EPFL
École polytechnique fédérale de Lausanne

Neuro X Institute

CHEMINA
Laboratory of Chemical Nanotechnology

Applications
Lesson 14

MSE 304

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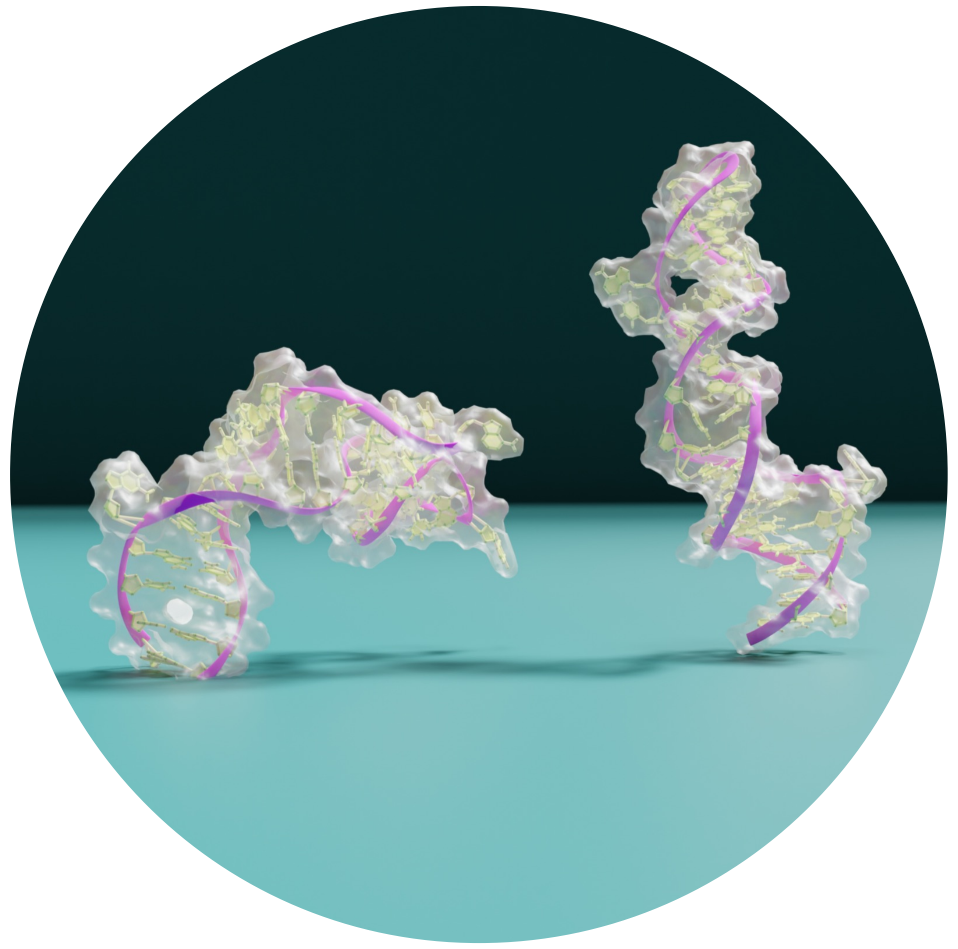
December 20th 2024



Goals We Set at the Start of the Section on Applications

- Be mesmerized by the diverse applications where surfaces & interfaces play a key role
- Observe how the fundamentals you learned in prior classes can be applied
- Recap on some basic chemistry concepts to understand surfaces & interfaces
- Learn techniques that enable characterization of surfaces & interfaces

What we recap in today's class:

- Surface Chemistry/Functionalization
- Nanoscience and Plasmonics
- Biosensors
- Catalysis
- Techniques to monitor surfaces

Diverse Applications of Surfaces & Interfaces

Catalysis

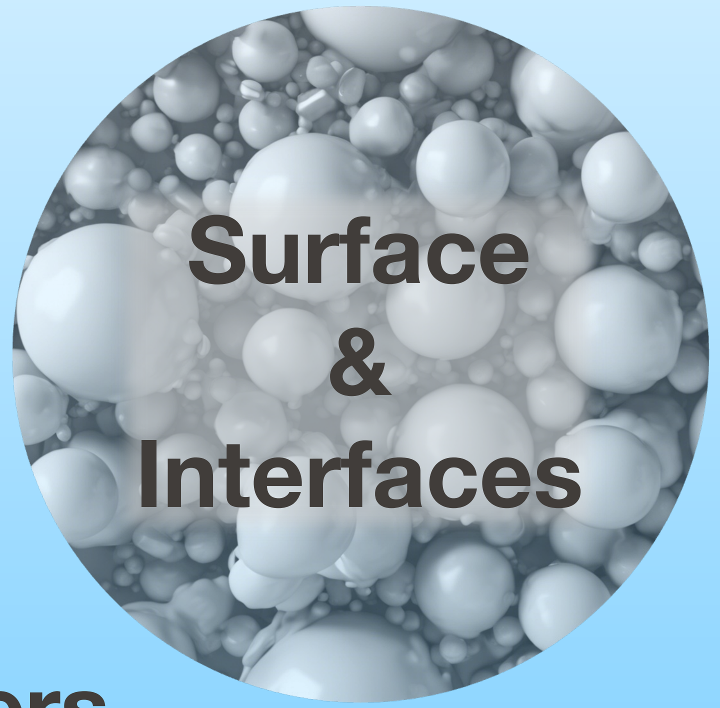
Functionalization (coatings)

Corrosion

Biosensing

semiconductors

metals



Surface & Interfaces

Integrated circuits

polymers

biomaterials

Lubrication (tribology)

Magnetic storage

Biointerfaces

Batteries

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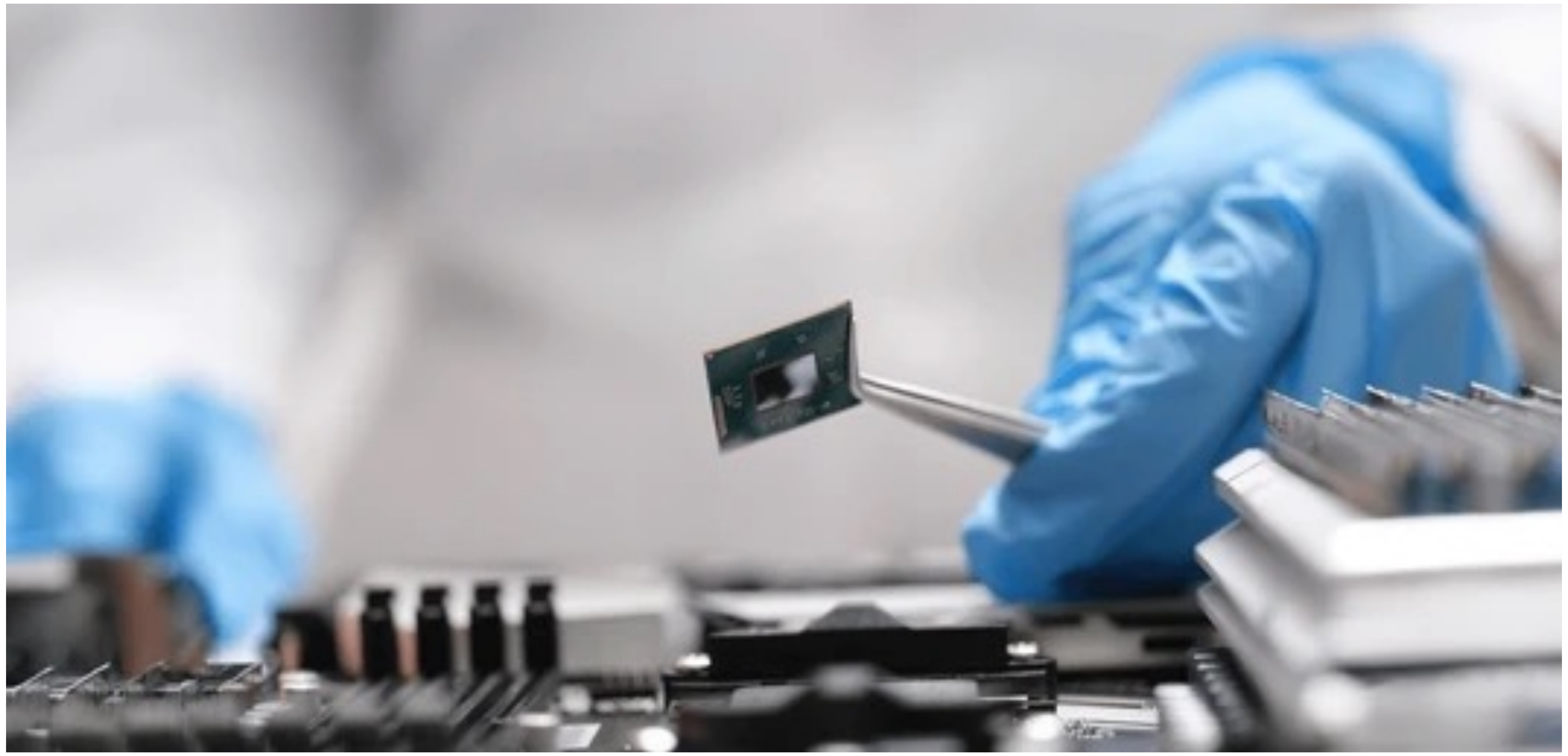
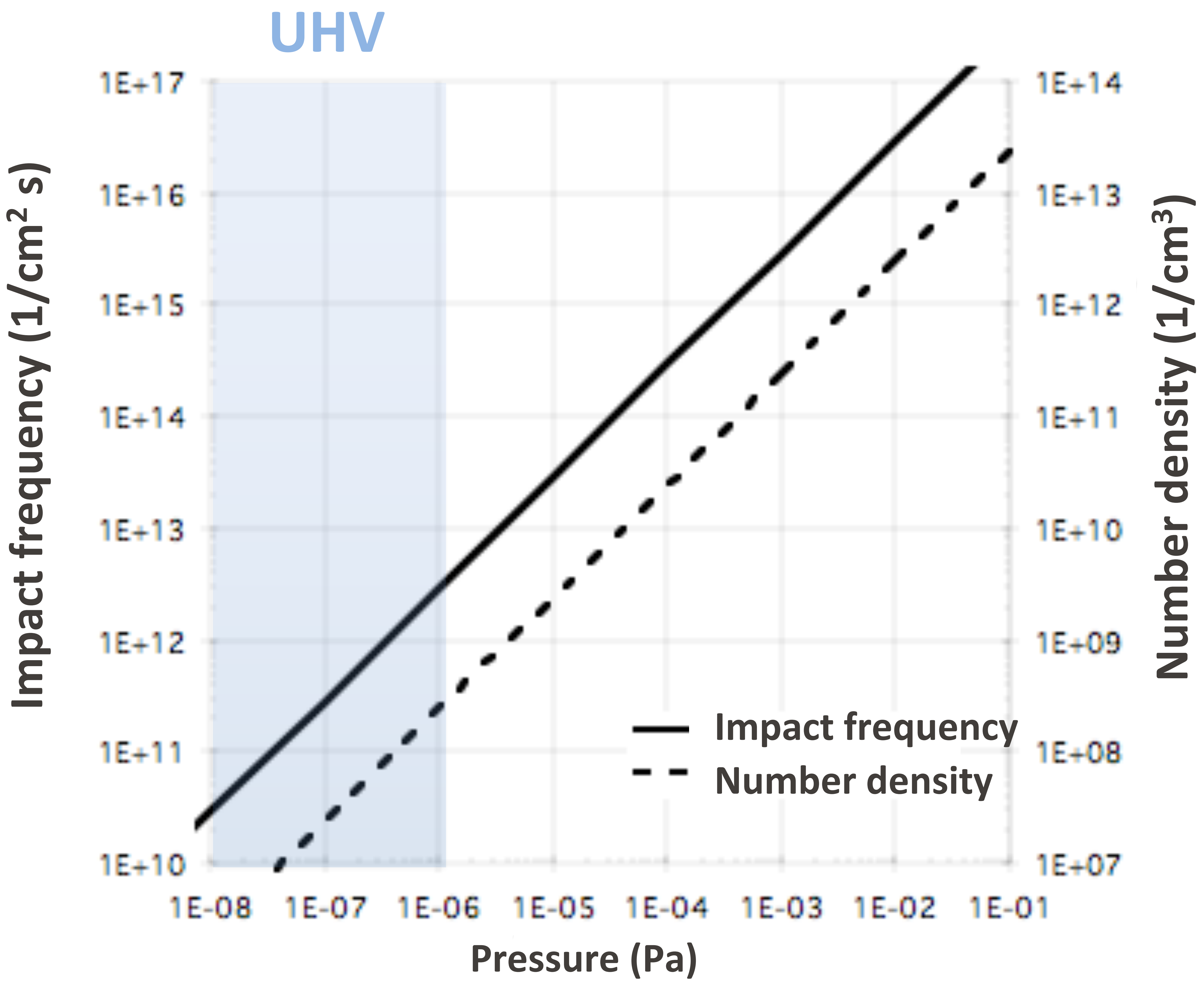
Challenge of Studying Surfaces

How can vacuum influence contamination?



Ultra High Vacuum (UHV) Needed for Ultra Clean Surfaces

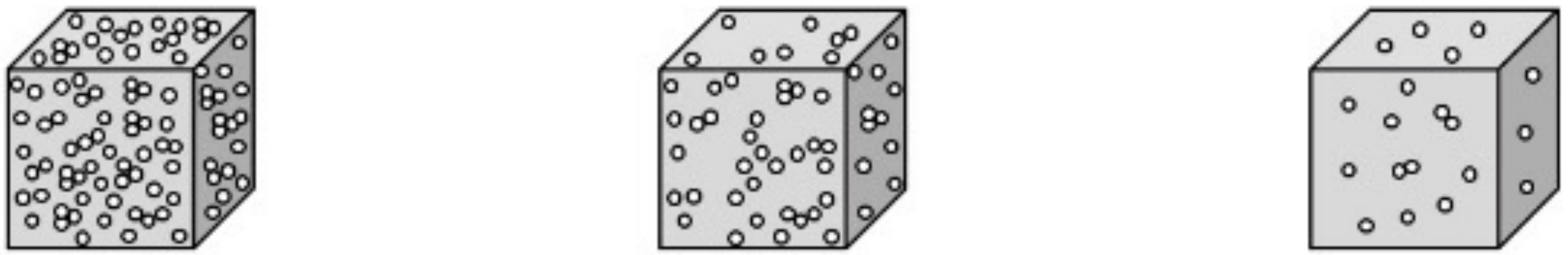
The number of impacts per second per cm^2 can only be decreased by pressure reduction



Impact frequency/unit area and number density
as a function of the pressure for an ideal gas

Vacuum Levels Significantly Impacts Monolayer Formation

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

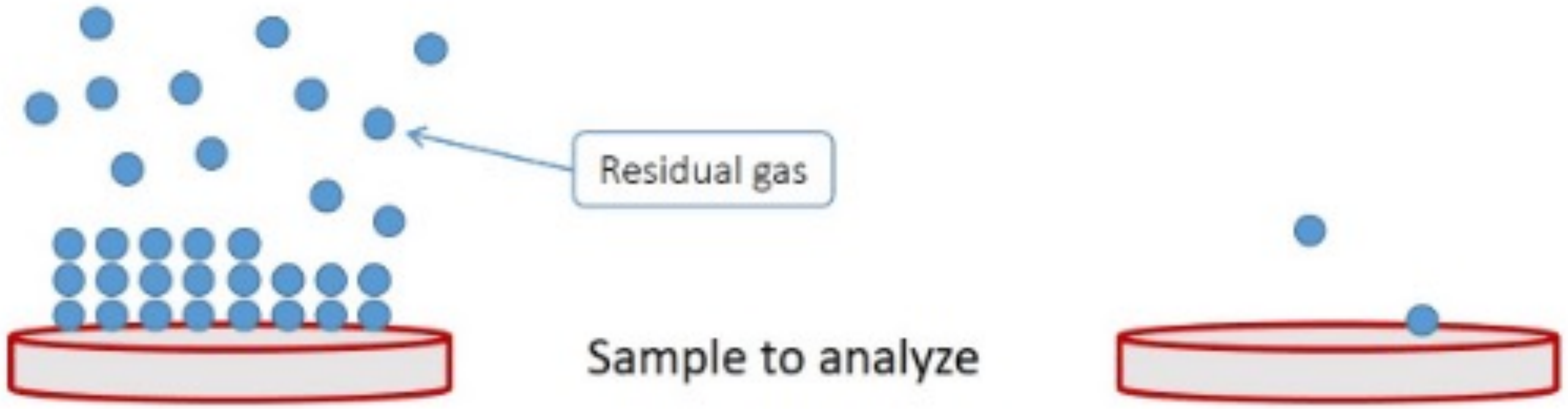


1×10^{-3} Torr	1×10^{-6} Torr	1×10^{-11} Torr
10^{13} atoms/cm^3	10^{10} atoms/cm^3	10^{5} atoms/cm^3

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

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

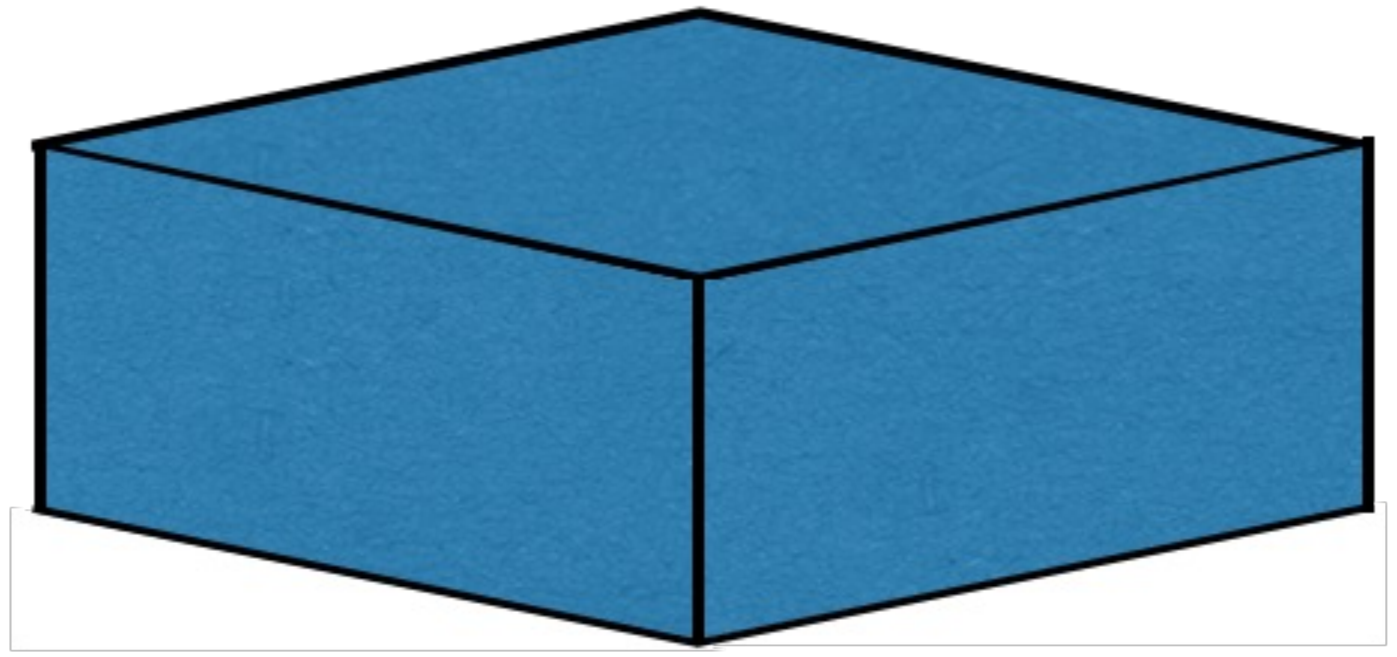
High Vacuum

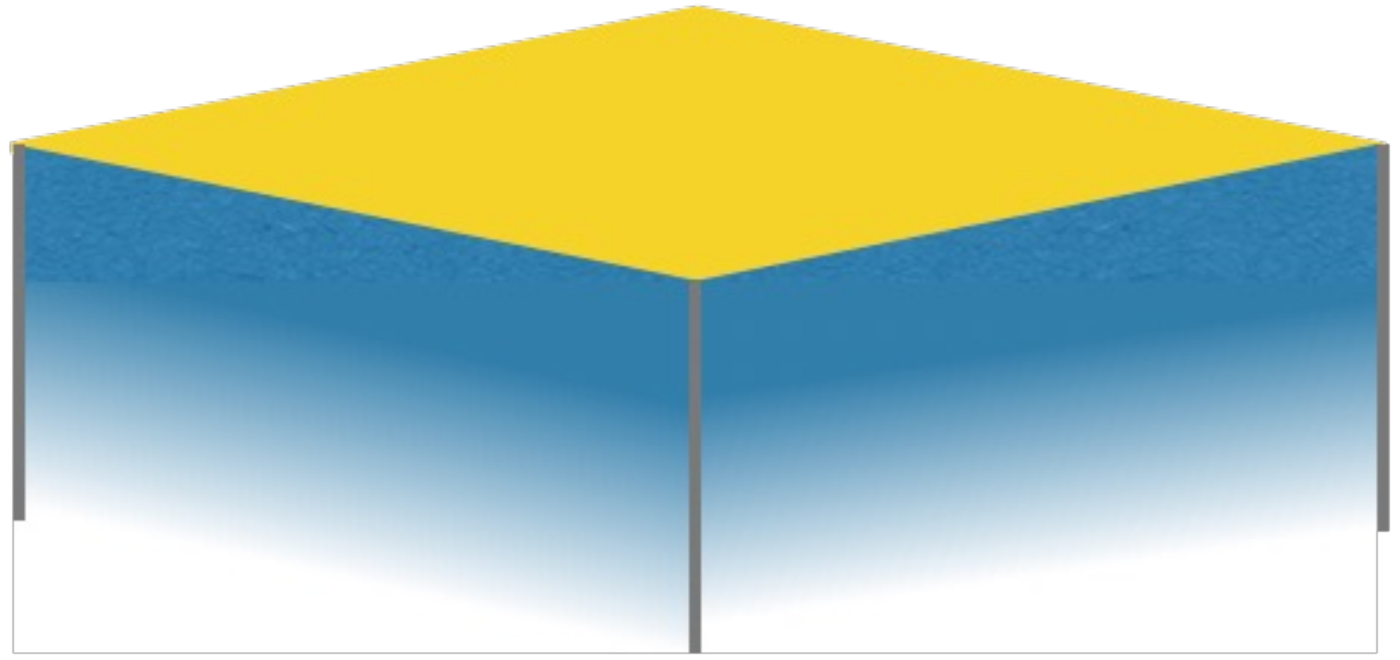


UHV

Surface Chemistry – Why Functionalize Surfaces?

