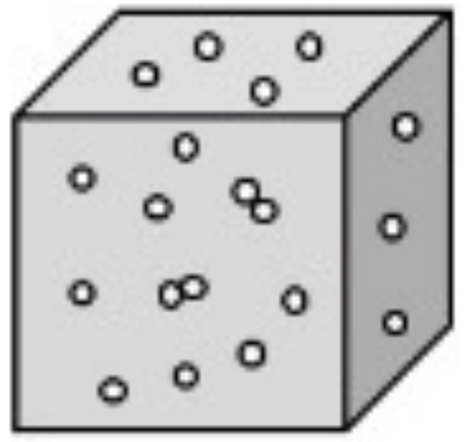
Rough Vacuum	High Vacuum	Ultra High Vacuum
1 atm – 10^{-3} Torr	10^{-3} Torr - 10^{-8} Torr	10^{-8} Torr - 10^{-12} Torr



1 x 10^{-3} Torr
10^{13} atoms/cm^3



1 x 10^{-6} Torr
10^{10} atoms/cm^3

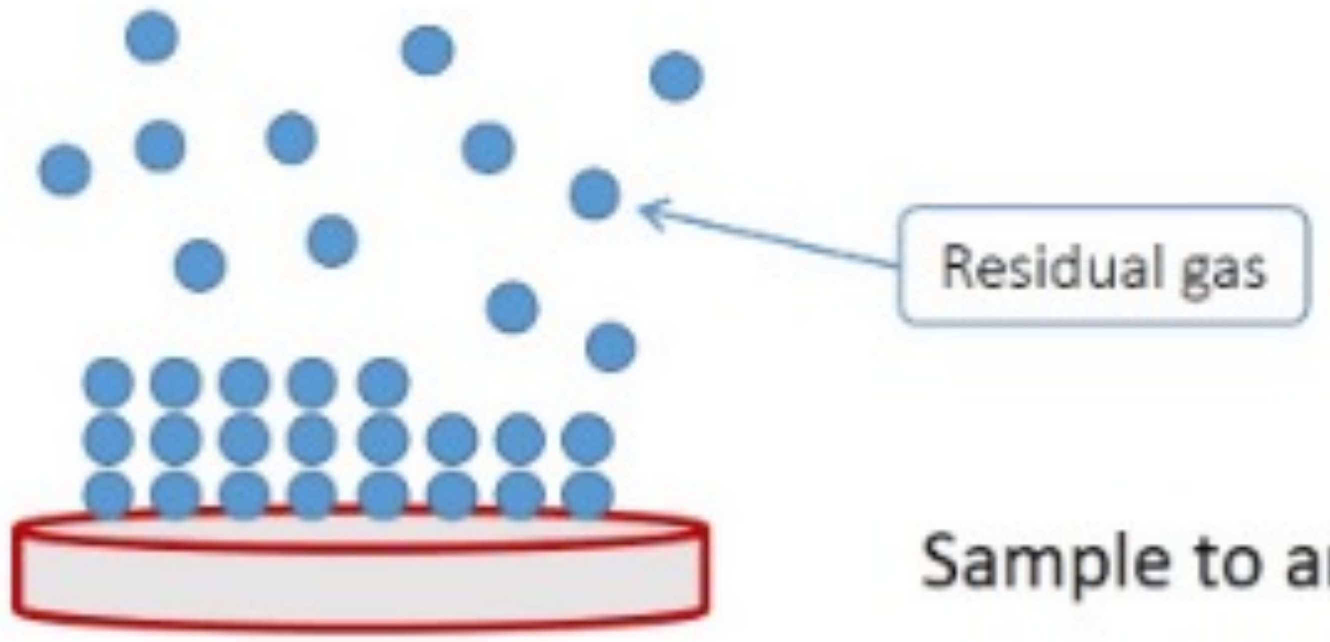


1 x 10^{-11} Torr
10^{5} atoms/cm^3

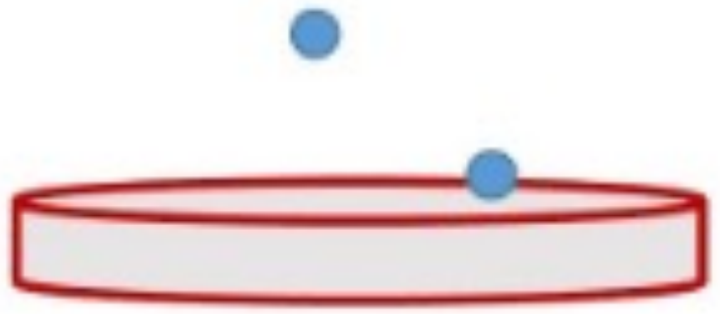
1 residual gas **monolayer**
every **4 SECONDS**

1 residual gas **monolayer**
every **4 DAYS**

High Vacuum



Sample to analyze

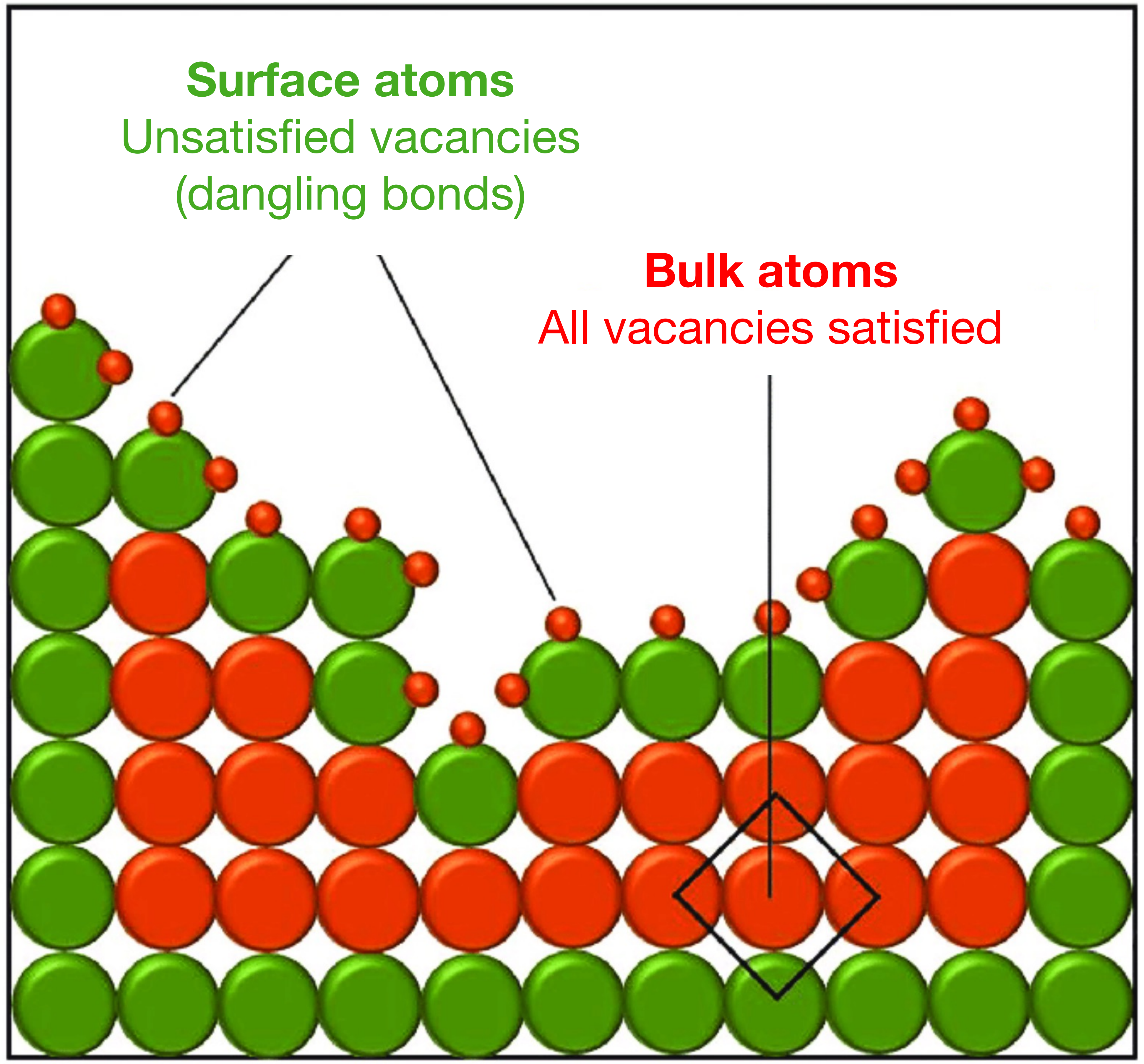


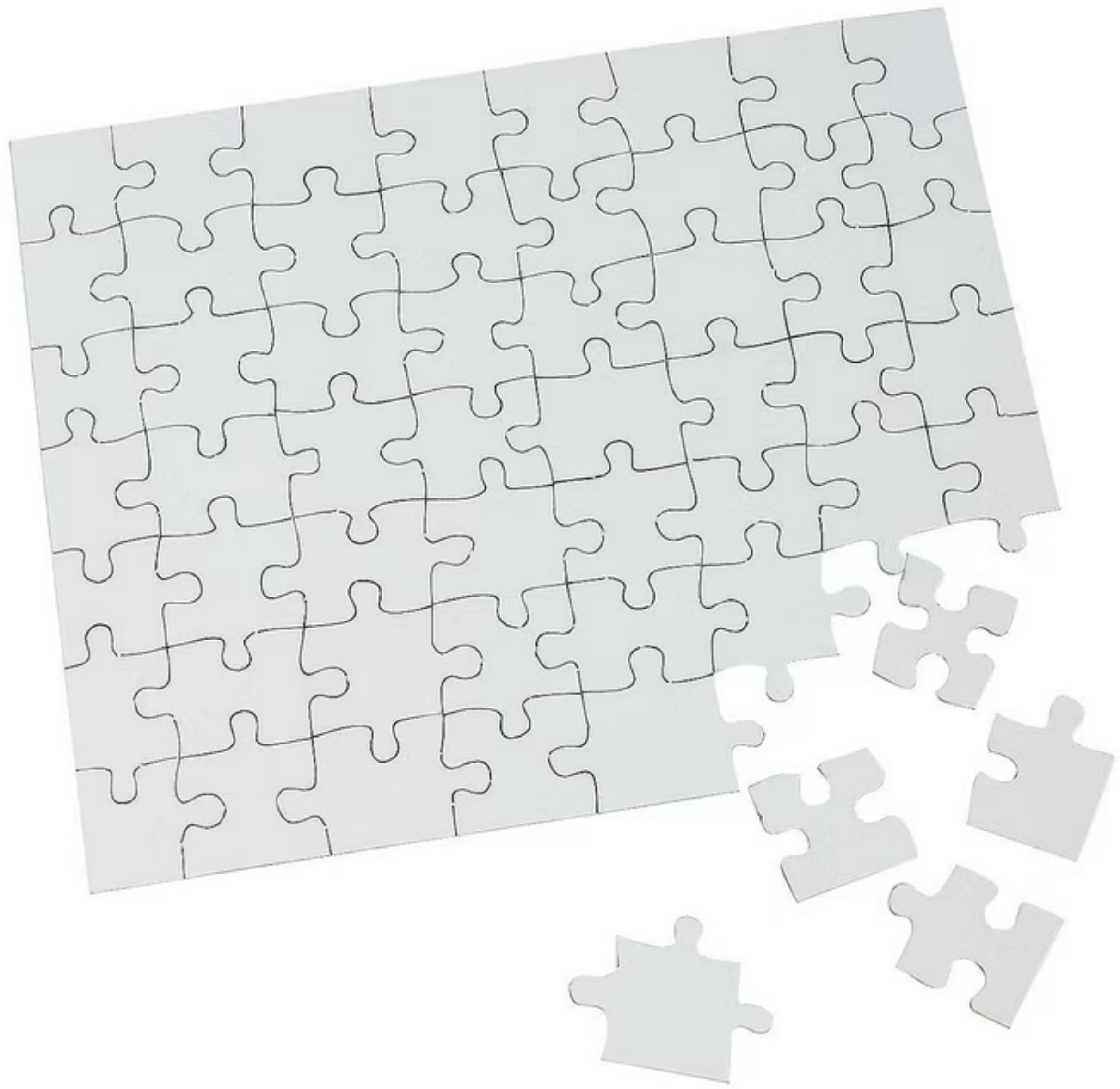
UHV

Clean Surfaces are High Energy – Coatings Lower Energy

Surface energetically unfavorable compared to bulk

Clean surface has a high surface energy and wants to reduce this





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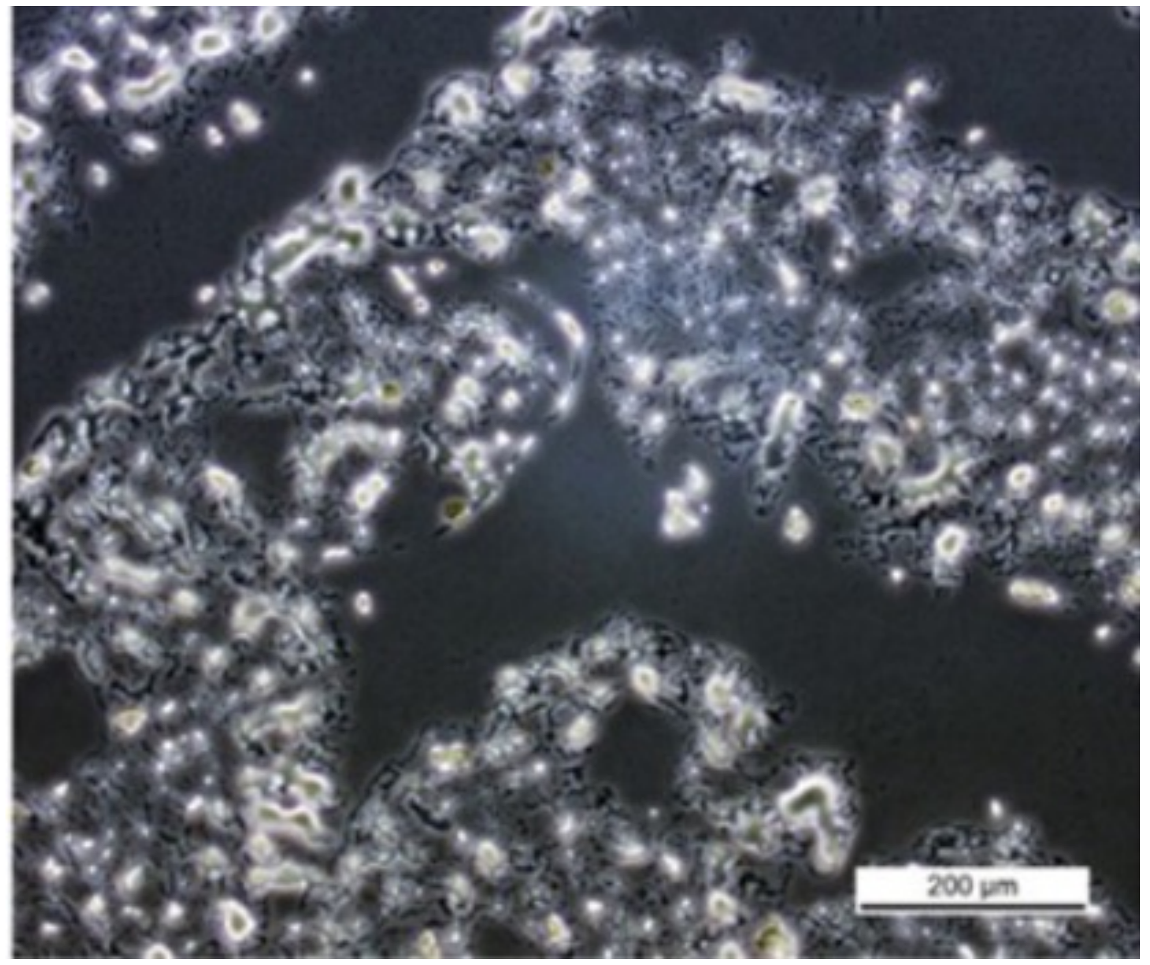
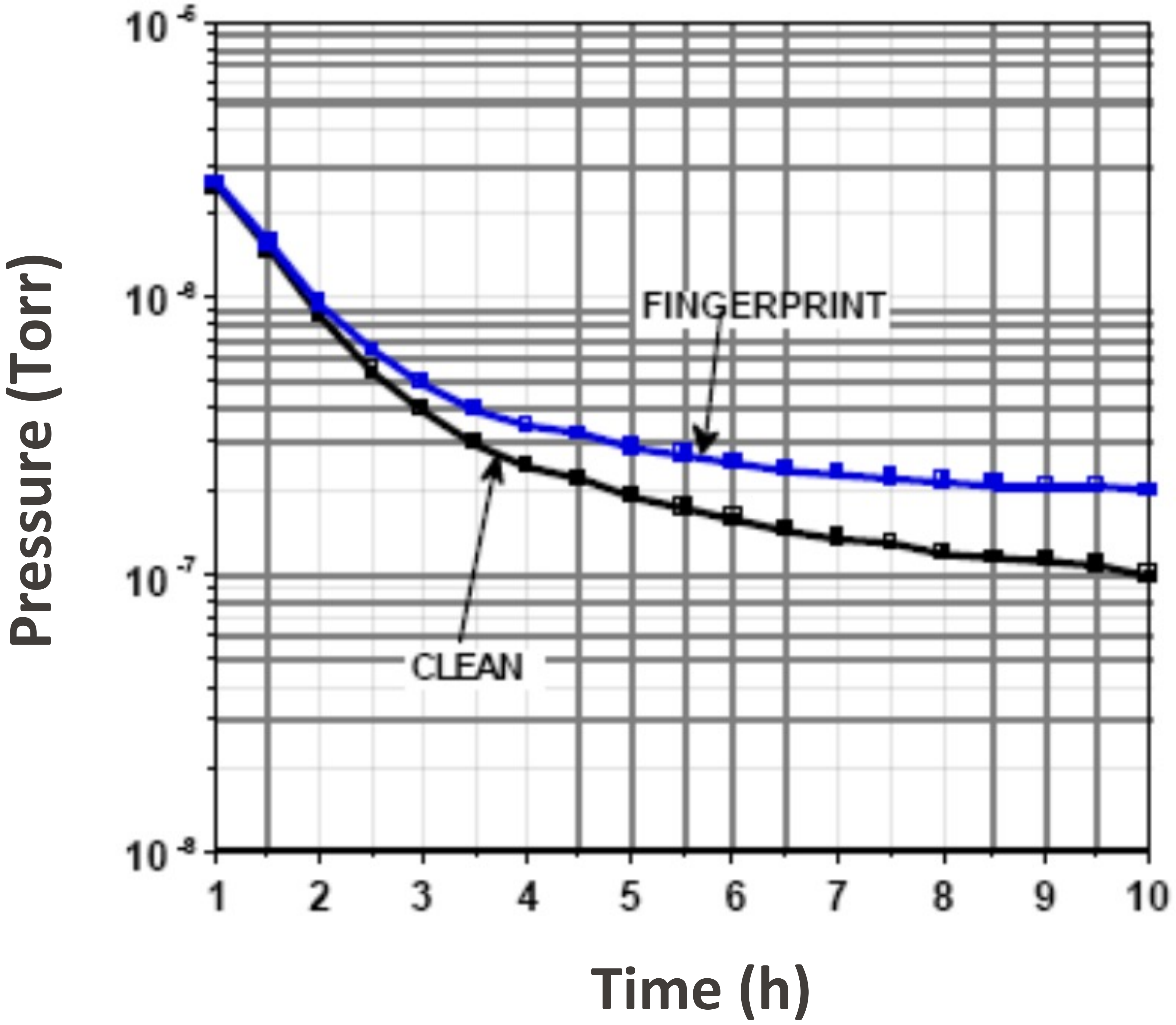
Sources of Surface Contamination

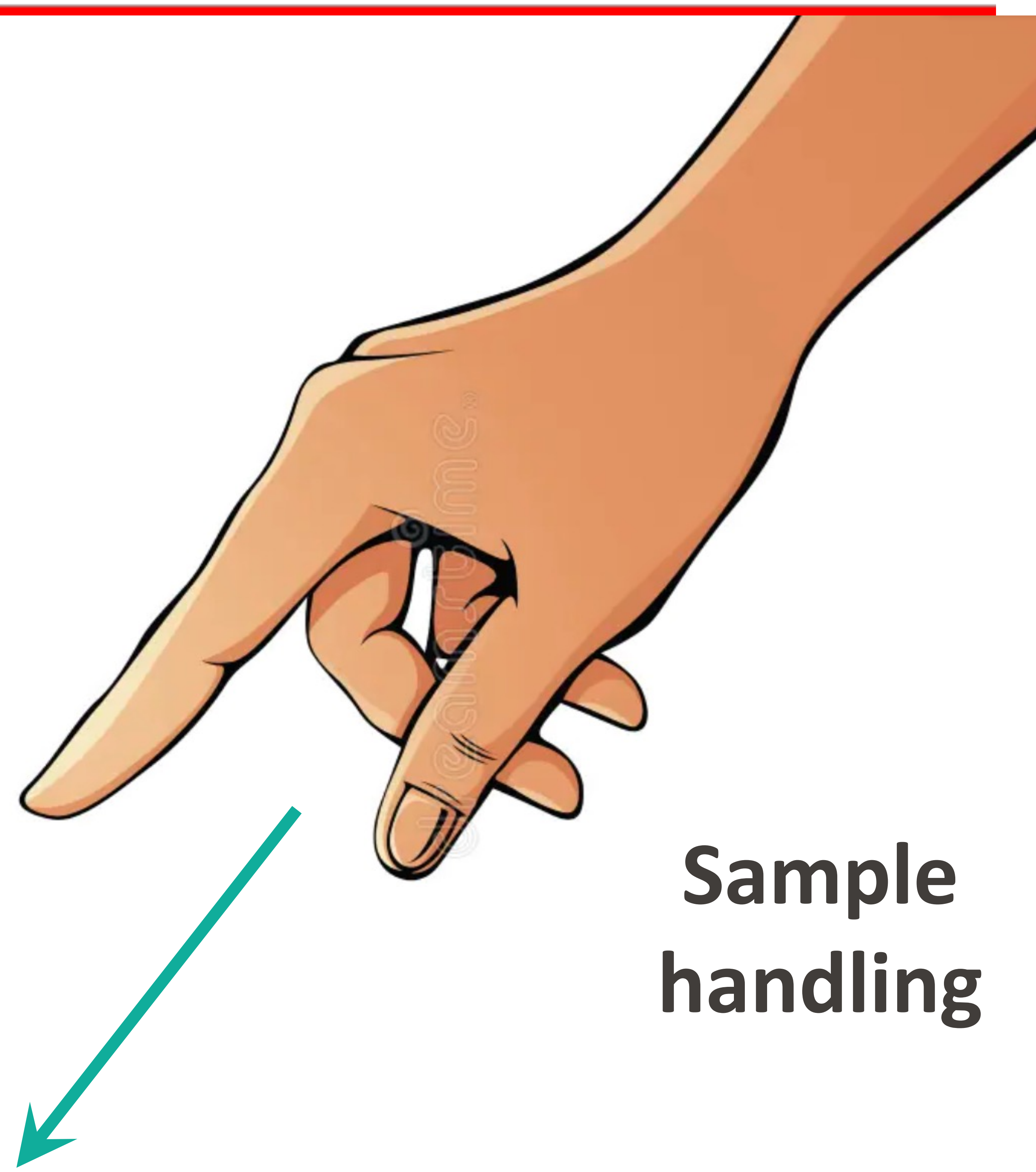
Single Fingerprint Has a Large Effect on Vacuum Pumpdown

1 fingerprint = 1 x 10^{19} molecules!



Moret *et al.* | *Forensic Sci. Int.* | 2018





Sample handling

Empa
Materials Science and Technology

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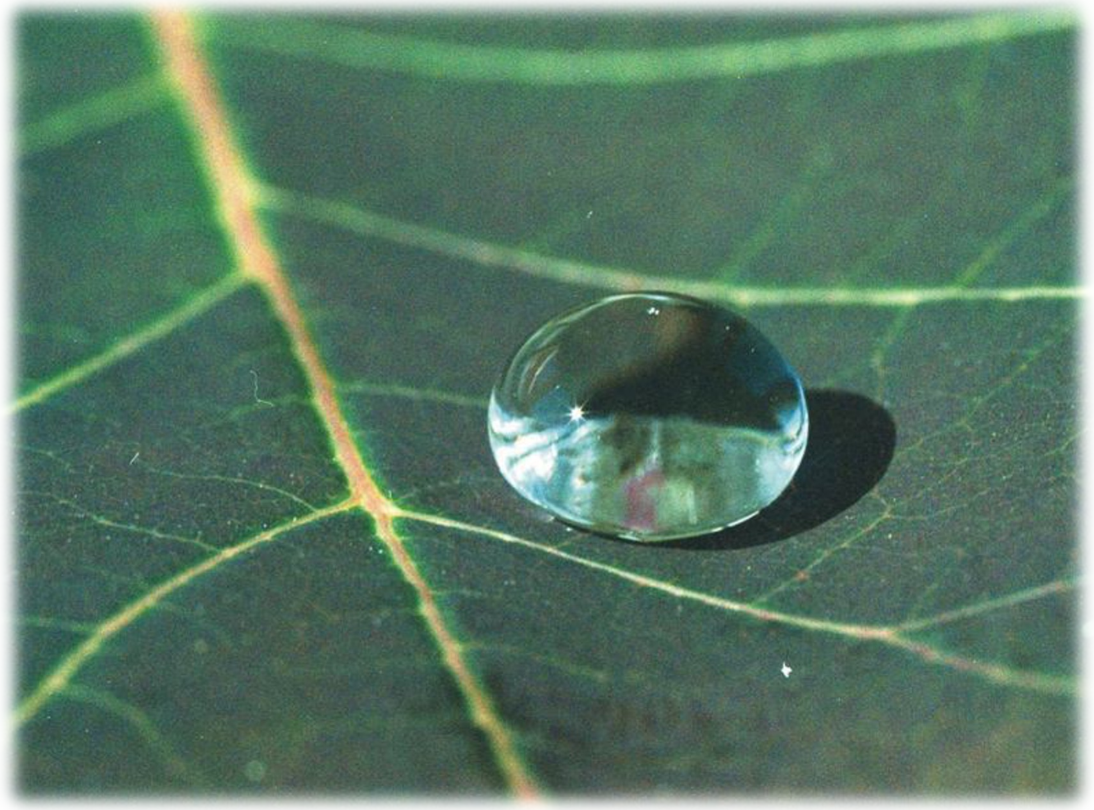
Careful: Adsorption *vs.* Absorption

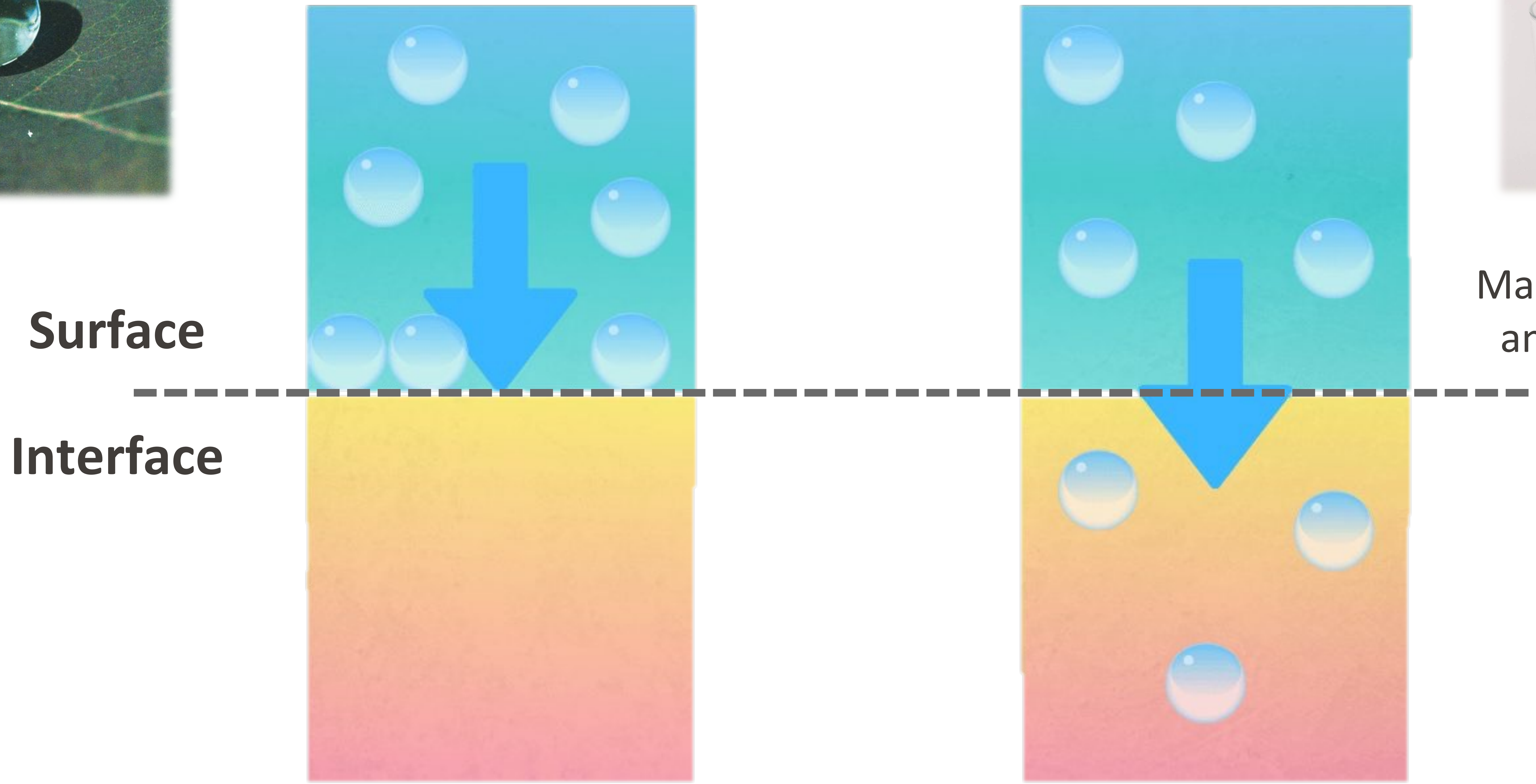


Adsorption

Sticking to the surface
of the other phase

Absorption

Soaking into the bulk
of the other phase



Mass transfer **into**
another matrial

SCIENCE NOTES

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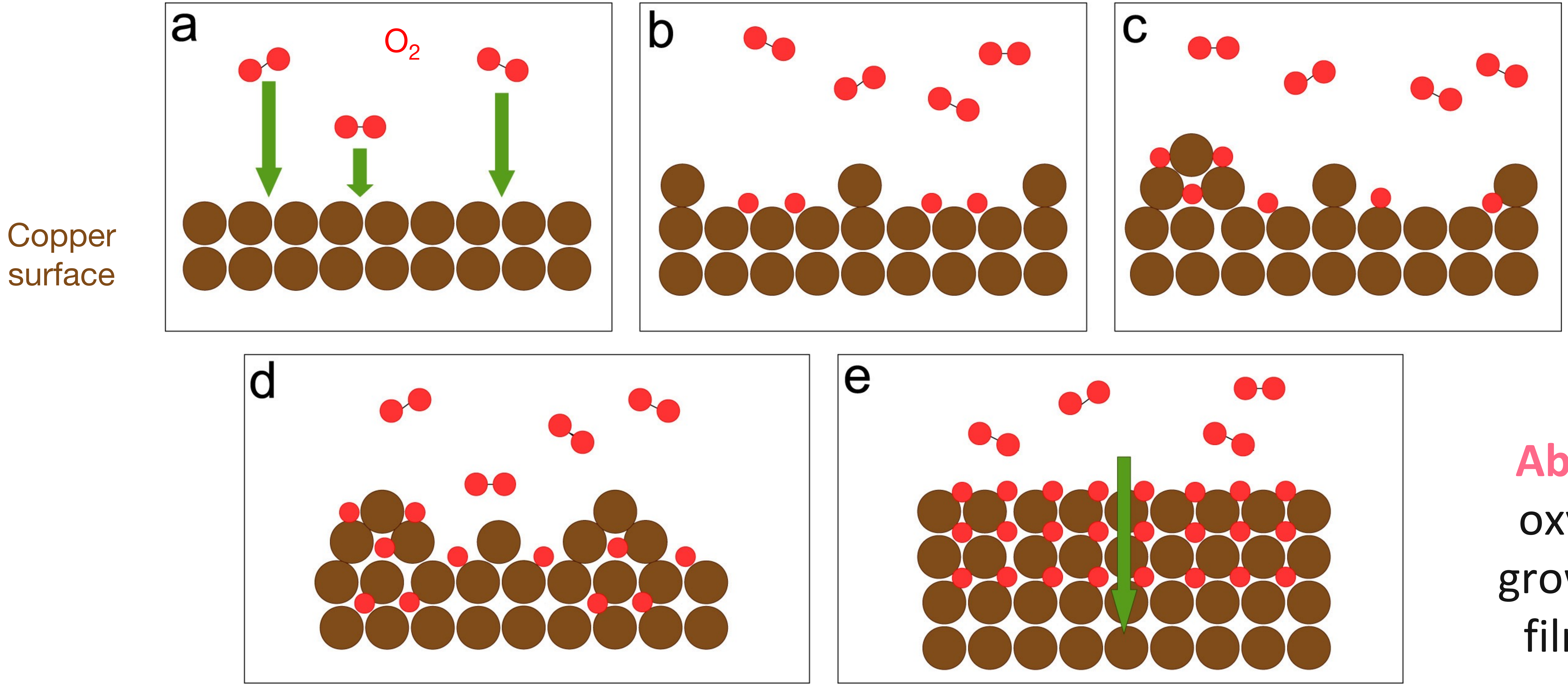
Careful: Adsorption *vs.* Absorption

Adsorption	Absorption
Accumulation onto surface	Accumulation into another substance
Surface phenomenon	Bulk phenomenon
Exothermic process	Endothermic process
Favored by lower temperature	Mostly unaffected by temperature
Rate dependent on surface sites until equilibrium reached	Occurs at uniform rate
Surface concentration differs from internal concentration	Concentration eventually becomes the same throughout material

Metal Oxidation – Adsorption + Absorption

Surfaces in air are mostly covered with multilayers of molecules from the gas phase

(H_2O, hydrocarbons, air components)



Step 1:
Adsorption of O_2 onto copper surface

Step 2:
Absorption of oxygen drives growth of oxide film into bulk

Gattinoni & Michaelides | *Surf. Sci. Rep.* | 2015

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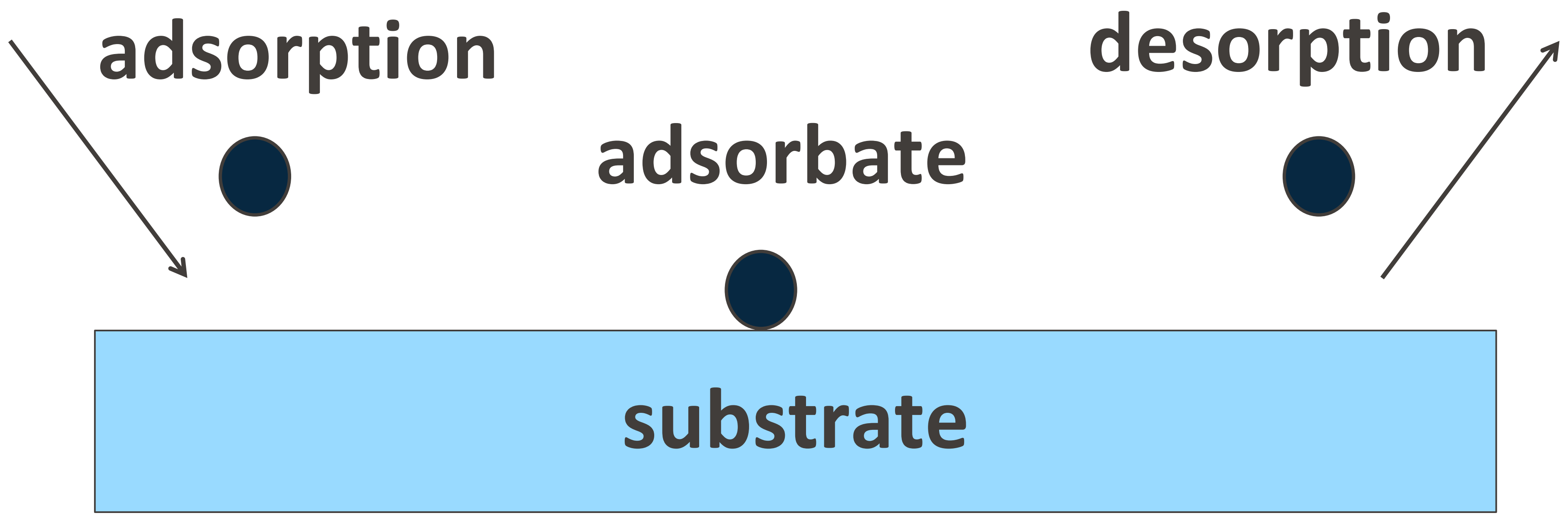
The Different Forms of Adsorption on Surfaces



$$\theta = \frac{\text{Number of occupied adsorption sites}}{\text{Number of adsorption sites present}}$$

θ = 0 clean surface

θ = 1 monolayer

Physisorption

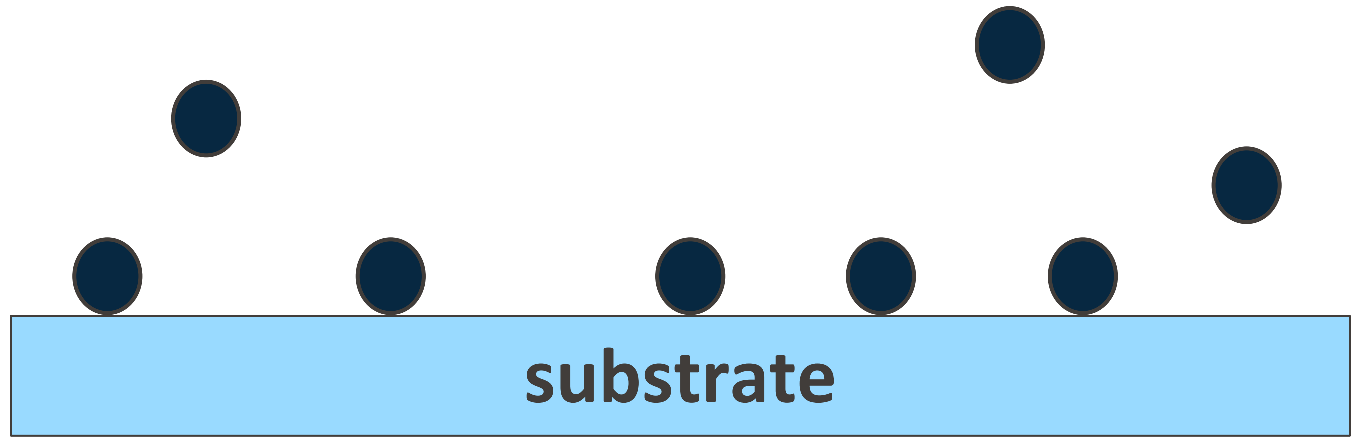
Van der Waals interactions between adsorbate and substrate

non-specific and weak

$\Delta H_{des} \approx 20$ kJ/mol

multilayer growth possible

observed mostly at low temperatures



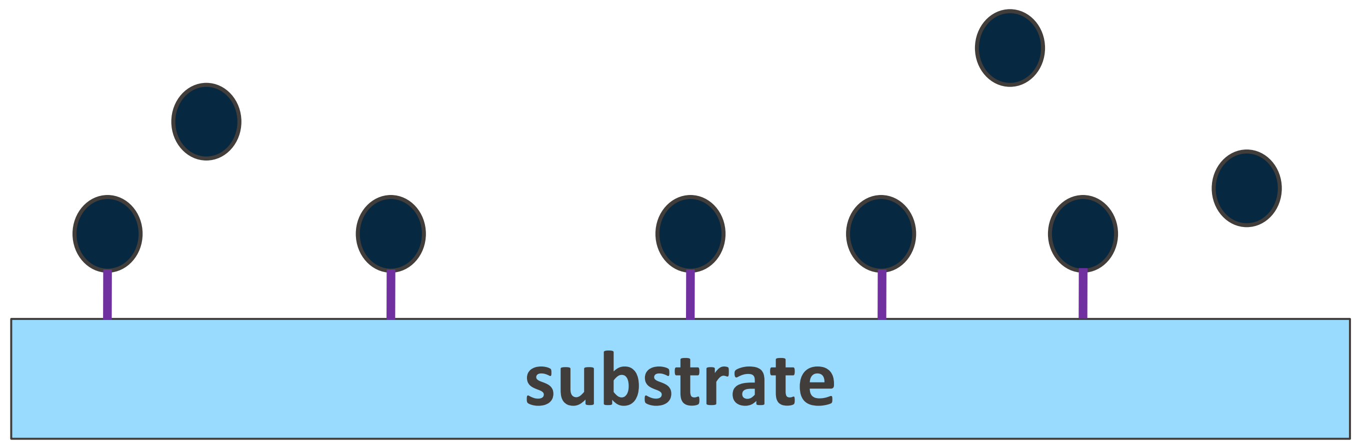
Chemisorption

Chemical bond between adsorbate and substrate

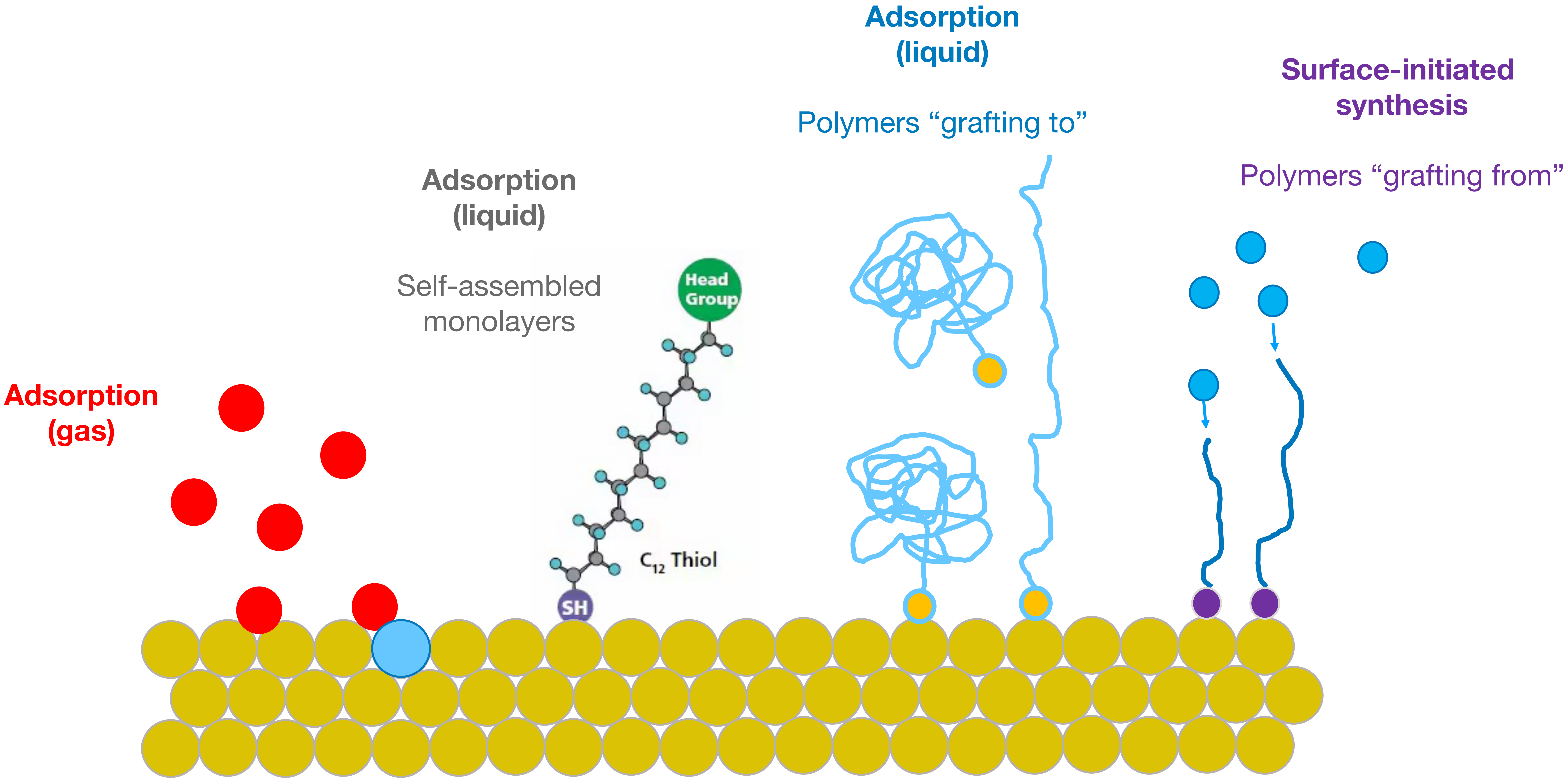
Generally kinetically stable at RT

$\Delta H_{des} \approx 200$ kJ/mol

maximum coverage is 1 monolayer (θ = 1)



Chemisorption (Surface Chemistry) In Future Lessons



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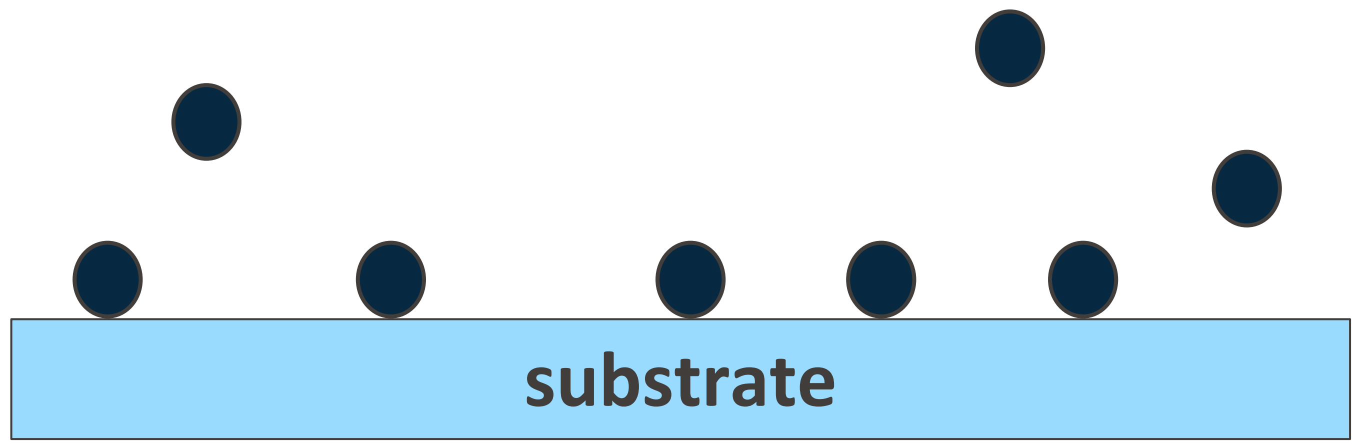
Potential Energy Change for Physisorption *vs.* Chemisorption

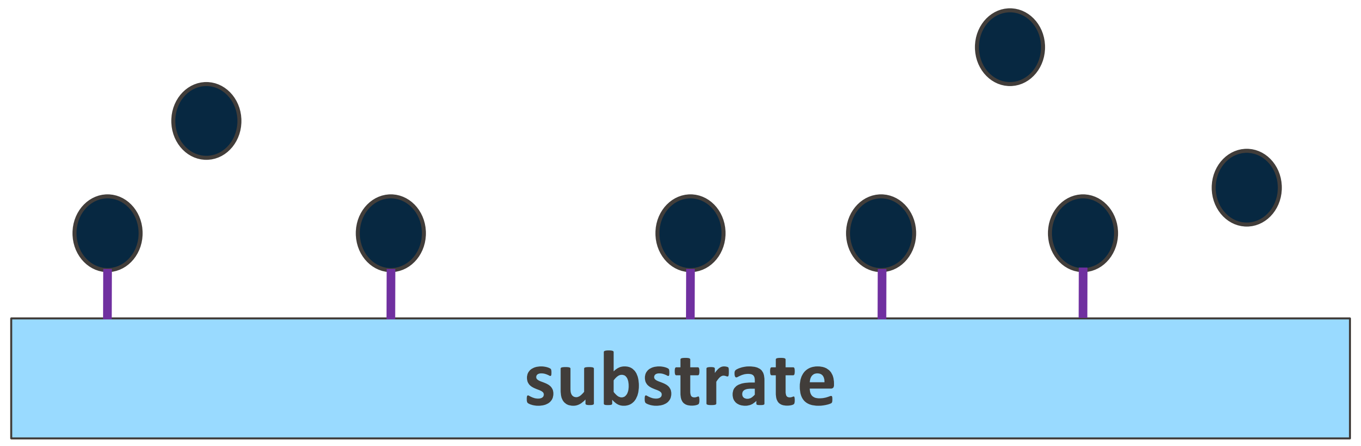
Physisorption

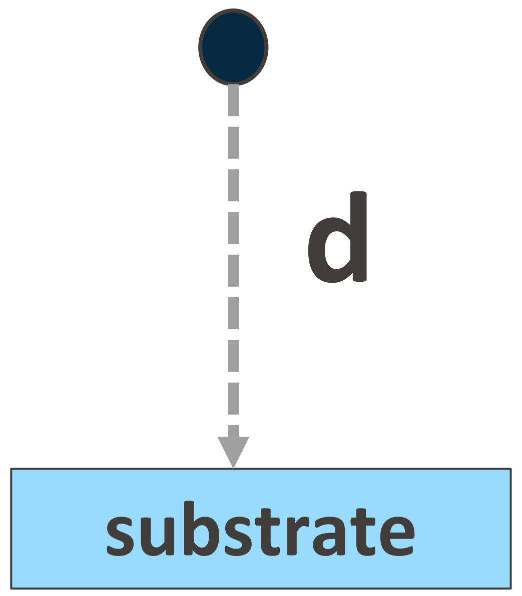
Van der Waals interactions between adsorbate and substrate