The goal is to combine ideal bulk properties with ideal surface properties





Bulk Properties

Reflect behavior of atoms/molecules within interior of material

Porosity

Thermal conductivity

Electrical conductivity

Density

Elasticity

Tensile strength

Magnetism

Surface Properties

Properties unique to atoms on material's surface where they are less coordinated and experience different forces

Wettability

Biocompatibility

Corrosion resistance

Roughness

Lubricity/ease-of-cleaning

Catalytic activity

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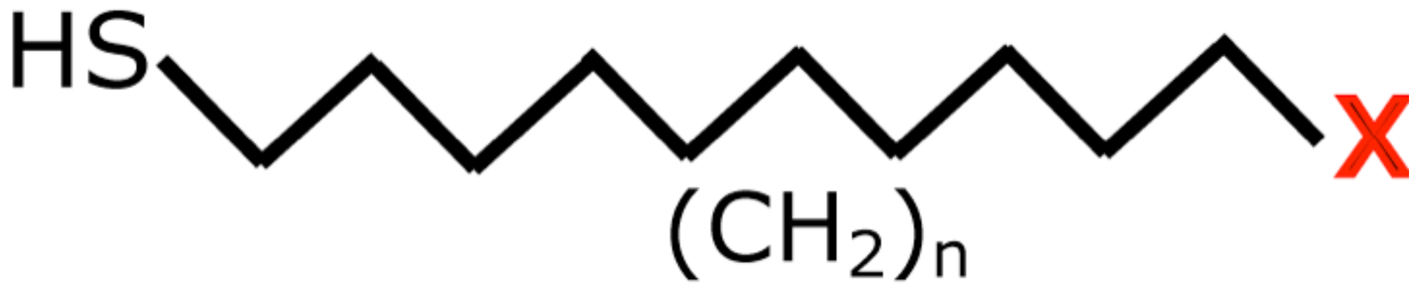
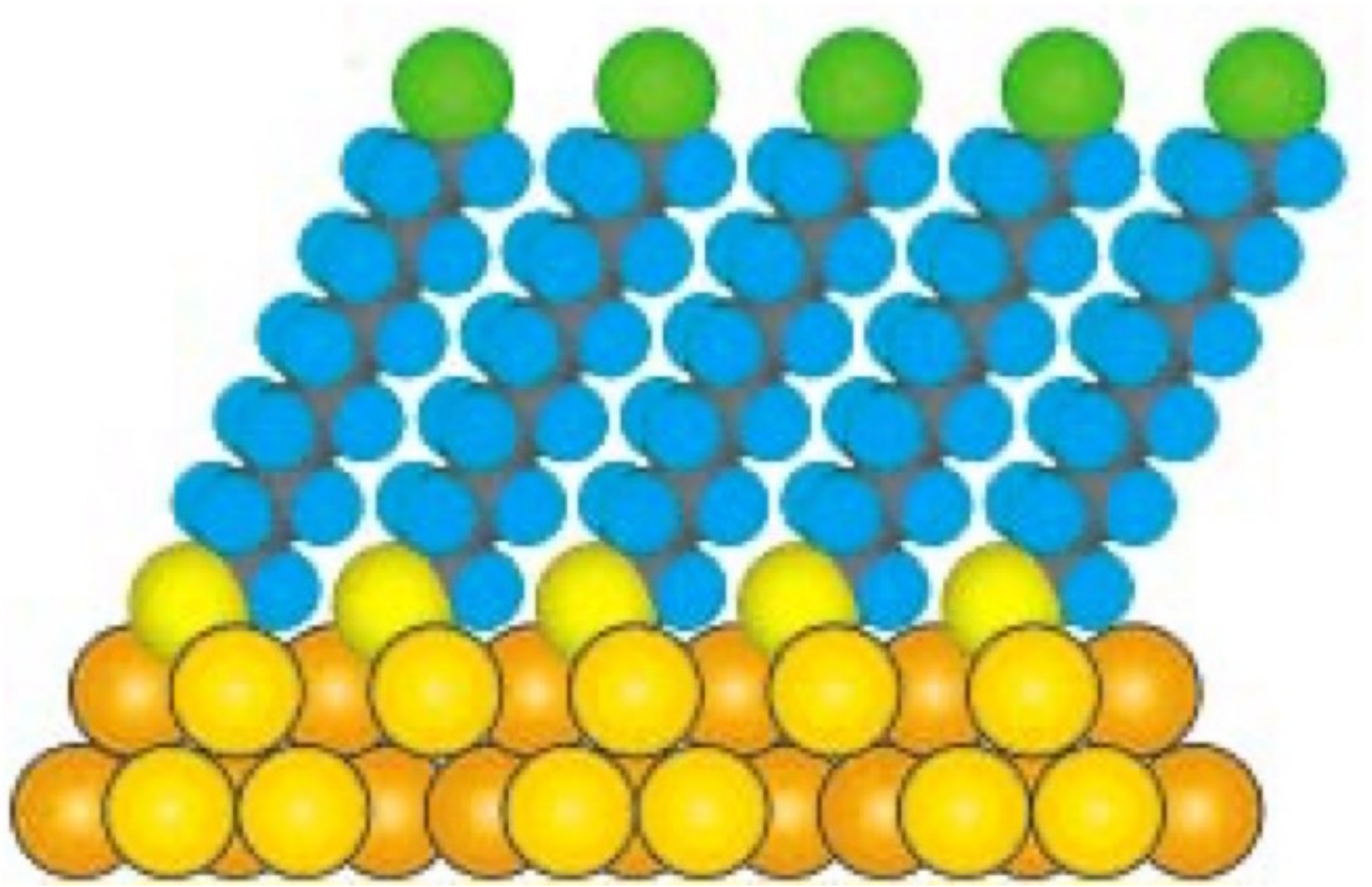
How to Functionalize Surfaces? Self-Assembled Monolayers

Examples of alkanethiols that spontaneously self-assemble on surfaces:



X = tail group/functional group

CH_3, OH, COOH, NH_2, *etc.*



Functional group: mainly determines surface properties

Hydrocarbon chain: interchain van der Waals interactions

Head/anchoring group: interacts with substrate (chemisorption)

Spontaneously adsorbed, single layer of species with a high degree of lateral organization

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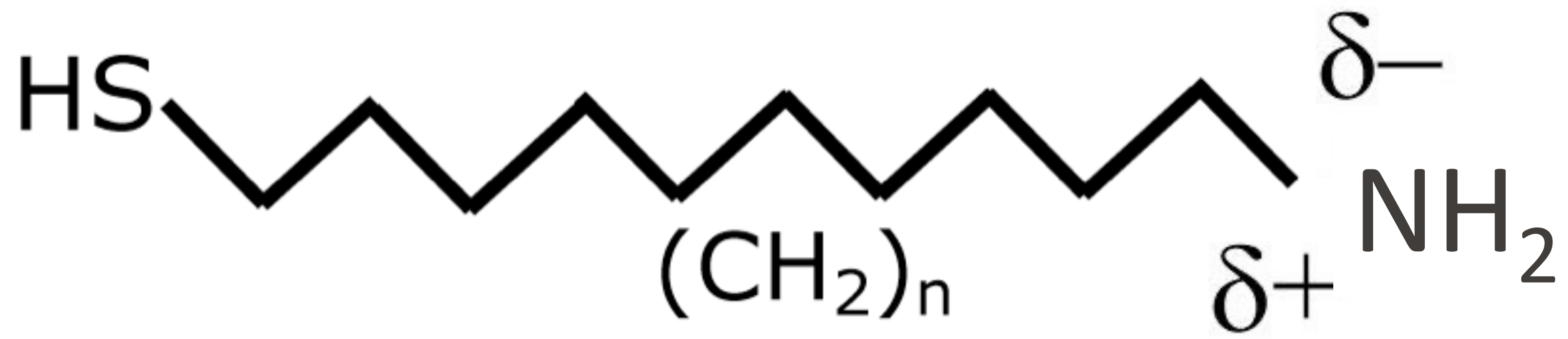
Hydrophilic *vs.* Hydrophobic Terminal Groups

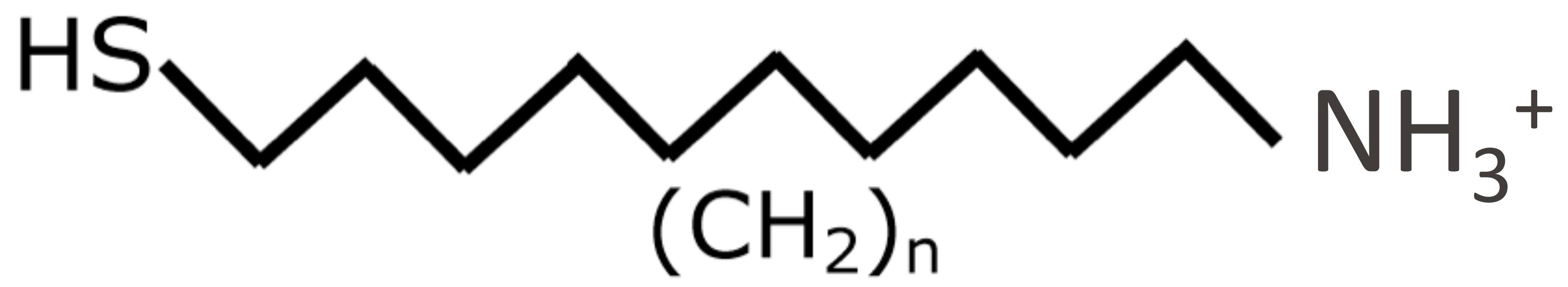
Hydrophilic terminal groups

- OH (hydroxyl)
- COOH (carboxyl)
- NH_2 (amine)

Polar

Hydrogen-bonds or ionic interactions with H_2O



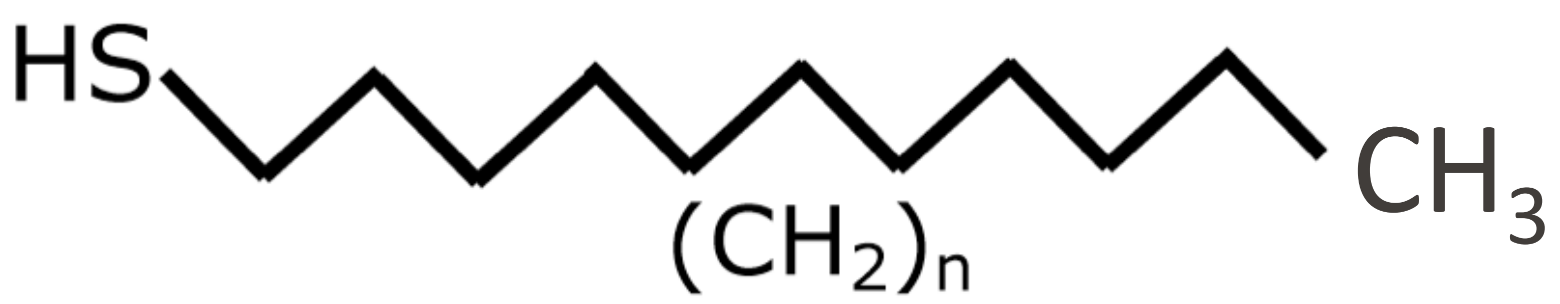


Hydrophobic terminal groups

- CH_3 (methyl)
- CF_3 (triflyoromethyl)
- C_6H_5 (phenyl group)

Non-polar

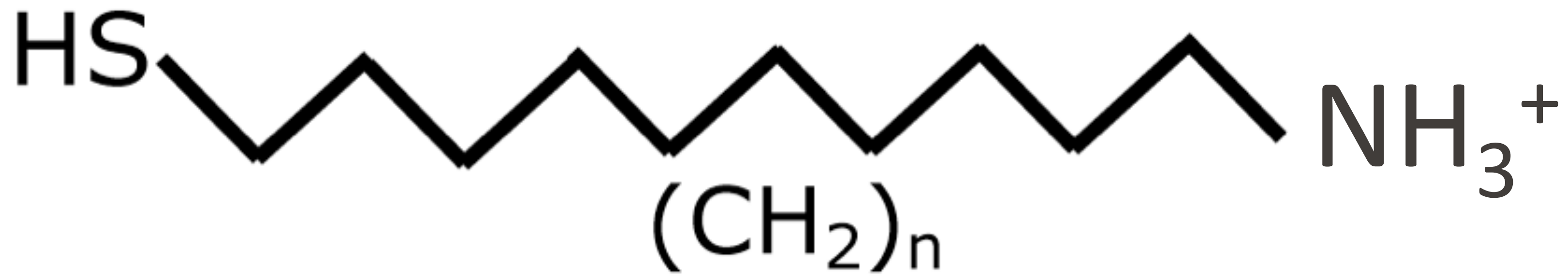
Minimal interactions with water due to low polarity



Which form of the amine-group is more hydrophilic?

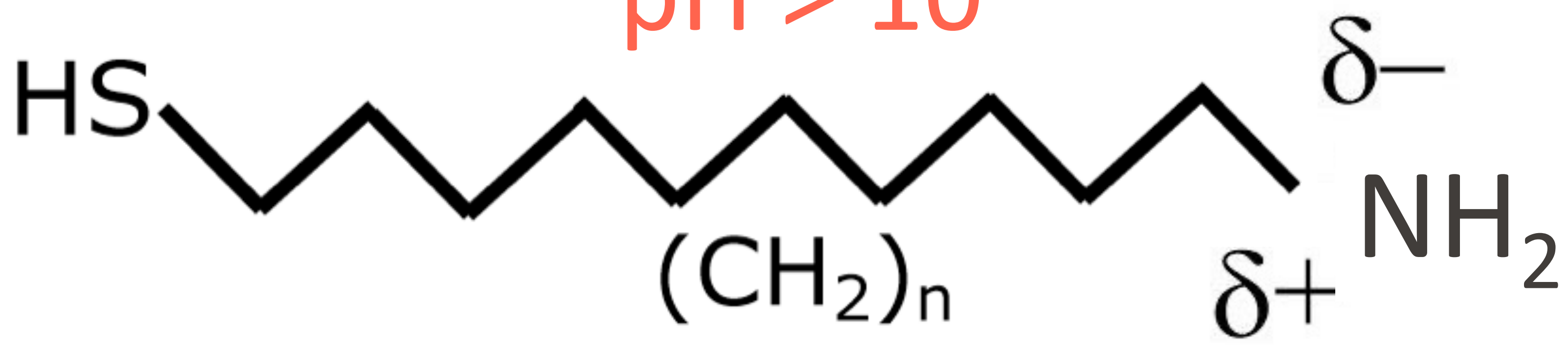
Recall the Strength of Intermolecular Interactions/Forces

pH < 10



pKa ~ 10

pH > 10



Acid dissociation

$$HA \rightleftharpoons H^{+} + A^{-}$$

$$K_a = \frac{[A^-][H^+]}{[HA]}$$

Intermolecular Forces	Formed by attraction between:
Ion-dipole	Ion + polar molecule
Hydrogen bond	Molecules with H, N, O, F atoms
Dipole-dipole	Two polar molecules
Ion-induced dipole	Ion + nonpolar molecule
Dipole-induced dipole	Polar + Nonpolar molecule
Van der Waals forces	Two nonpolar molecules

Strength of force

Henderson-Hasselbach equation

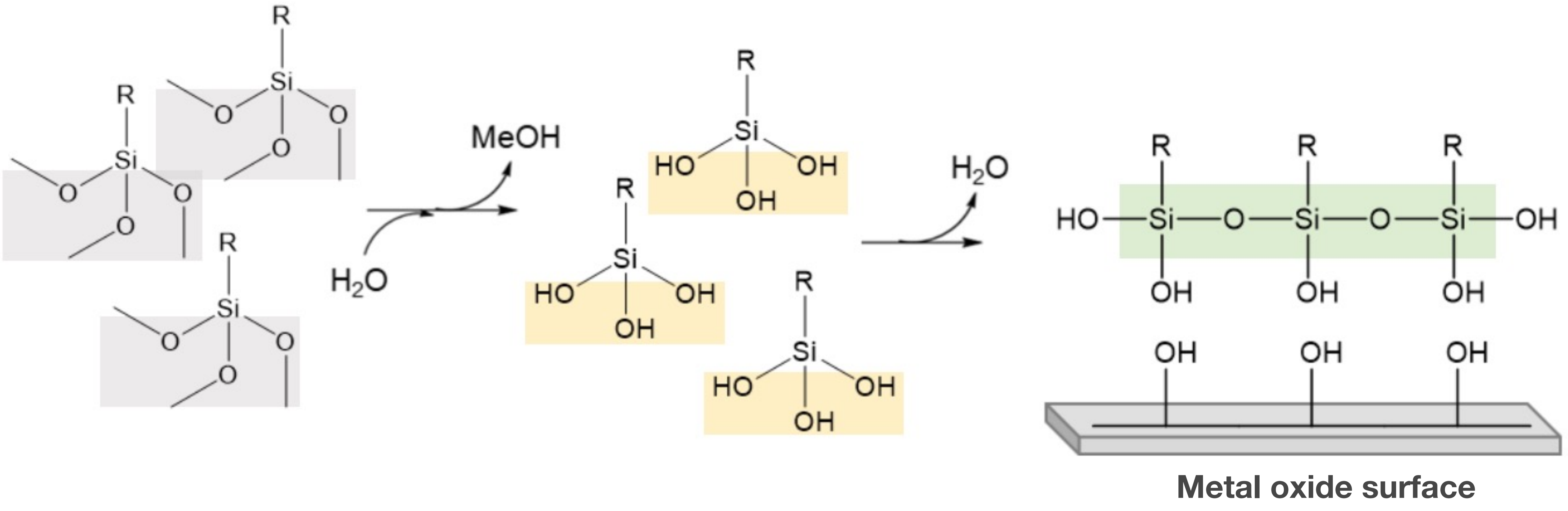
$$pH = pK_a + log\frac{[A^-]}{[HA]}$$

pH < pKa ➔ protonated
pH > pKa ➔ deprotonated

Beyond Alkanethiol-Gold Surface Chemistry

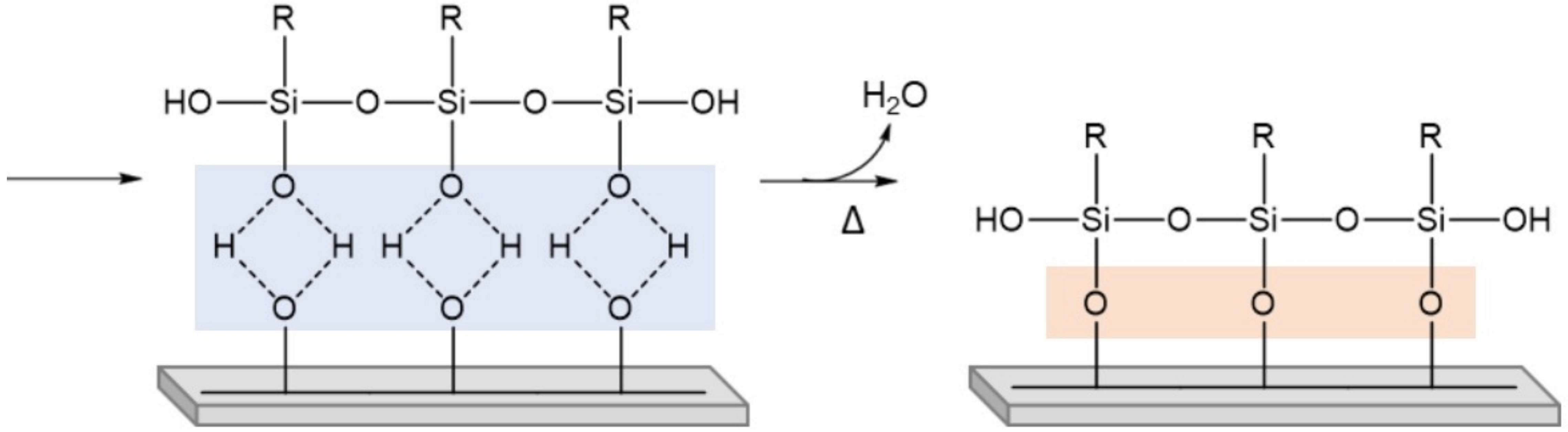
Silane chemistry for surfaces with –OH groups (*e.g.,* metal oxides)