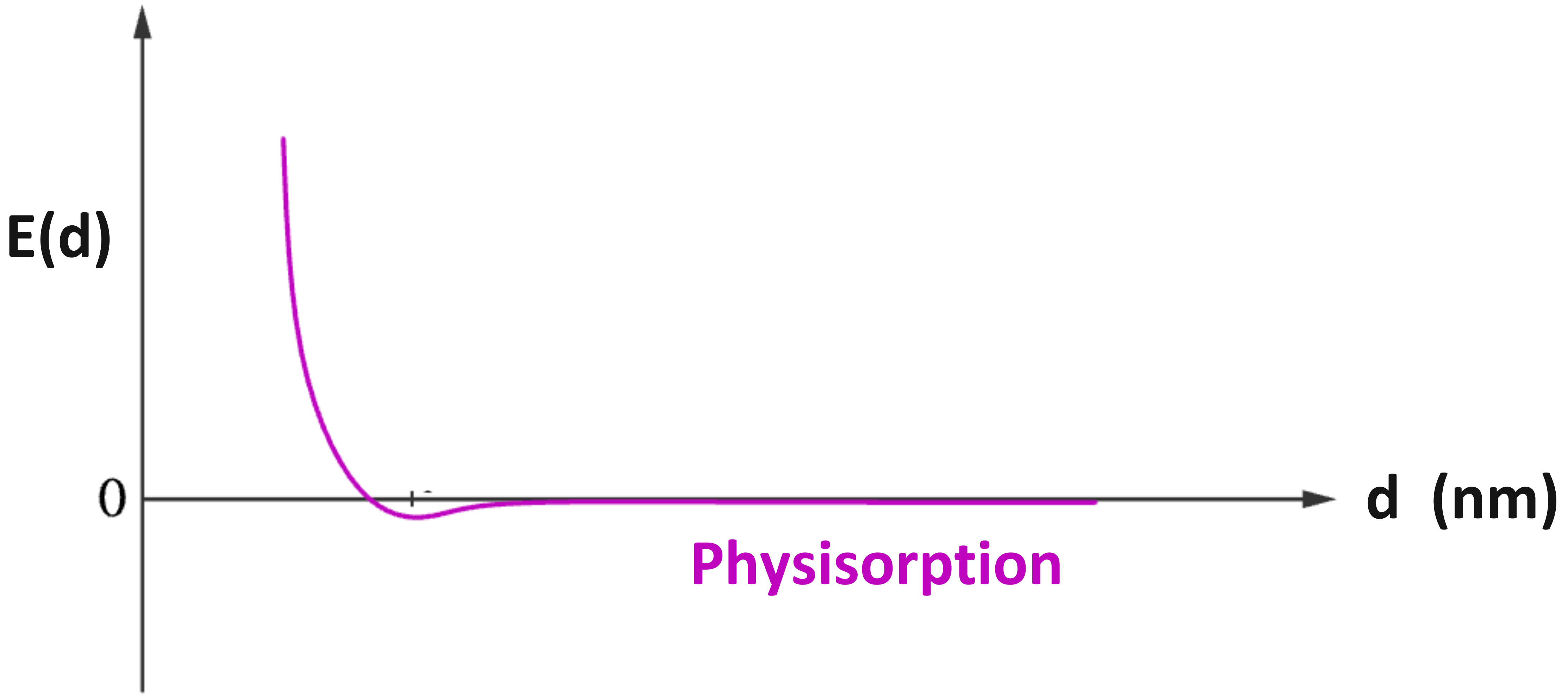


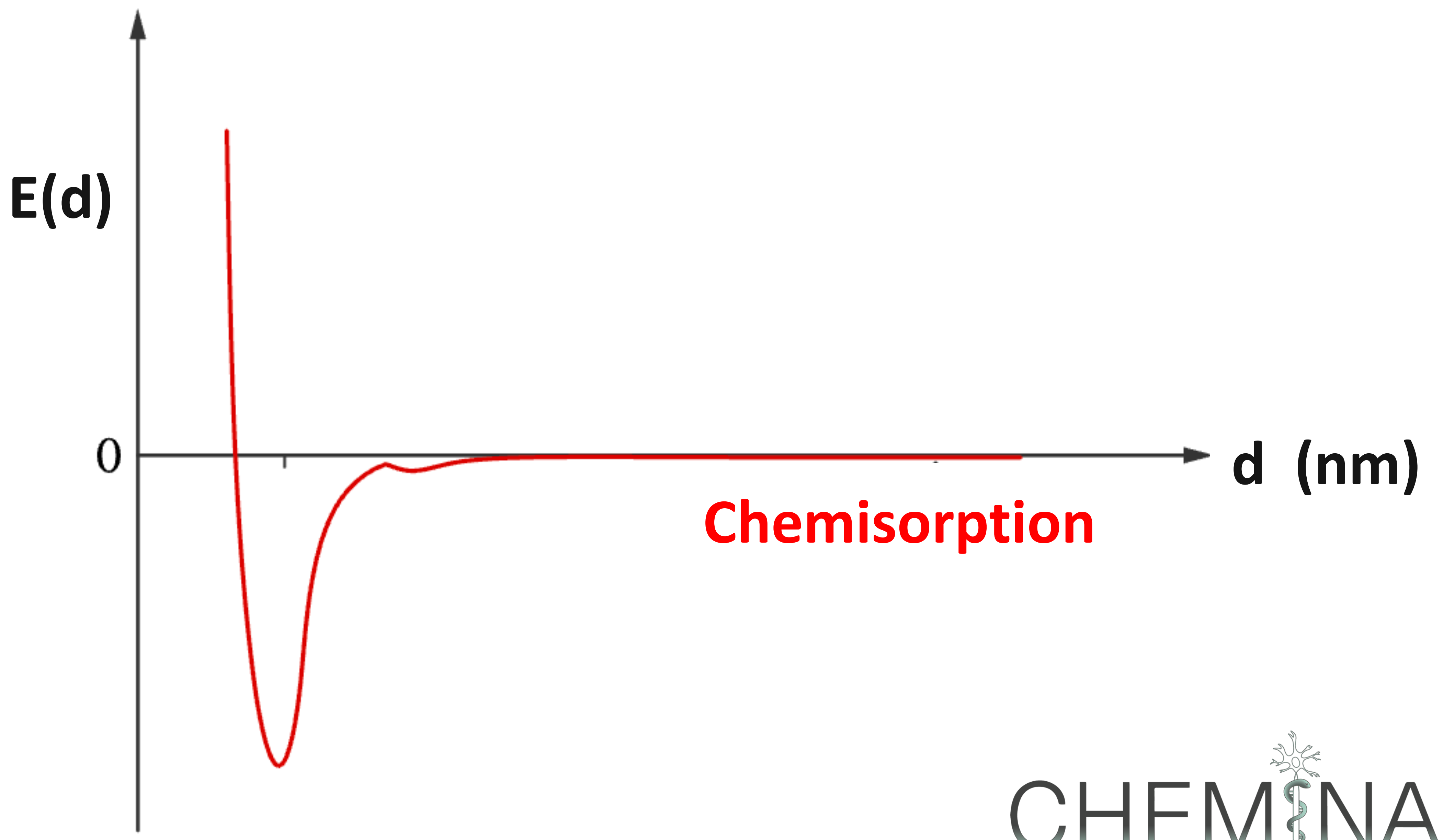
Chemisorption

Chemical bond between adsorbate and substrate





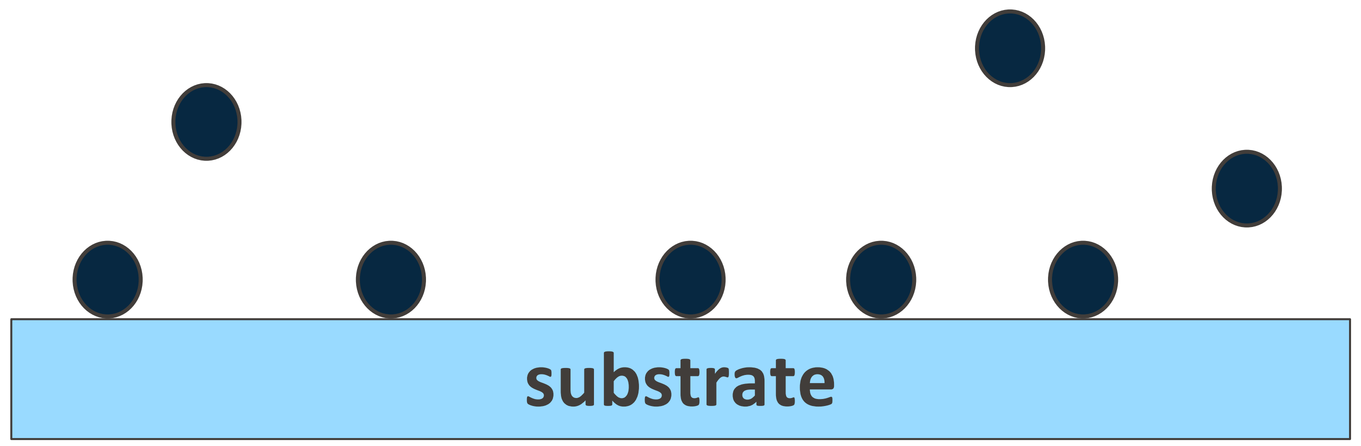




Chemisorption Typically Slower Due to Activation Barrier

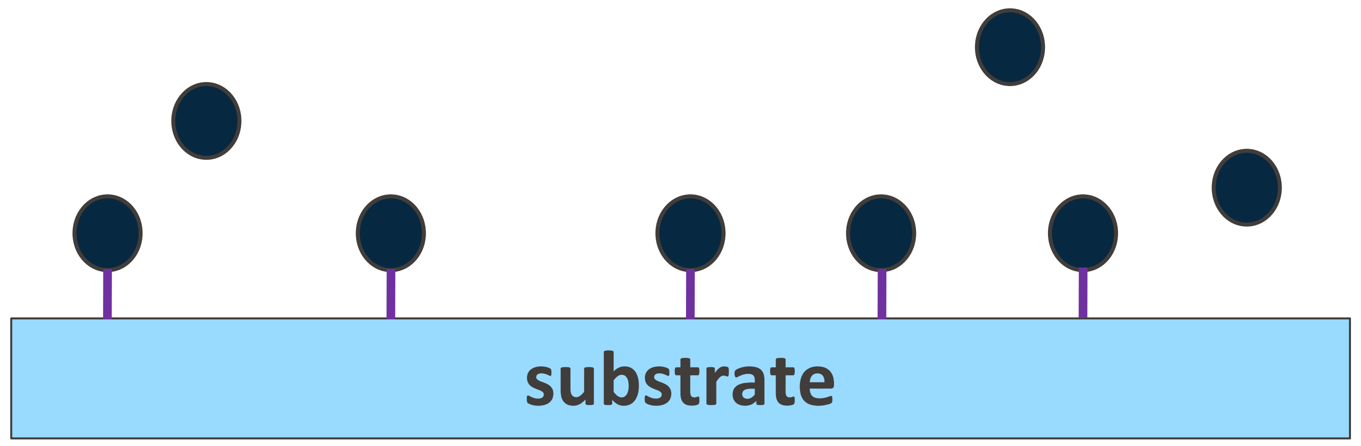
Physisorption

Van der Waals interactions between adsorbate and substrate

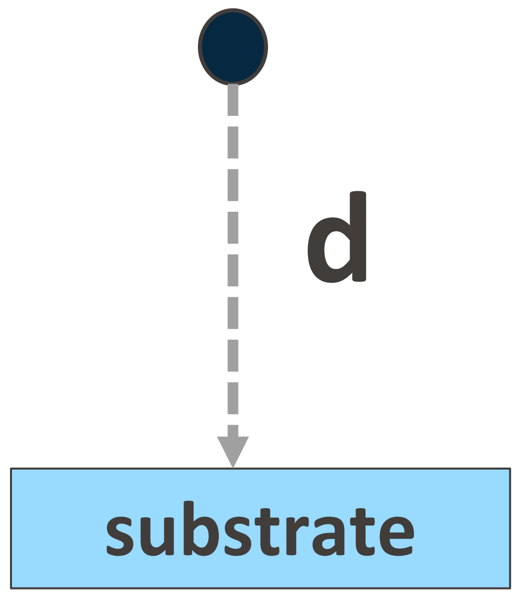


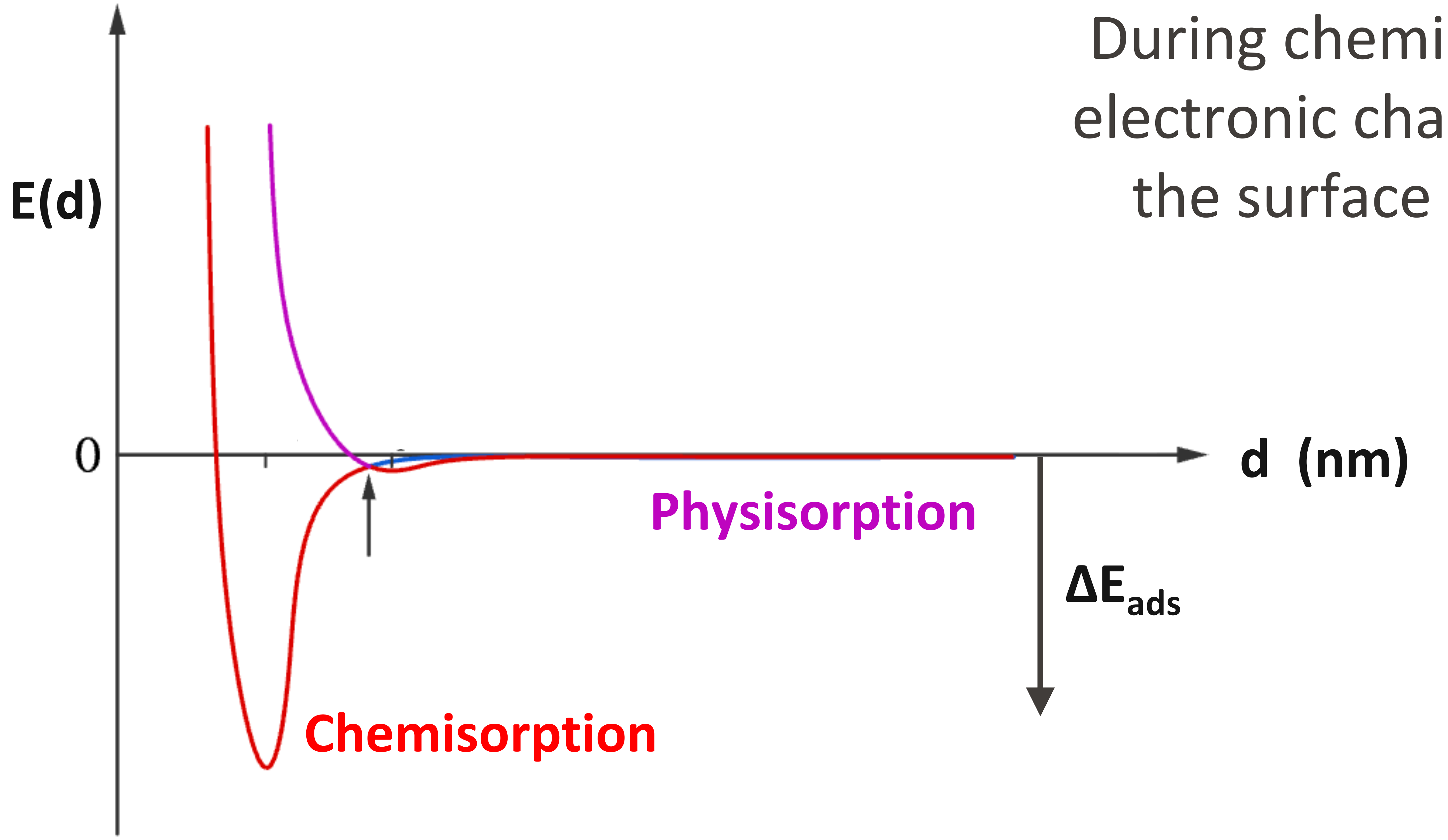
Chemisorption

Chemical bond between adsorbate and substrate

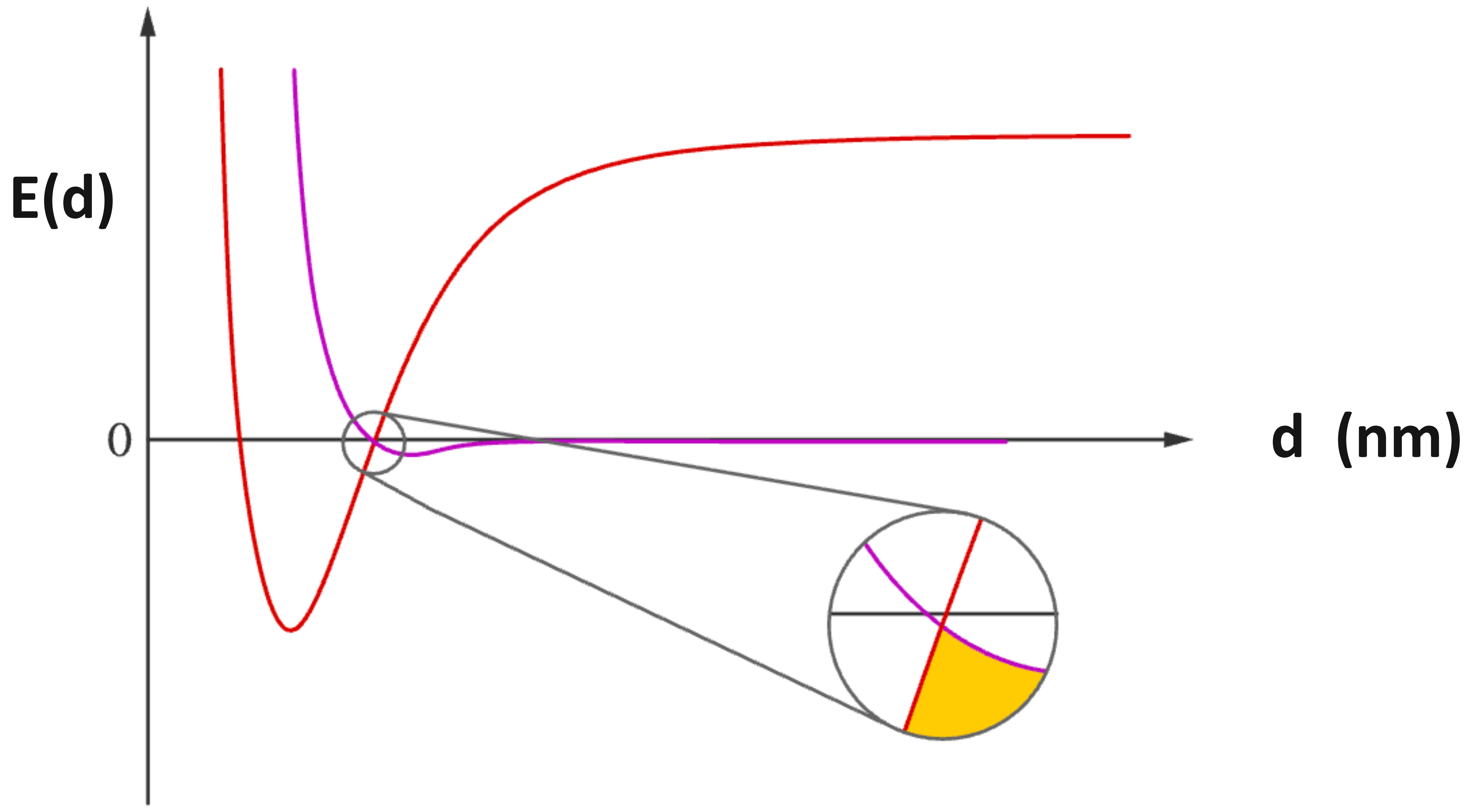


During chemisorption, the electronic characteristics of the surface can change

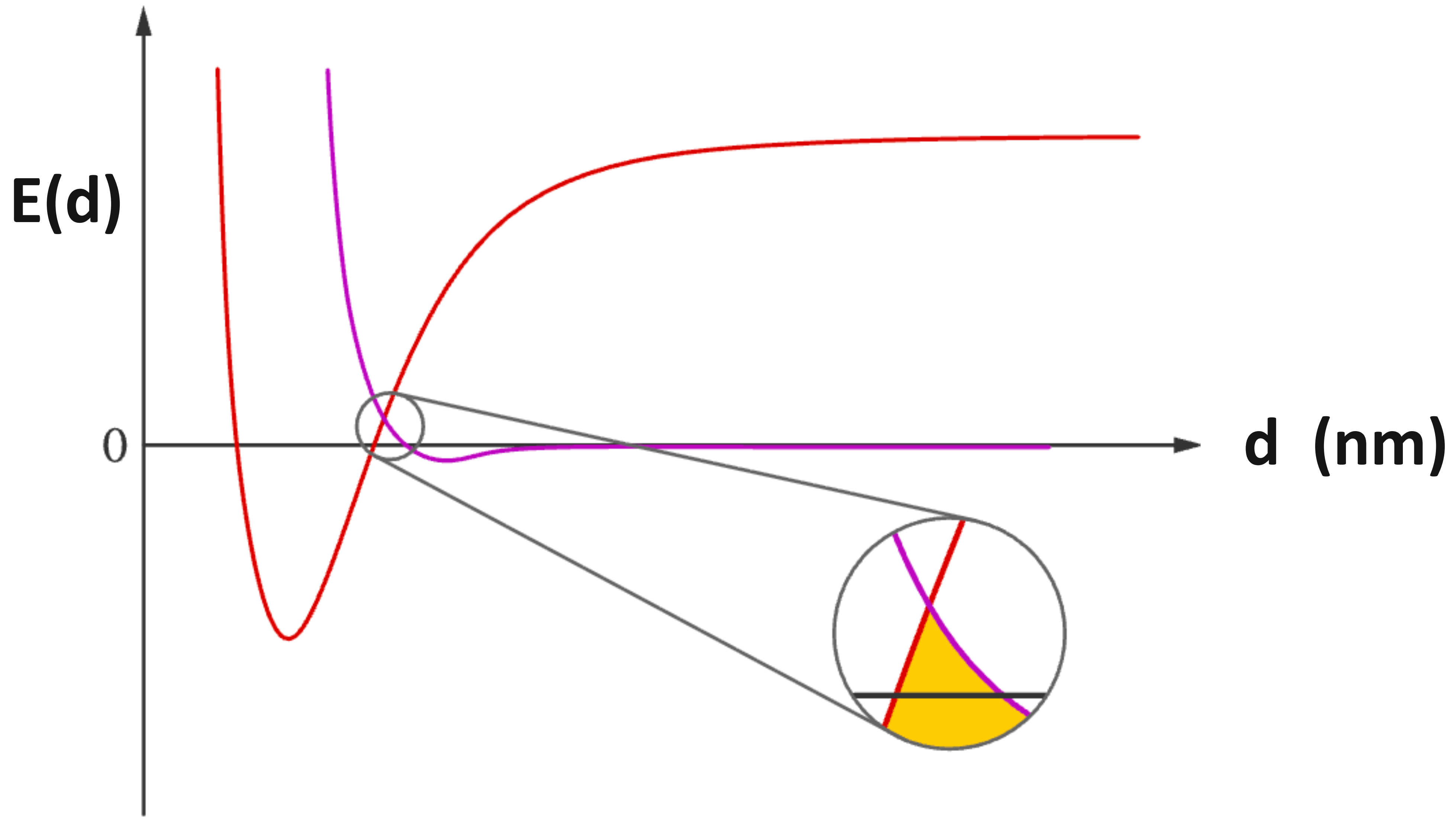




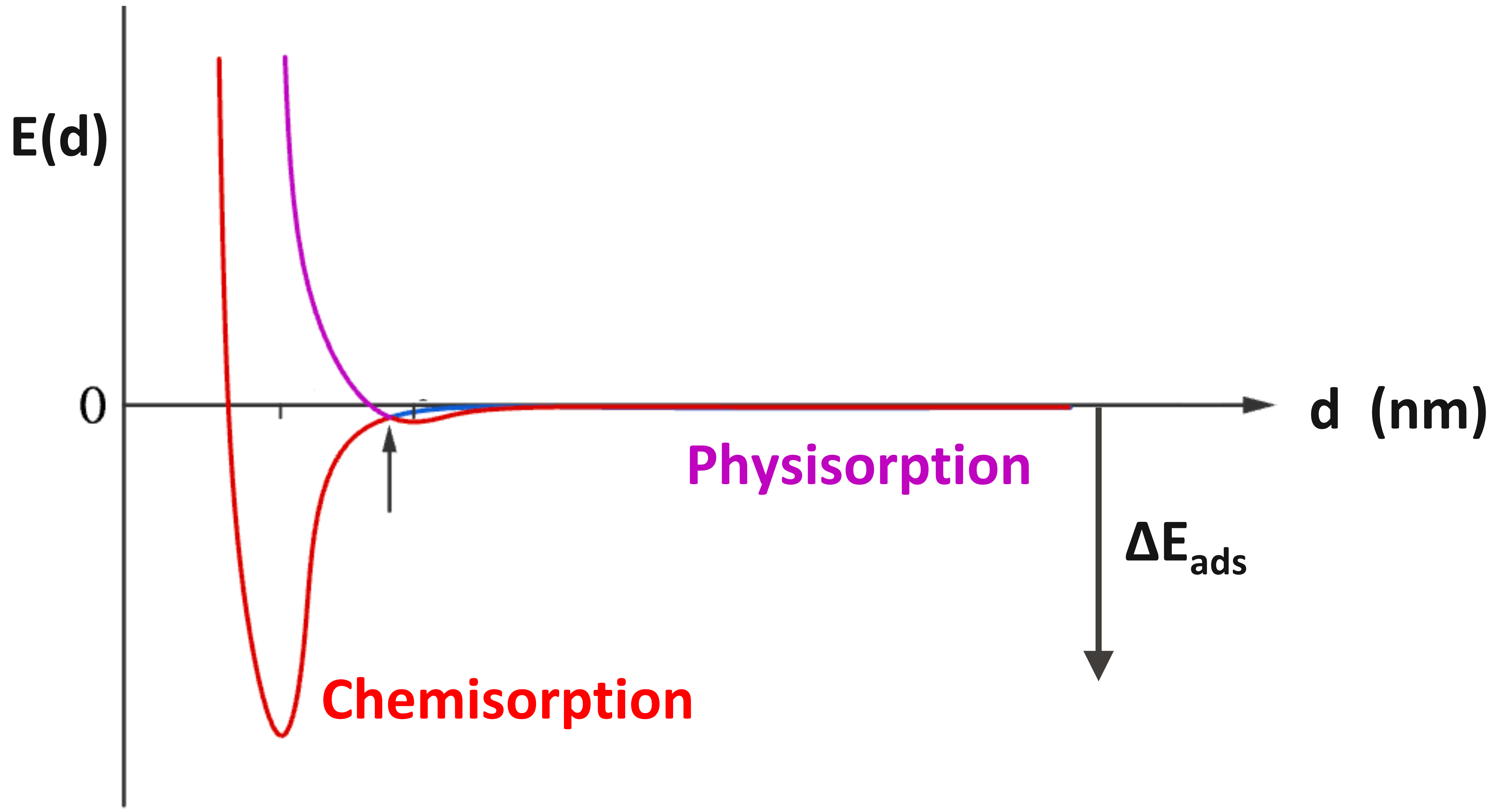
Crossover Point of Chemisorption/Physisorption Curves



No direct activation barrier for chemisorption to happen



Activation barrier for chemisorption to happen



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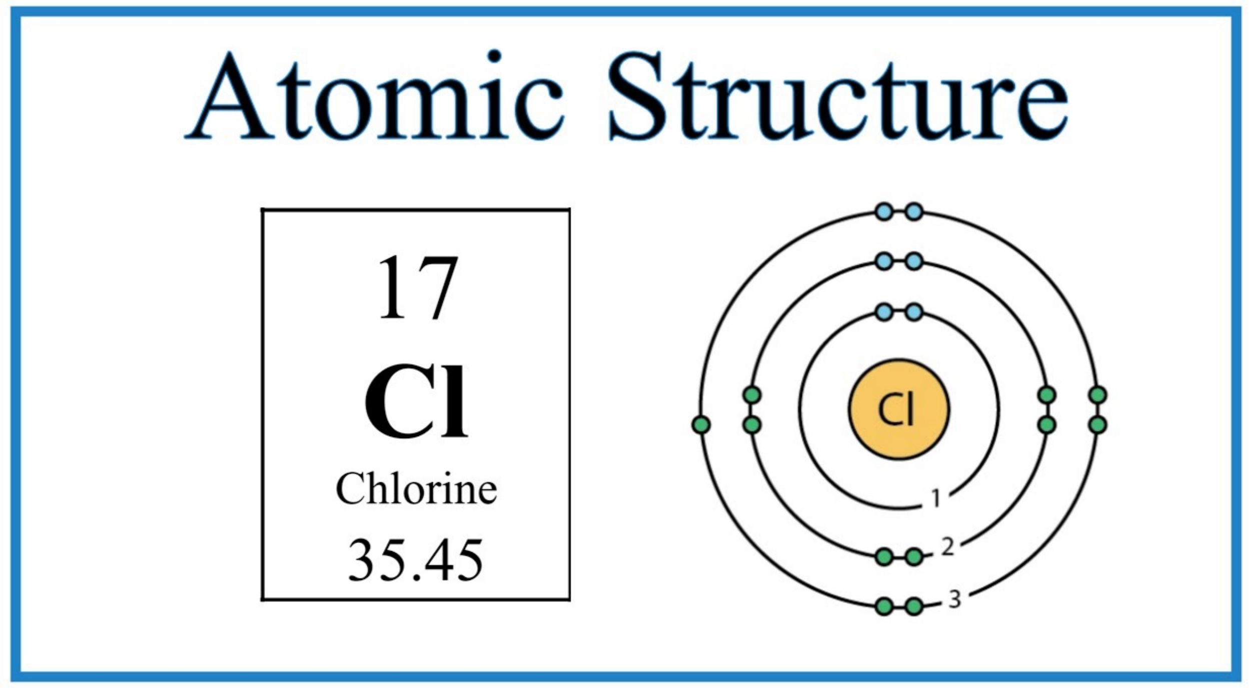
Chemisorption on Surfaces Often Occur After Physisorption



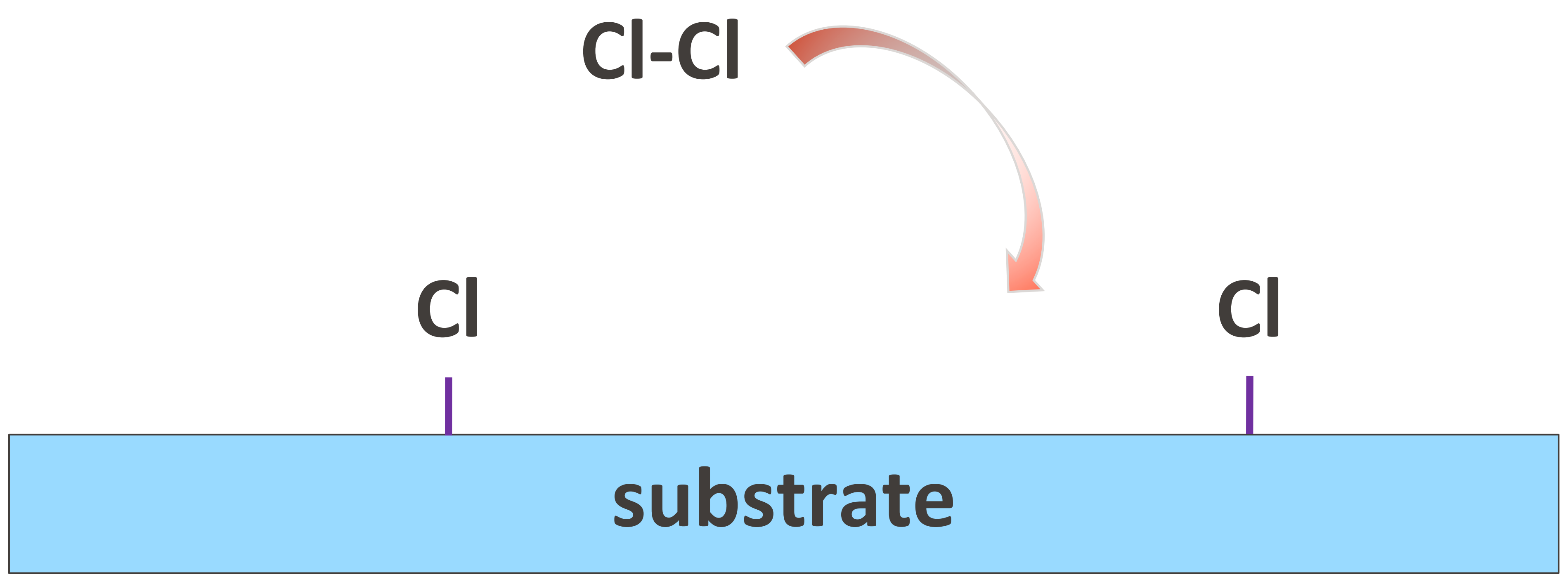
Spontaneous process: $\Delta G<0$

Adsorbate loses degrees of freedom upon adsorption: $\Delta S<0$

$$\Delta G = \Delta H - T\Delta S \rightarrow +$$

Almost always exothermic: $\Delta H<0$

Dissociation energy (strength of chemical bond) high in gas phase



Surface interactions reduce energy required to break Cl-Cl bond

Metal surfaces (*e.g.*, Platinum) ➔ empty d orbitals
Semiconductors (*e.g.*, Silicon) ➔ displace H atoms to create Si-Cl bonds

Catalytic surfaces inherently promote bond breaking!

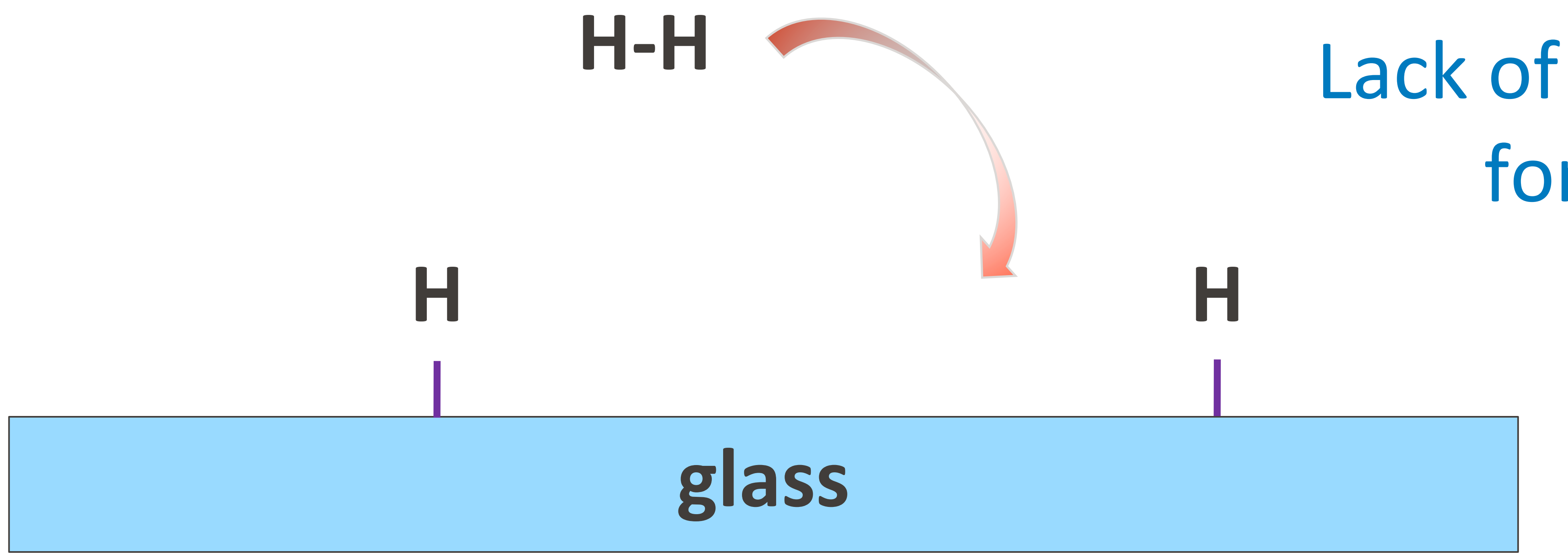
Chemisorption Exception: H_2 on Glass

Spontaneous process: ΔG<0

Endothermic reaction: ΔH>0

$\Delta G = \Delta H - T\Delta S$ → -

ΔS>0 meaning that entropy *increases*



Lack of strong bond formation

Inert nature of glass – lack of strong binding interactions

Adsorbed H diffuses readily on glass and therefore the two diffusing atoms have more degrees of freedom than the gas-phase diatomic molecule

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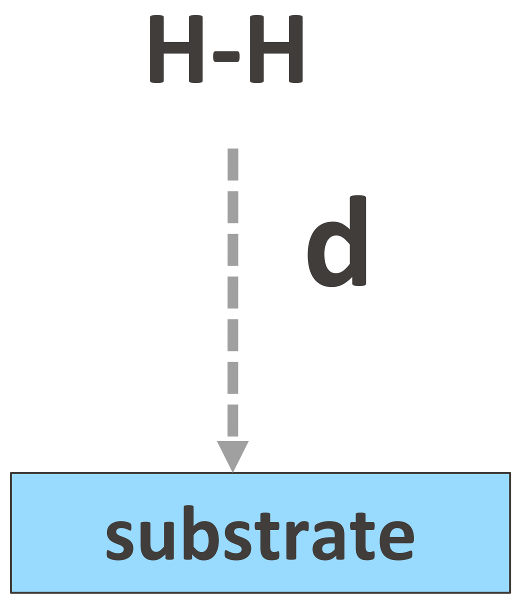
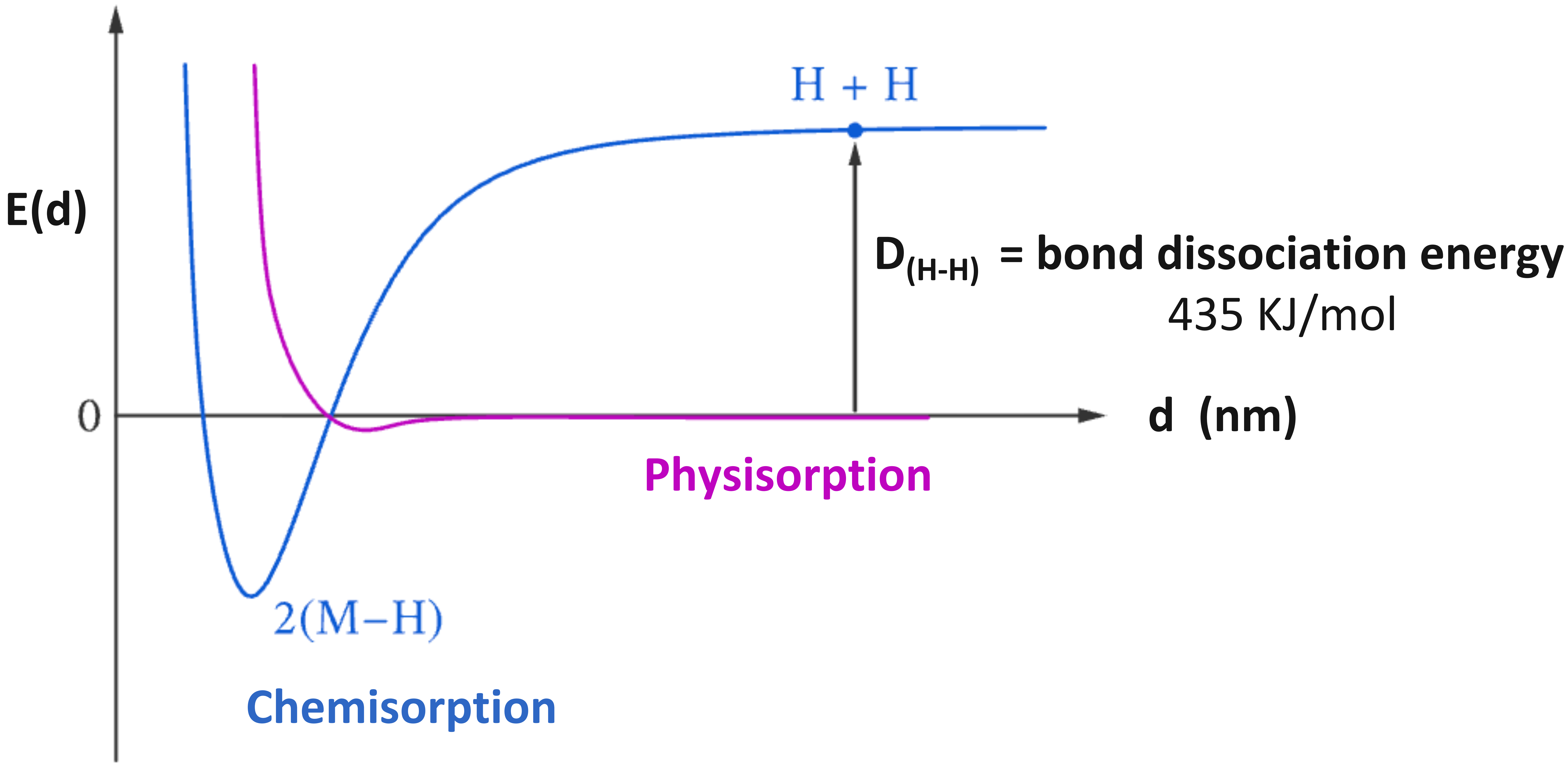
The Different Paths For H_2 Adsorption to the Surface





This concept is important for how catalysis works in a future lesson

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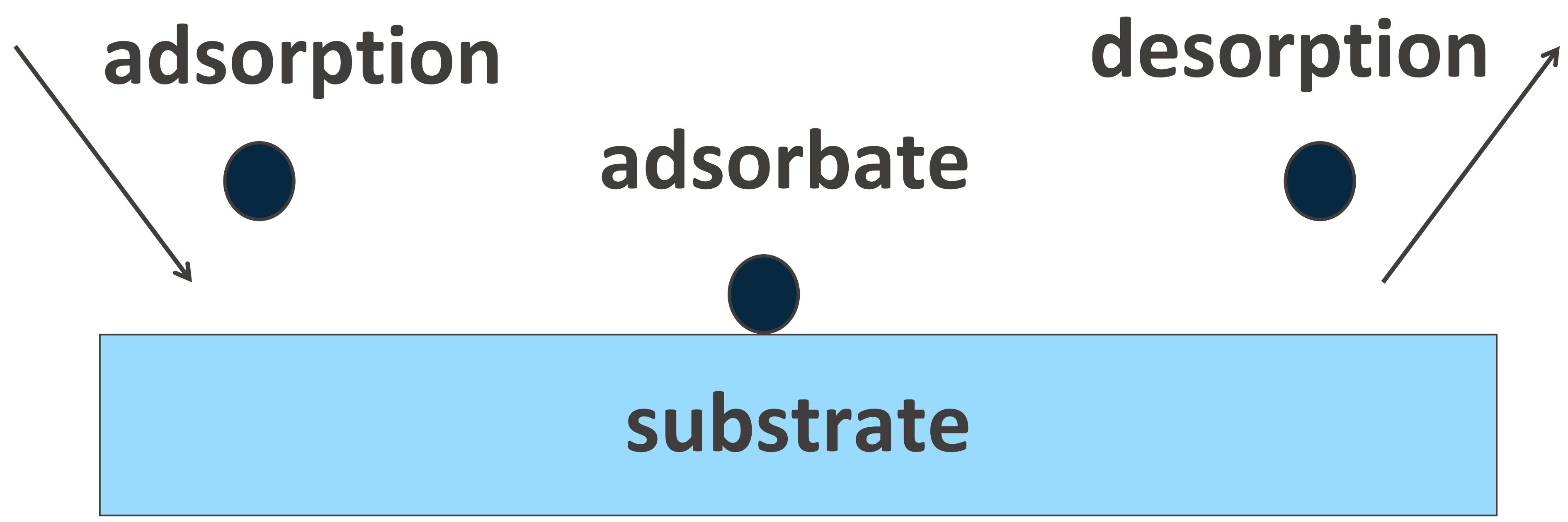
Desorption from the Surface



Breaking of chemical bonds and removal of adsorbed species from the surface

Molecule requires sufficient energy to activate the desorption (E_d)

Desorption is temperature dependent and is described by:

$$-\frac{dN_i}{dt} = \nu_i N_i^m \cdot \exp\left(\frac{-E_{d,i}}{RT}\right)$$

Polanyi-Wigner equation

N_i: surface concentration of the adsorbate
v_i: frequency factor
E_{di}: desorption activation energy
m: order of the desorption reaction

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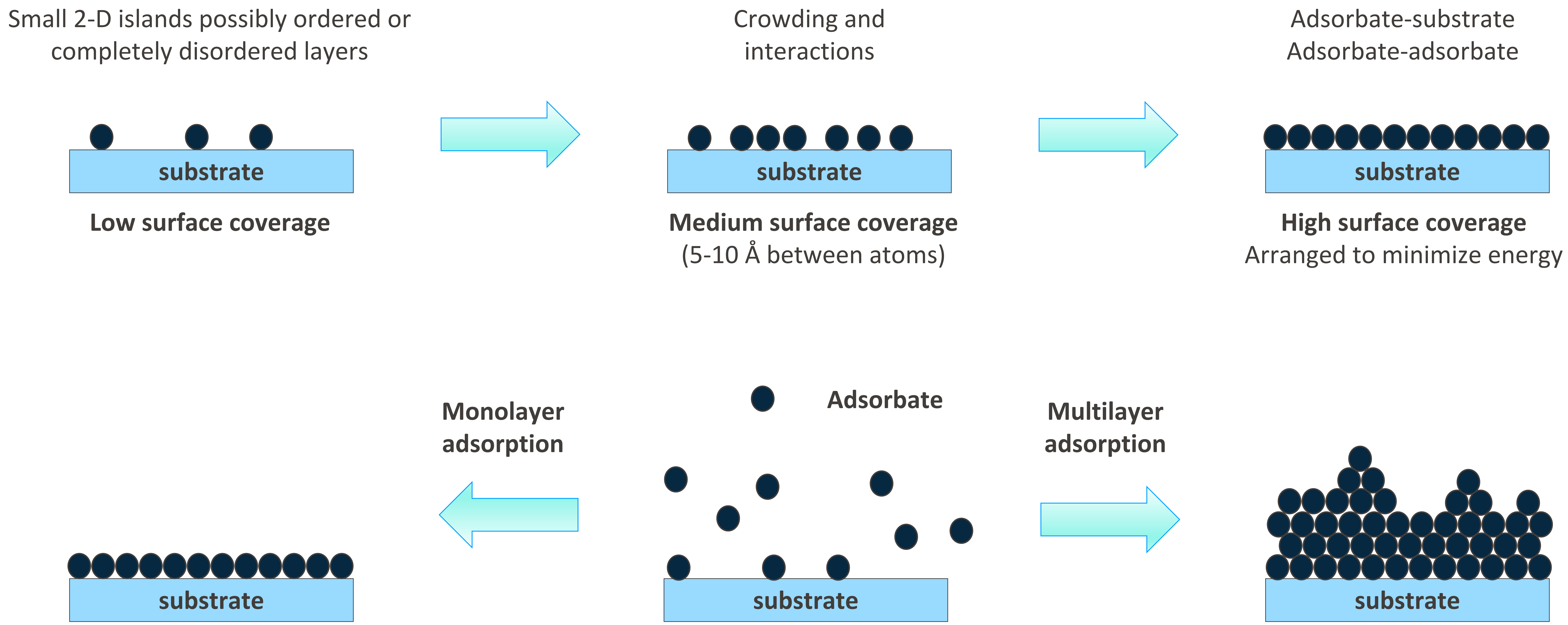
Ordered Adsorbate Layers



Crystal structure of the surface dictates where molecules adsorb

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Key Takeaways

Contamination comes from air, humidity, residues, dust, handling, etc.

Adsorption = surface, Absorption = bulk

Physisorption = weak and reversible, Chemisorption = strong and permanent

Adsorbates are arranged on surfaces to minimize surface energy

How are adsorbates arranged on surfaces?