*The precise mechanism of assembly is unknown



Hydrolysis

Condensation

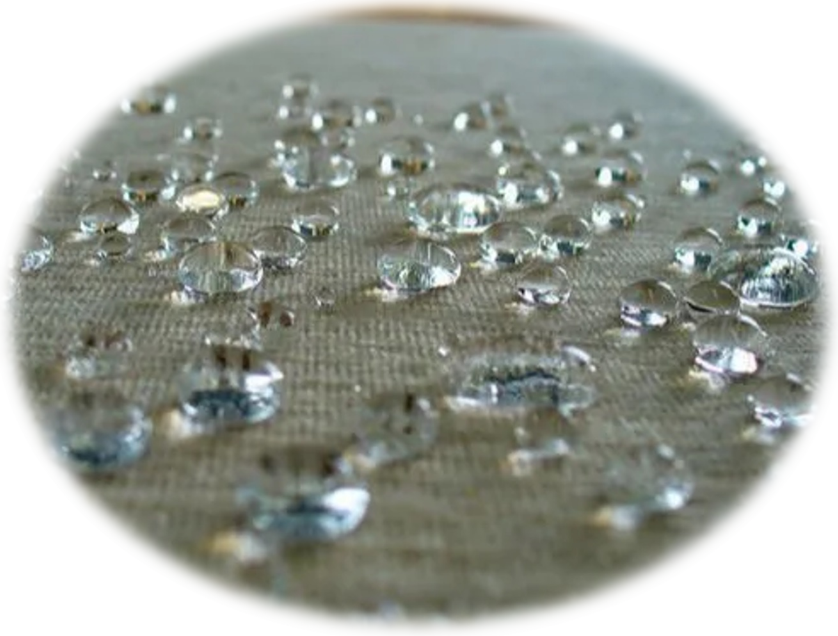


Hydrogen bonding

Covalent bond formation

Arkles, *CHEMTECH, 7,* 766, **1977**

Applications of silane chemistry



Water repellant coatings

Adhesives, primers, paints

Antifog

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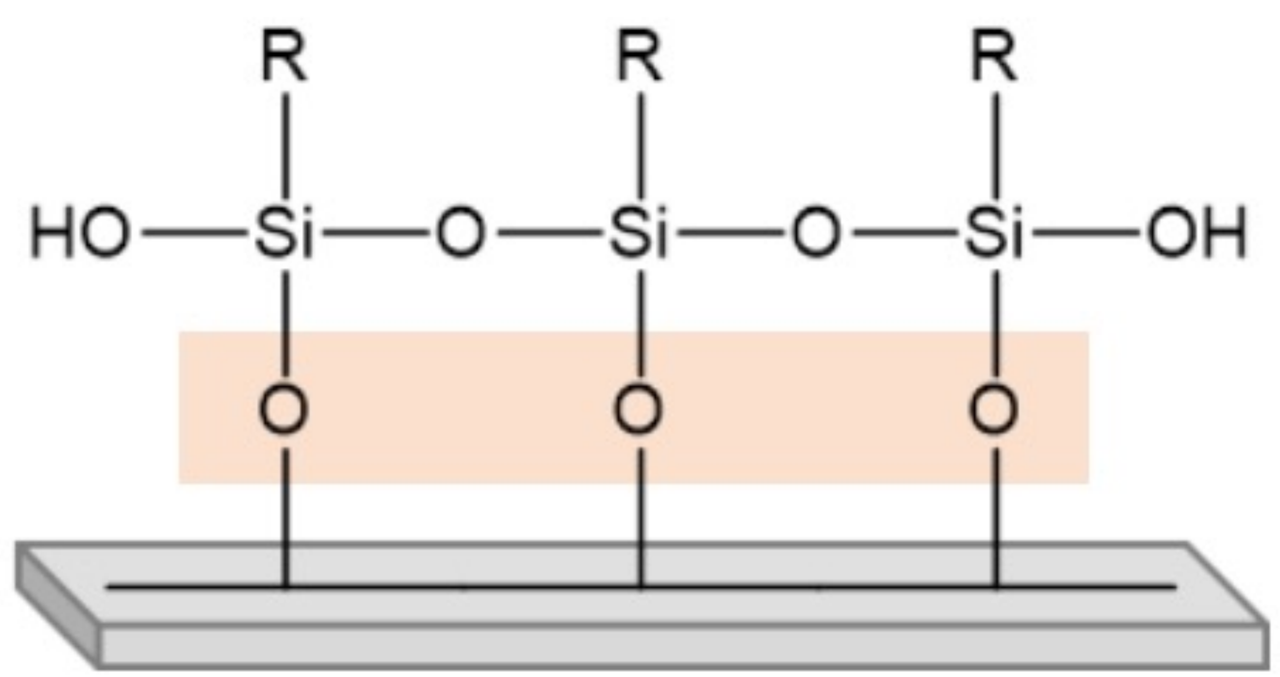
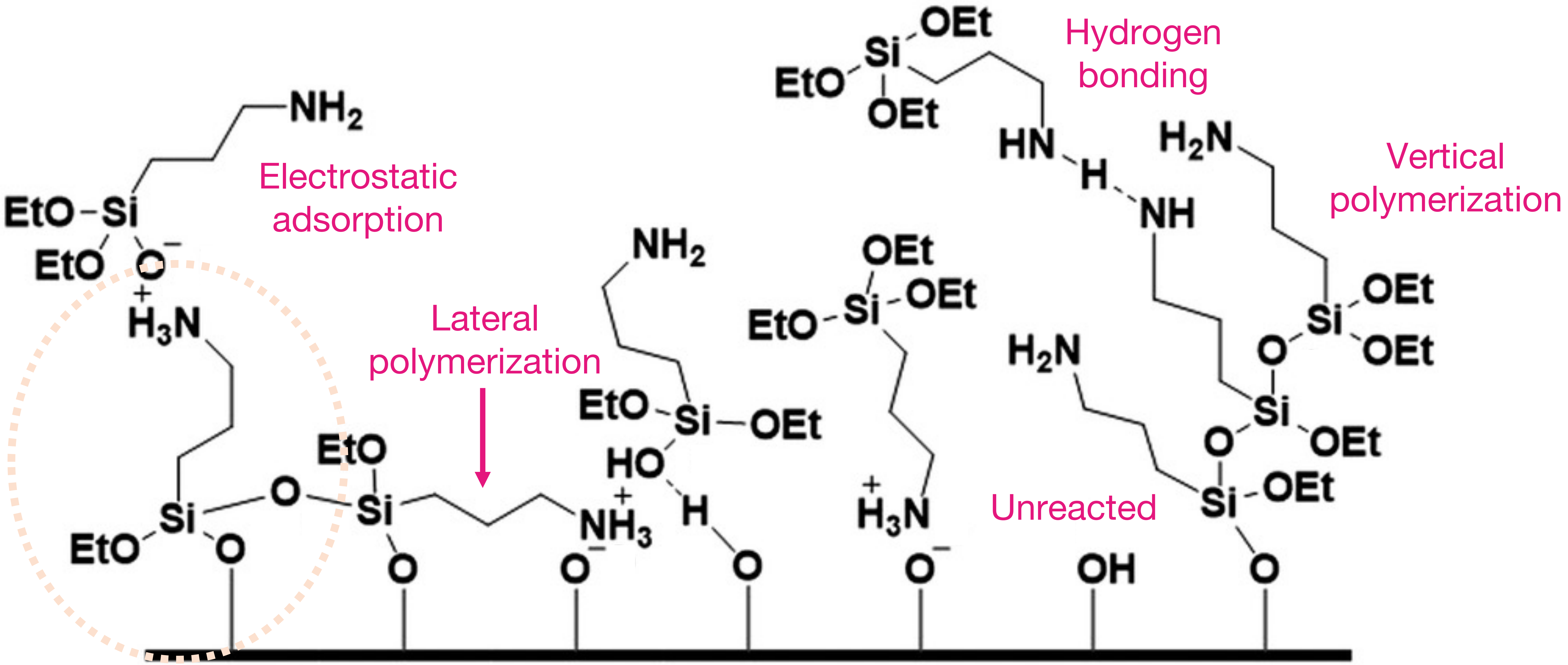
Challenges of Homogenous and Reproducible Silane Chemistry

Expectation ☺



Metal oxide surface

Reality ☹

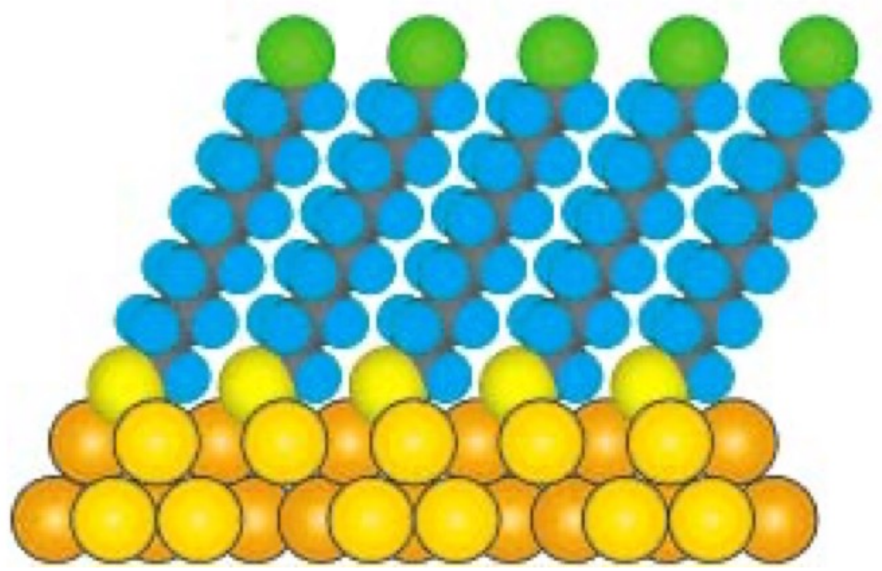


Layer characteristics are heavily influenced by solvent, water content, environmental humidity, pH, silane concentration, reaction time, temperature, etc.

Duleba *et al., Phys. Chem. Chem. Phys.,26, 15452,* **2024**

The Pros and Cons of Alkanethiols vs. Alkylsilanes

Alkanethiols



Metal surface *(e.g.,* Au*)*

Selective bonds formed with noble metal surfaces

Many different functional end groups commercially available

Easy to prepare (Au chemically inert)

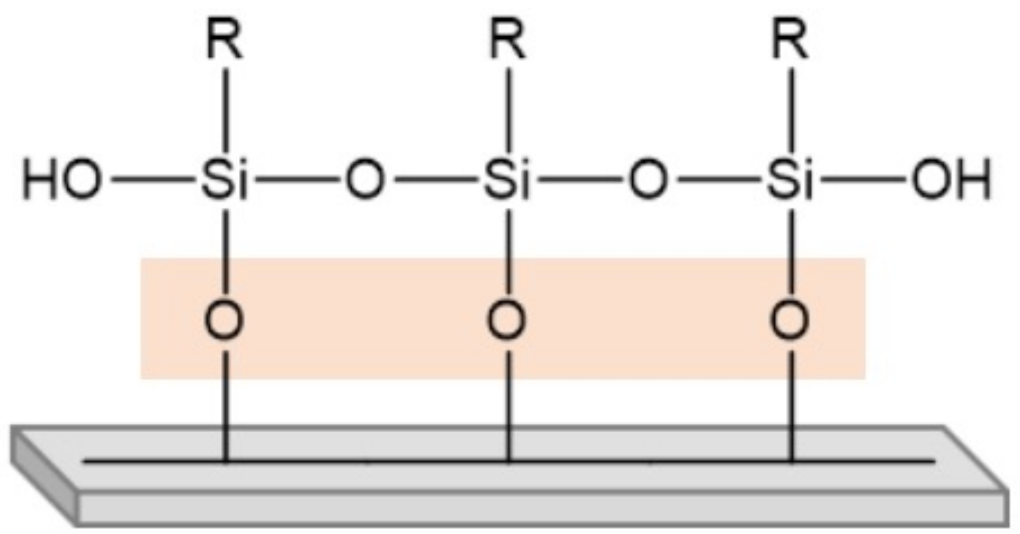
Very well studied (order and packing well known)

Patterning is possible

Do not absorb on most technologically important materials

Sensitivity to oxidation leads to low stability

Alkylsilanes



Metal oxide surface (-OH)

Only requirement for substrate is presence of –OH groups

Many functionalized silanes commercially available

High stability due to polysiloxane formation

Limitation in functional groups due to possible reactivity with head/anchor group

Reproducible sample prep can be difficult

Multilayer formation is possible (and common)

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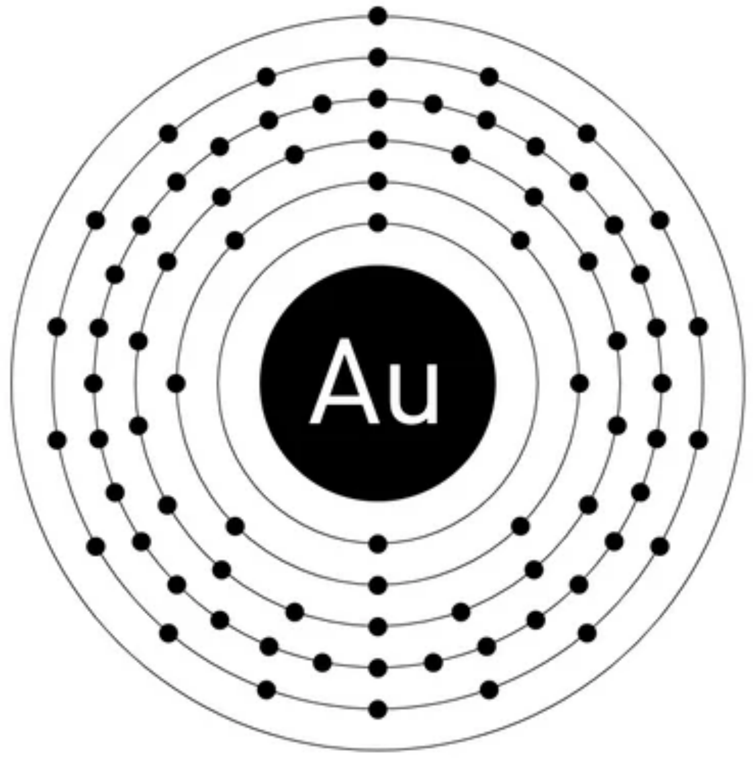
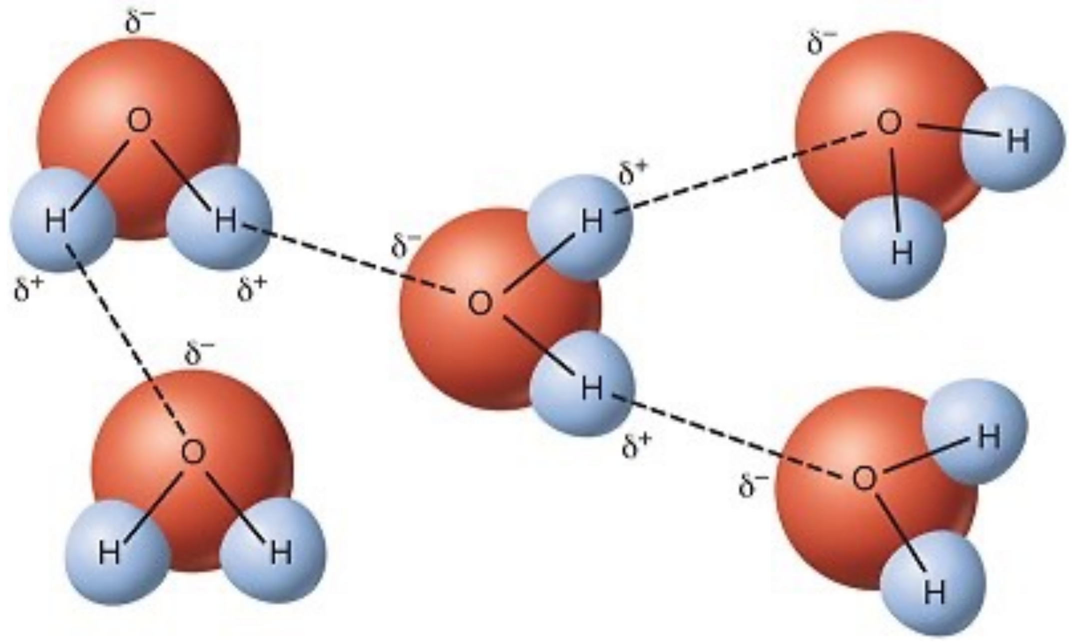
Surface Assembly of Polymers

Metal



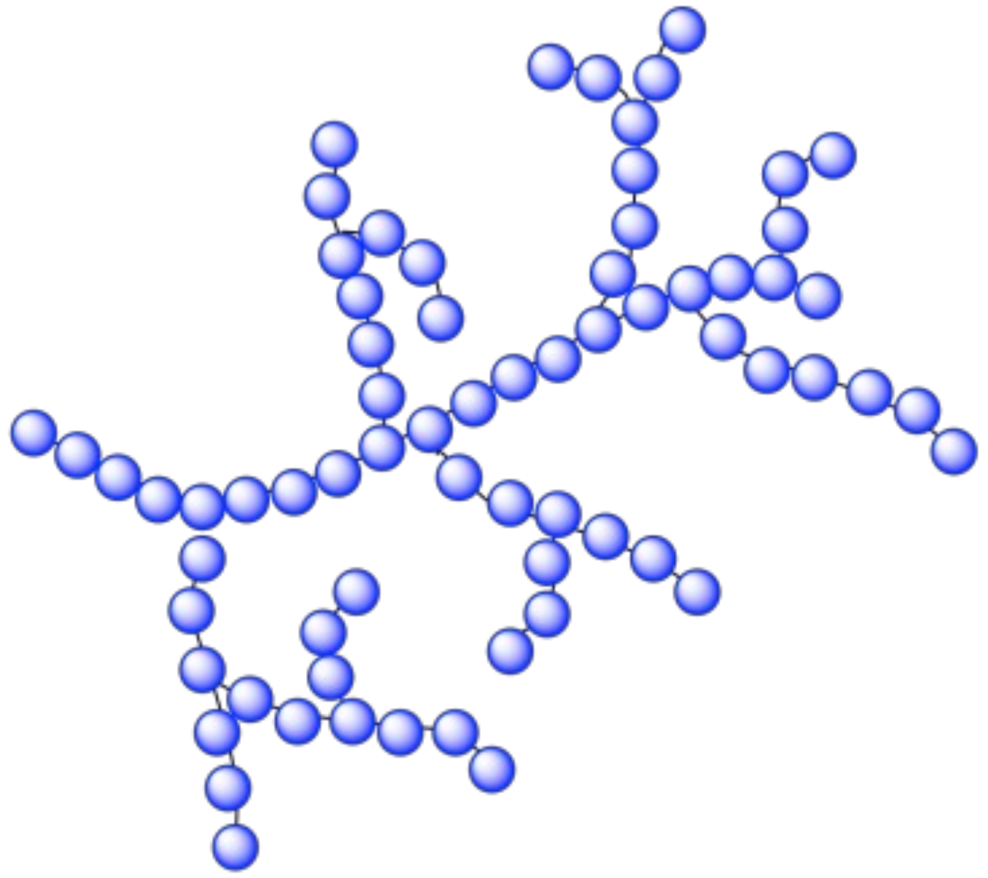
Atoms

Water



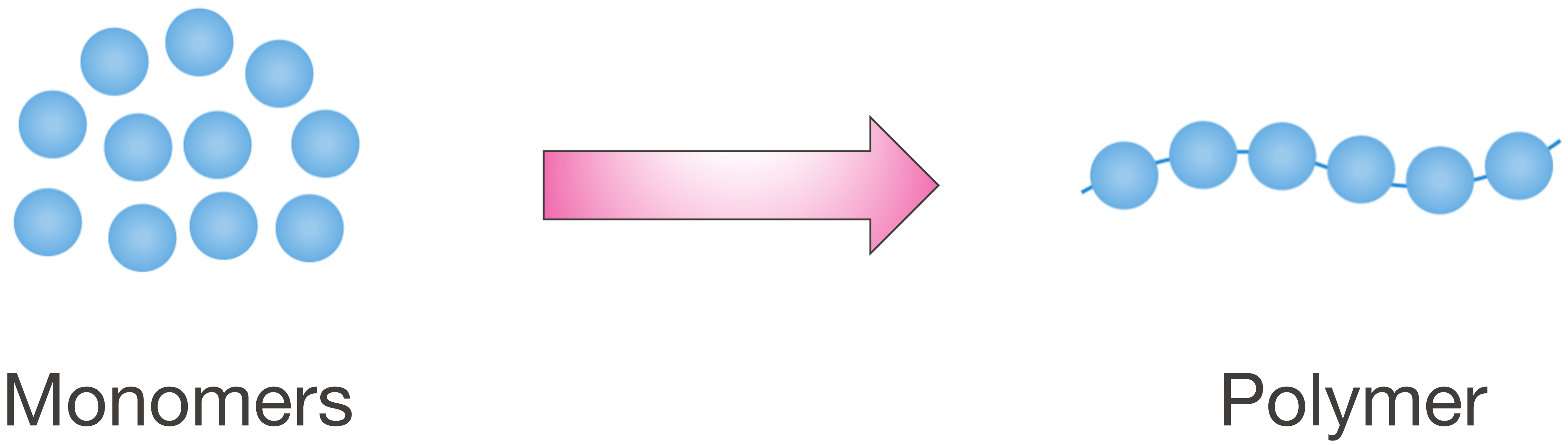
Molecules

Polymer

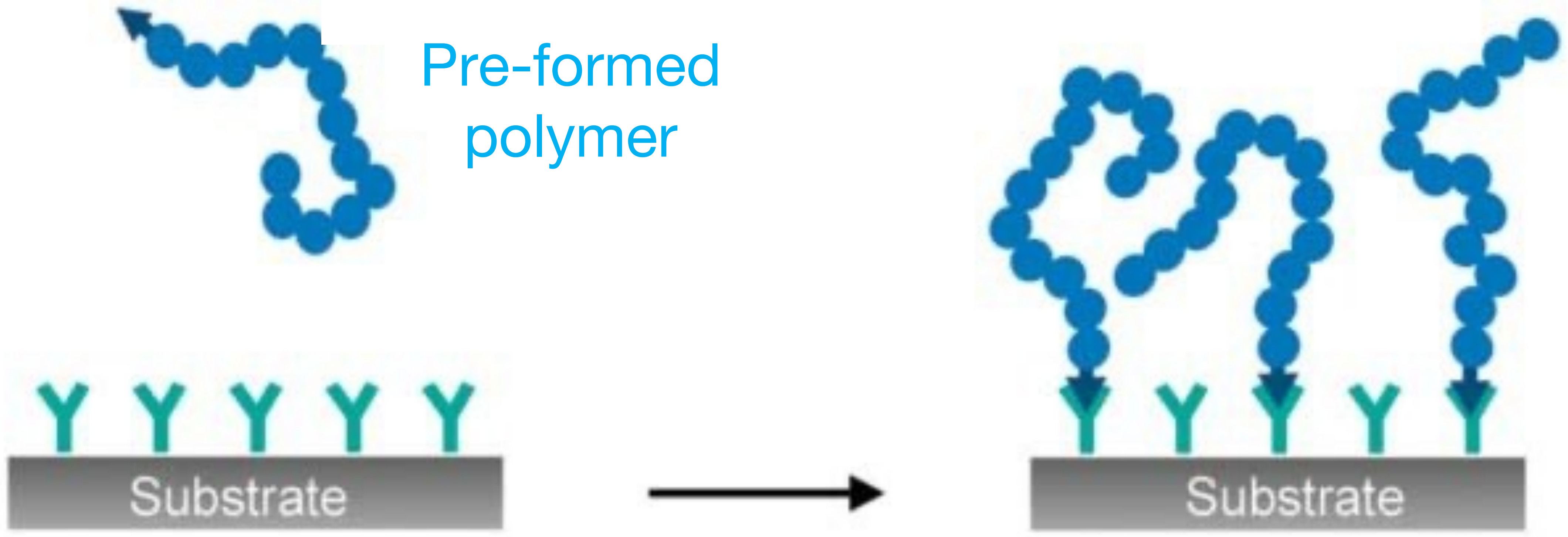


Chains of molecules

Surface Assembly of Polymers



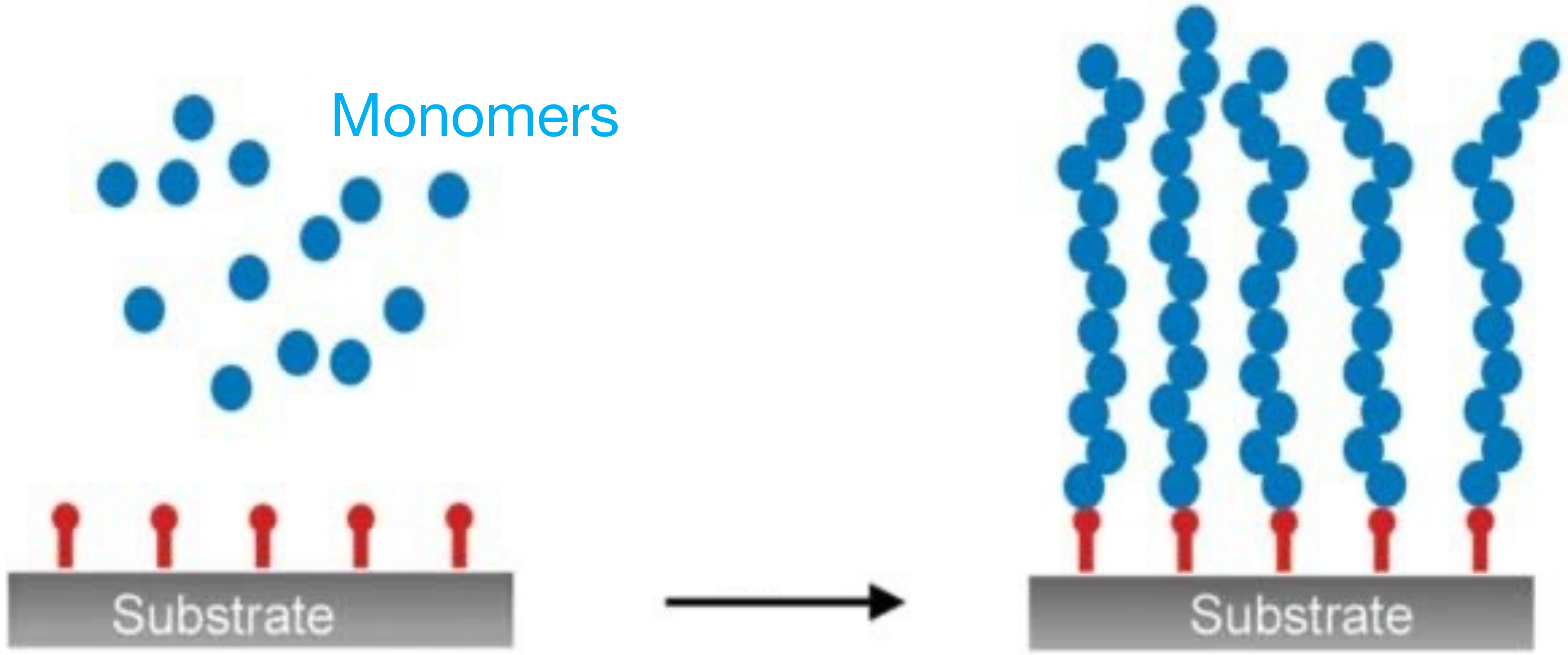
Top-down:
Grafting-to approach



Control over polymer properties

Limited surface density steric hindrance

Bottom-up:
Grafting-from approach



High grafting density and stronger bonding

Less control over polymer properties

Comparing Polymer Brushes to SAMs

	Polymer brush		SAM (self-assembled monolayer)
	Grafting-to	Grafting-from	
Grafting molecule	Almost all types of polymers		Mainly alkanethiol & alkyl silane
Micro-architecture	Various and complex polymeric structures		Well assembled molecular monolayer
Scaffold materials	Glass, titanium, gold, silver, silicon, etc		Gold thin film, oxide-formed substrate
Thickness	High tunability by adjusting polymer chain length		Thin: one molecular layer
Coating defects	Presence: short polymer chain Self-healing of defects: long polymer chain		Presence of defects and pinhole
In vivo stability	High stability		Low stability
Coating density	Loosely packed	Densely packed	Densely packed
Fabrication approach	Various chemical coupling between polymer and surface	Various polymerization on the surface	Thiol-gold bond & silane linkage

Kim & Jung, *Phys. BMB Rep.,49, 12,* **2016**

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Unique Properties at the Nanoscale

Increased surface-to-volume ratio ➔ dominance of surface effects over bulk properties

Bulk gold

Gold nanoparticles

Optical properties of metal nanoparticles are dependent on their sizes and geometries

Why?

H!Q

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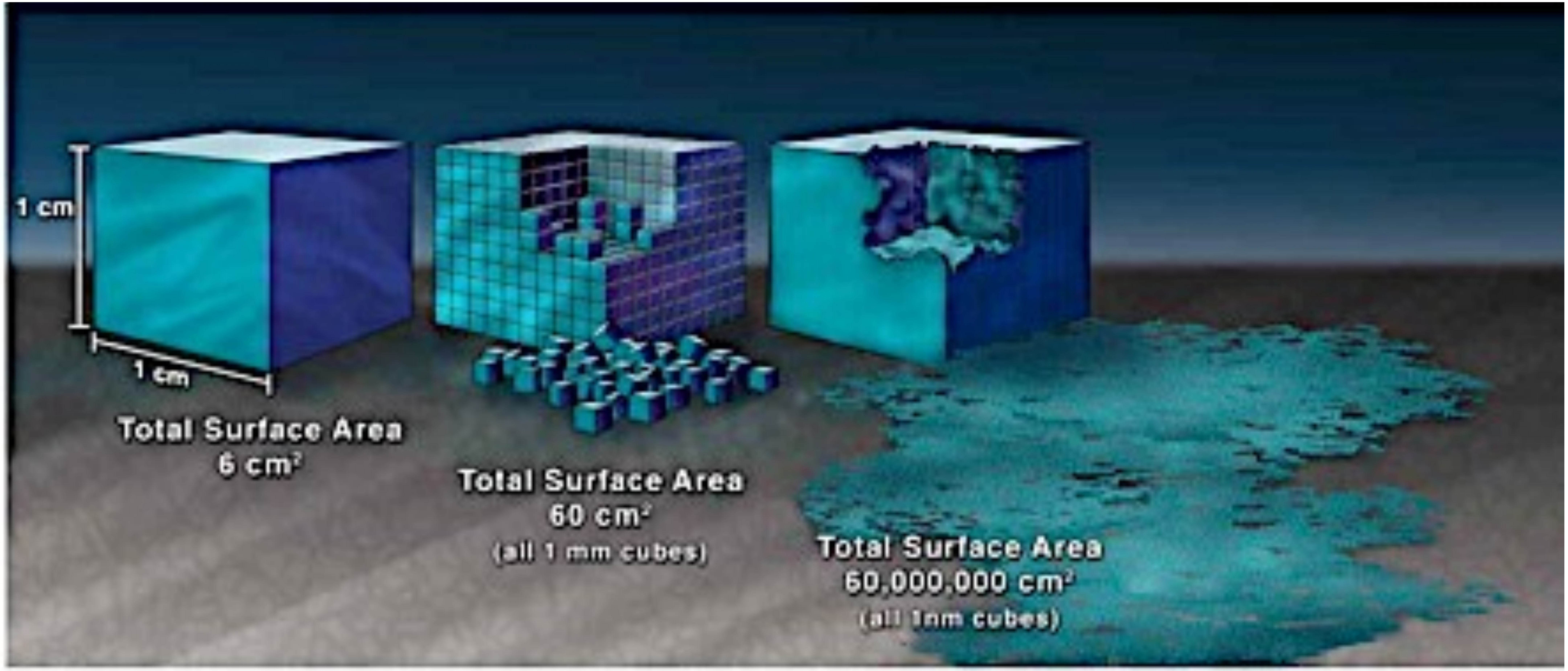
Why Nanoscale Matters for Electronic Properties at Surfaces

Increased surface-to-volume ratio ➔ significant number of electrons are at or near the surface, leading toe enhanced surface effects



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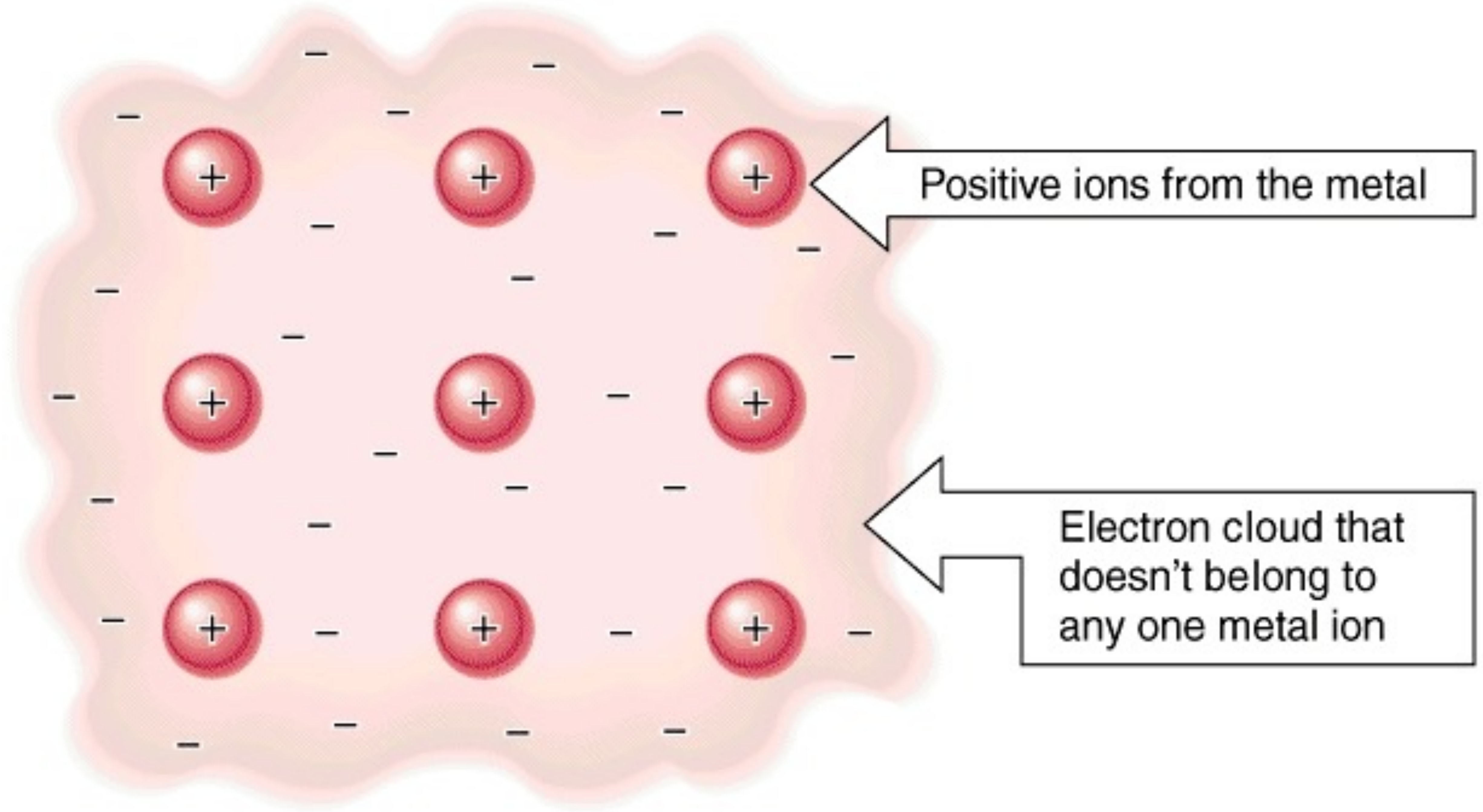
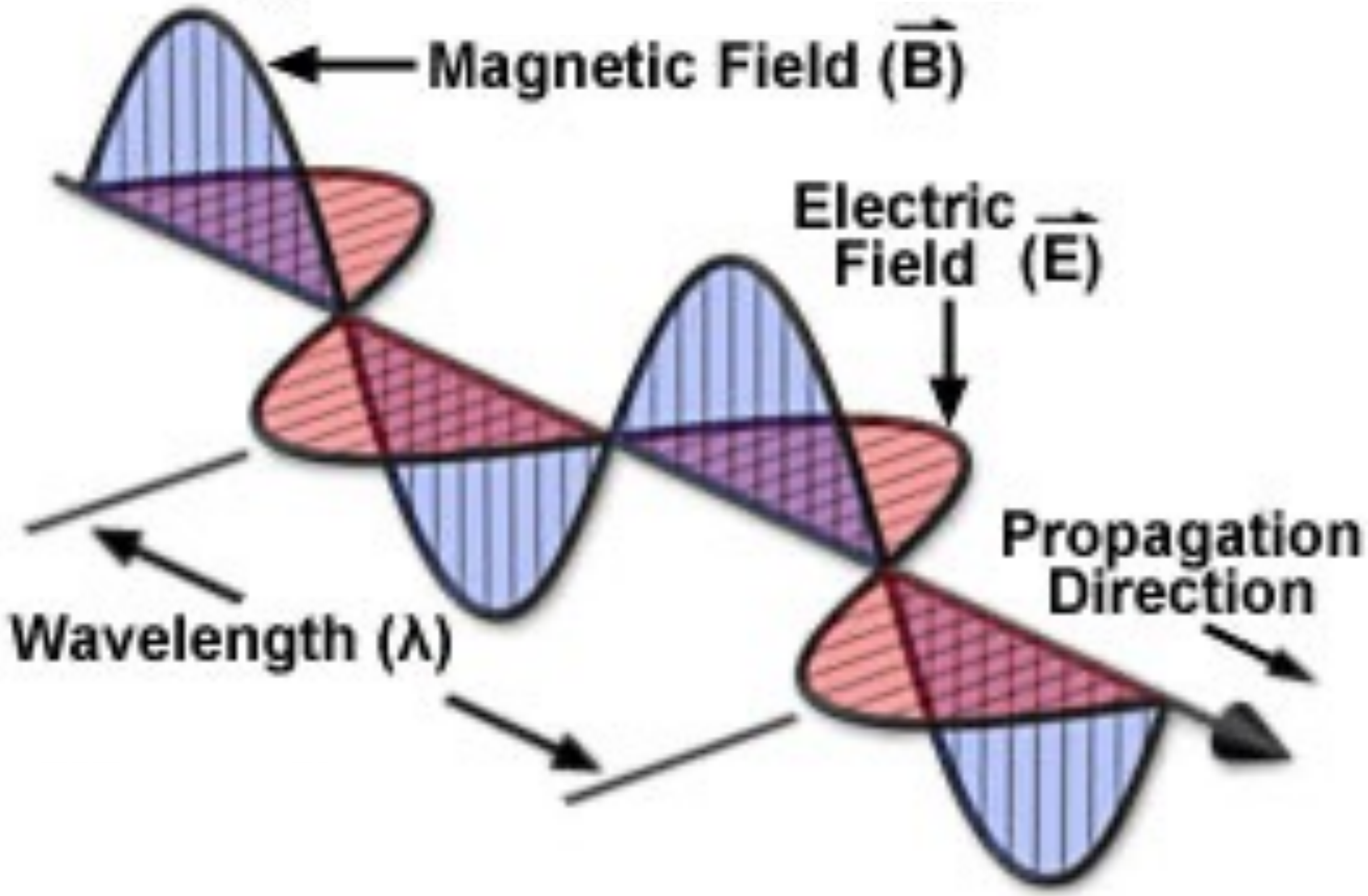
Influencing the Sea of Electrons on Surfaces Using Light