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Solid Surfaces: Short Recap of Lattice Structures

Amorphous solids

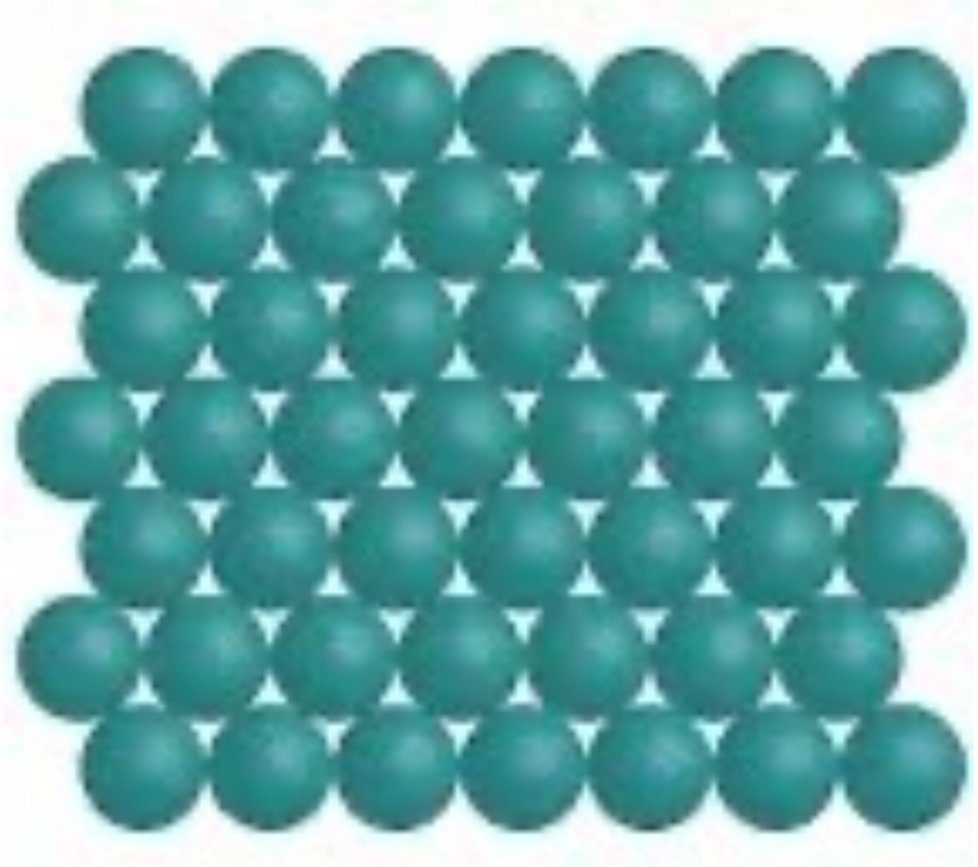
Random arrangement

No definite shape, can be molded

Softens over range of temperatures

Glass, plastic, gels

Crystalline solids



Regular repeating lattice

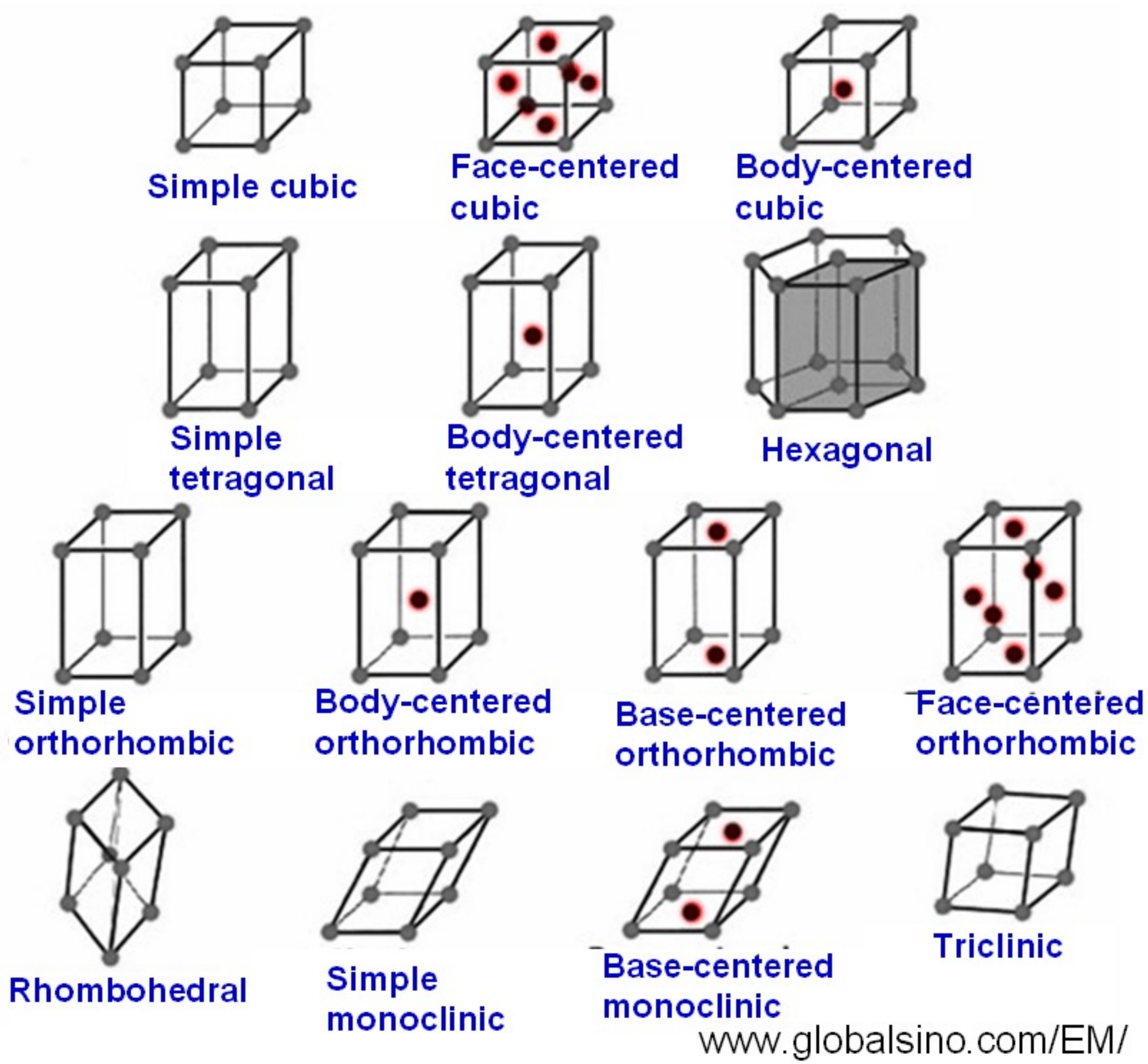
Definite geometric shape

Sharp, well-defined melting point

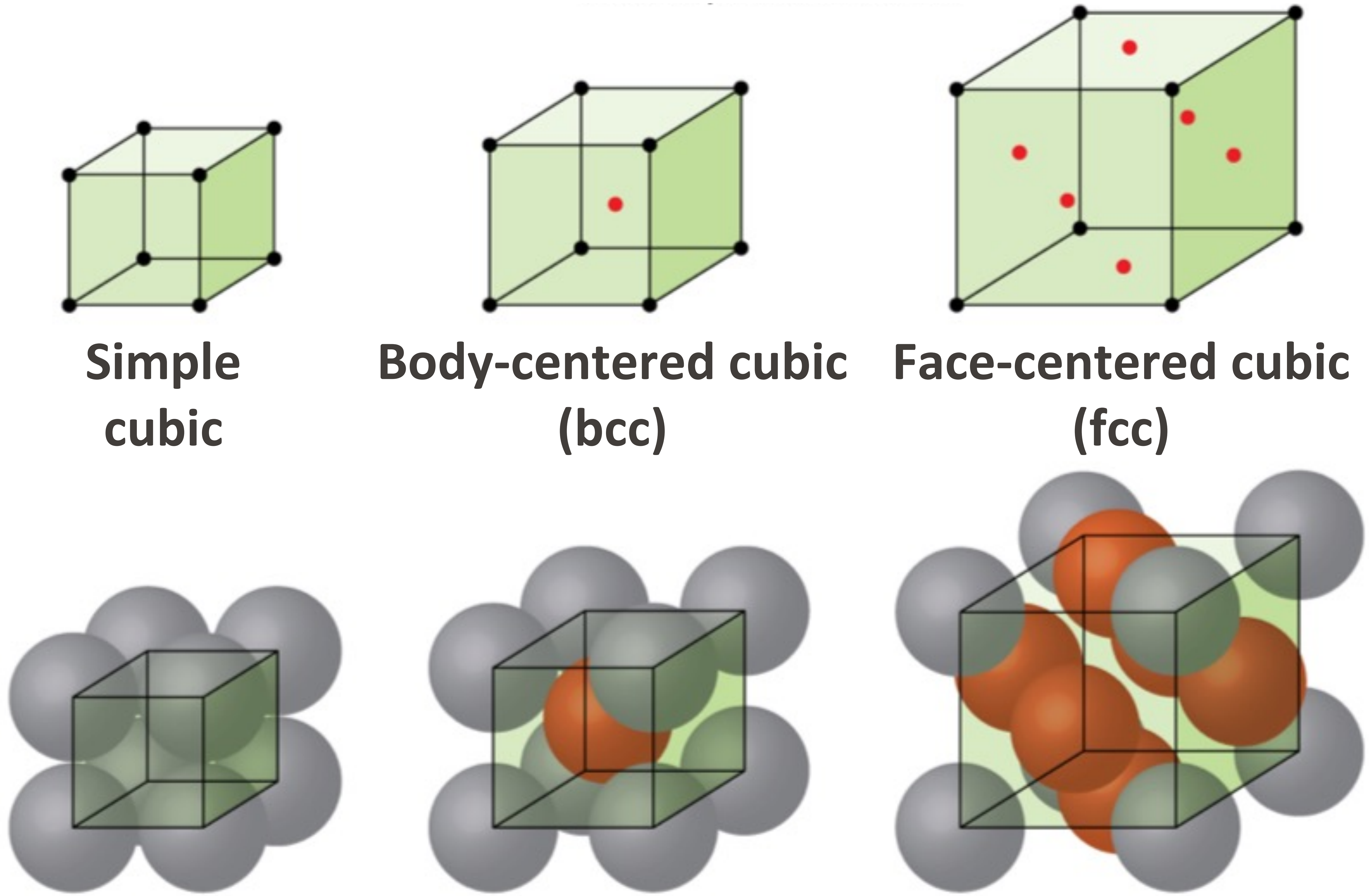
Salt, diamond, sugar

The 14 Bravais Lattices for all 3-D Crystals

All 3-D crystals can be described by one of these lattices. What matters is remembering that a crystal is a periodic arrangement of atoms, and depending on how we slice it, you expose different planes



Common Cubic Lattices for Surface Science



Polonium (rare in Nature)

Iron, Tungsten Chromium, Molybdenum

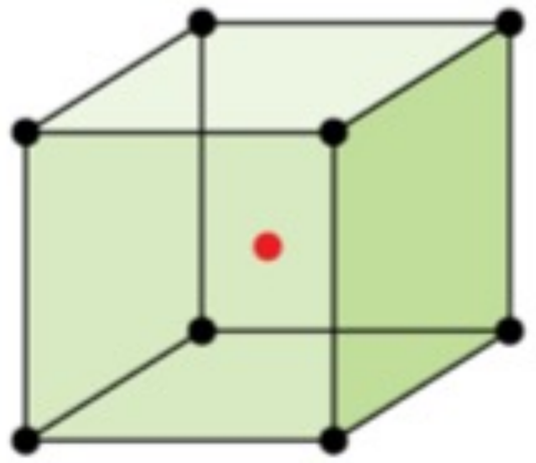
Copper, Nickel Aluminum, Platinum Gold, Lead

Close-Packed Structures: Role in Adsorption/Absorption

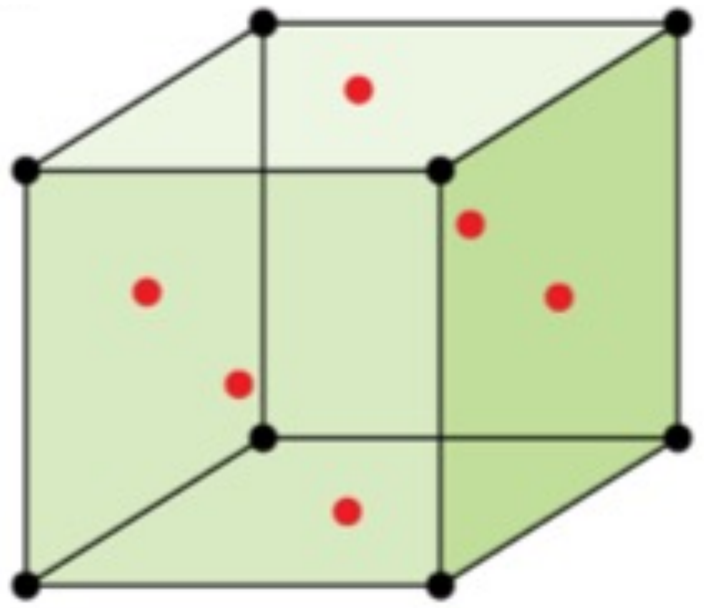
Structures where atoms are packed as closely as possible and minimizing empty space

$$Packing\ efficiency = \frac{Volume\ occupied\ by\ atoms}{Volume\ of\ unit\ cell} \times 100$$

68%

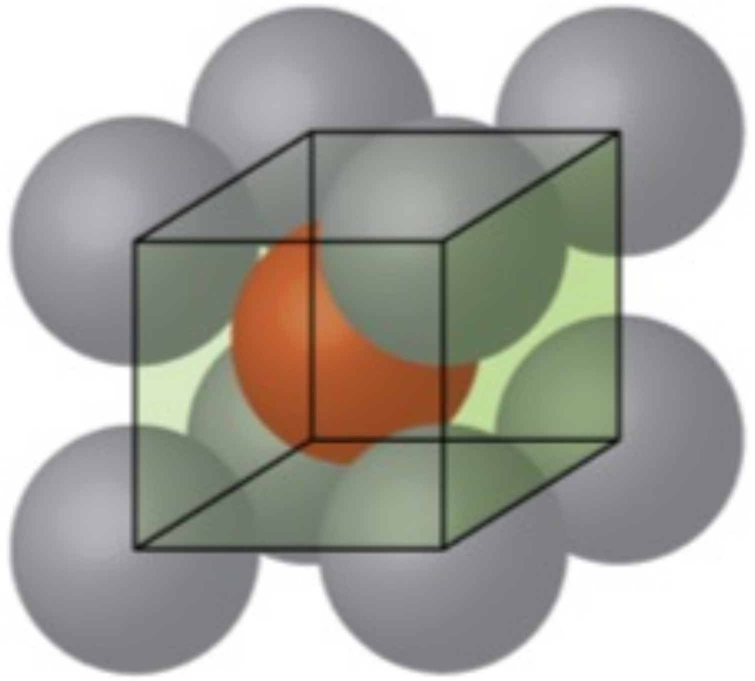


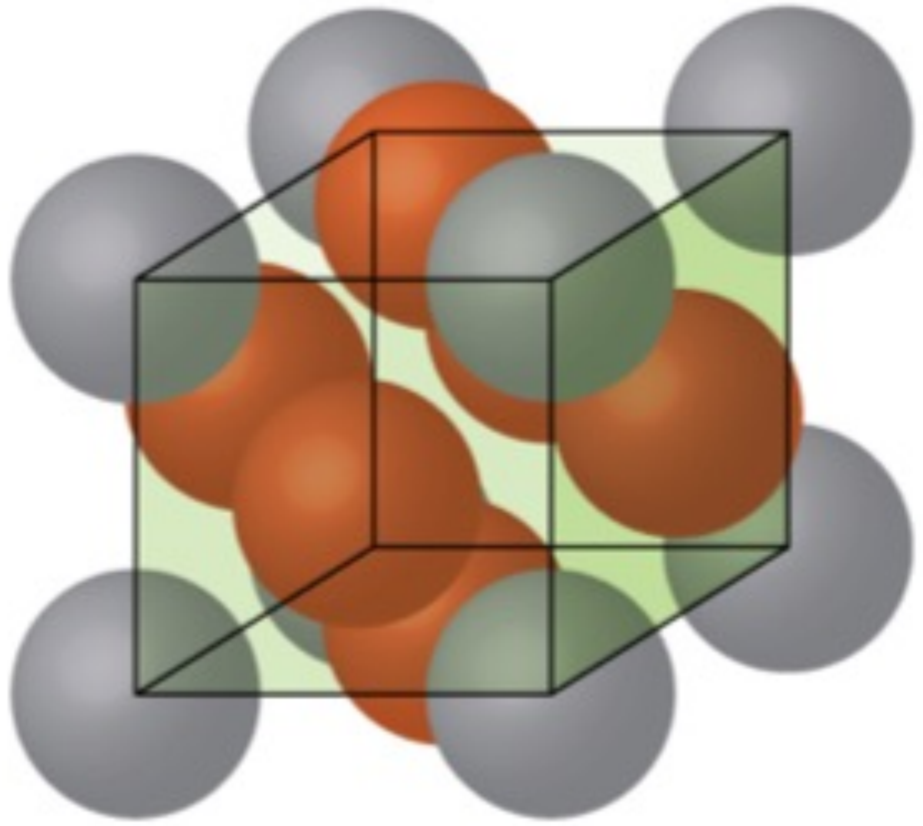
Body-centered cubic (bcc)



Face-centered cubic (fcc)

74%

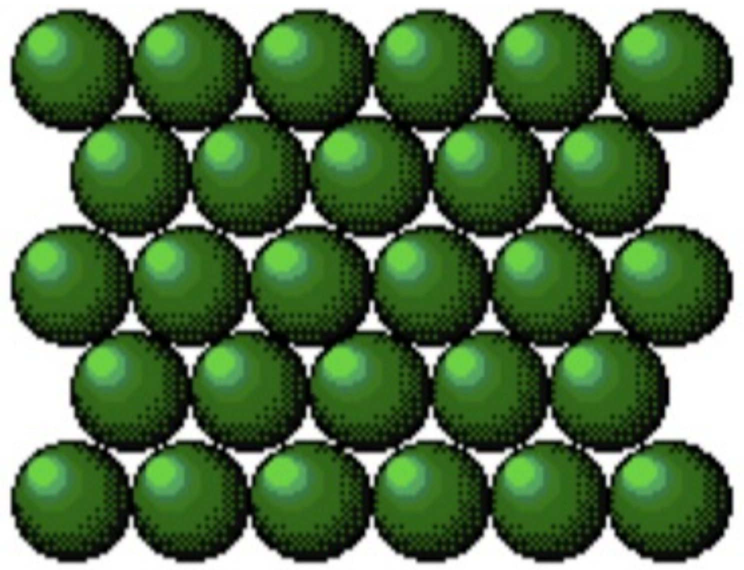




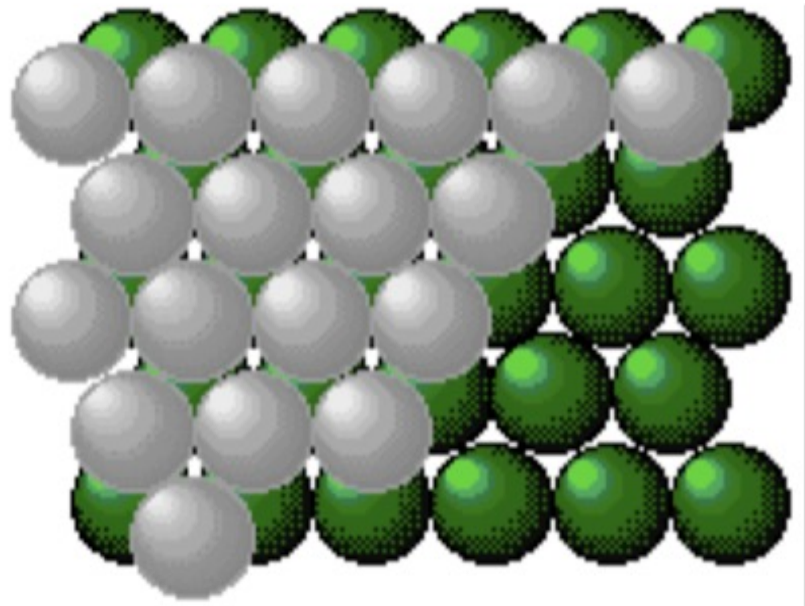
Close-Packed Structures: Role in Adsorption/Absorption

Structures where atoms are packed as closely as possible and minimizing empty space

1st layer: close packed atoms

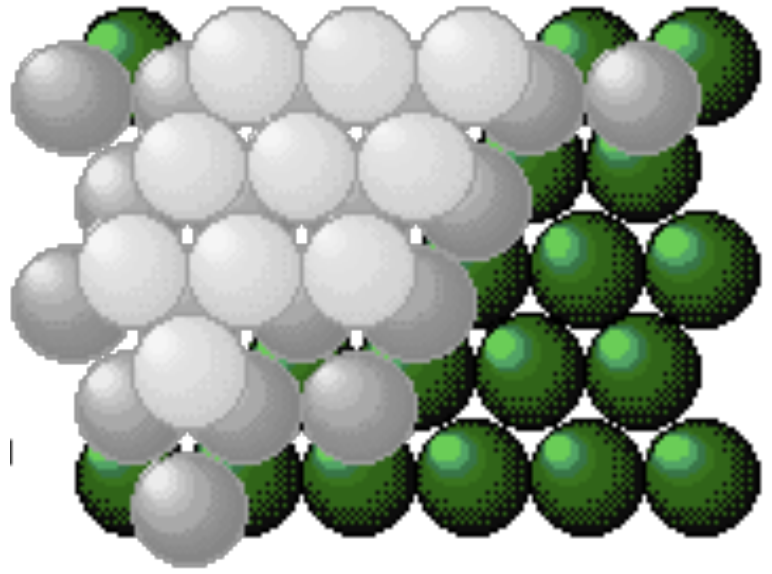


2nd layer: atoms are situated over gaps in the 1st layer



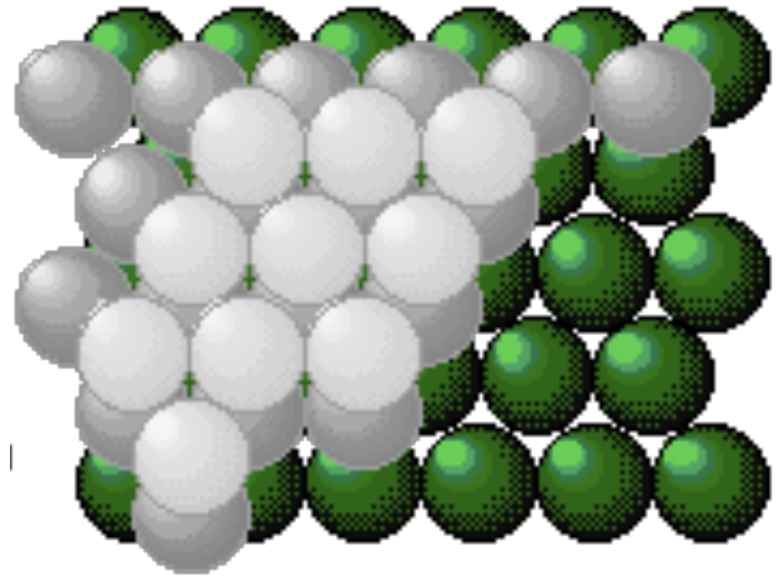
3rd layer: atoms are situated over the gaps in the 2nd layer

Two possibilities:



and over the atoms of the first layer

Hexagonal close packed



Over the gaps in the first layer

Cubic close packed

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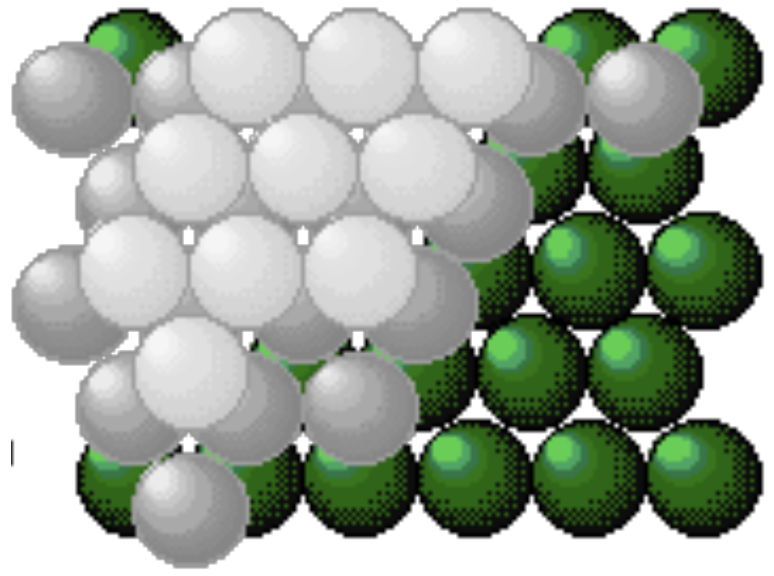
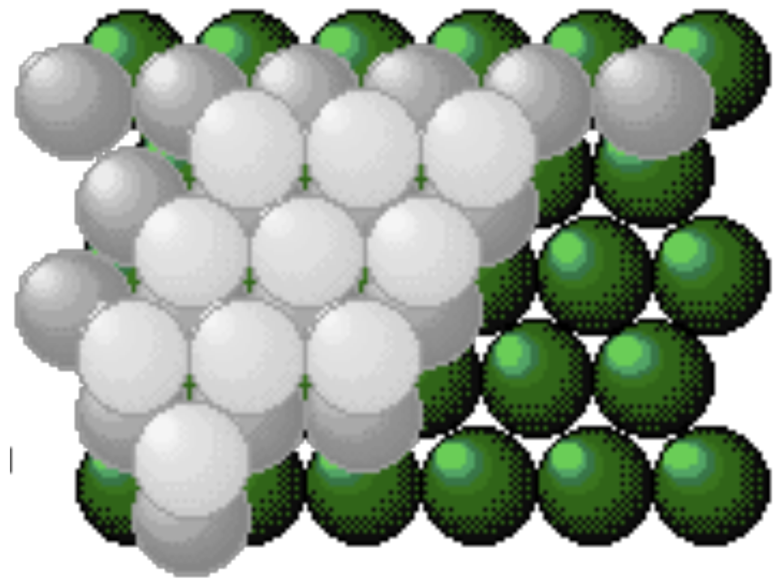
Close-Packed Structures: Role in Adsorption/Absorption

The packing efficiency influences both surface interactions (adsorption) and bulk interactions (absorption)



and over the atoms of the first layer

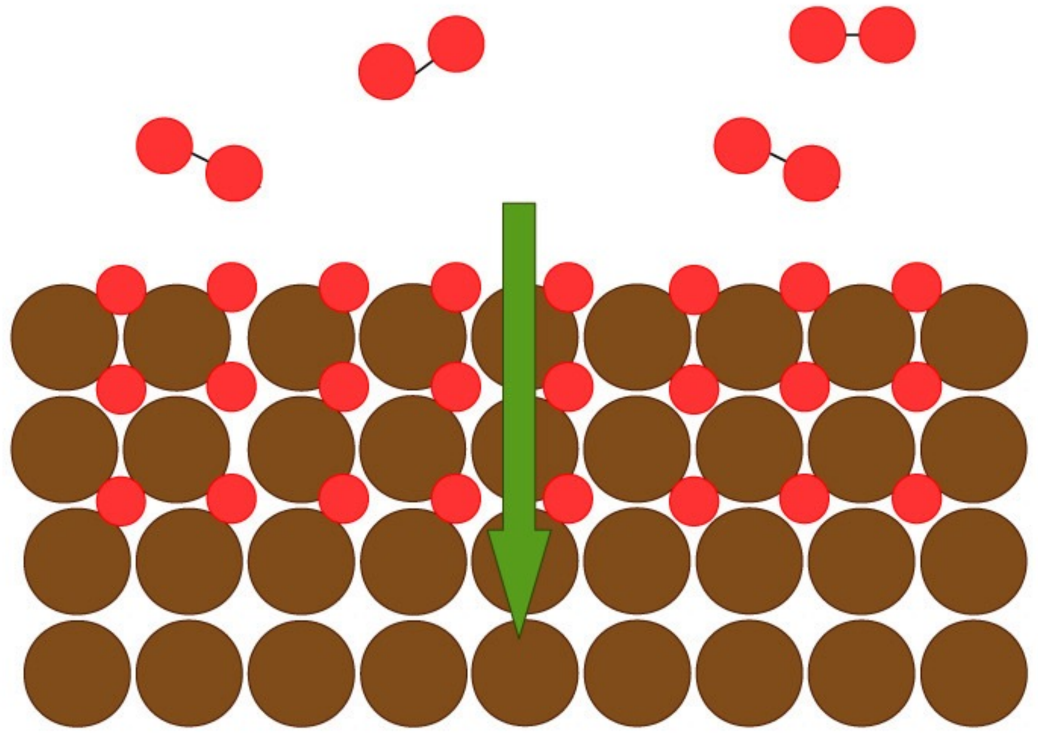
Hexagonal close packed



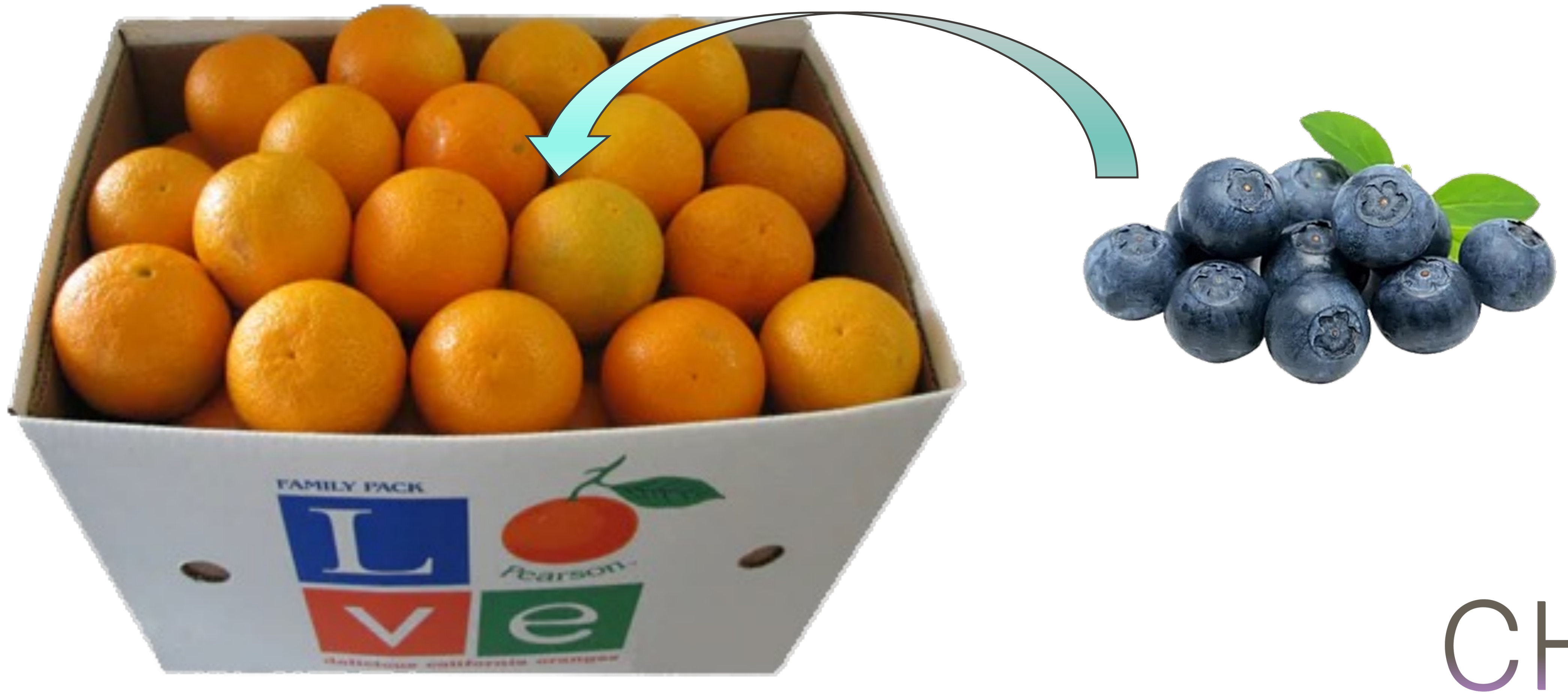
Over the gaps in the first layer

Cubic close packed

Interstitial sites (gaps between atoms in crystal lattices) define absorption pathways



Gattinoni & Michaelides | *Surf. Sci. Rep.* | 2015



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Miller Indices to Describe Crystal Planes

1. Identify where planes intersect the three axes

↓

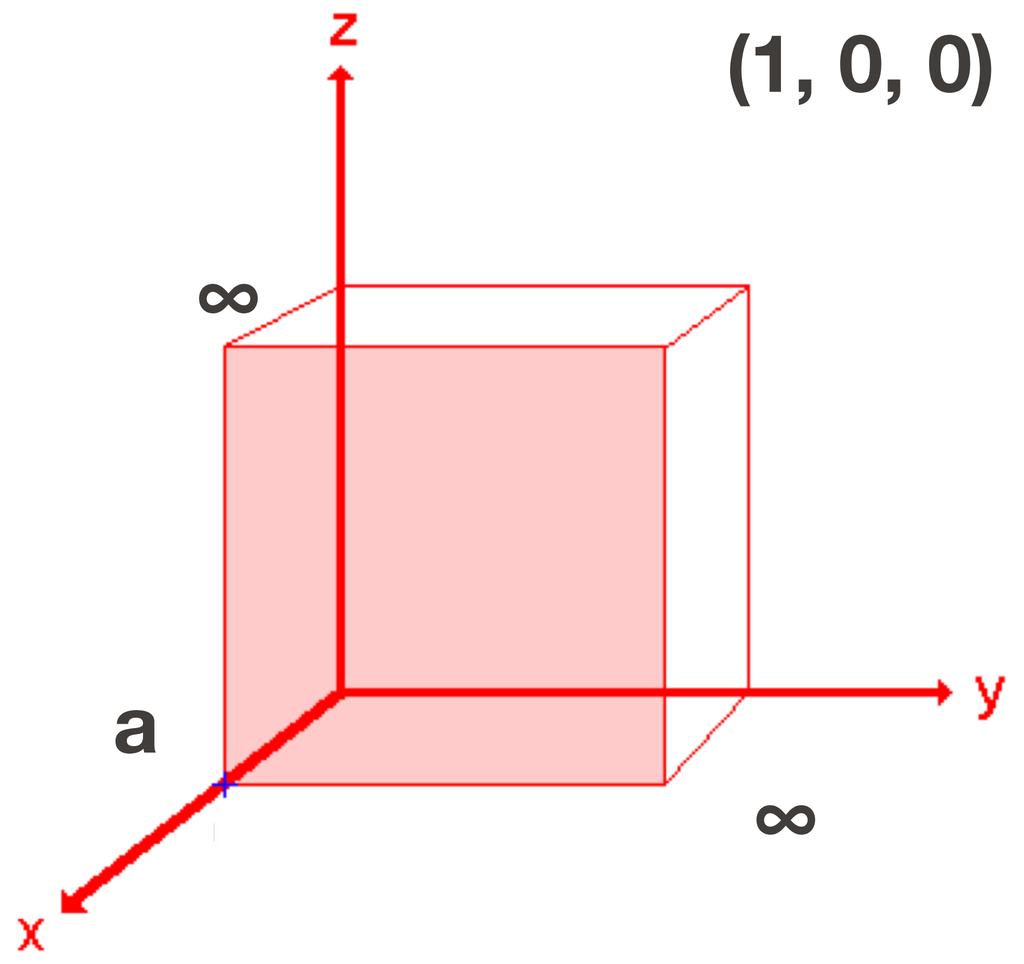
2. Take reciprocals of these locations in terms of lattice parameters a, b, c. If no intersection (parallel) then intersect is infinity (reciprocal is 0)

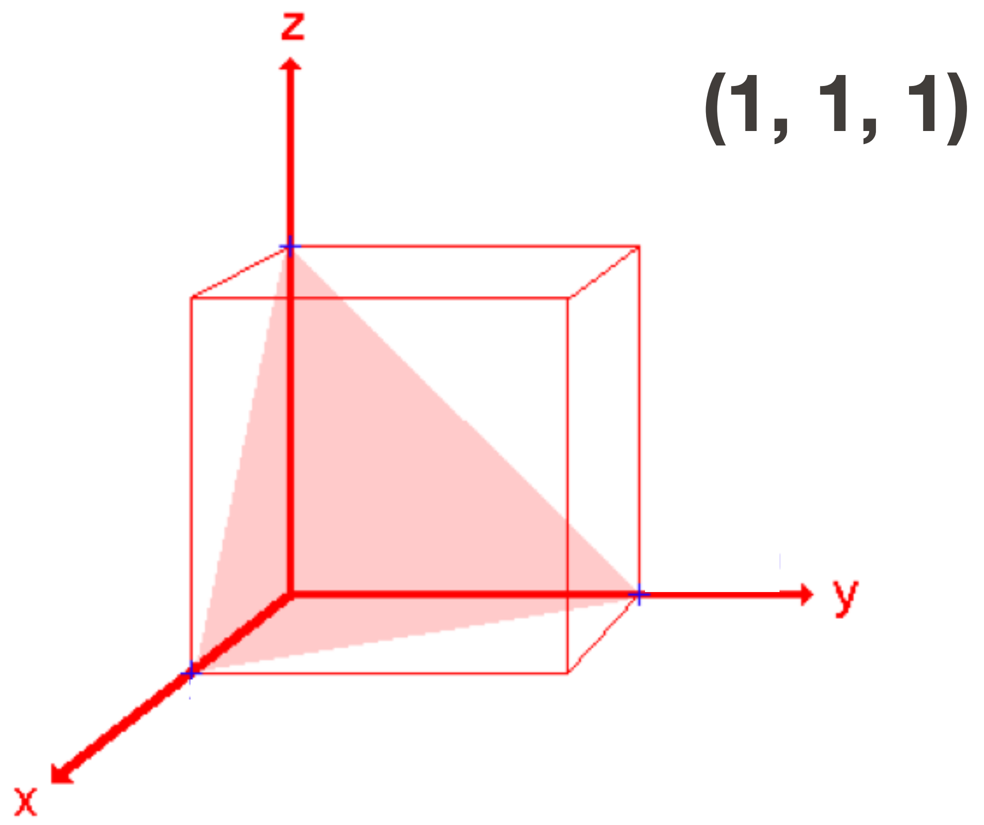
↓

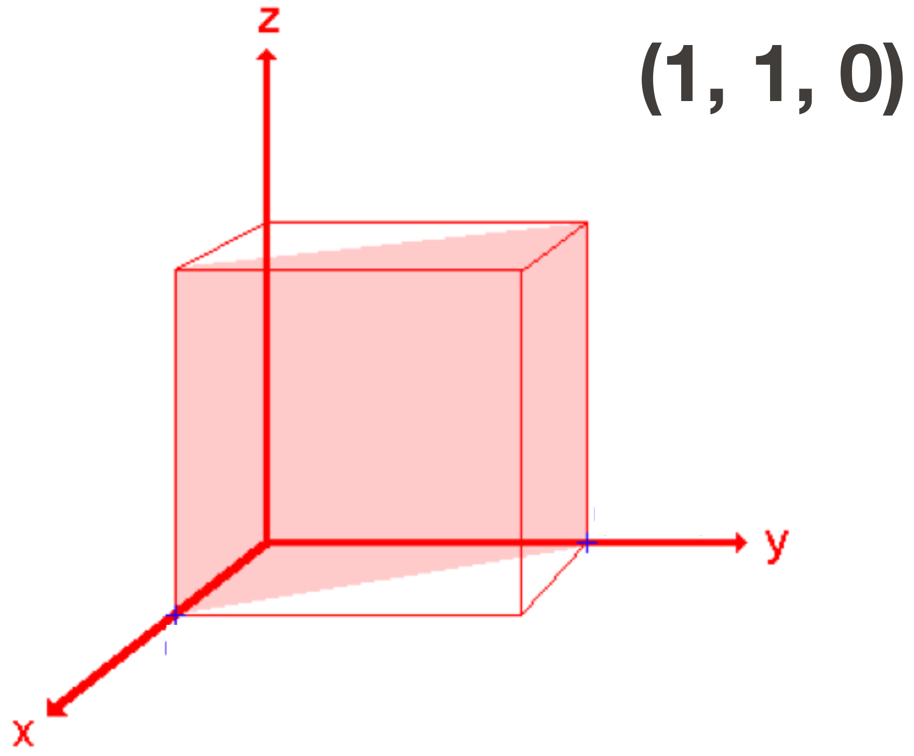
3. Use smallest whole numbers (1, 0, 0)

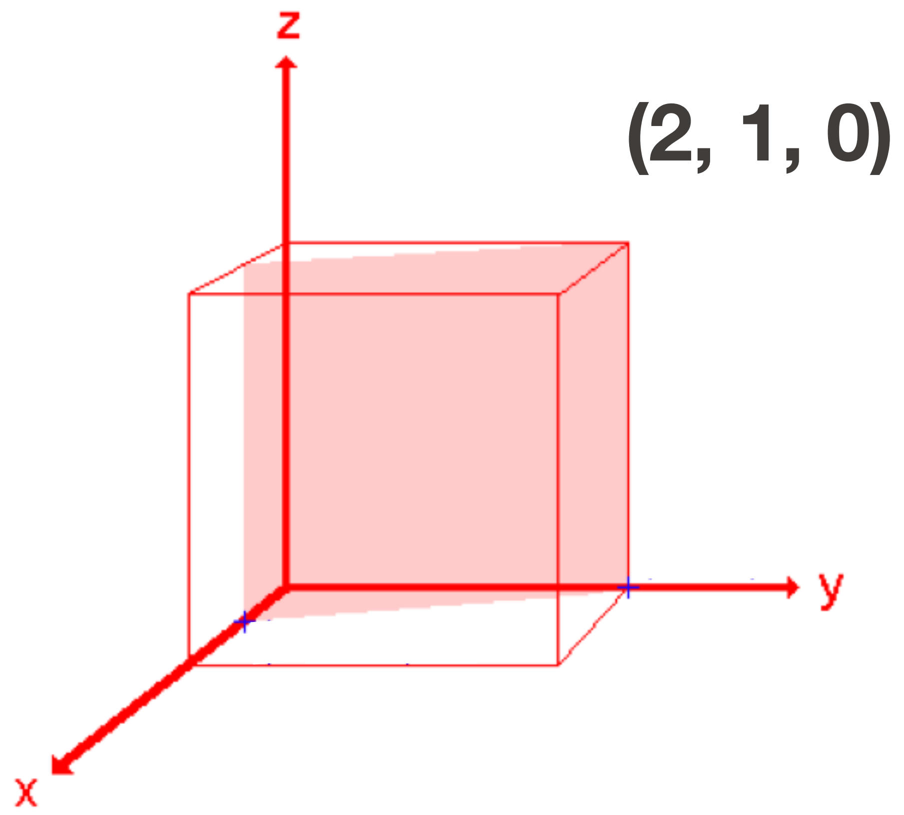
↓

4. Put integers into parentheses to get Miller indices









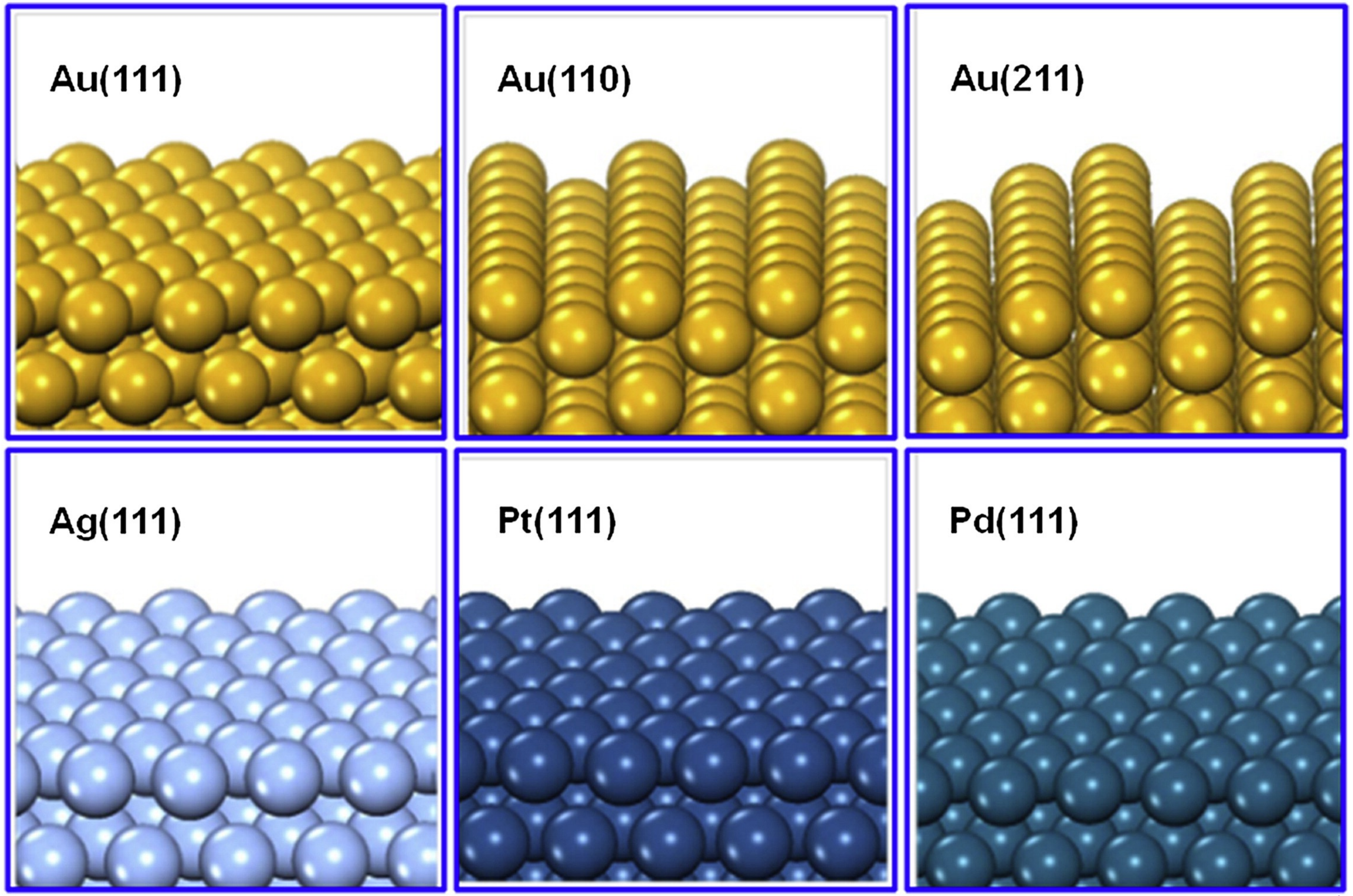
Atomic Arrangements of Atoms on Different Planes

Miller indices describe crystallographic planes in crystalline material

Each orientation represents specific arrangement of atoms on the surface of the crystal lattice, with distinct geometric and chemical properties

Variations in:

- Atomic density
- Surface energy
- Geometry
- Stability



Li *et al.*, | **Biomaterials** | 2023

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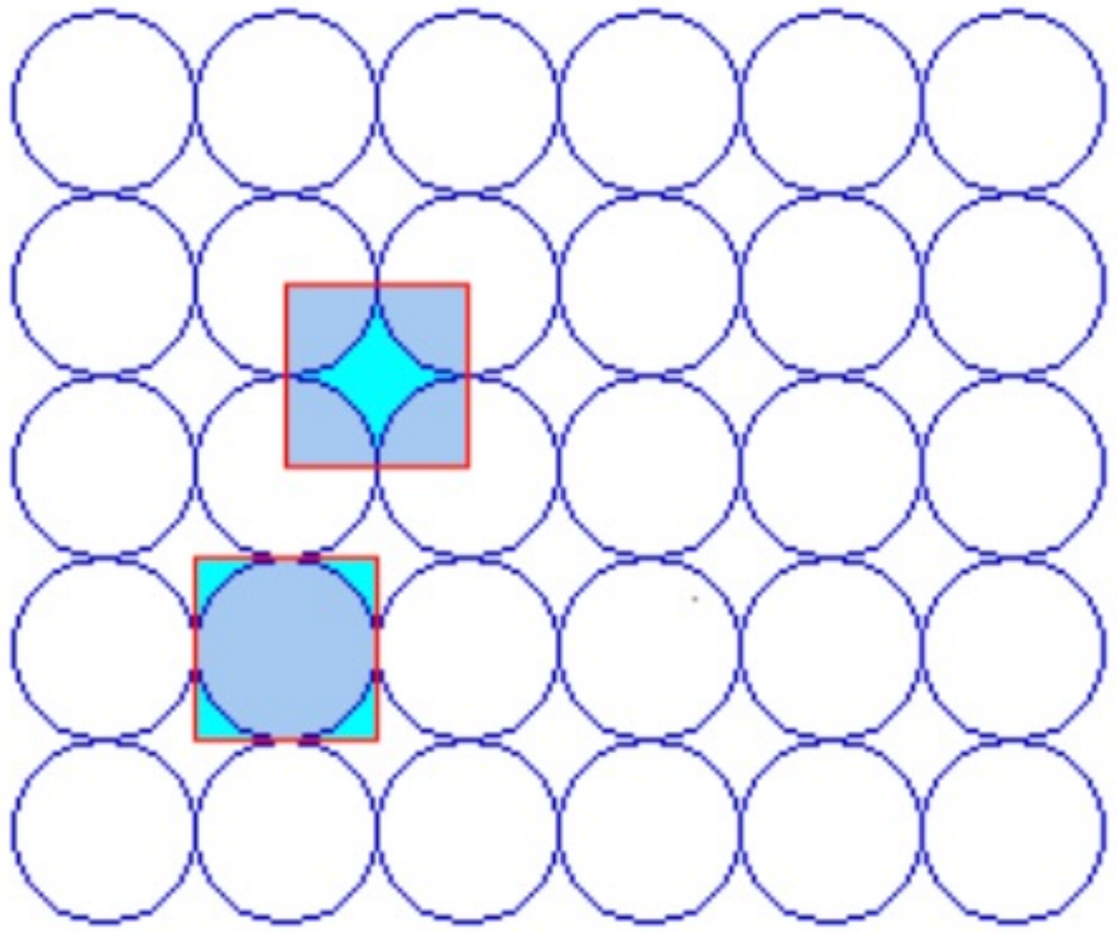
Ordered Adsorbate Layers in Relation to Substrate's Elementary Cell

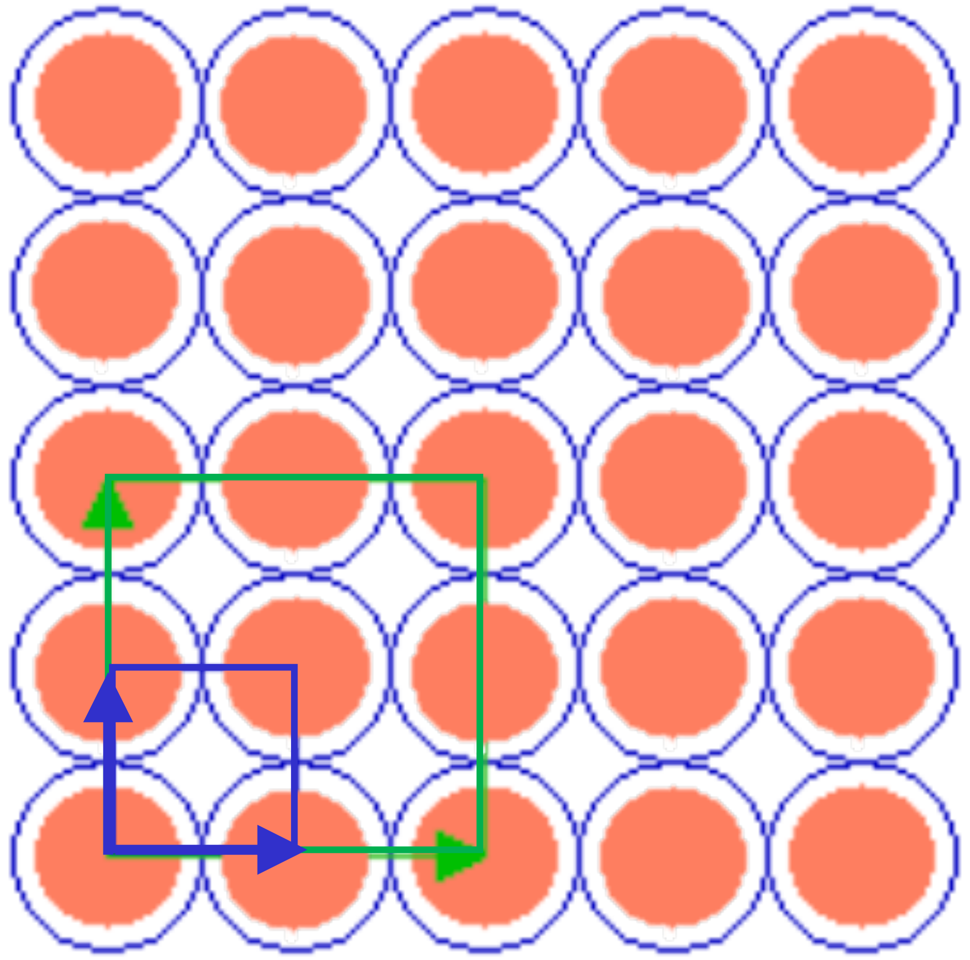
fcc(100) lattice



Two possible choices of unit cell

Substrate provides periodic grid of atoms

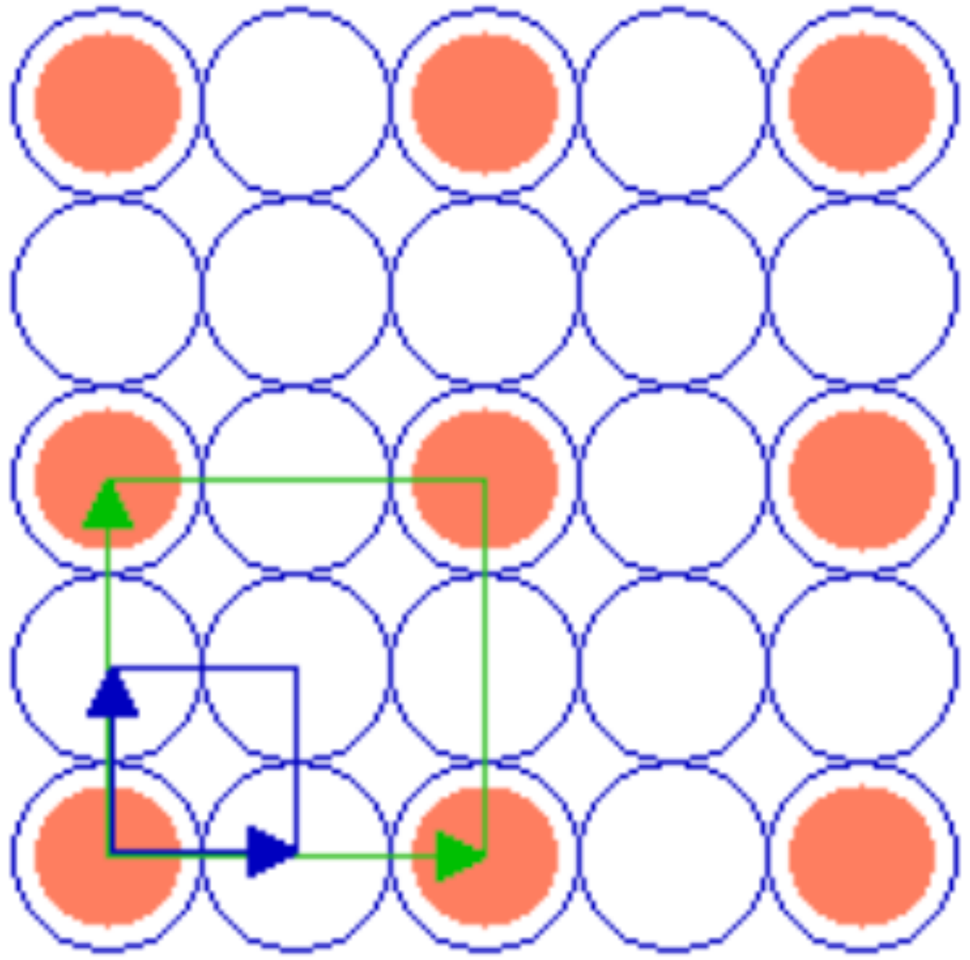
Adsorbates



(1x1)

θ = 1

coverage

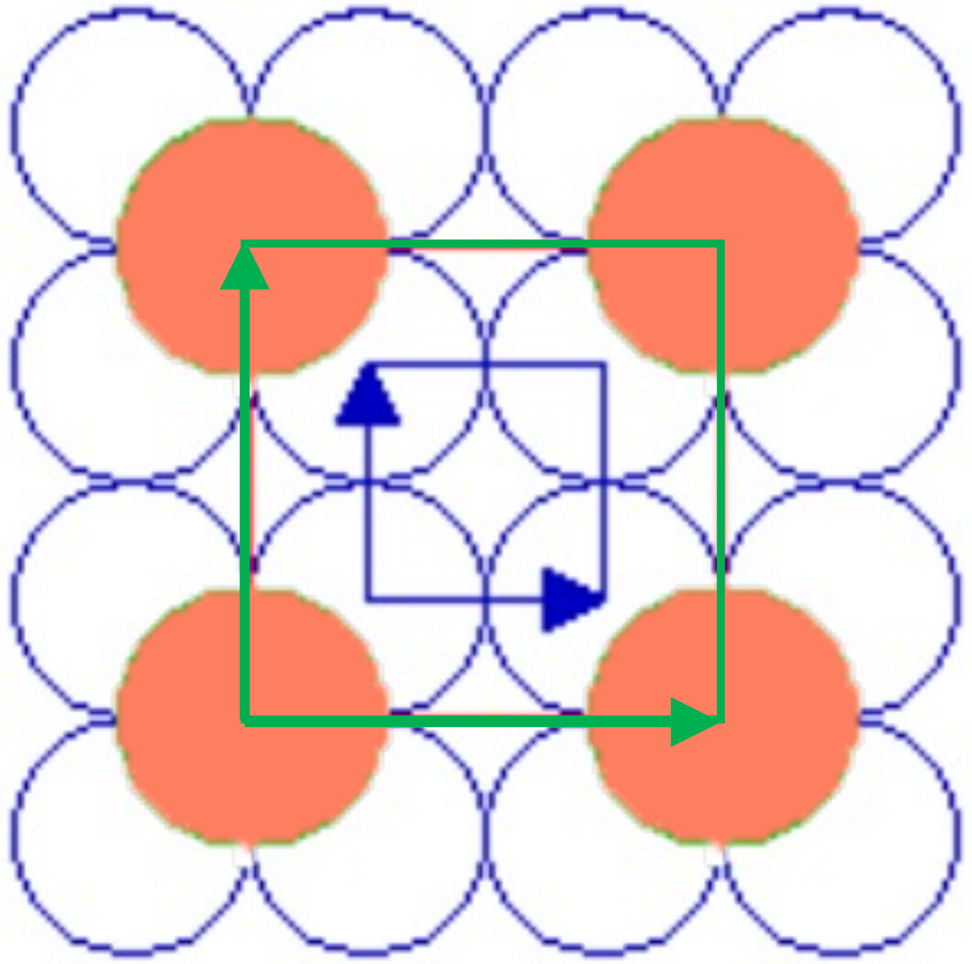


(2x2)

θ = 1/4

Adsorbate unit cell

Substrate unit cell



c(2x2)

θ = 1/2

*c = centered

Adsorbates don't just stick randomly — they form ordered patterns based on substrate lattice

How to Read Wood's Notation (Adsorbate Address)

Substrate orientation

Miller indices

Adsorbate superstructure

Adsorbate species

Si(111)-(1x1)-O

W(211)-(2x2)-H

Cu(100)-c(2x2)-Cl

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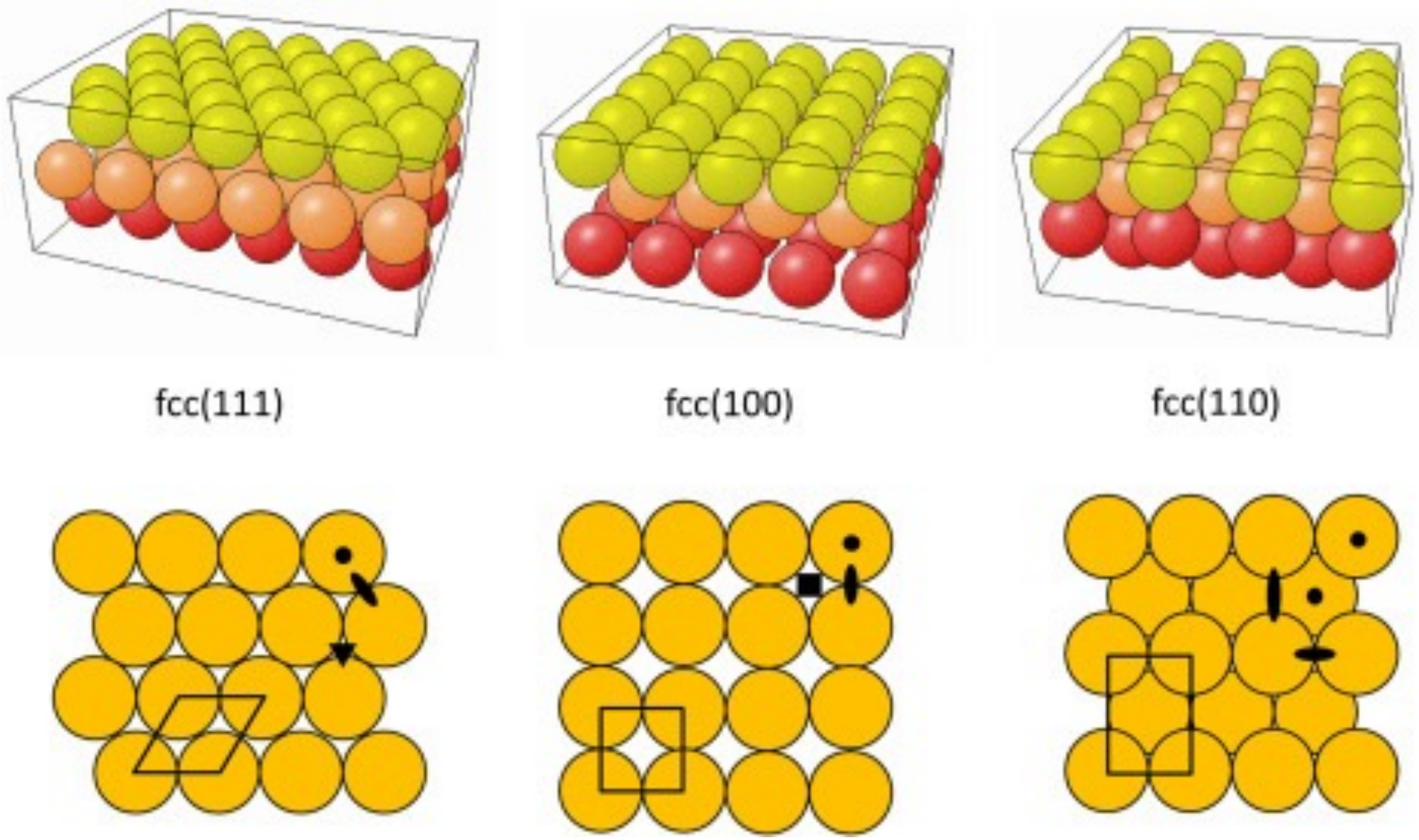
Face-Specific Behavior of Adsorption

Chloride ions adsorption on copper electrode surfaces



Wandelt | *Surf. Sci. Electrochem.* | 2018

Most symmetric adsorption sites are marked by the shapes

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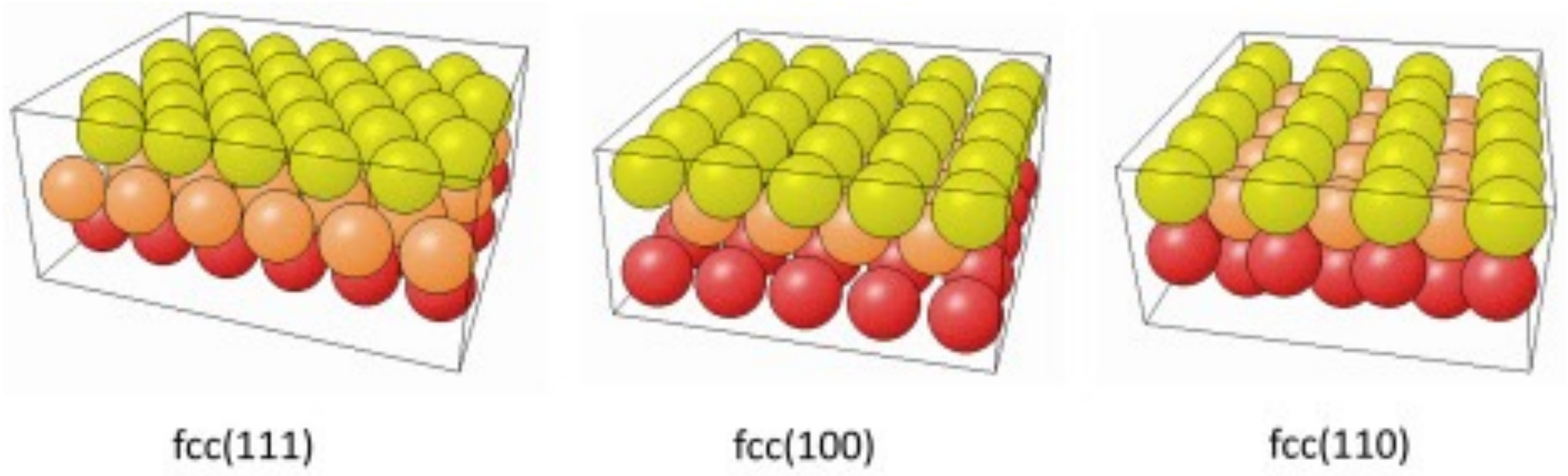
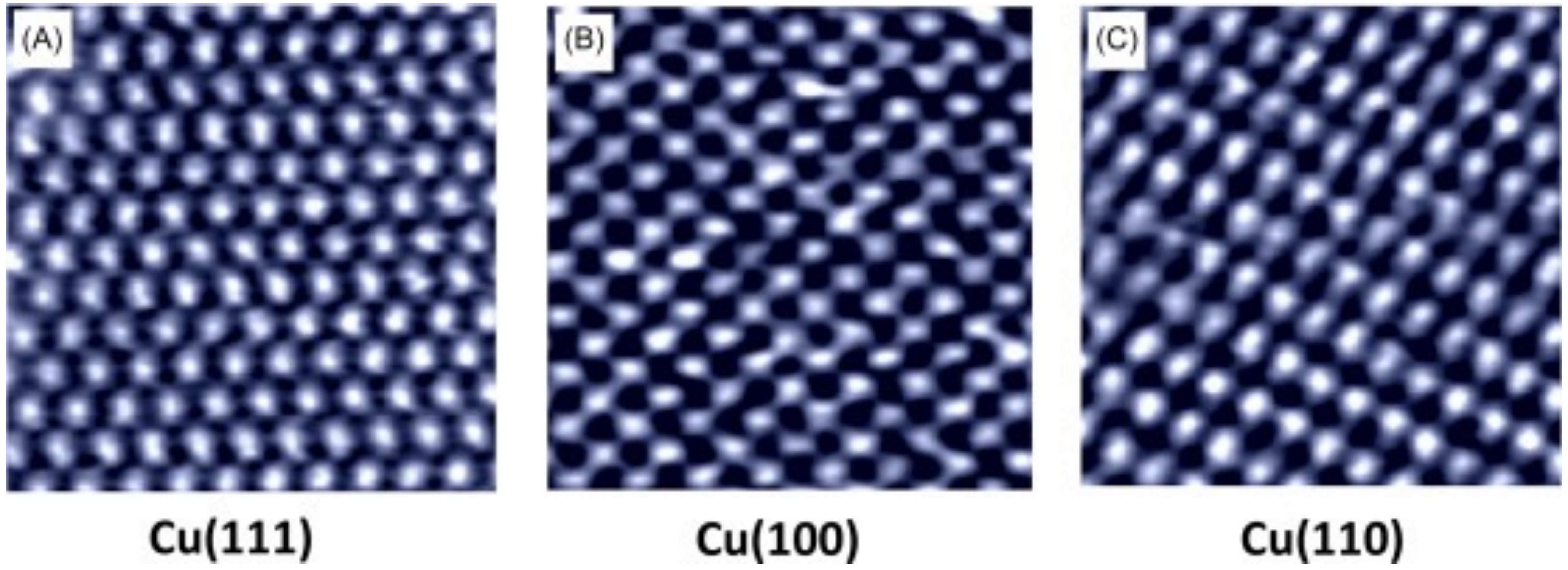
Visualizing Face-Specific Structure of Surfaces

Chloride ions adsorption on copper electrode surfaces



Scanning tunneling microscopy (STM) images of anion-free copper surfaces



Scale:
~ 3 x 3 nm

Wandelt | *Surf. Sci. Electrochem.* | 2018

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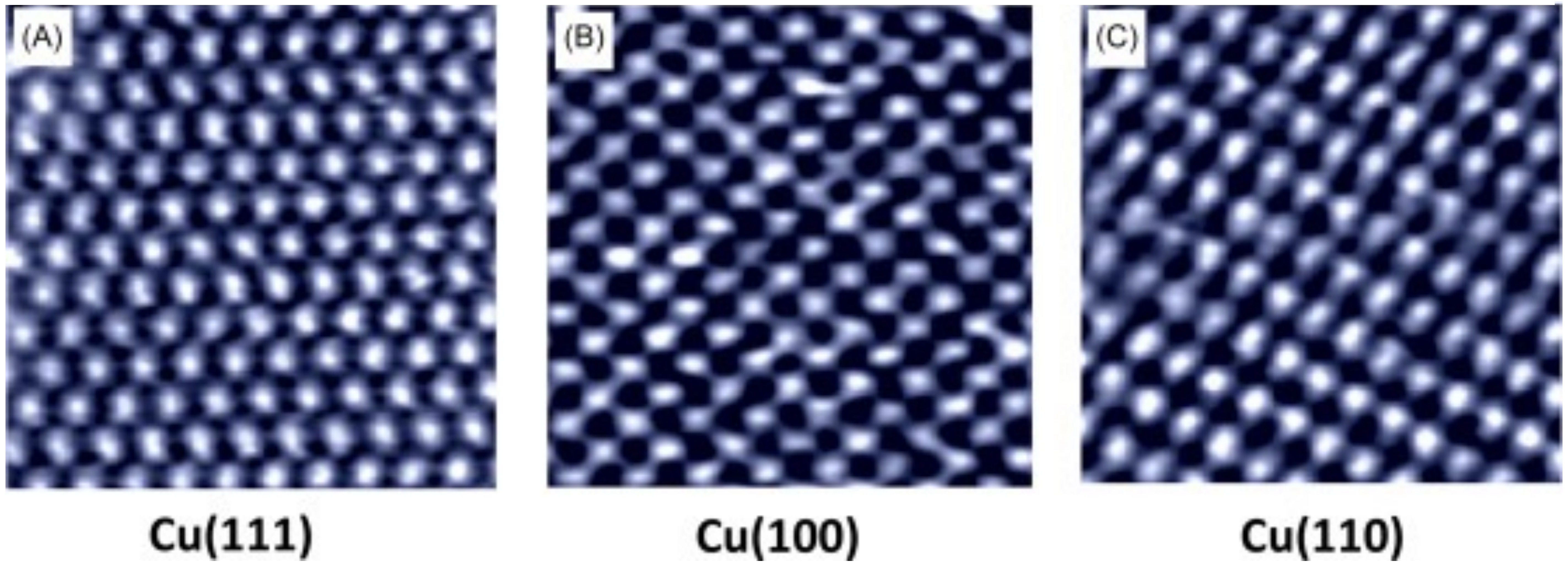
Extracting Face-Specific Parameters

	Cu(111)	Cu(100)	Cu(110)
Lattice constants (nm)	$\vec{a} = \vec{b}$ =0.256; α=60°	$\vec{a} = \vec{b}$ =0.256; α=90°	a=0.256, b=0.362; α=90°
Density (atoms/cm²)	1.767×10^{15}	1.530×10^{15}	1.082×10^{15}
Coordination number	9	8	7
Missing neighbors	3	4	5
Interlayer spacing (nm)	d=0.212	d=0.181	d=0.128
Workfunction (eV)	4.94	4.59	4.48

Scanning tunneling microscopy (STM) images of anion-free copper surfaces



Scale: ~ 3 x 3 nm

Wandelt | *Surf. Sci. Electrochem.* | 2018

Key Takeaways

Crystal lattice structures of surfaces defines how adsorbates stick

Packing of lattice structure influences adsorption/absorption

Adsorbates form ordered patterns on the substrate lattice (adsorbate address)

Depending on the cut of the crystal, adsorption behavior will change

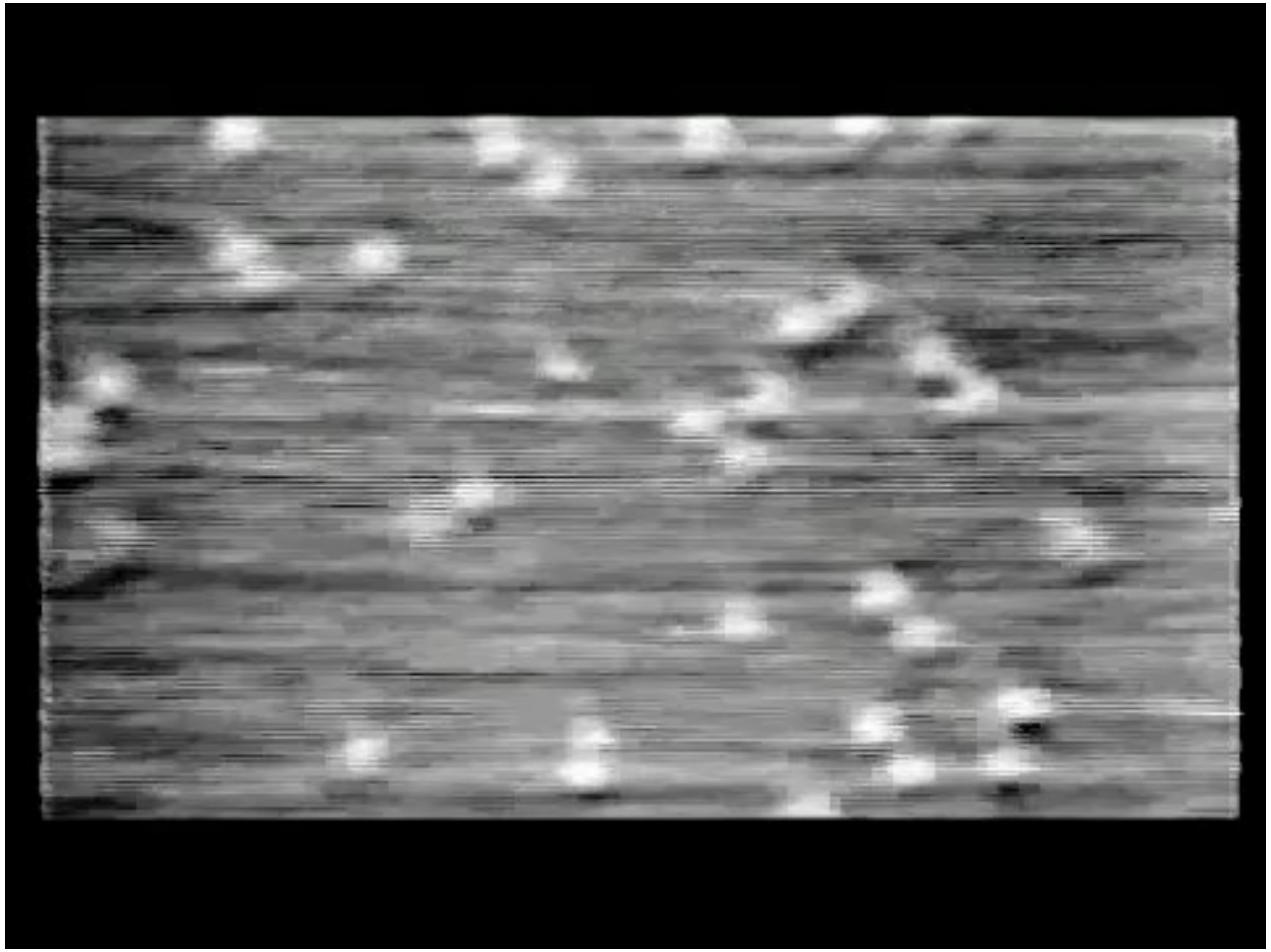
How can we characterize/visualize this phenomenon?