The Free Electron Sea

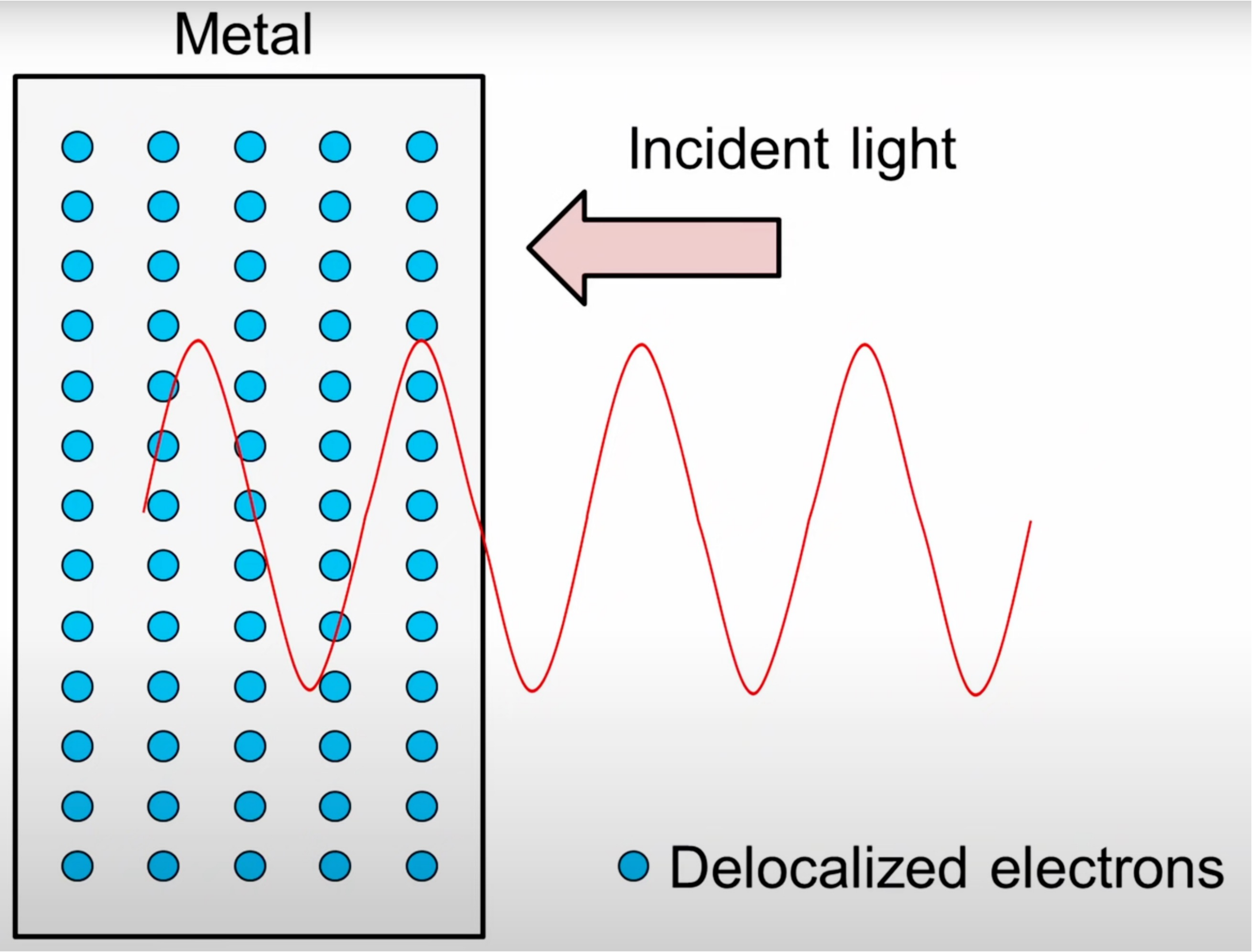


Light as an oscillating electromagnetic field



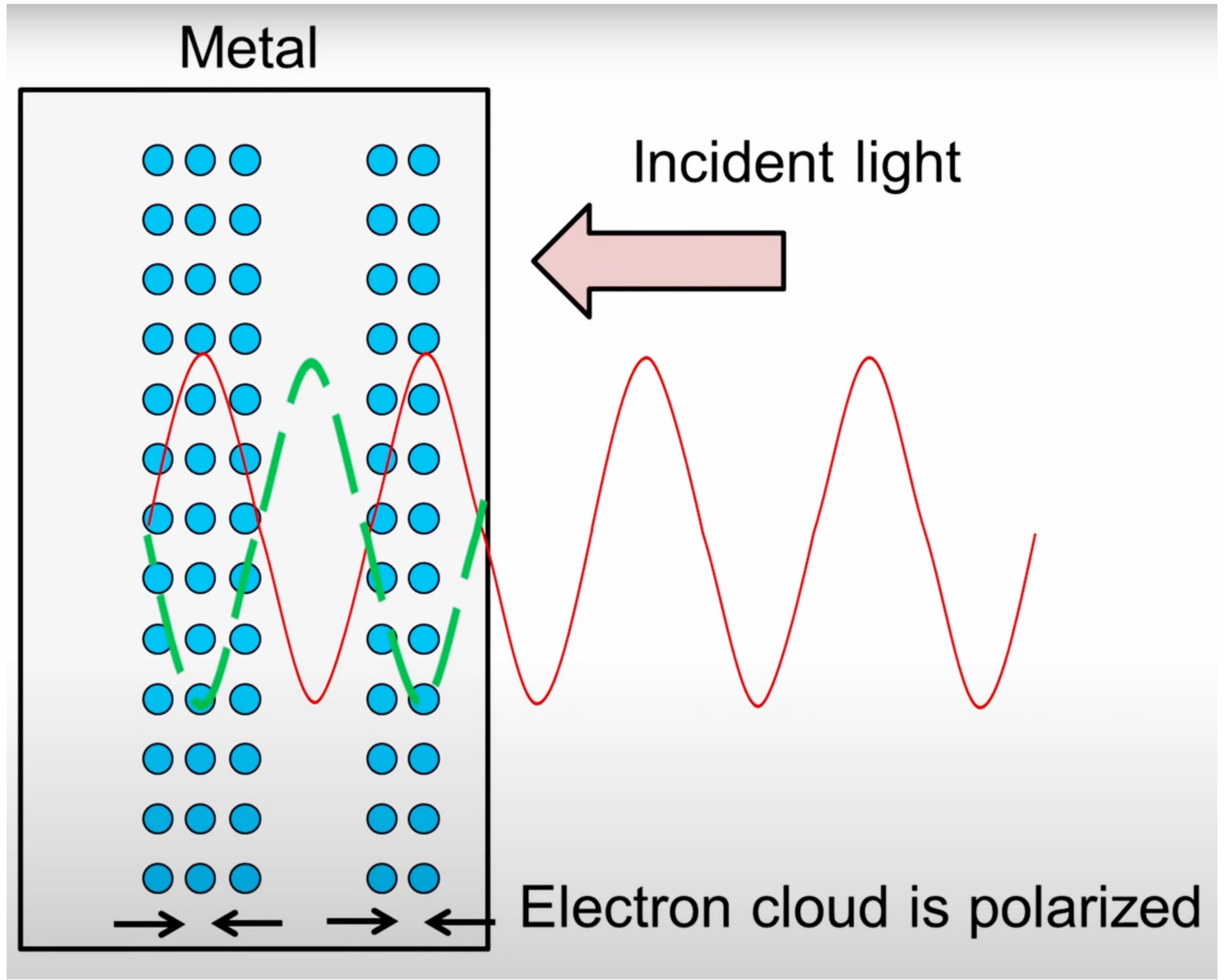
Electrons in metal are affected by the electromagnetic field from light incident to surface

Effect of Plasmon Resonance



Incident light excites electrons on metal surface

Oscillating field of light interacts with free electrons



Electron cloud is perturbed

Electrons begin to oscillate collectively as a polarized cloud (plasmon)

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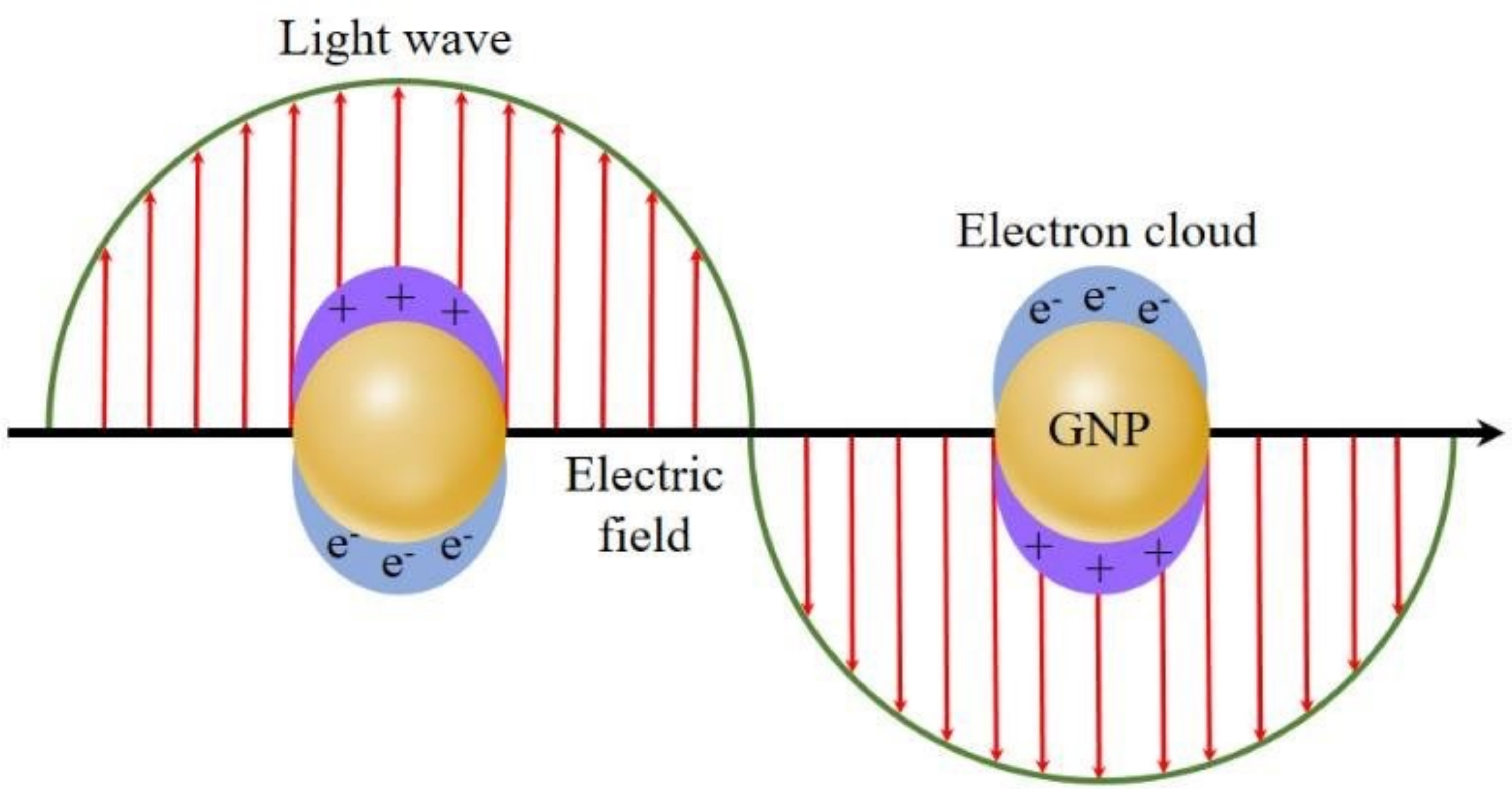
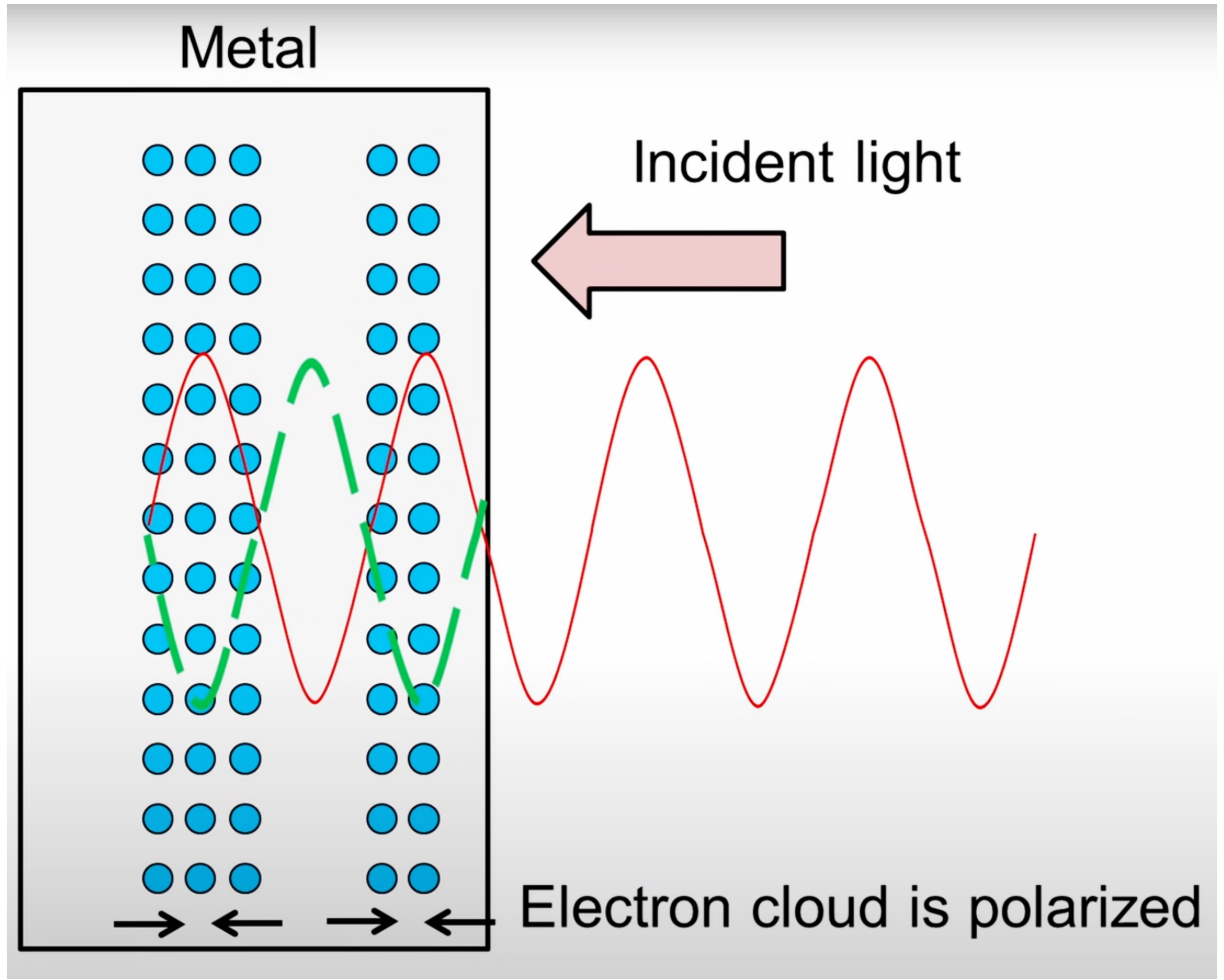
Effect of Plasmon Resonance





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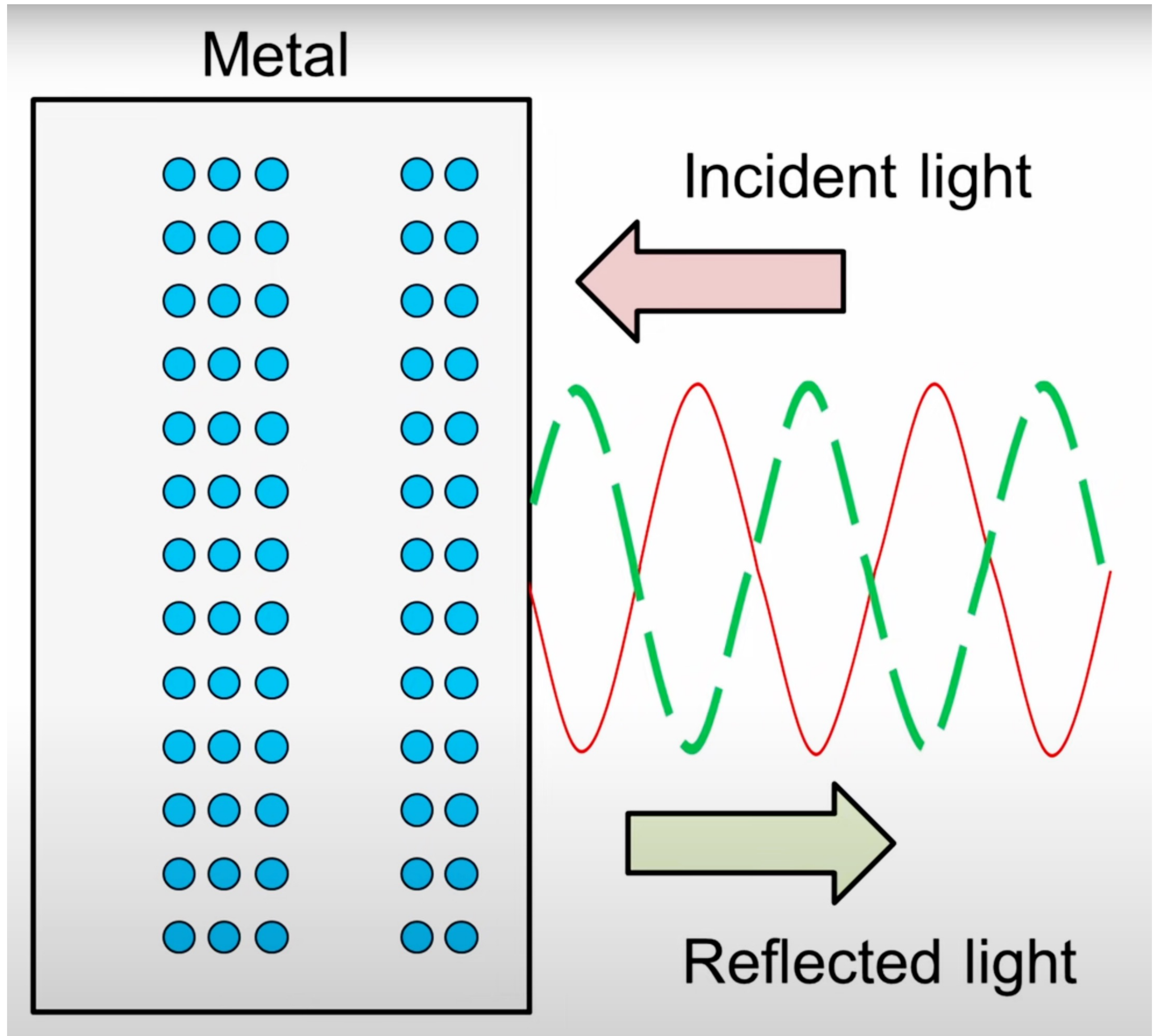
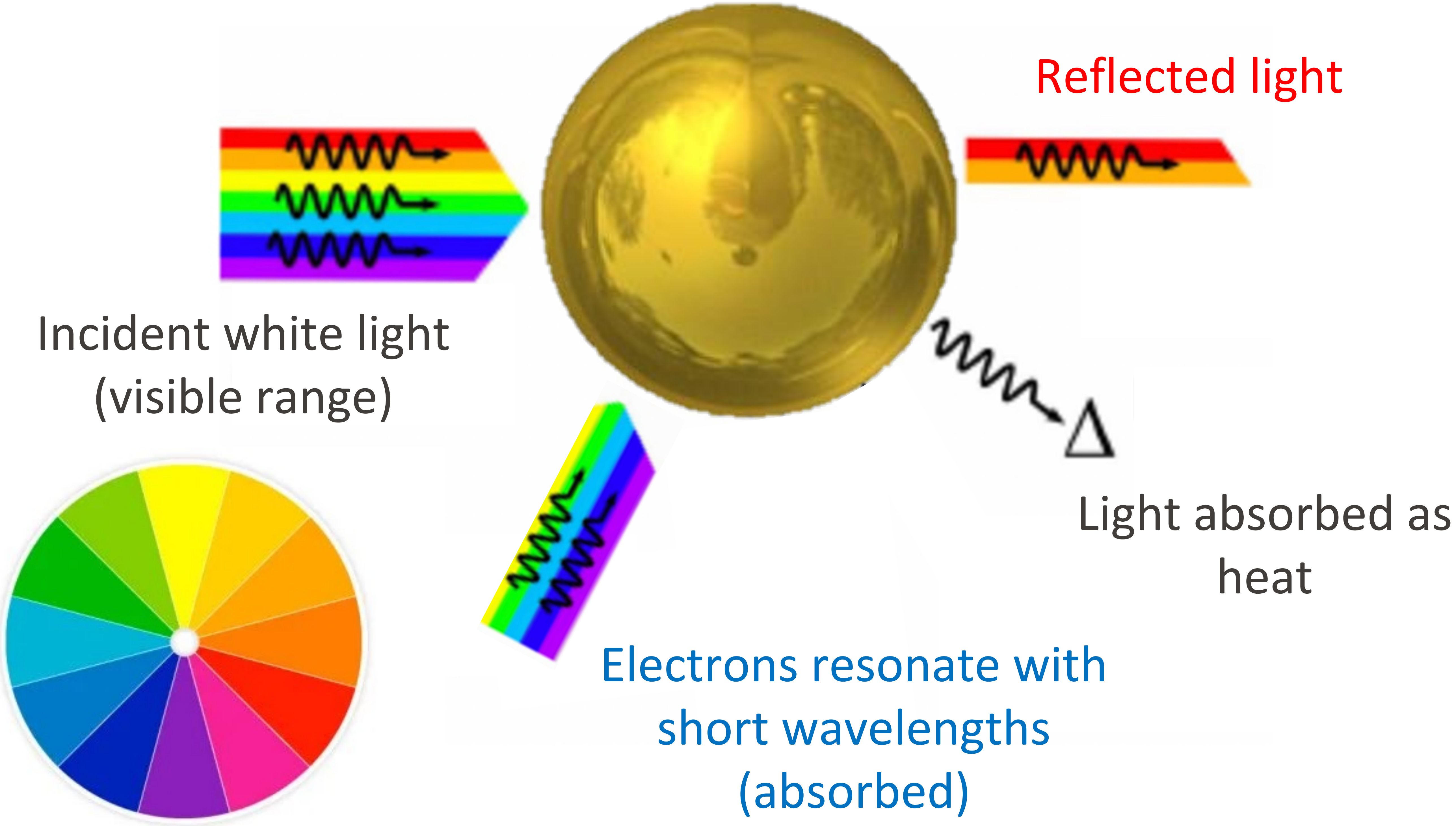