Real-Time Observation of Oxygen on Ruthenium Surface

Scanning tunneling microscopy (STM) images the random walk of individual oxygen atoms on Ru at 300 K

θ < 0.25

θ = 0.25 corresponds to a complete, ordered (2x2) overlayer



10 Å

Experiments conducted in a UHV chamber

Wintterlin | *Surface Science* | 1997

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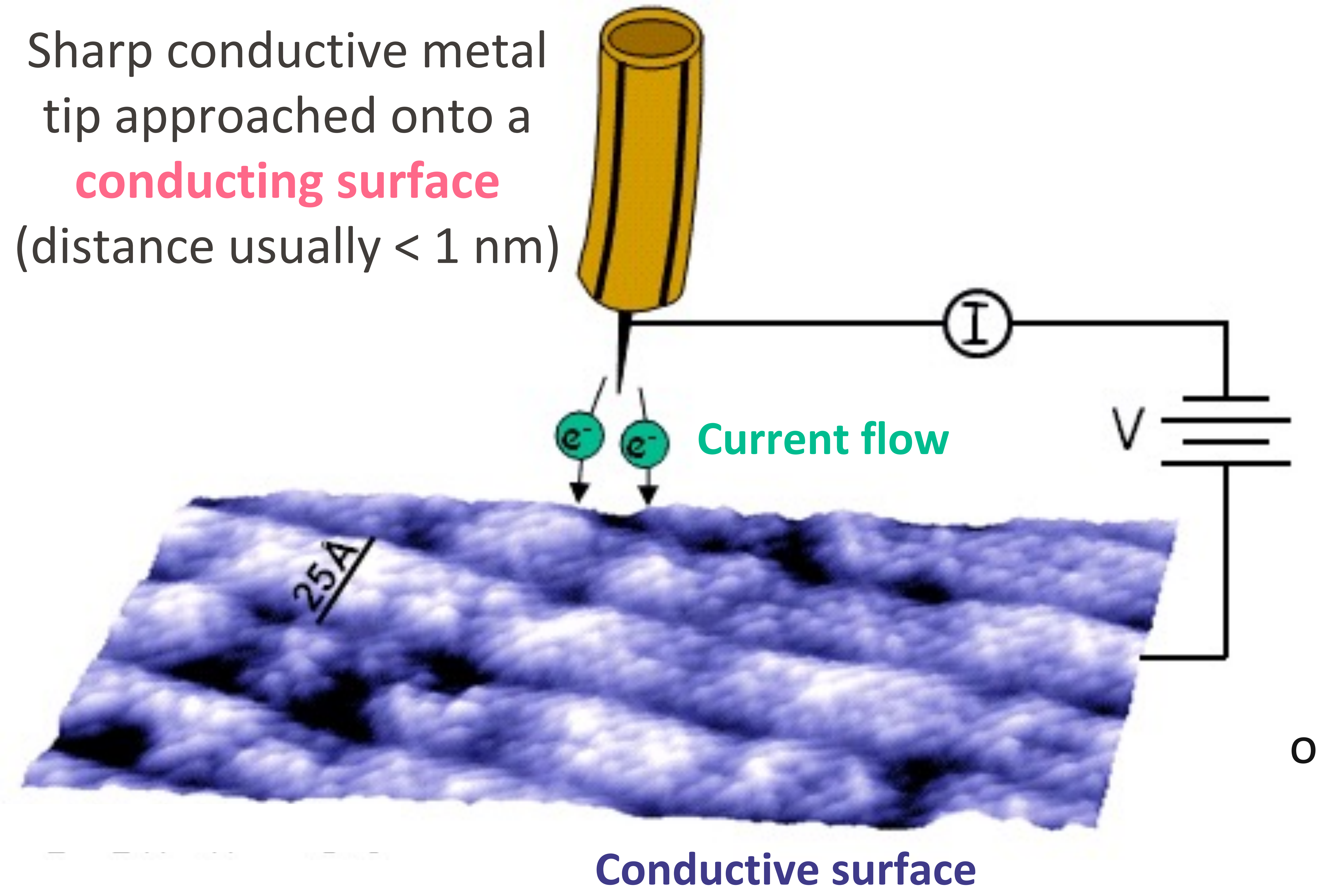
Seeing Surfaces with Atomic-Scale Resolution

Scanning Tunneling Microscopy (STM)

Sharp conductive metal tip approached onto a **conducting surface** (distance usually < 1 nm)



STM provides information on:

1) Electron-density distribution
2) Electronic work function
3) Surface topography

A 3-D image of the "surface" can be obtained with atomic resolution

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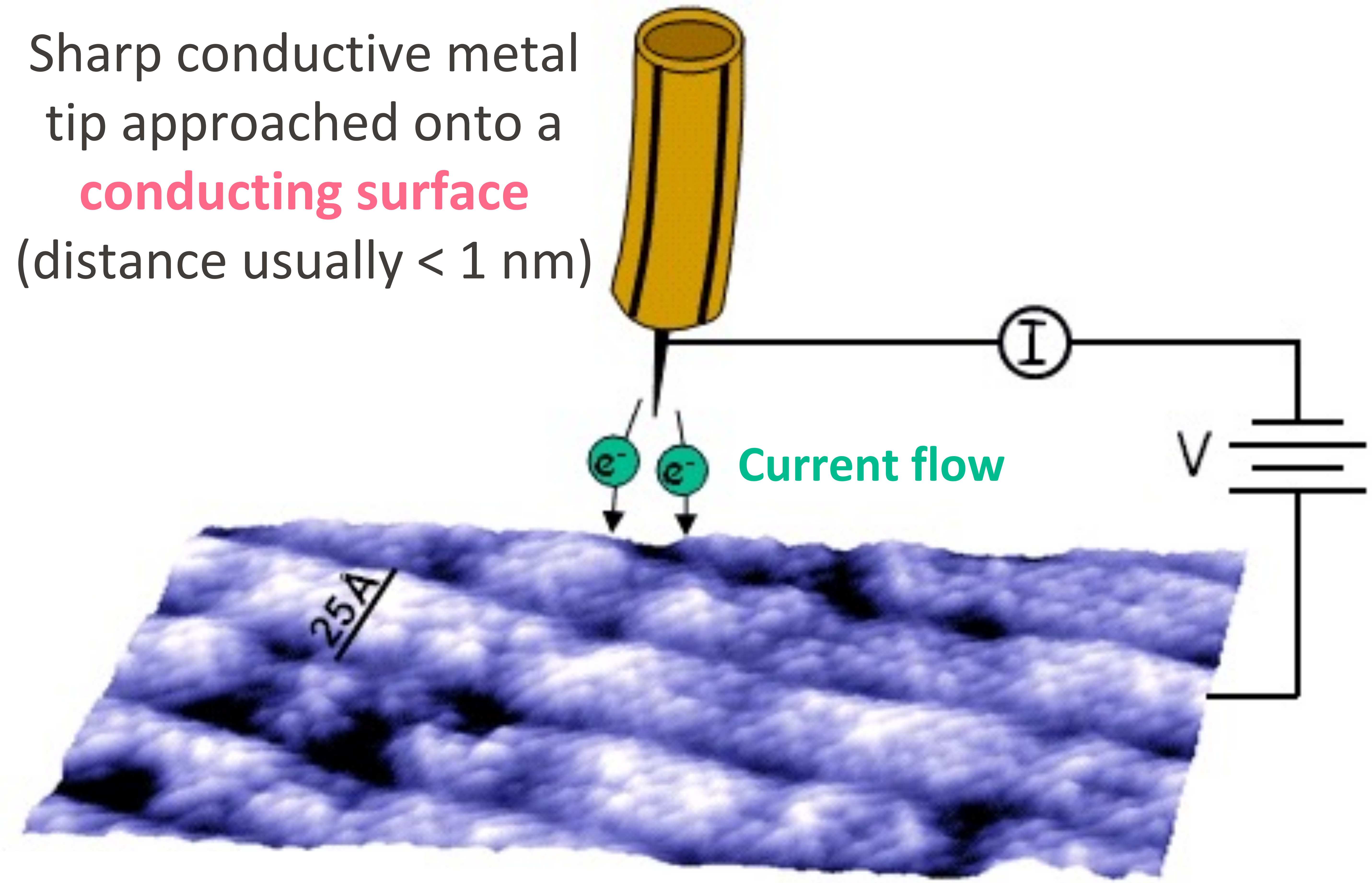
Seeing Surfaces with Atomic-Scale Resolution

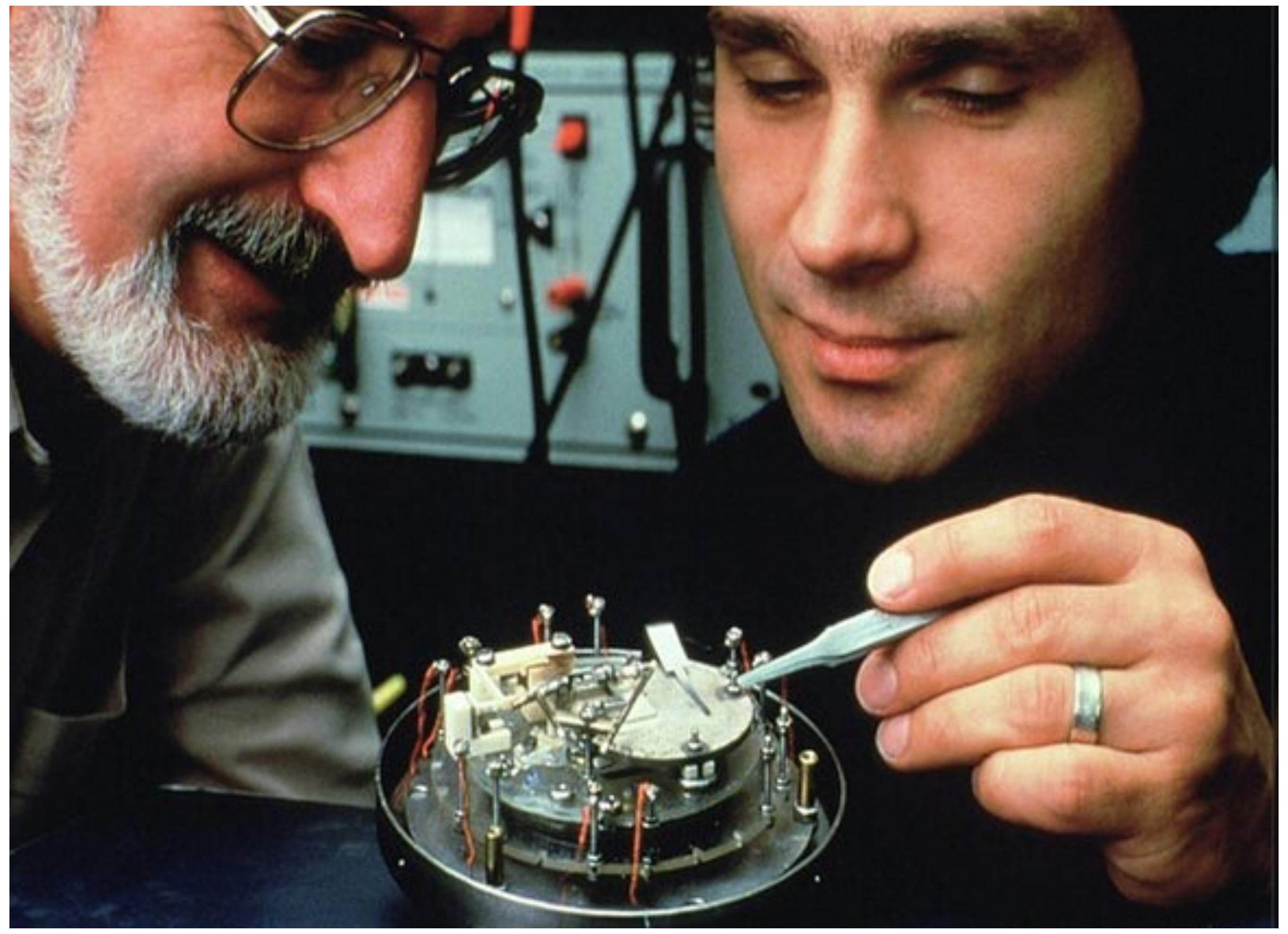
Scanning Tunneling Microscopy (STM)

Sharp conductive metal tip approached onto a **conducting surface** (distance usually < 1 nm)



Conductive surface

1981 IBM Rüschlikon



Heinrich Rohrer & Gerd Binnig

Nobel Prize in Physics for invention of STM (1986)

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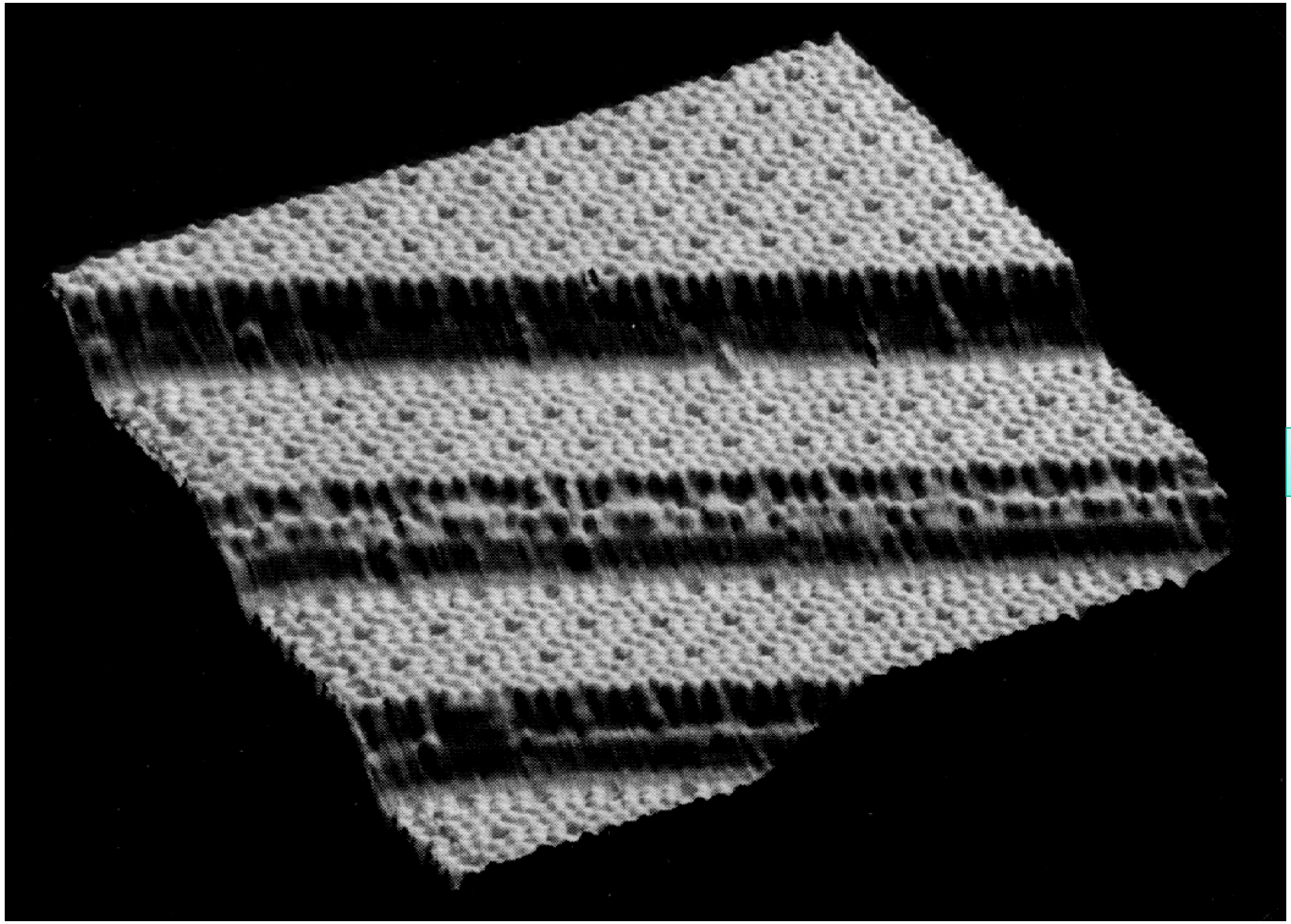
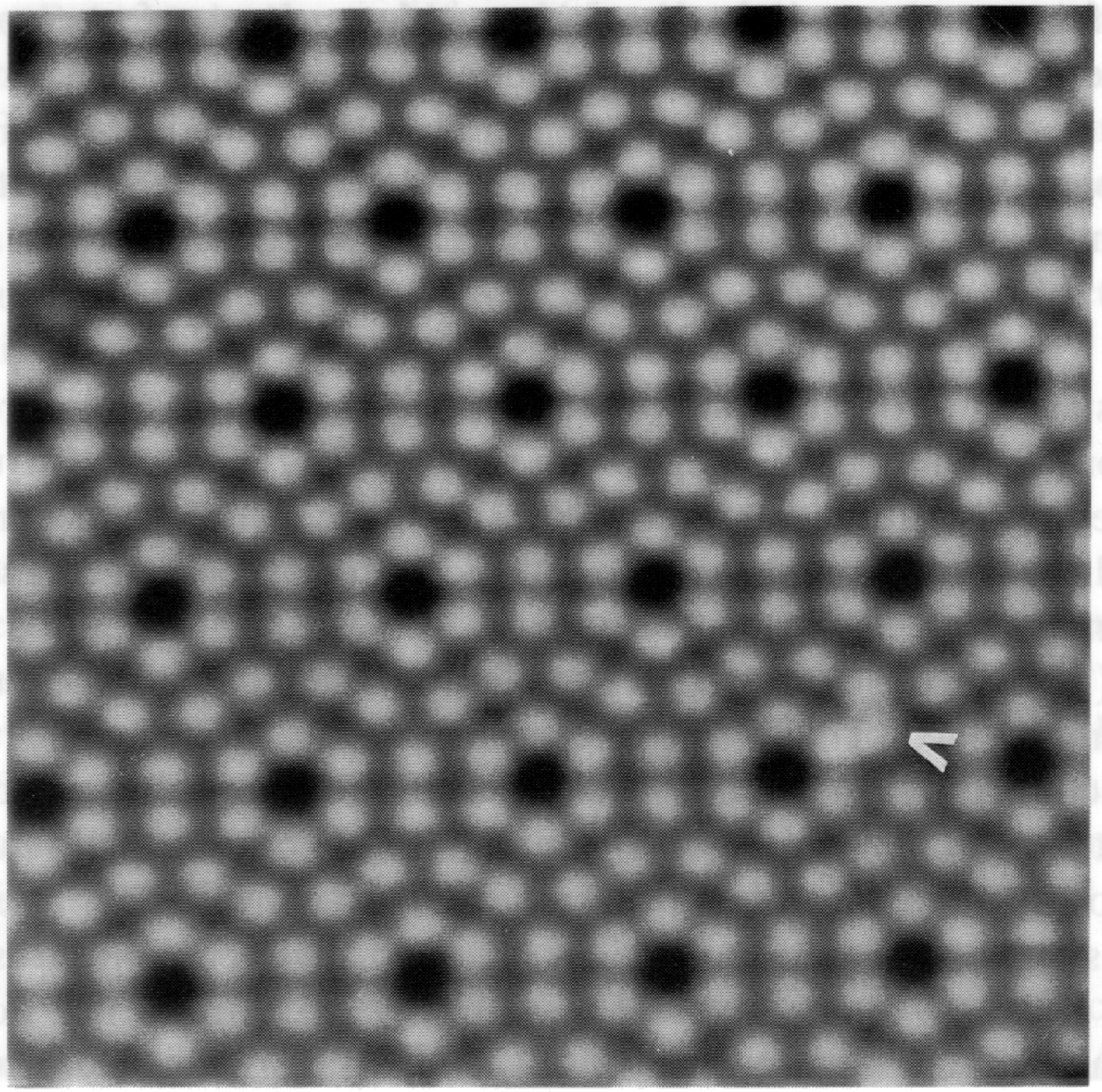
Seeing Surfaces with Atomic-Scale Resolution



Perspective STM image of a 32 x 36 nm area of a Si(111) surface showing atomic layers



Source: Lucio Isa

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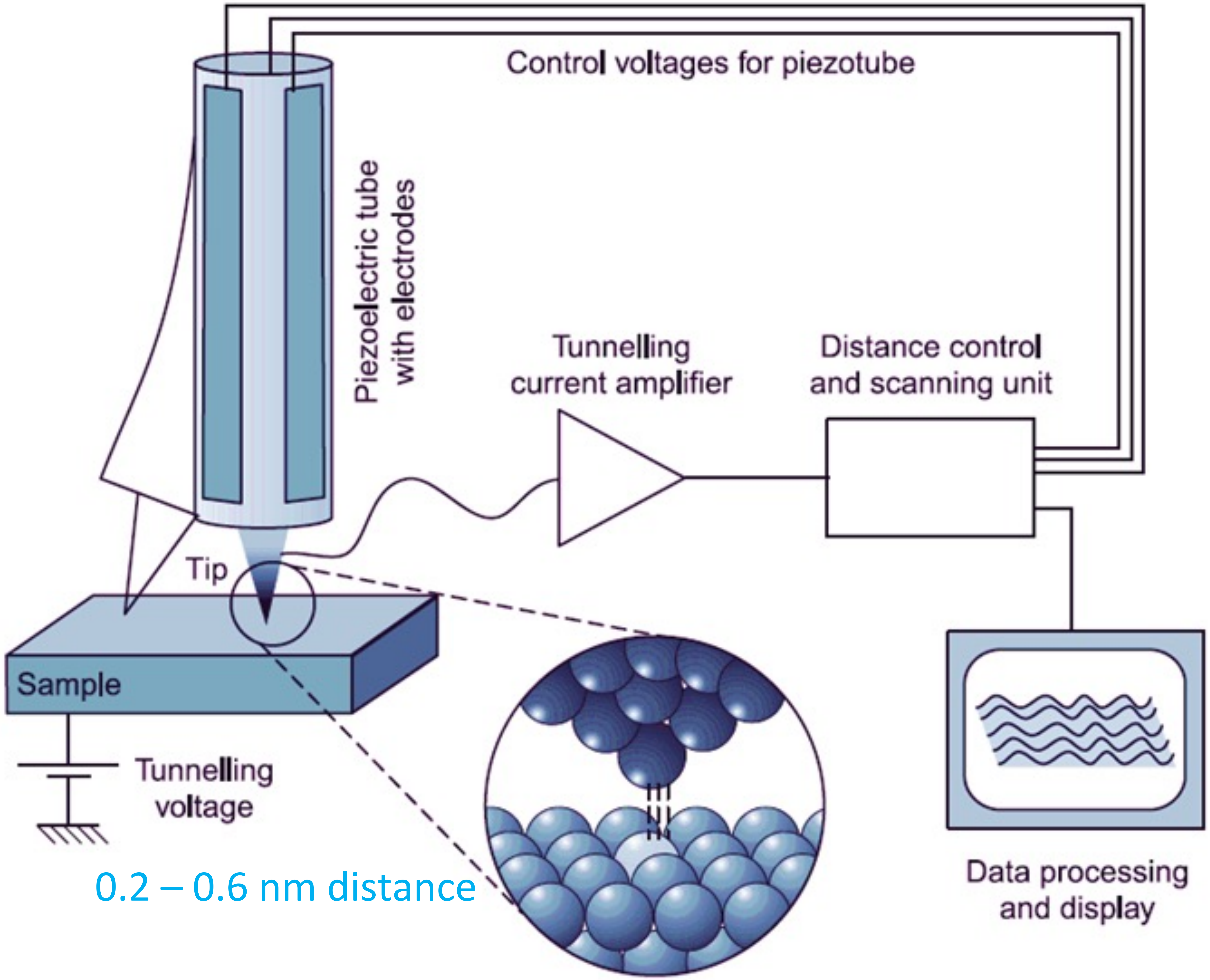
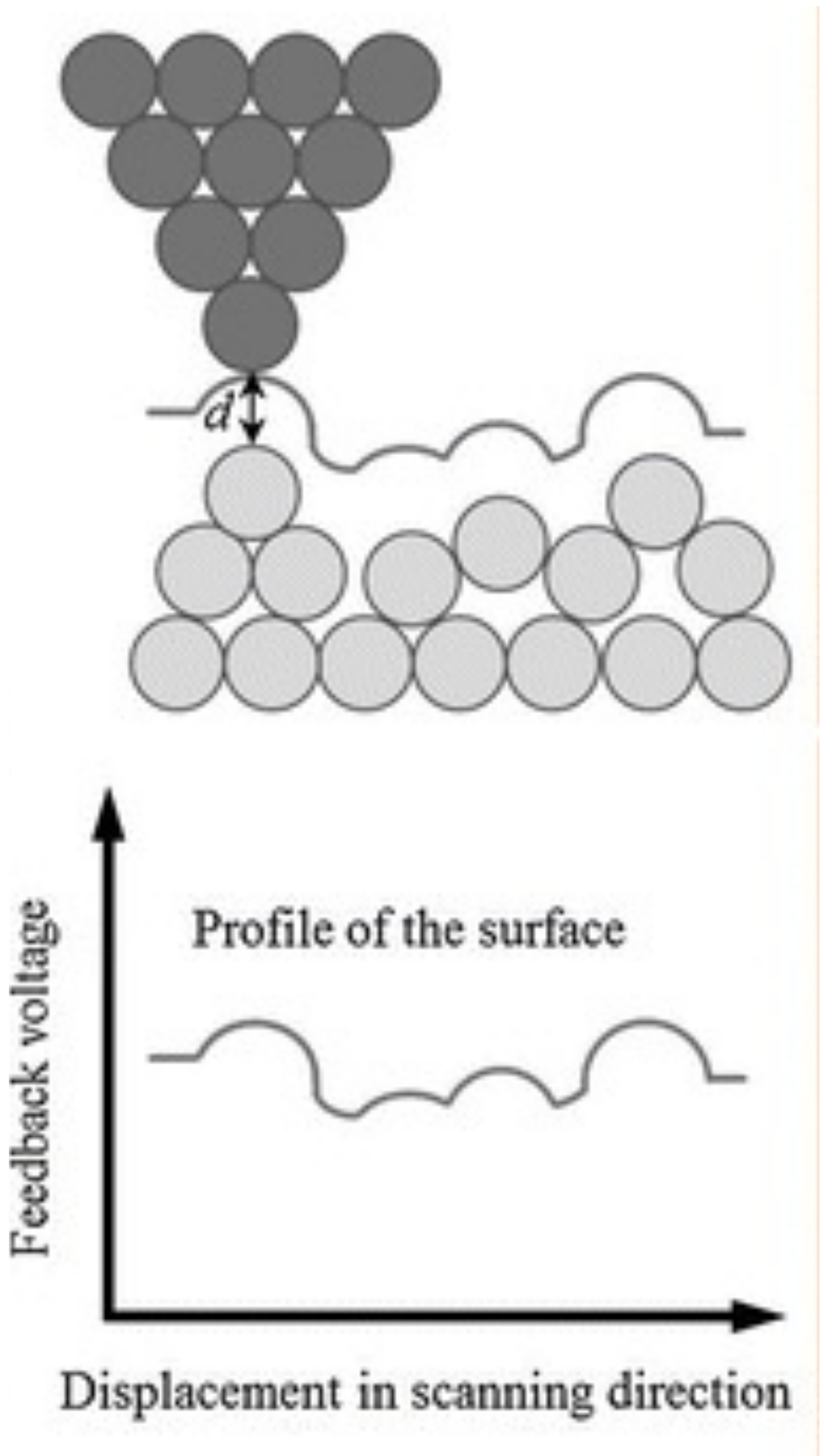
STM Uses a Tunneling Current to Map Atoms on Surfaces

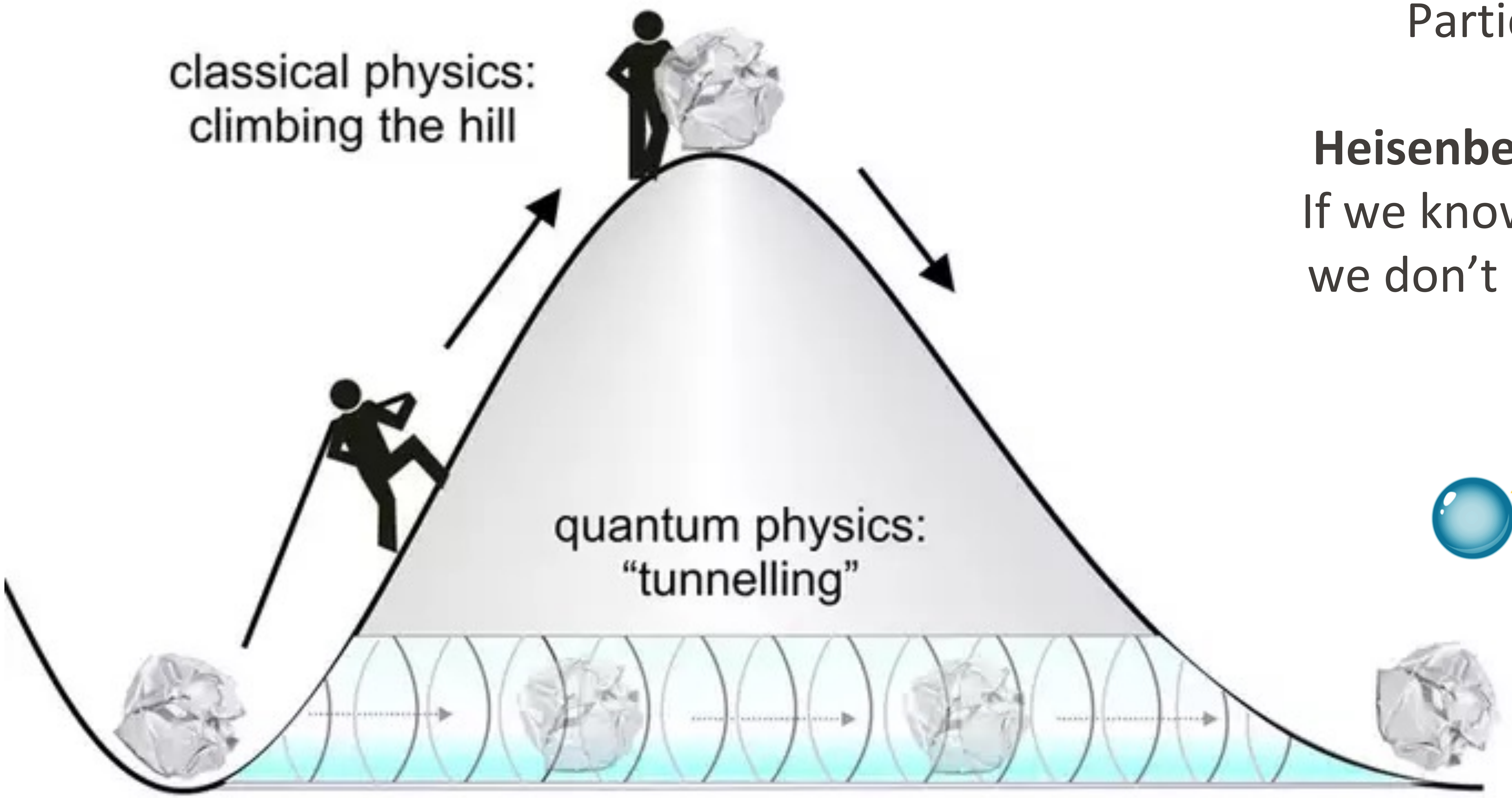


0.2 – 0.6 nm distance



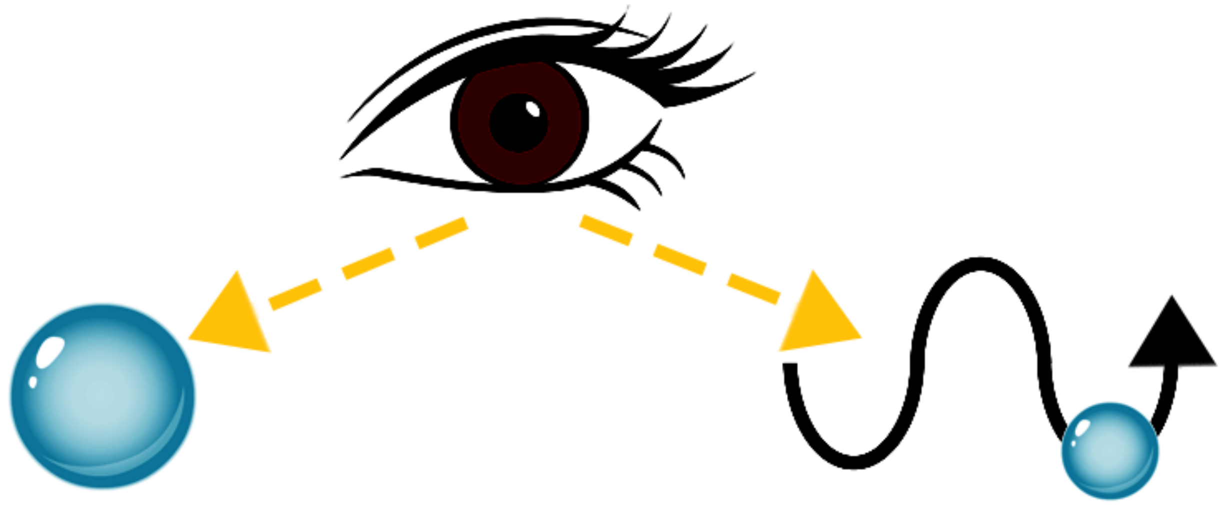
Source: Wikipedia

What is Quantum Tunneling?