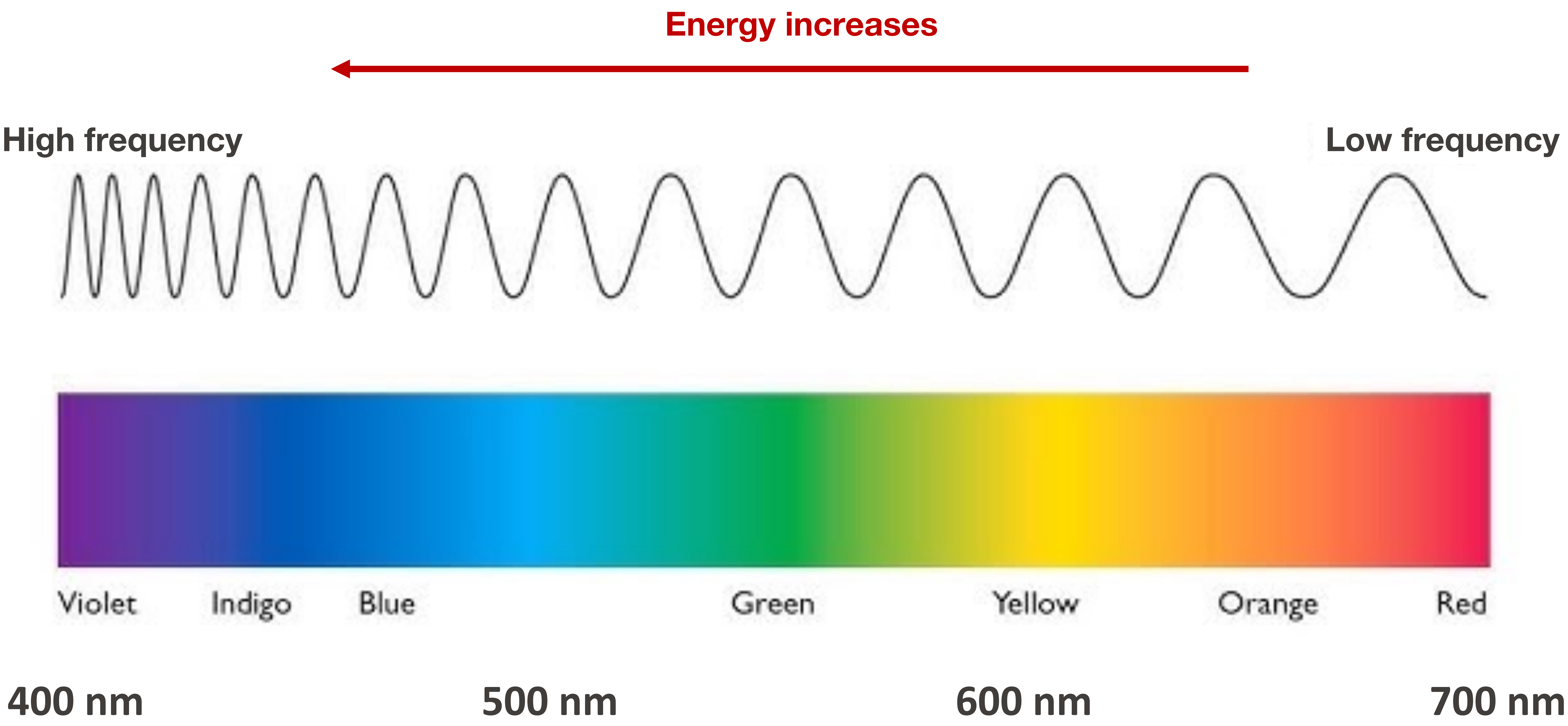


At resonance frequency, incident light energy transferred to oscillating electron cloud (plasmon excitation)

Only specific wavelengths of light are reflected back while others are absorbed or scattered

Relative contributions of absorption and scattering determined by size and shape of plasmonic particles

Visible Part of the Electromagnetic Spectrum



$$f = \frac{c}{\lambda}$$

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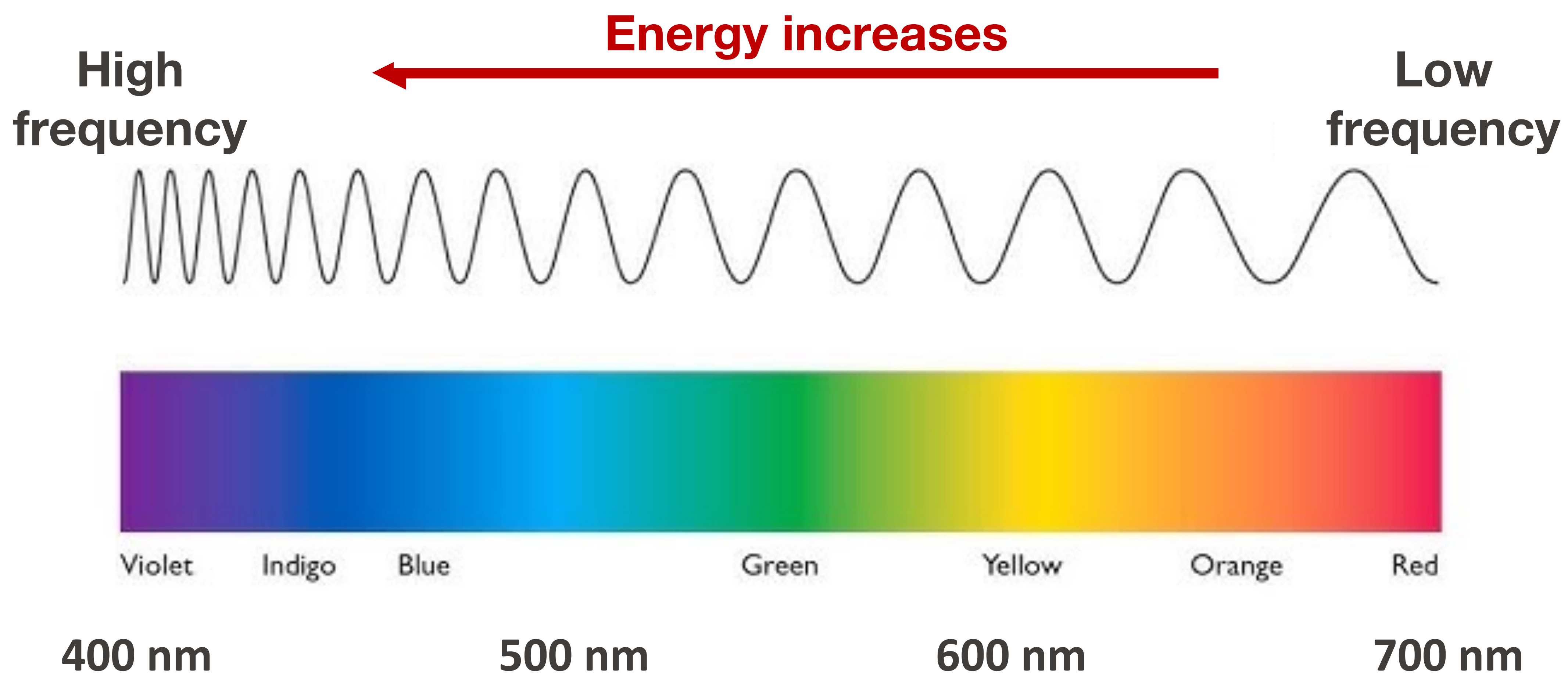
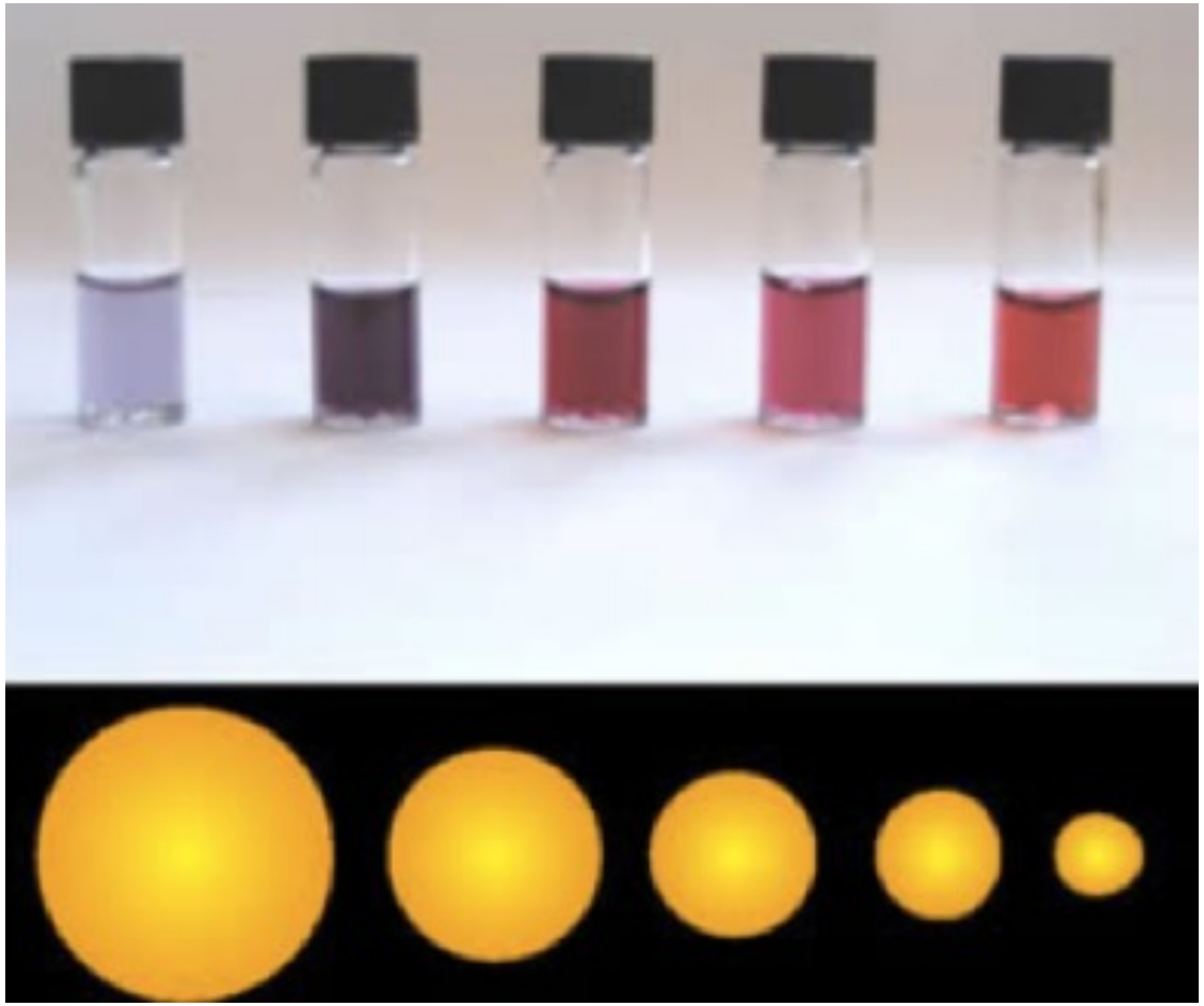
How We “See” Different Colored Nanoparticles

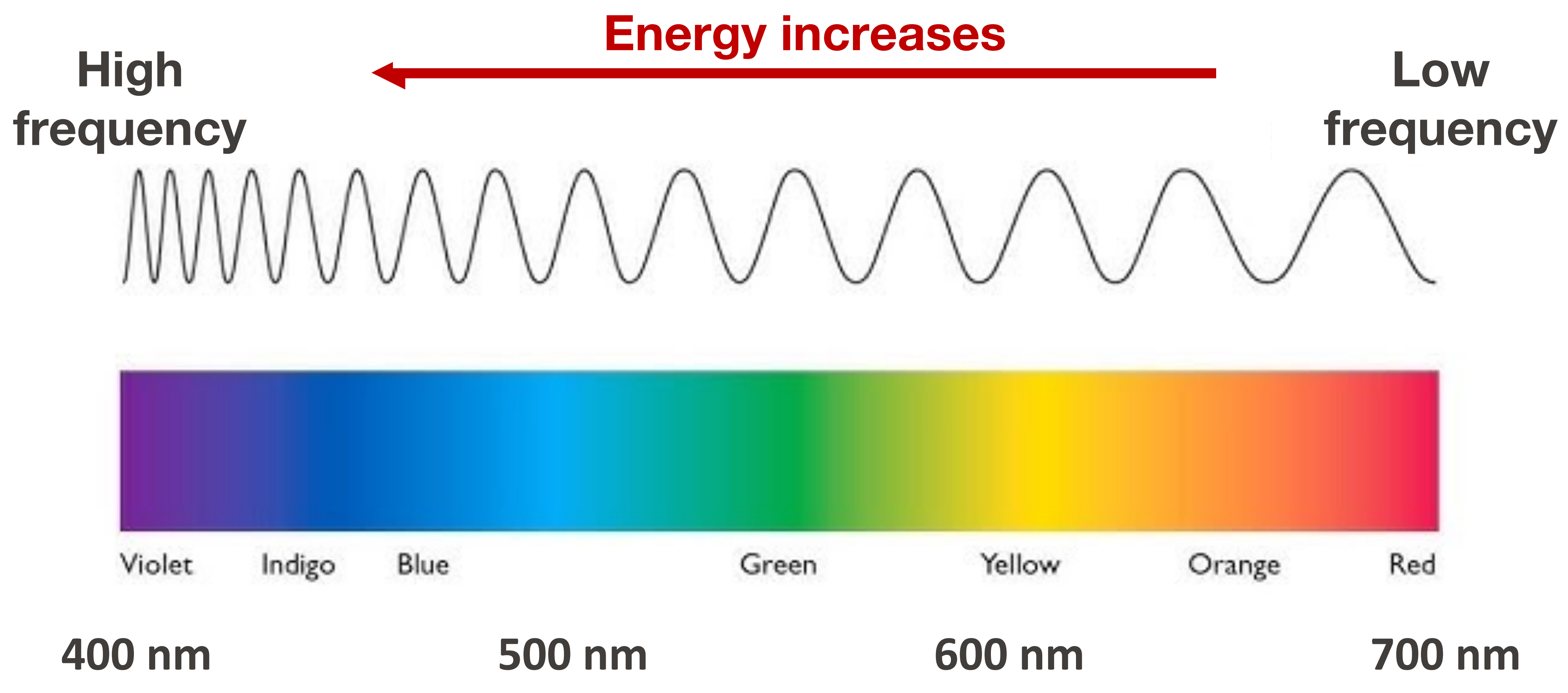


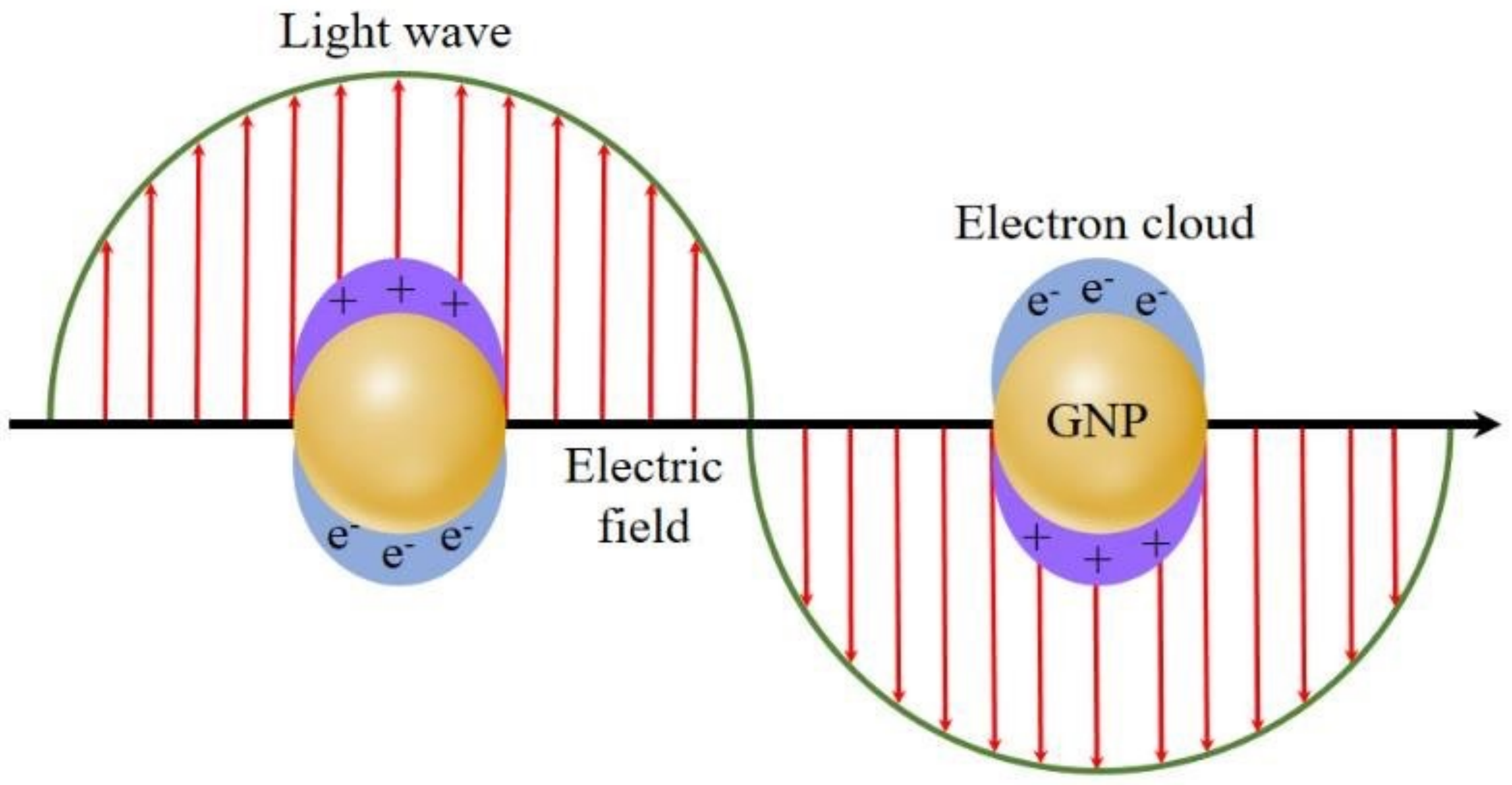


Small gold nanoparticles (10-20 nm) have plasmon resonance around 520 nm (green) leading to red color

Larger gold nanoparticles (50-100 nm) have plasmon resonance around 650 nm (orange light) leading to purple/blue color

How We "See" Different Colored Nanoparticles





Small gold nanoparticles (10-20 nm) have plasmon resonance around 520 nm (green) leading to red color

Larger gold nanoparticles (50-100 nm) have plasmon resonance around 650 nm (orange light) leading to purple/blue color

Smaller nanoparticles have less conduction electrons that can oscillate collectively (lower polarizability)

Electron cloud is more tightly confined
➔ shorter plasmon wavelength

Larger nanoparticles have more conduction electrons that can oscillate collectively (higher polarizability)

Electron cloud is less tightly confined
➔ longer plasmon wavelength

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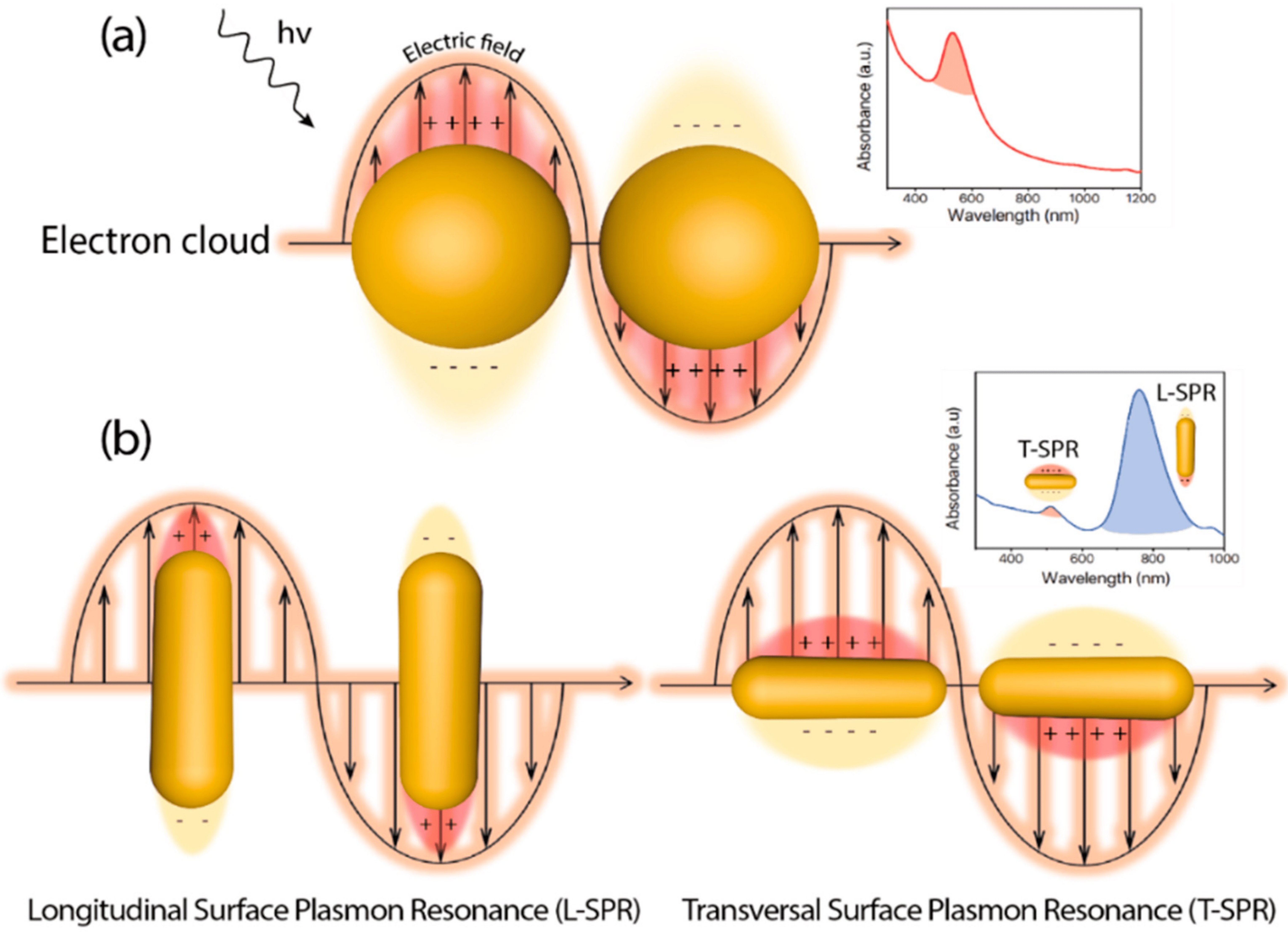
Broader Color Range with Asymmetric Nanostructures



While nanoparticles are symmetric, **nanorods** are anisotropic (different resonant frequencies depending on aspect ratio leading to multiple plasmon resonances

Garcia-Peiro *et al.*, *Catalysts, 10*, *12*, **2020**

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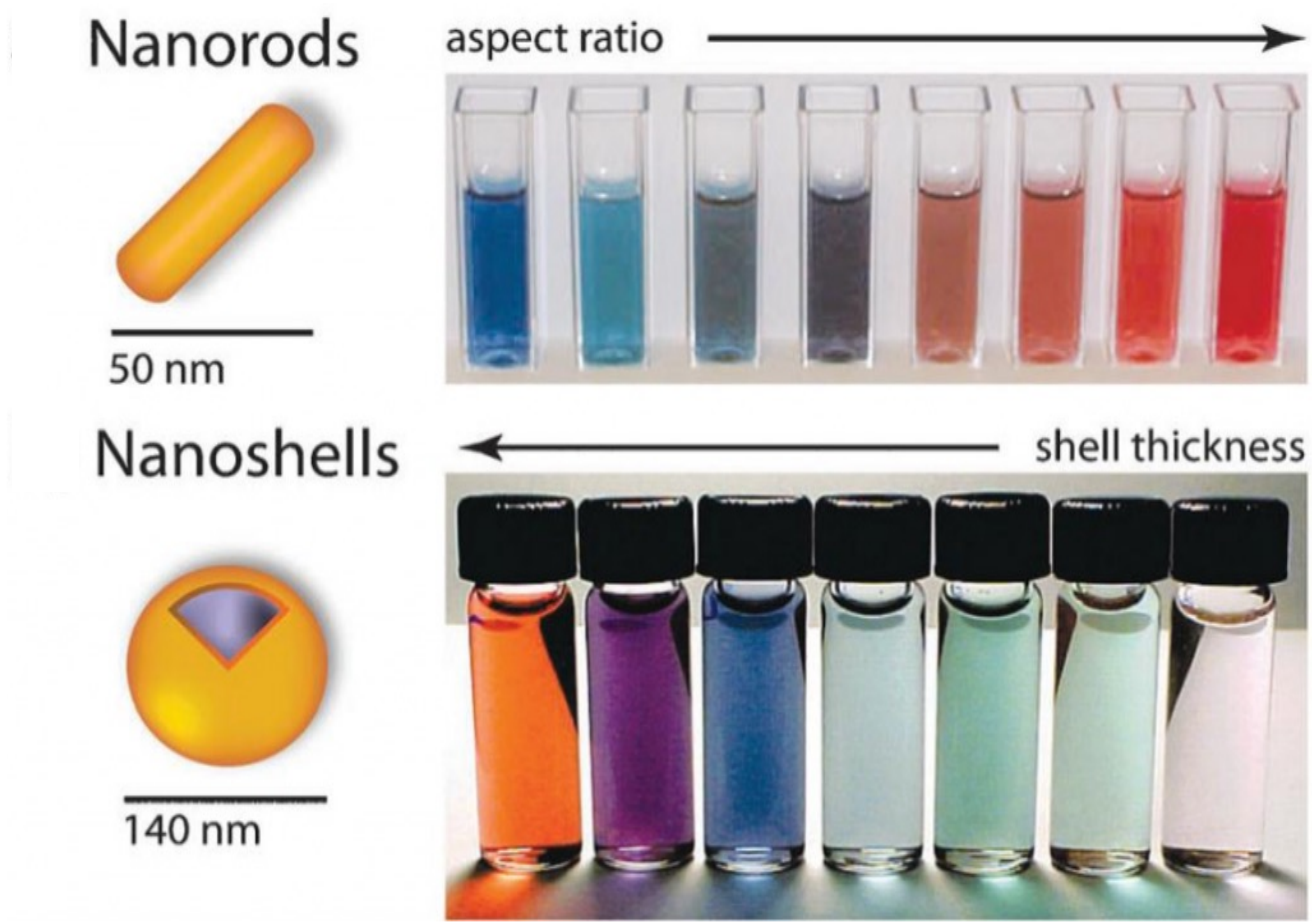
Broader Color Range with Asymmetric Nanostructures



While nanoparticles are symmetric, **nanorods** are anisotropic (different resonant frequencies depending on aspect ratio leading to multiple plasmon resonances

Nanoshells have inner and outer plamon modes with tunable optical properties based on shell thickness

Xiong *et al., Nanoscale, 6, 23,* **2014**

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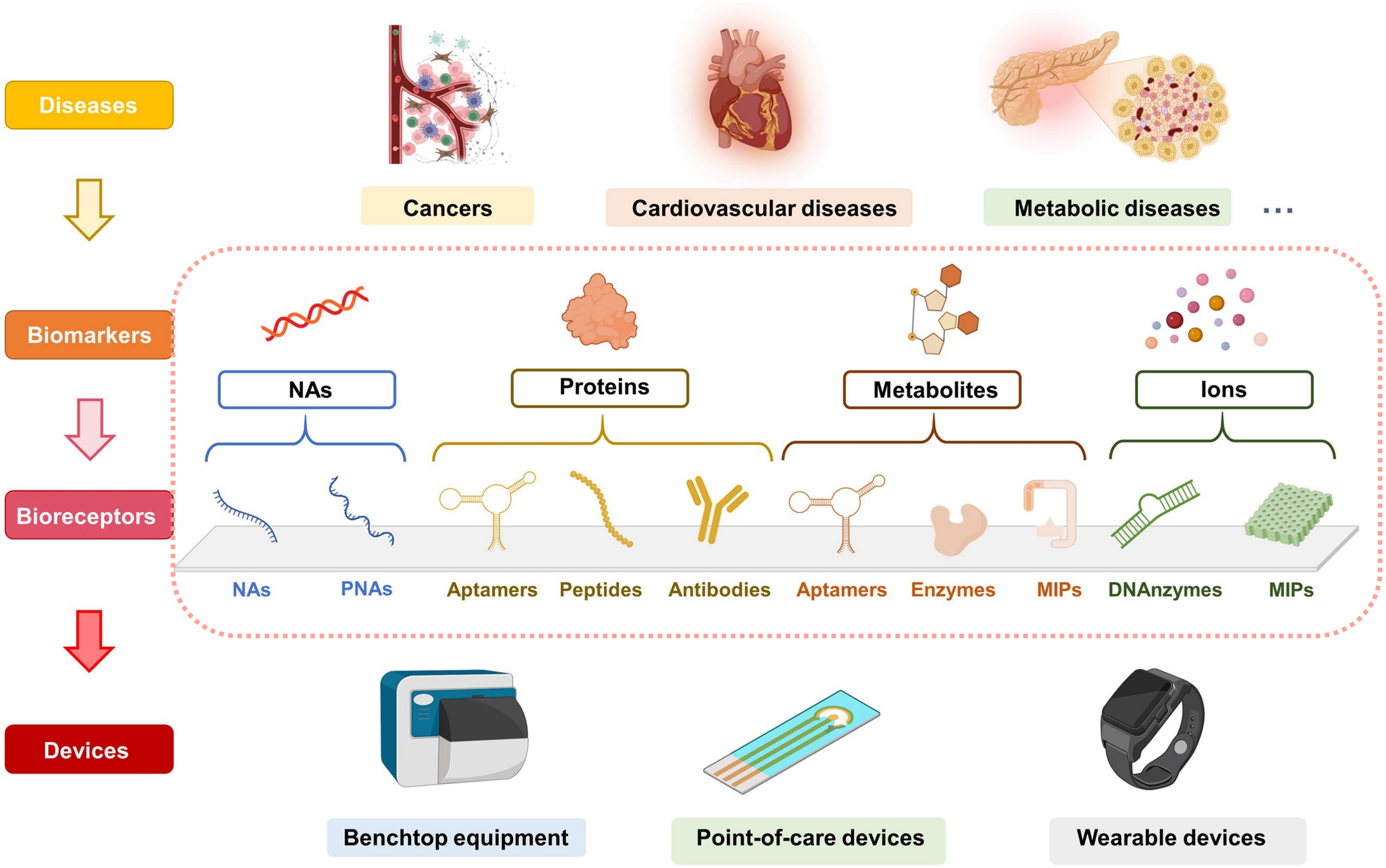
Biosensors For Human Health

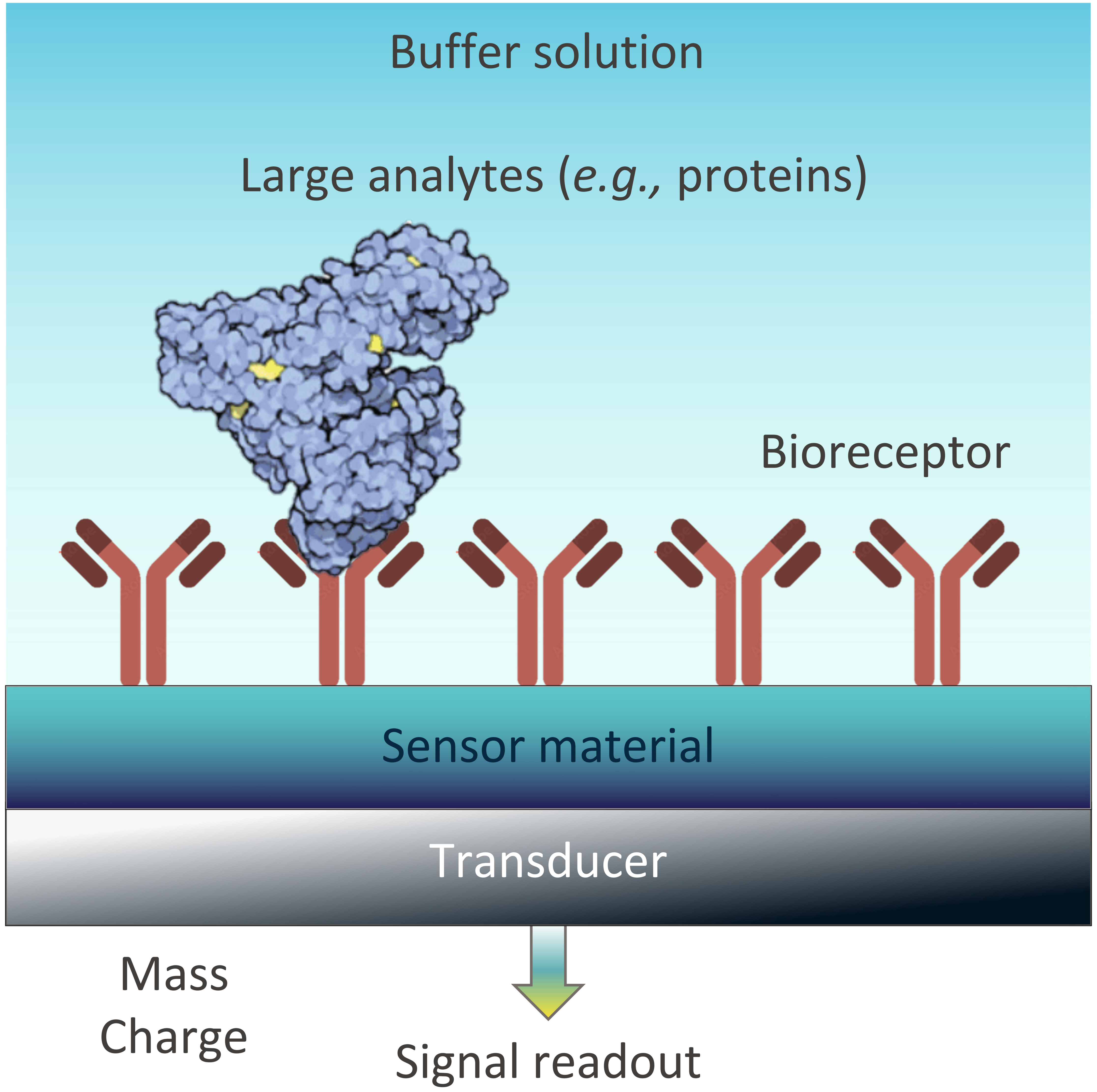


What are Bioreceptors?

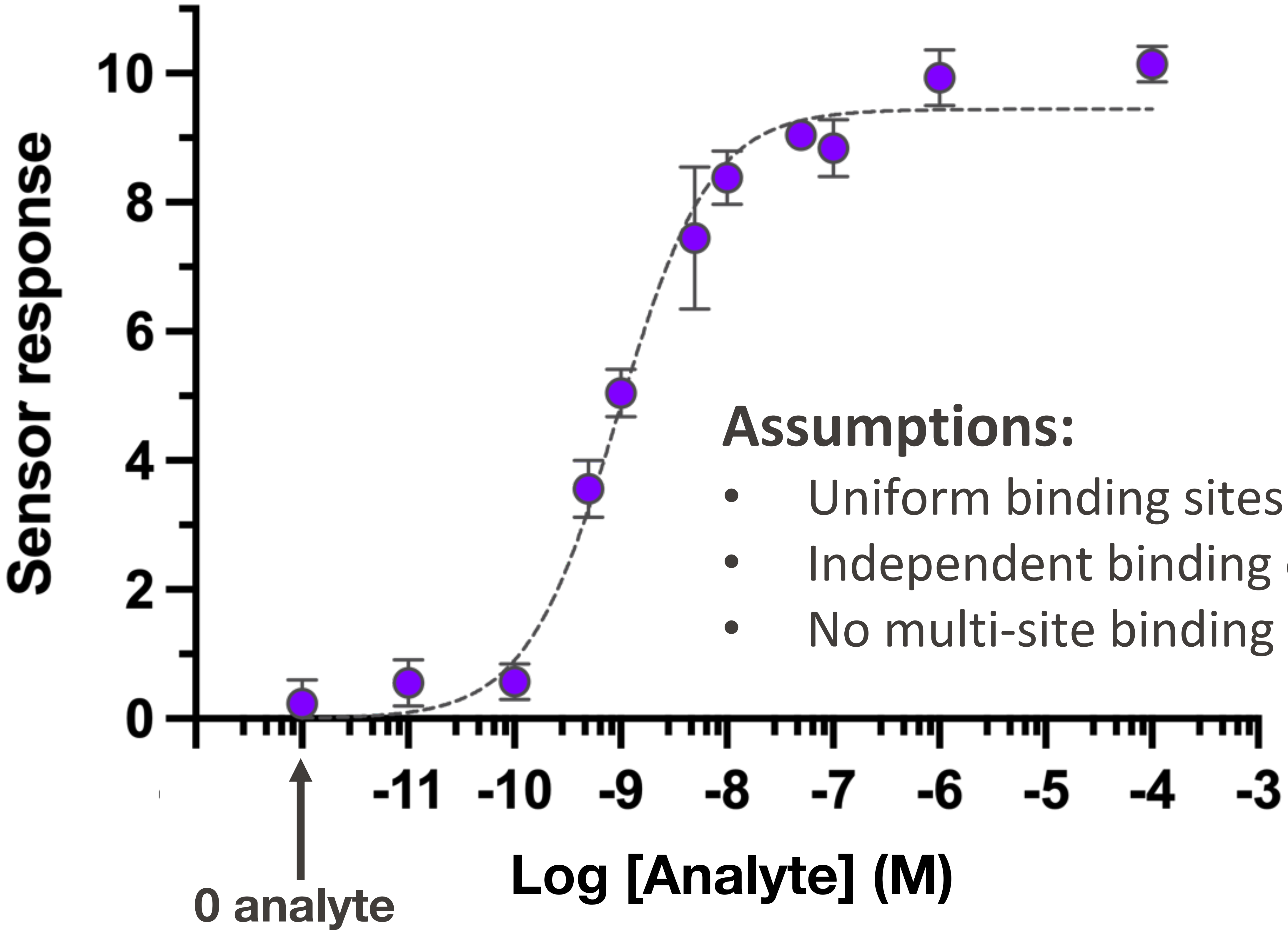
How does molecular recognition work?