Particles can act as waves

Heisenberg Uncertainty Principle:
If we know a particle’s momentum, we don’t know it’s precise position



MAX-PLANCK-GESELLSCHAFT

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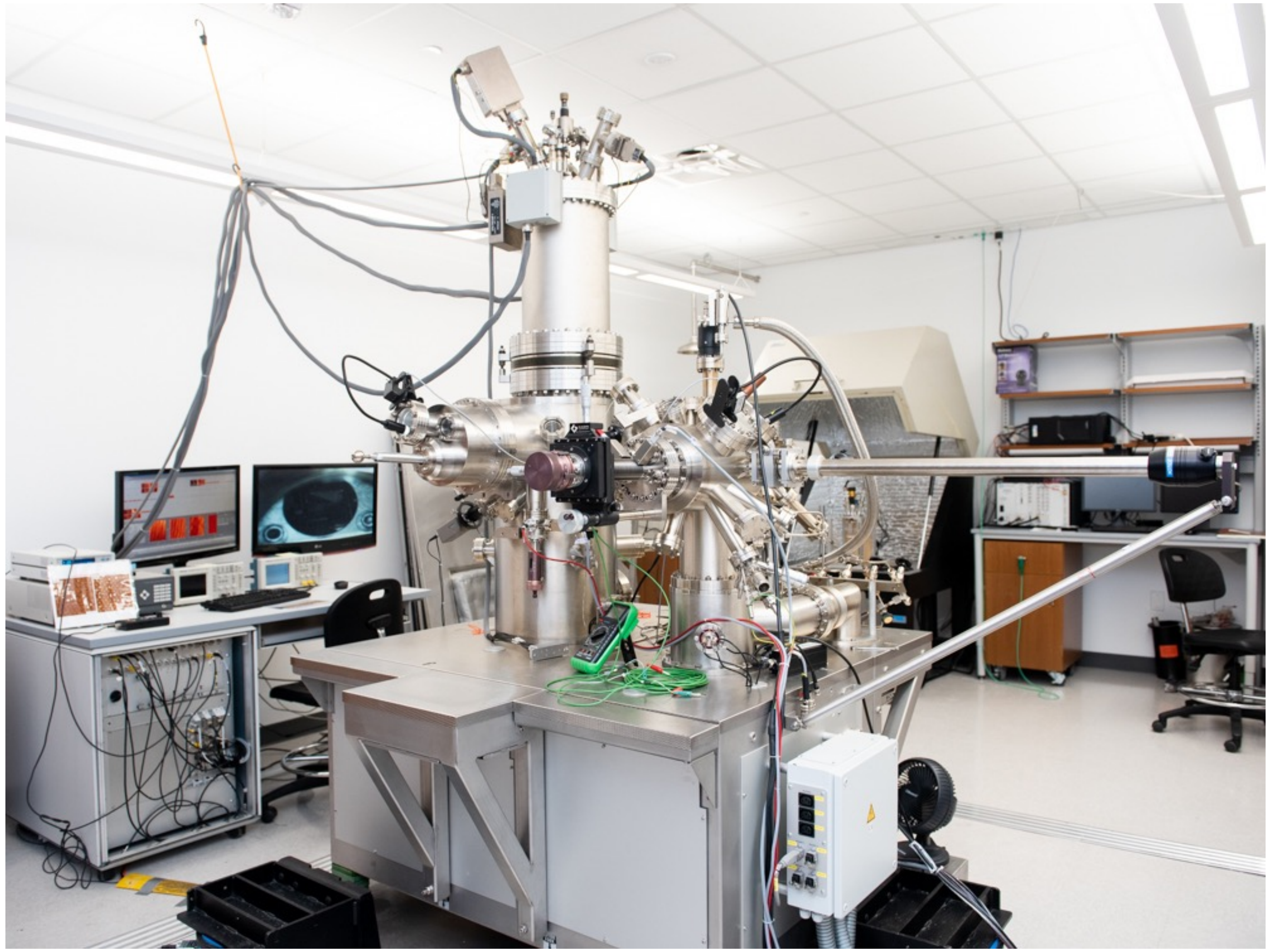
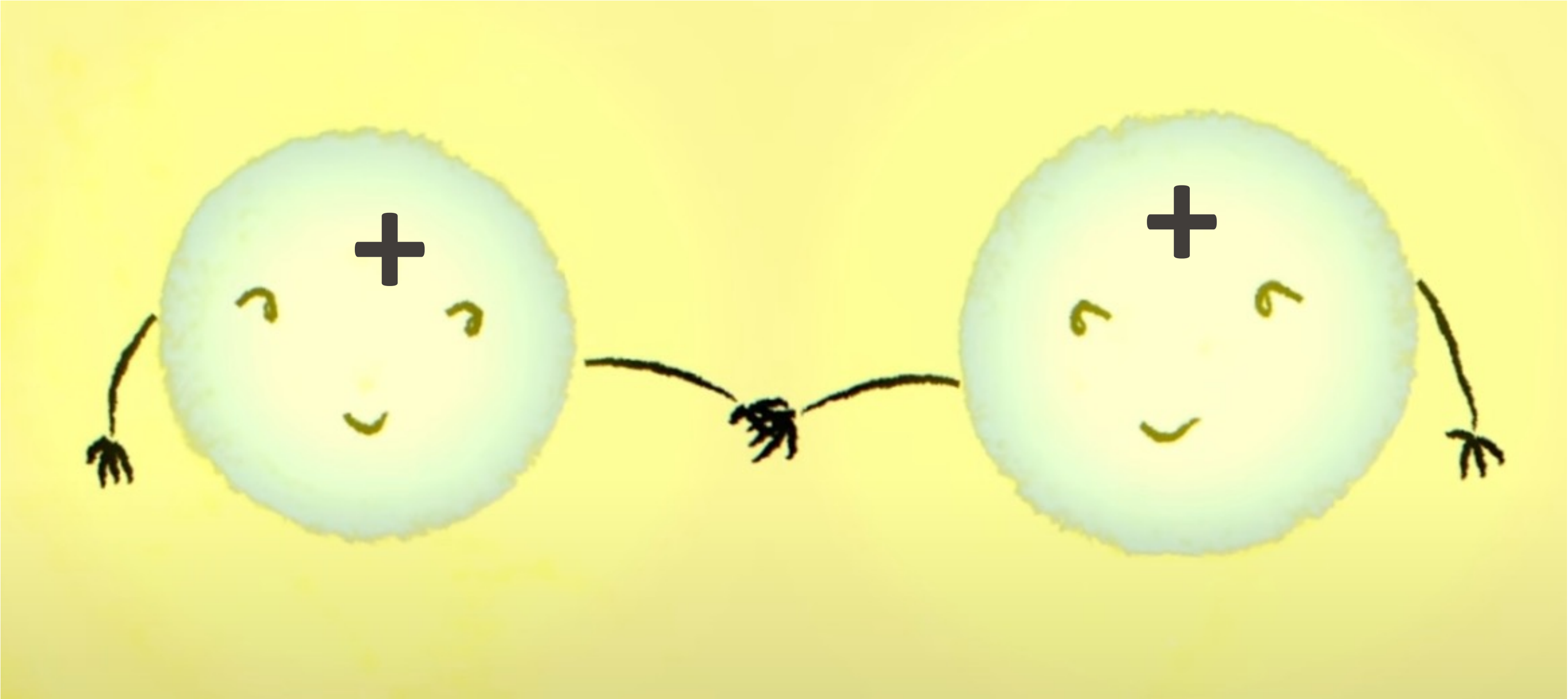
How is Quantum Tunneling Relevant in Our Lives?



Nuclear fusion of hydrogen atoms to form helium

Overcoming repulsion shouldn't be possible



Quantum tunneling
1 in a trillion encounters

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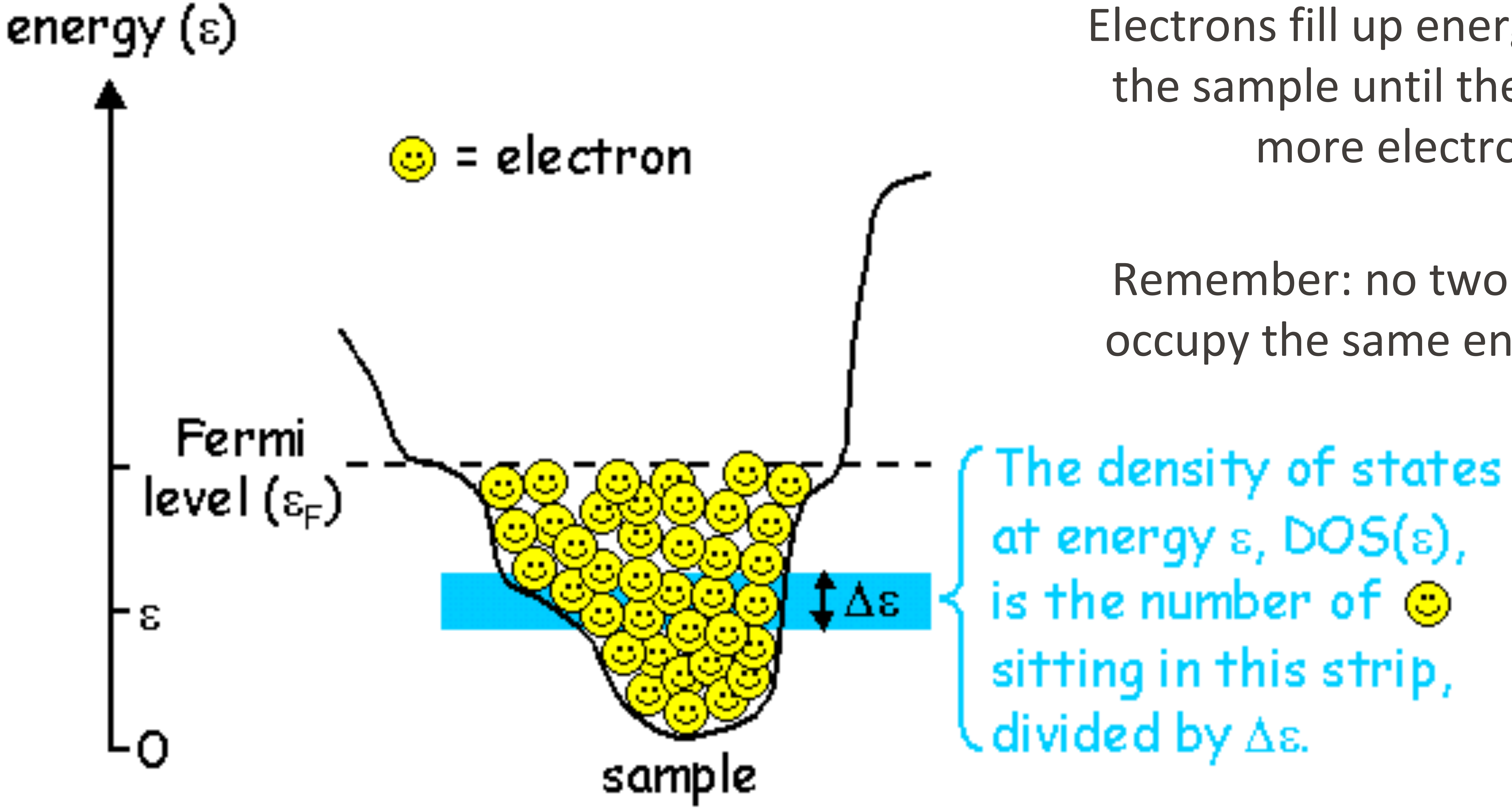
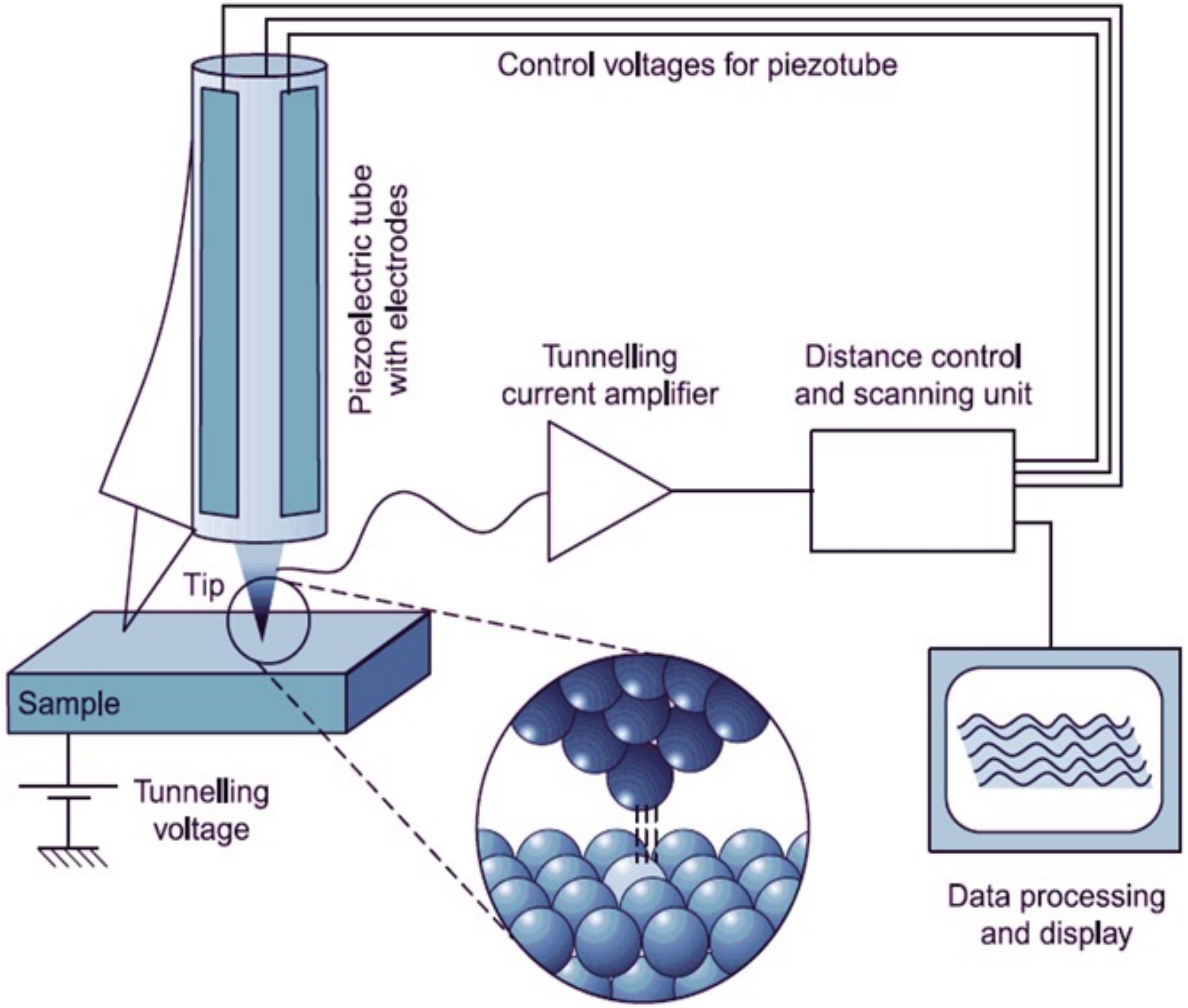
What is a Tunneling Current that Enables STM?



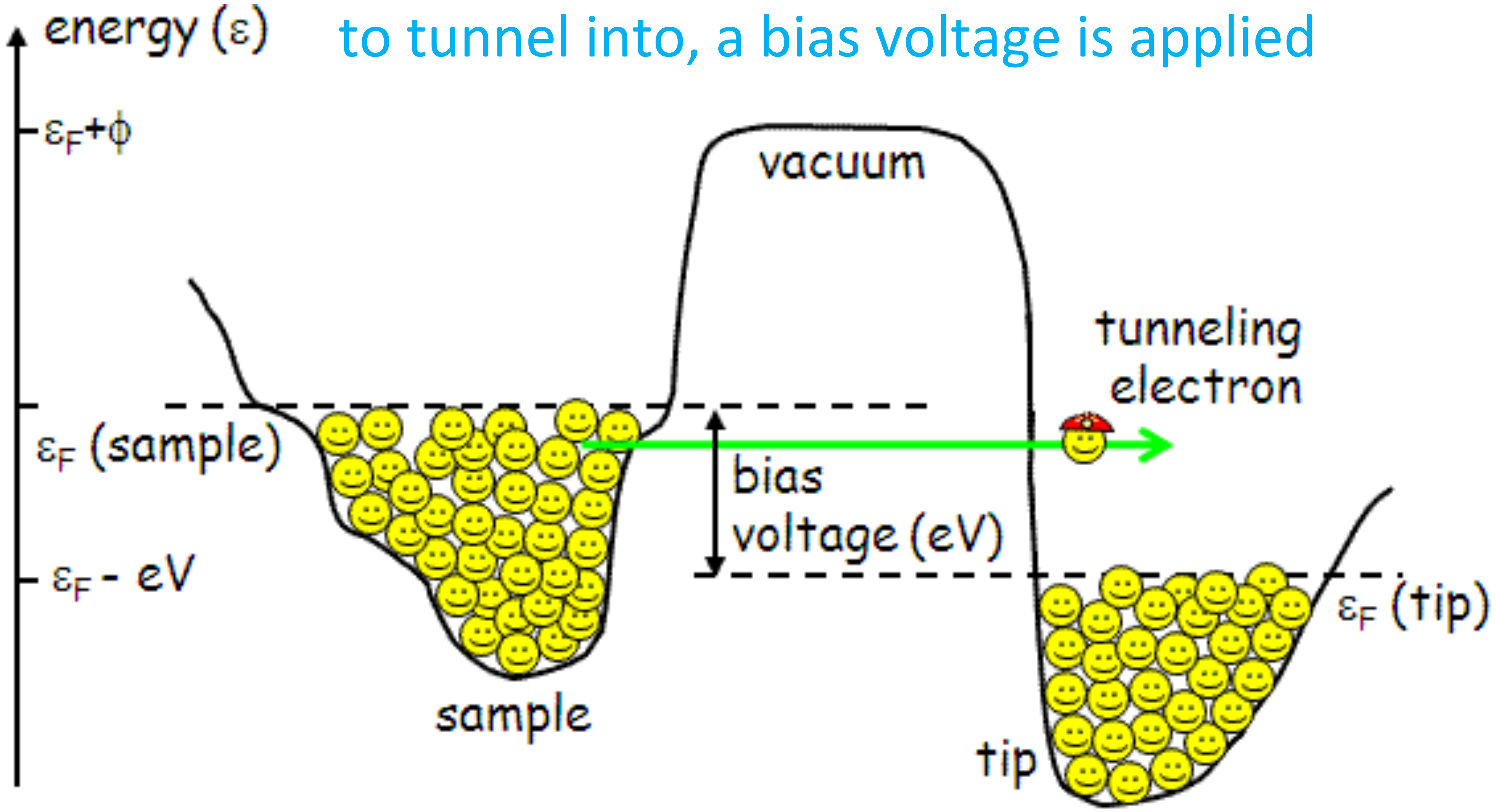
Electrons fill up energy valley in the sample until there are no more electrons

Remember: no two electrons occupy the same energy state

What is a Tunneling Current that Enables STM?



To create empty states for electrons to tunnel into, a bias voltage is applied



Tunneling current proportional to density of states in sample

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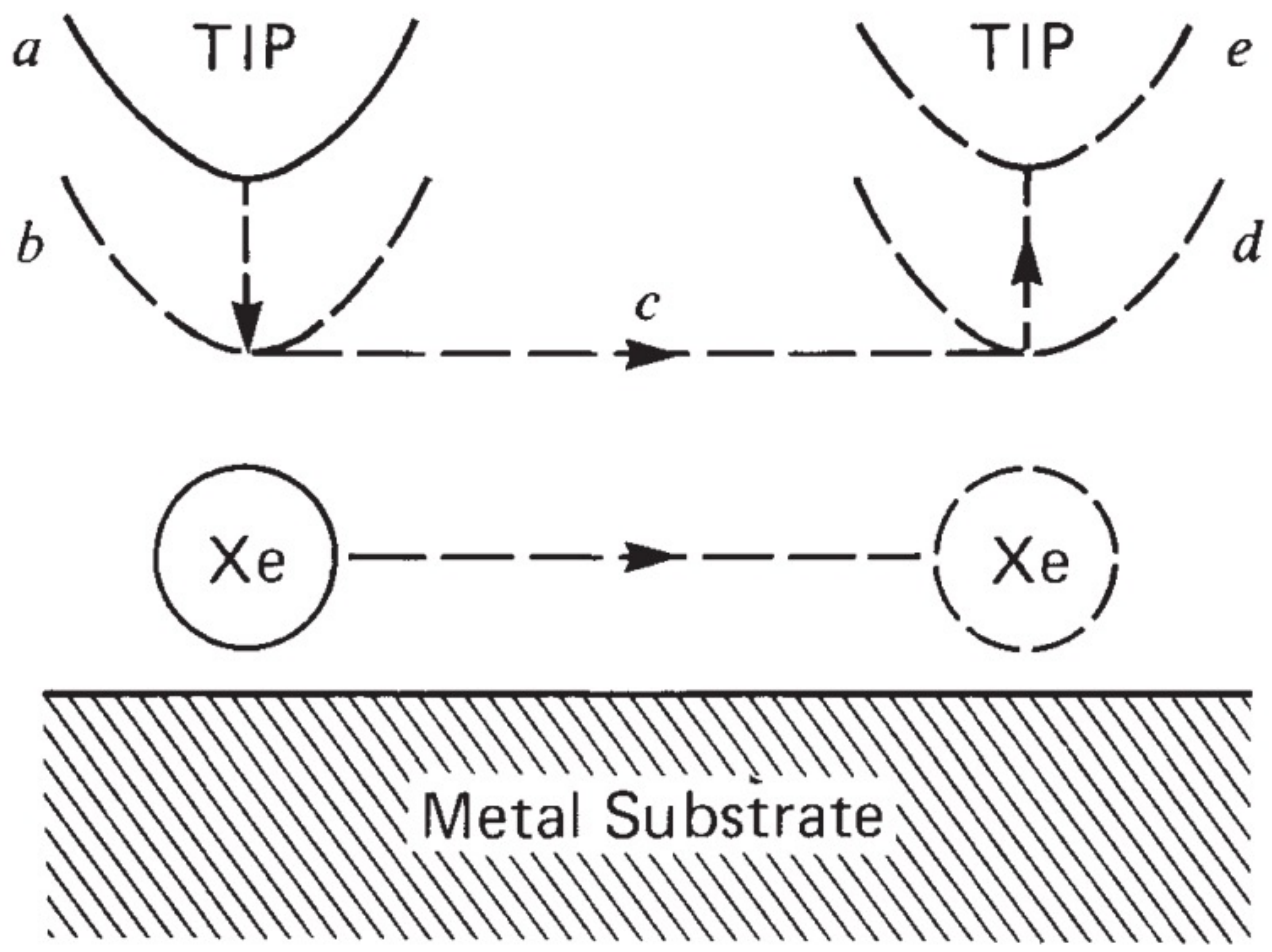
The Potential to Manipulate Atoms at the Nanoscale

Positioning single atoms with a scanning tunnelling microscope

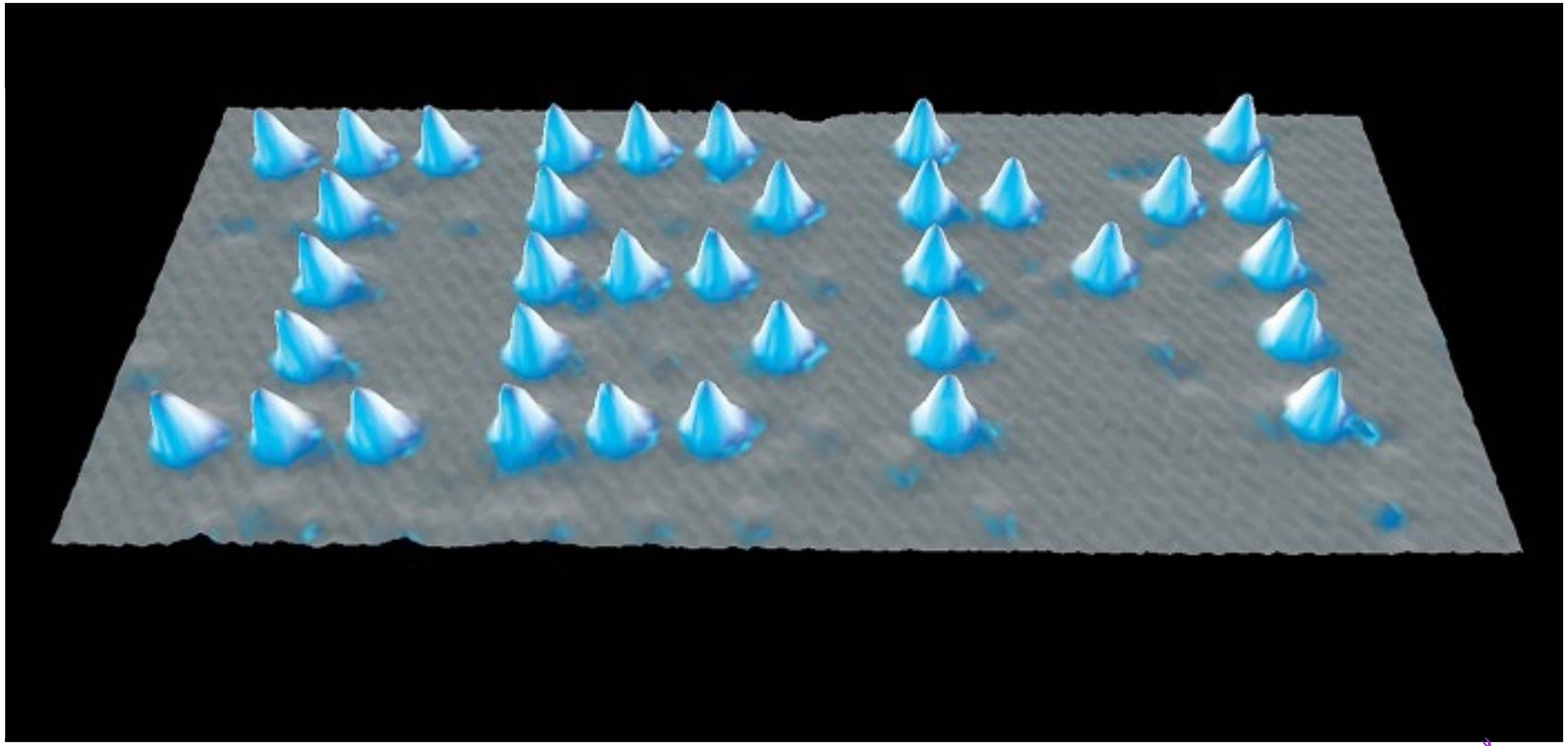
NATURE · VOL 344 · 5 APRIL 1990

D. M. Eigler & E. K. Schweizer*

IBM Research Division, Almaden Research Center, 650 Harry Rd, San Jose, California 95120, USA



Nickel (110)



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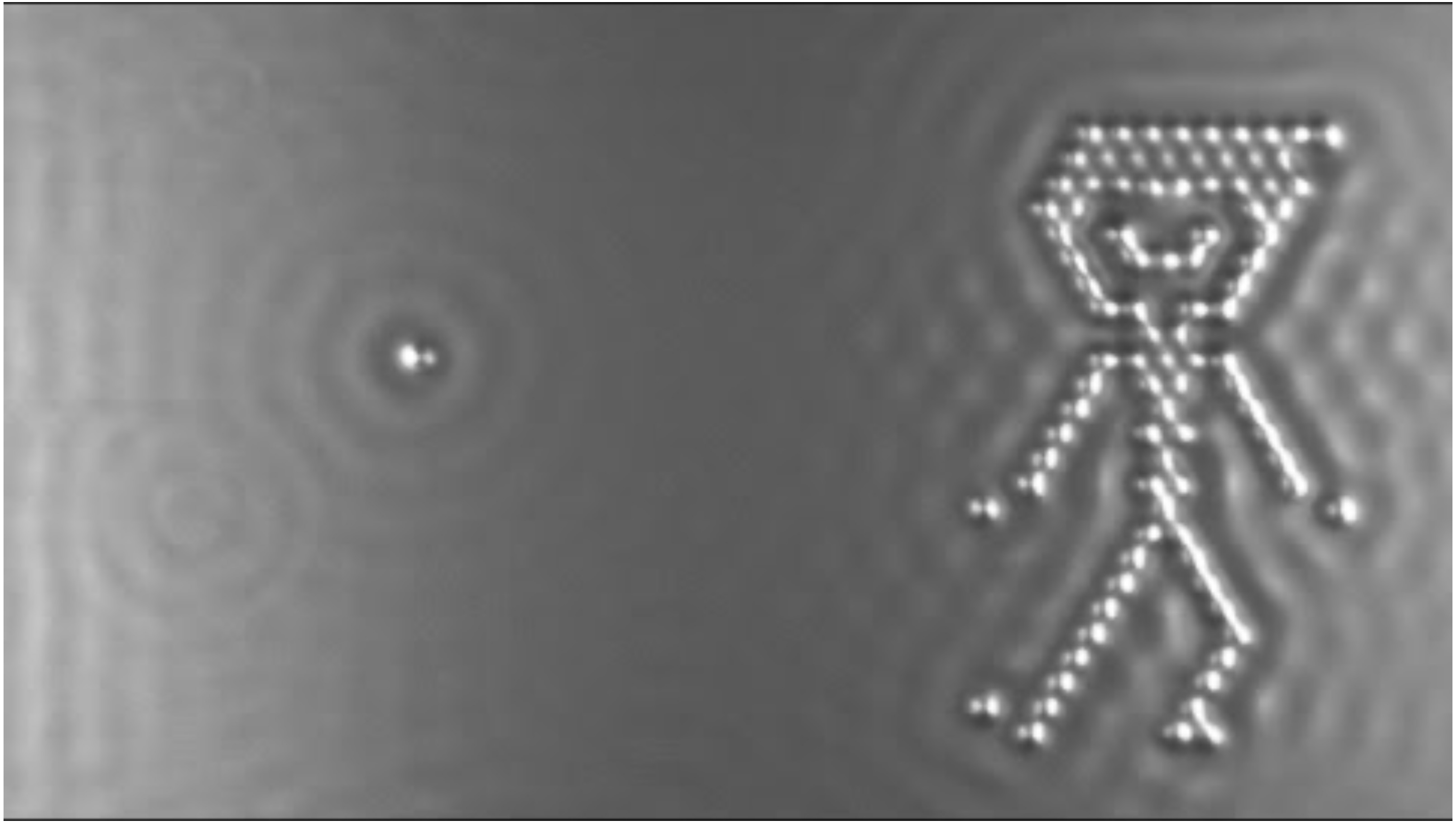
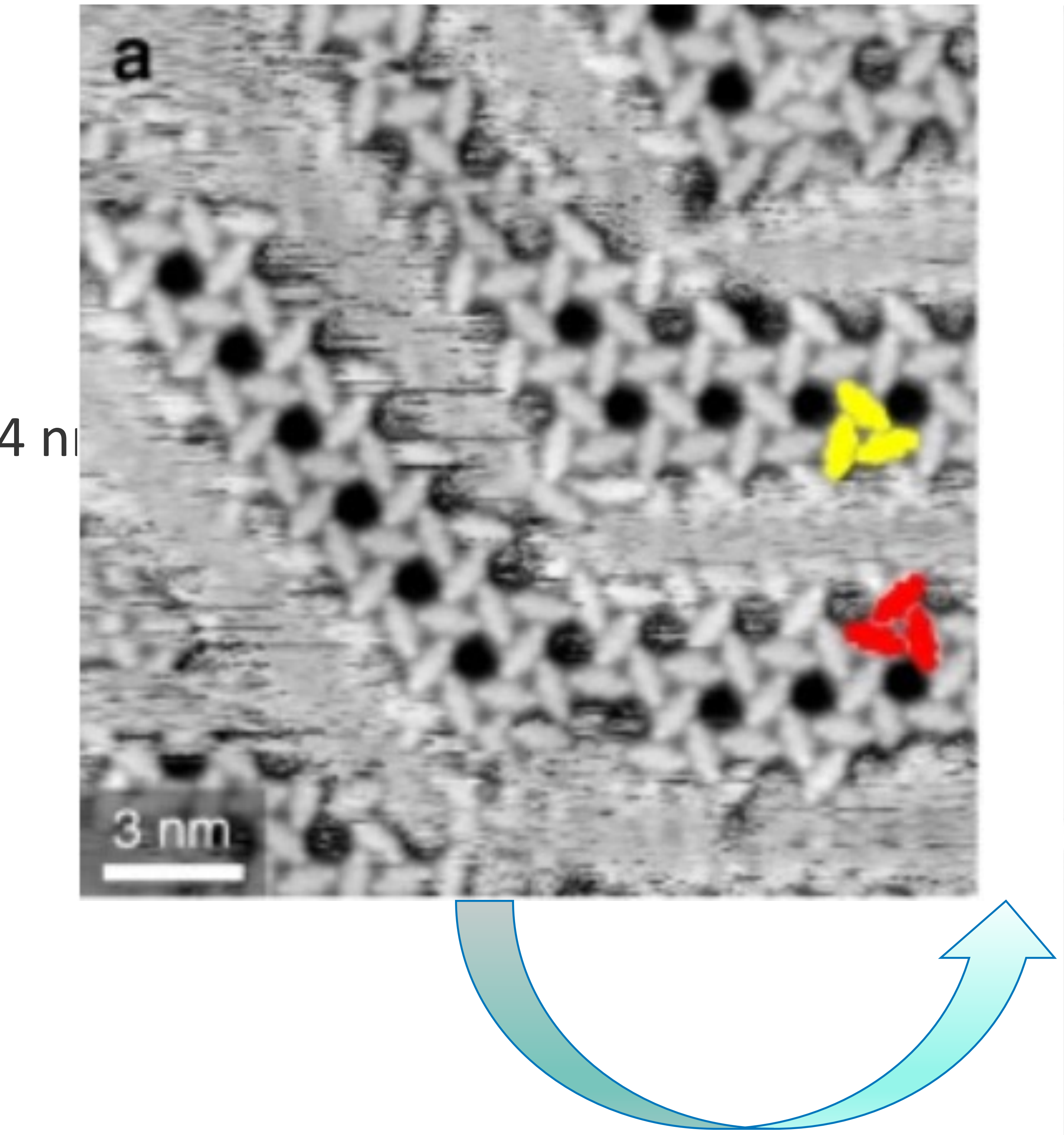
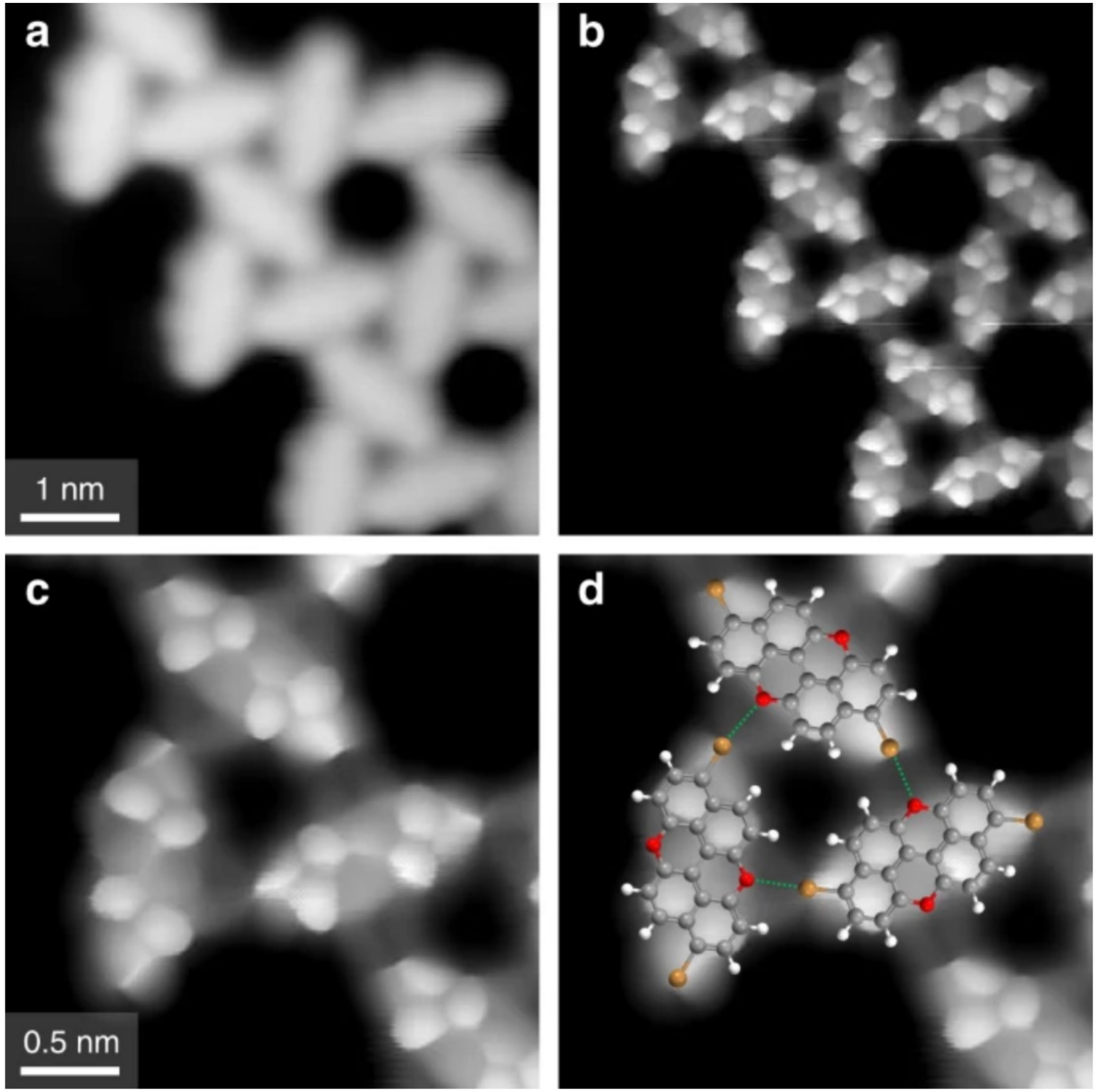
The World's Smallest Movie by IBM



The Power and Limitations of STM



Predicting intermolecular interactions with high-resolution STM



Lawrence *et al.* | *Nat. Commun.*| 2020

High resolution

Requires UHV and low temp.

Only conducting surfaces

Slow scanning

Sensitive to vibration

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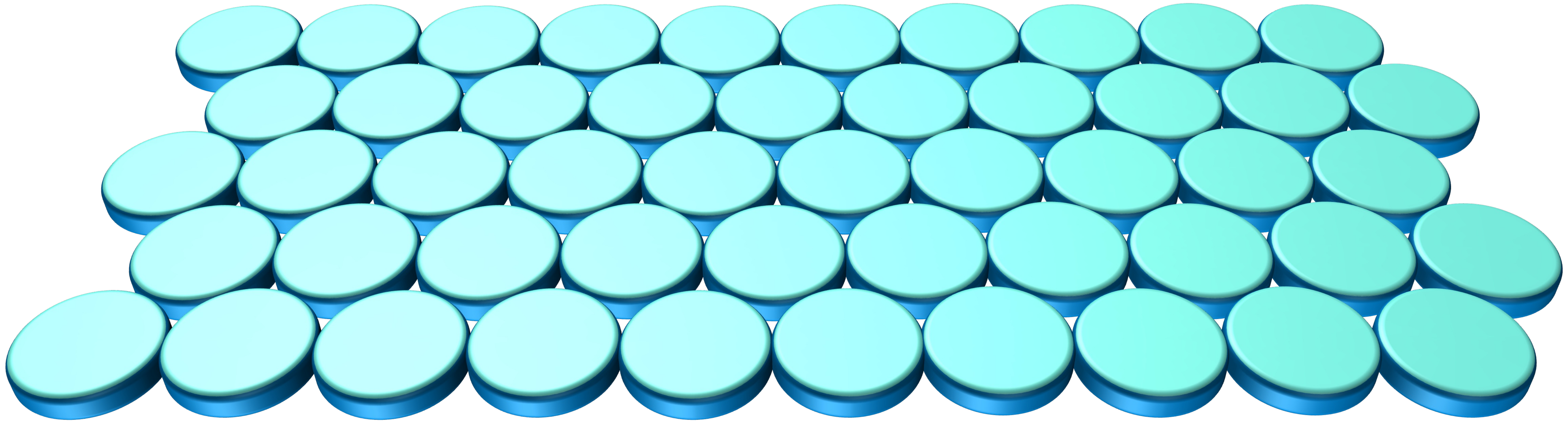
Ordered, Pristine Surfaces Do Not Last Long

Why Contamination on Surfaces is a Problem

Catalysis | **Biosensing** | **Energy storage**



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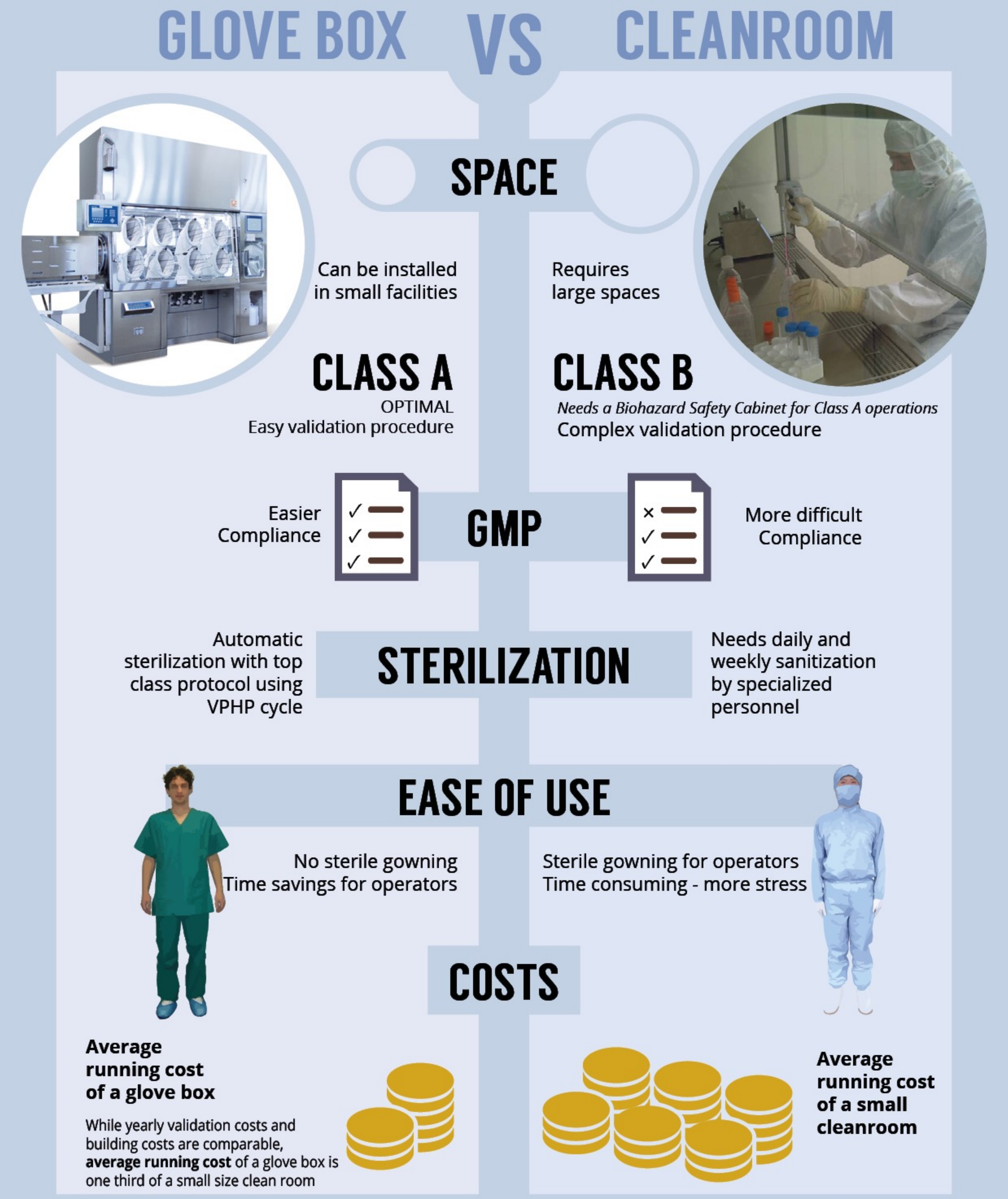
Controlled Environments to Limit Airborne Contaminants



COMECER an ATS company

Industries/applications

Pharmaceuticals

Biotechnology

Medical Devices

Nanotechnology

Semiconductor & Electronics

Aerospace

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Cleanroom: Controlled Environment to Limit Airborne Contaminants

Class	Maximum Particles/m³						FED STD 209E equivalent
	>0.1 um	>0.2 um	>0.3 um	>0.5 um	>1 um	>5 um	
ISO 1	10	2					
ISO 2	100	24	10	4			
ISO 3	1,000	237	102	35	8		Class 1
ISO 4	10,000	2,370	1,020	352	83		Class 10
ISO 5	100,000	23,700	10,200	3,520	832	29	Class 100
ISO 6	1,000,000	237,000	102,000	35,200	8,320	293	Class 1,000
ISO 7				352,000	83,200	2,930	Class 10,000
ISO 8				3,520,000	832,000	29,300	Class 100,000
ISO 9				35,200,000	8,320,000	293,000	Room Air

EPFL Center of MicroNano Technology (CMi)

EPFL CMi Cleanroom in the BM Building

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Surface Cleaning Hierarchy

Scale

Macroscopic (bulk cleaning)
Soap, detergents, sonication

- Visible dirt, grease, particles
- Leaves thin residues/adsorbed films

Chemicals/flame annealing
Piranha, acids, bases

- Organic layers, oxides
- Leaves chemical residues, roughens surface

Surface activation
Plasma/UV-ozone

- Hydrocarbons, polymers, residues
- Does not restore crystallinity, limited depth

Atomic-scale
Ion sputtering

- All adsorbates, damaged layers
- Expensive, requires UHV

Obtaining Clean Surfaces with Flame Annealing/Chemicals

Flame annealing of substrates

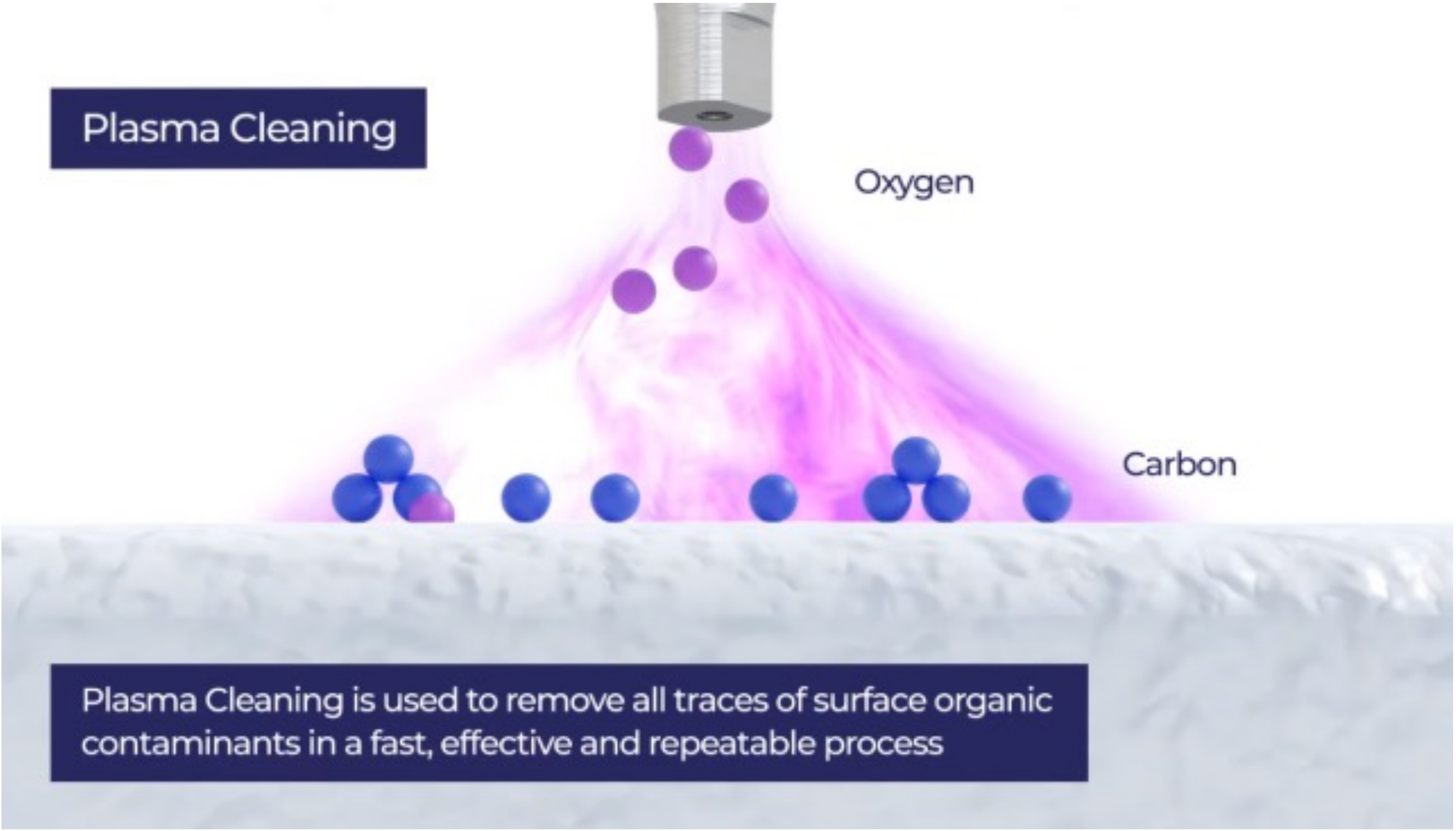
For samples covered by an oxide layer, which are not stable at high temperatures

Piranha cleaning

Concentrated sulfuric acid and hydrogen peroxide

Obtaining Clean Surfaces with Plasma Cleaning

Plasma cleaning to remove surface contaminants



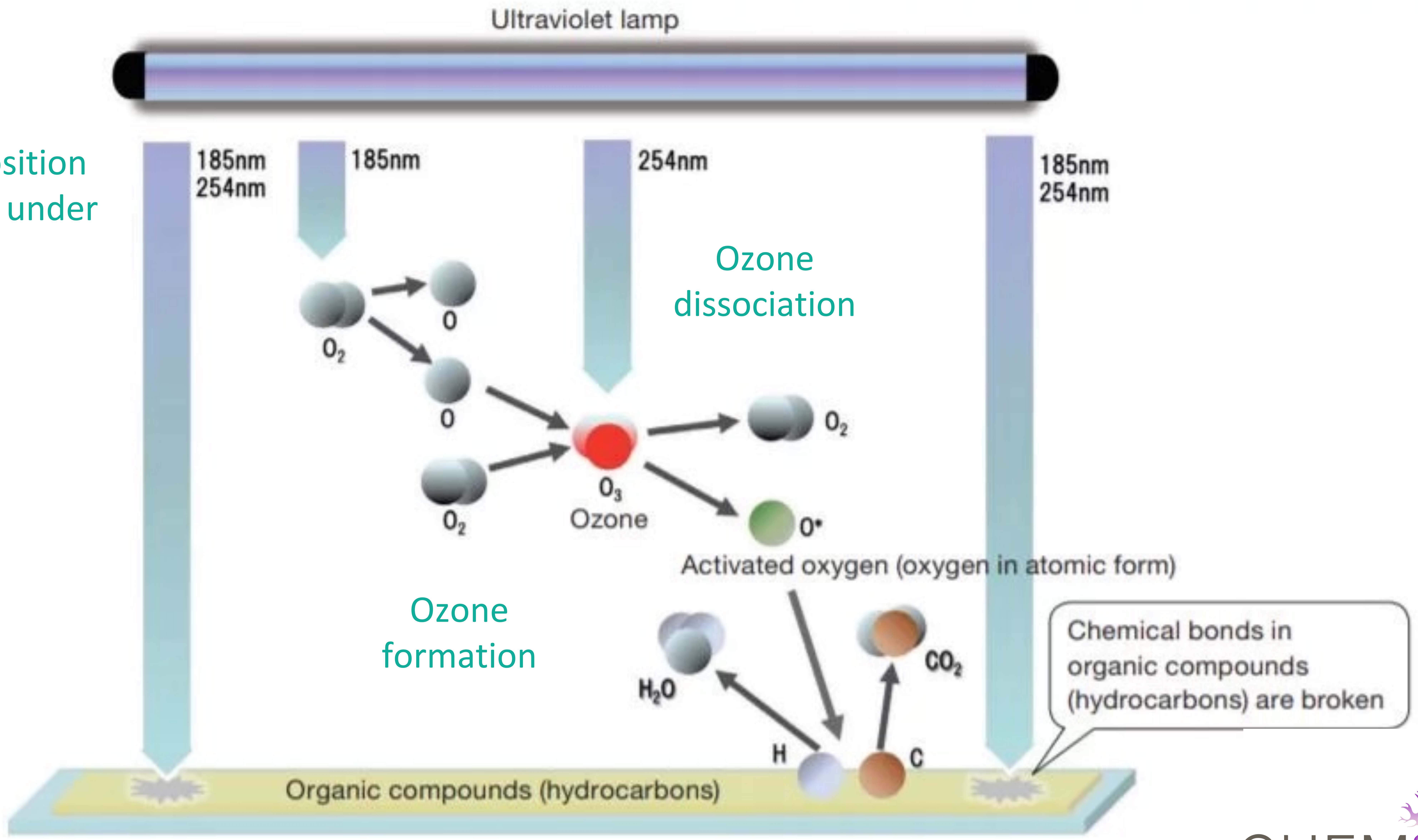
Plasma is generated by applying an electric field to a gas in a vacuum chamber

Oxygen radicals interact with carbon-based (organic) contaminants, breaking down into volatile compounds such as CO_2 and H_2O

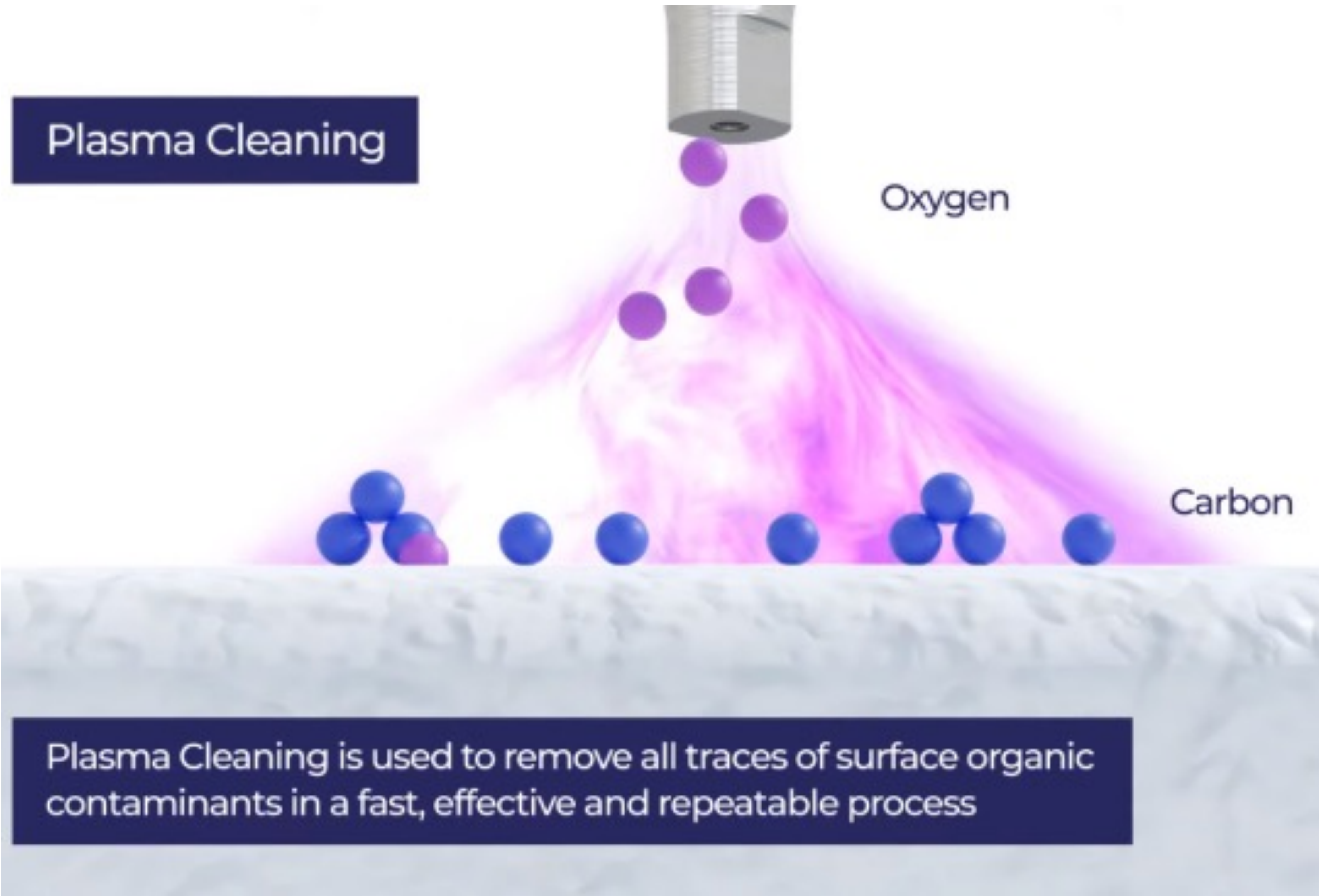
Reaction products often in gas form are carried away by vacuum system

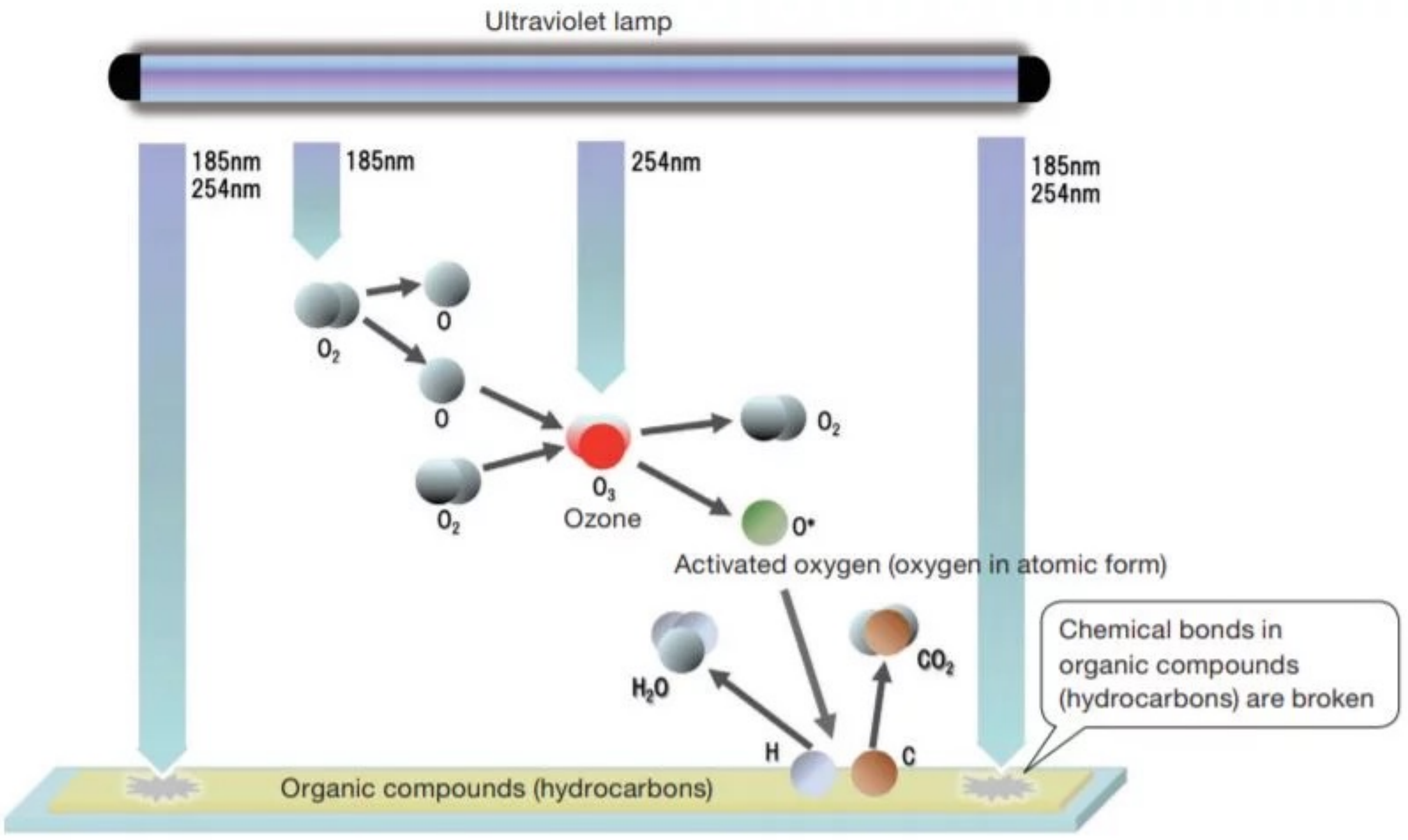
Obtaining Clean Surfaces with UV Ozone Cleaning

Direct decomposition of hydrocarbons under UV



Comparing Plasma *vs.* UV Ozone Cleaning





Energy source	Electrical discharge	UV light (185, 254 nm)
Speed	Fast (seconds – minutes)	Slow (minutes – hours)
Aggressiveness	More aggressive, can etch surface	Gentler treatment, mainly oxidizes

STInstruments
When Technology Matters

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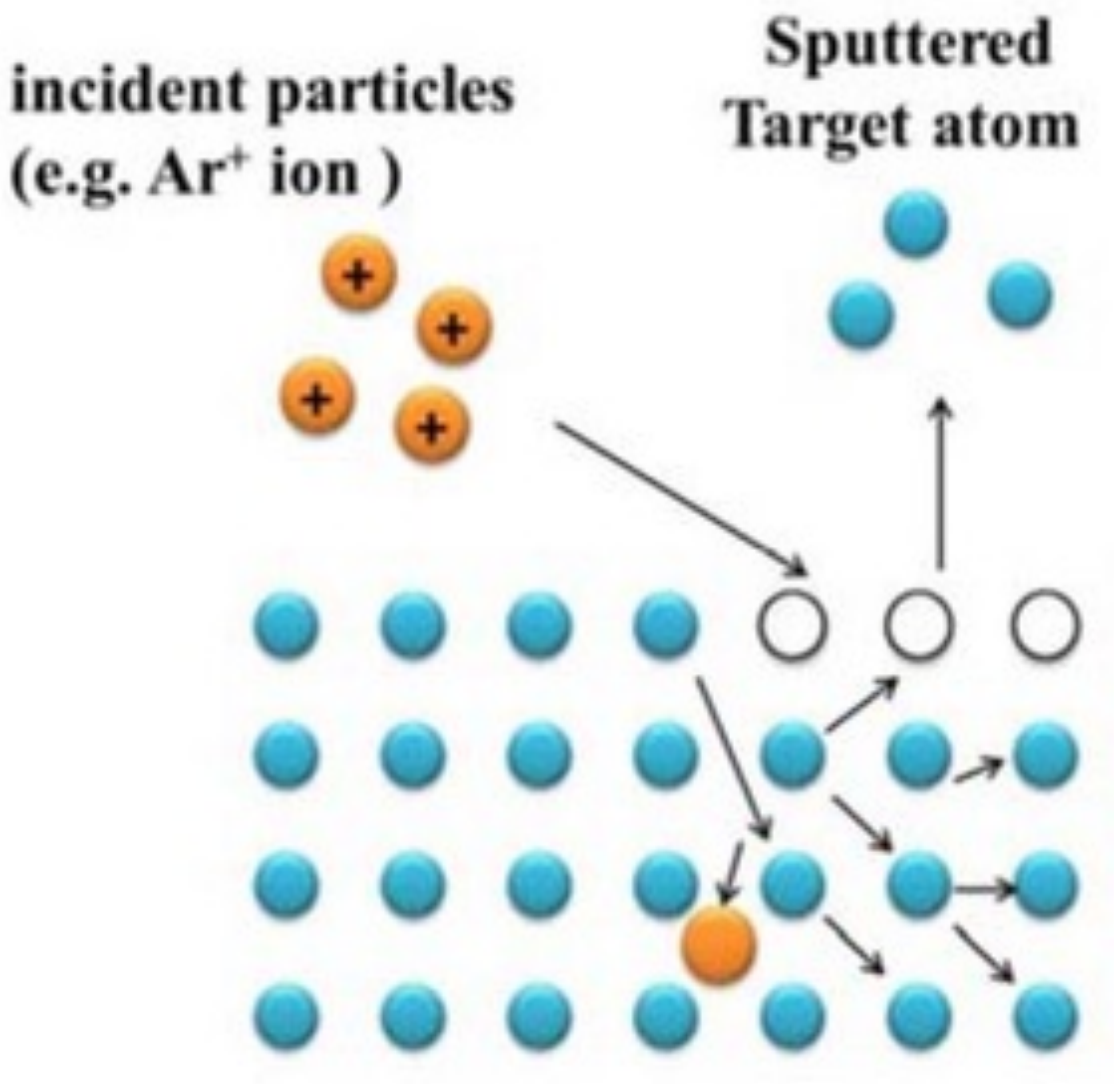
Obtaining Clean Surfaces with Ion Sputtering

Argon sputtering removes the top layer of a sample by sputtering with Ar ions, with subsequent heating to remove surface defects



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Creating New Surfaces Rather than Cleaning

Fracture of a material: possible to obtain pure and very smooth surfaces (mica)

Newly cleaved surface atomically flat and clean

No solvents, plasmas, or chemicals required

Only works for materials with good cleavage planes (mica, graphine, silicon)

Clean surface contaminated if left in air

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Key Takeaways

Contamination on surfaces affect many areas of research

We can tackle contamination in controlled environments like the cleanroom

There are different methods to clean the surface from the macroscale to atomic-scale

It’s important you can choose how to clean your surface depending on the contamination

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Summary of Today's Class

- Adsorption *vs.* Absorption
- Physisorption *vs.* Chemisorption
- Crystal lattice of substrates order adsorbates
- STM can visualize surfaces at atomic resolution
- How to tackle the challenge of contamination

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https://www.epfl.ch/labs/chemina/