Wang *et al.*, *Cell Rep. Phys. Sci.*, 5, 2, **2024**

How to Read Out the Signal of a Biosensor



Langmuir isotherm



Assumptions:

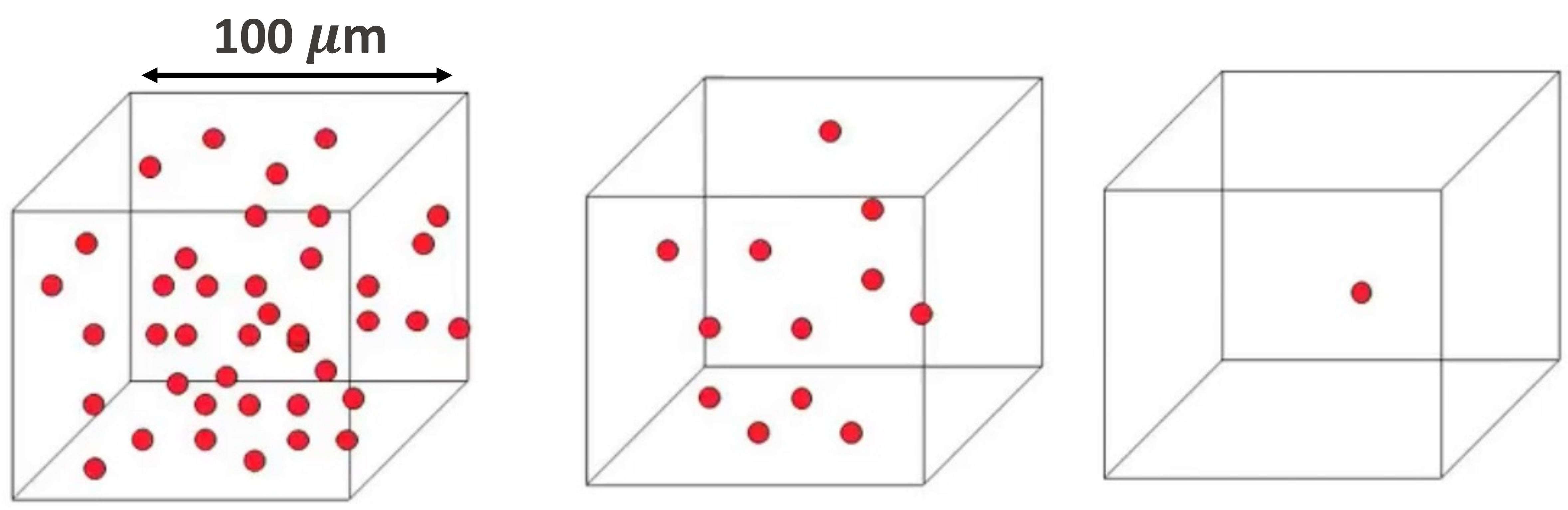
- Uniform binding sites
- Independent binding event
- No multi-site binding

Concentration – What Do these Values Mean?

1 M = 1 mol/L = 6 x 10^{23} molecules/L

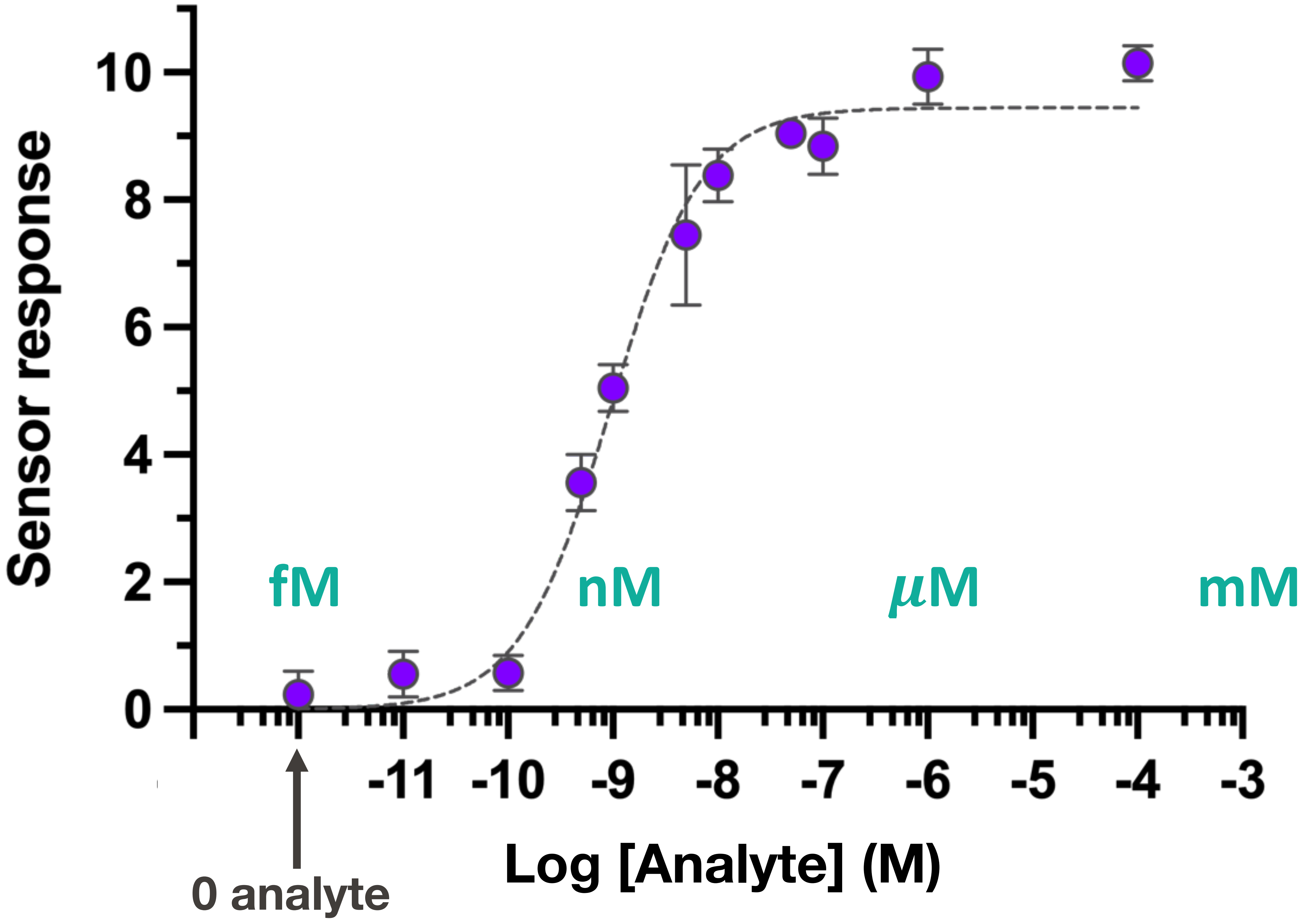
Note: Avogadro's number: 6 x 10^{23} molecules/mol

1 M ~ 1 x 10^{15} molecules/100 μm^3

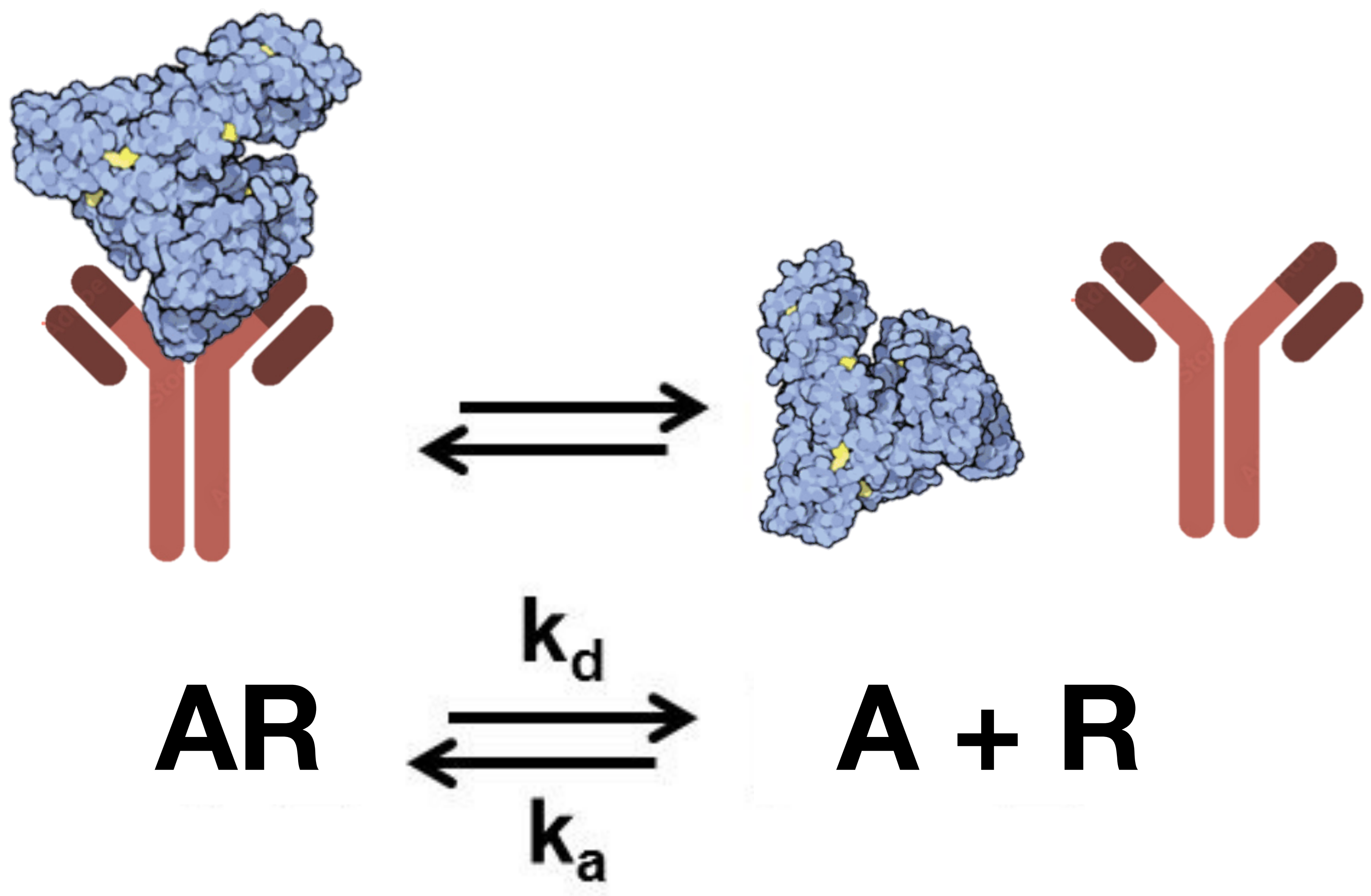


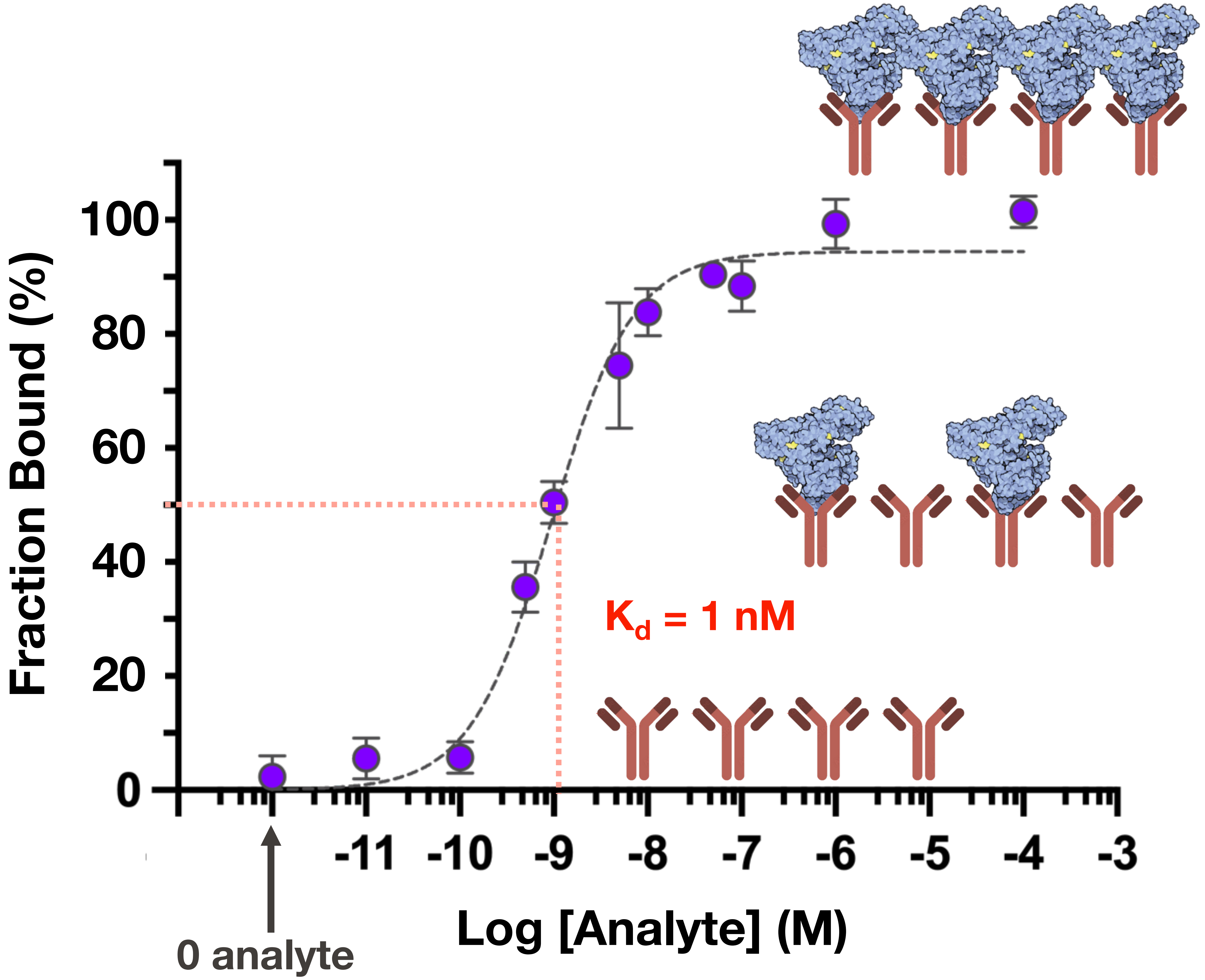
1 μM ~1 billion **1 pM ~1000** **1 fM ~1**

Single molecule of salt in several Olympic-sized swimming pools!



How to Read Out the Signal of a Biosensor





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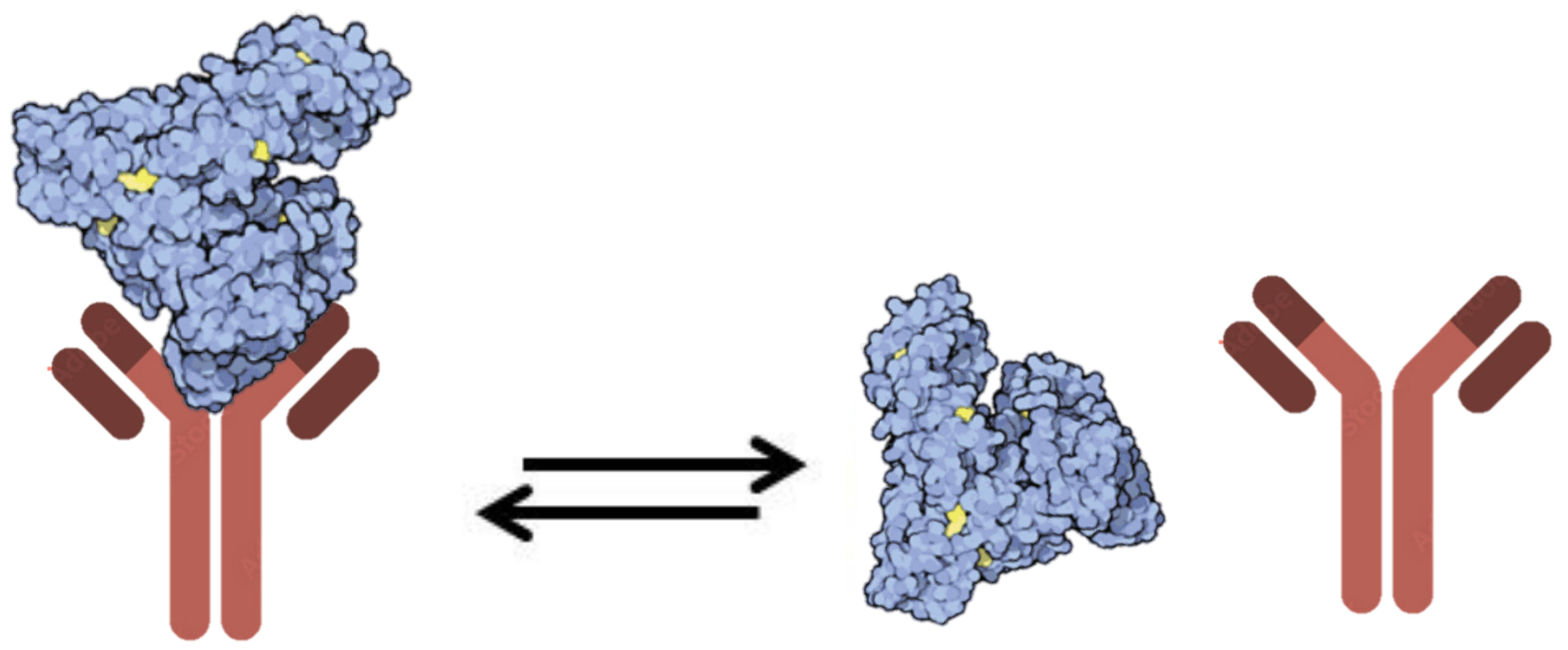
How to Calculate the Equilibrium Binding Affinity (K_d)



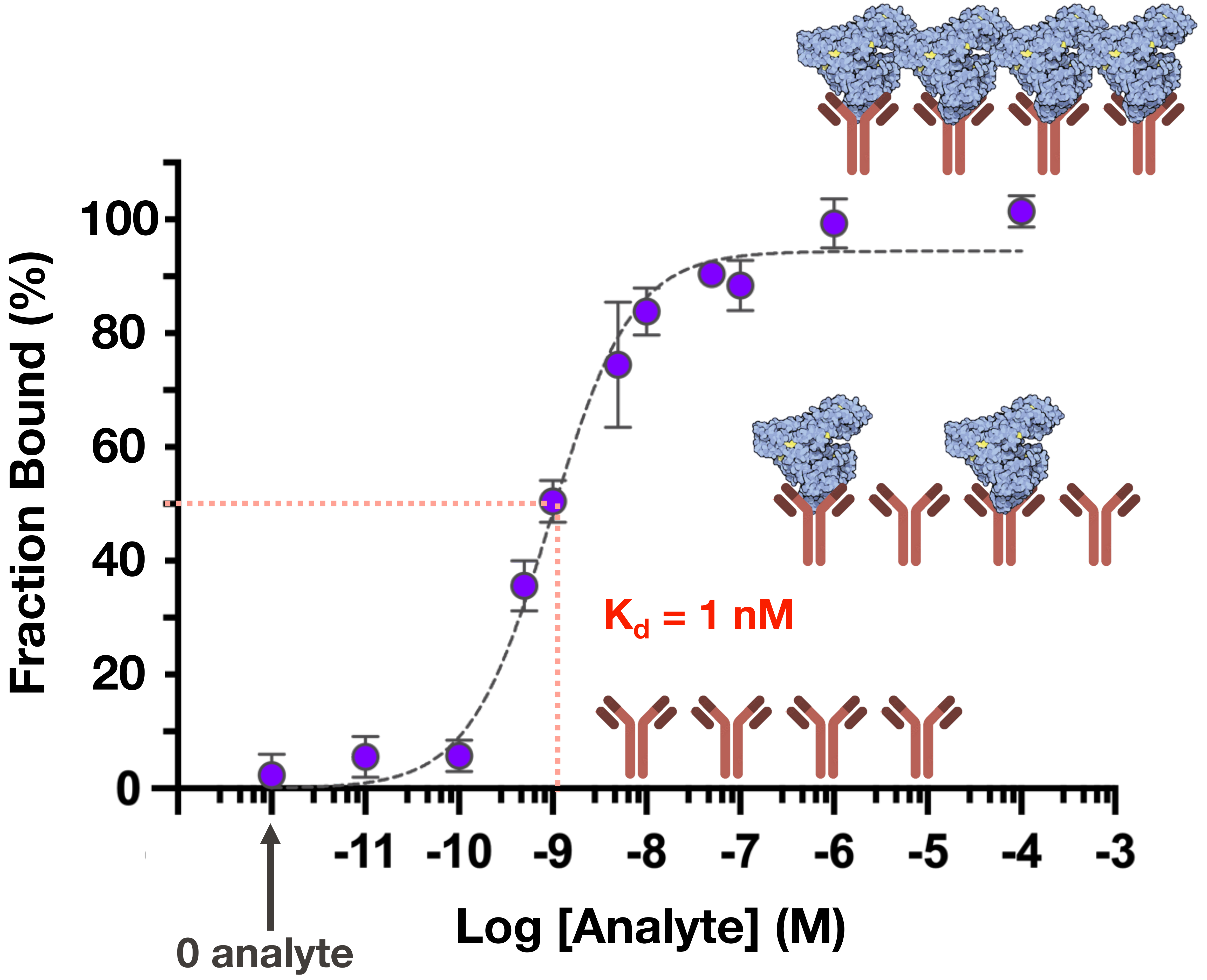
$$AR \underset{k_a}{\overset{k_d}{\rightleftharpoons}} A + R$$

Fractional occupied receptor density

$$\phi = \frac{[AR]}{[R_0]}$$

Target-bound receptors

Total number of receptors



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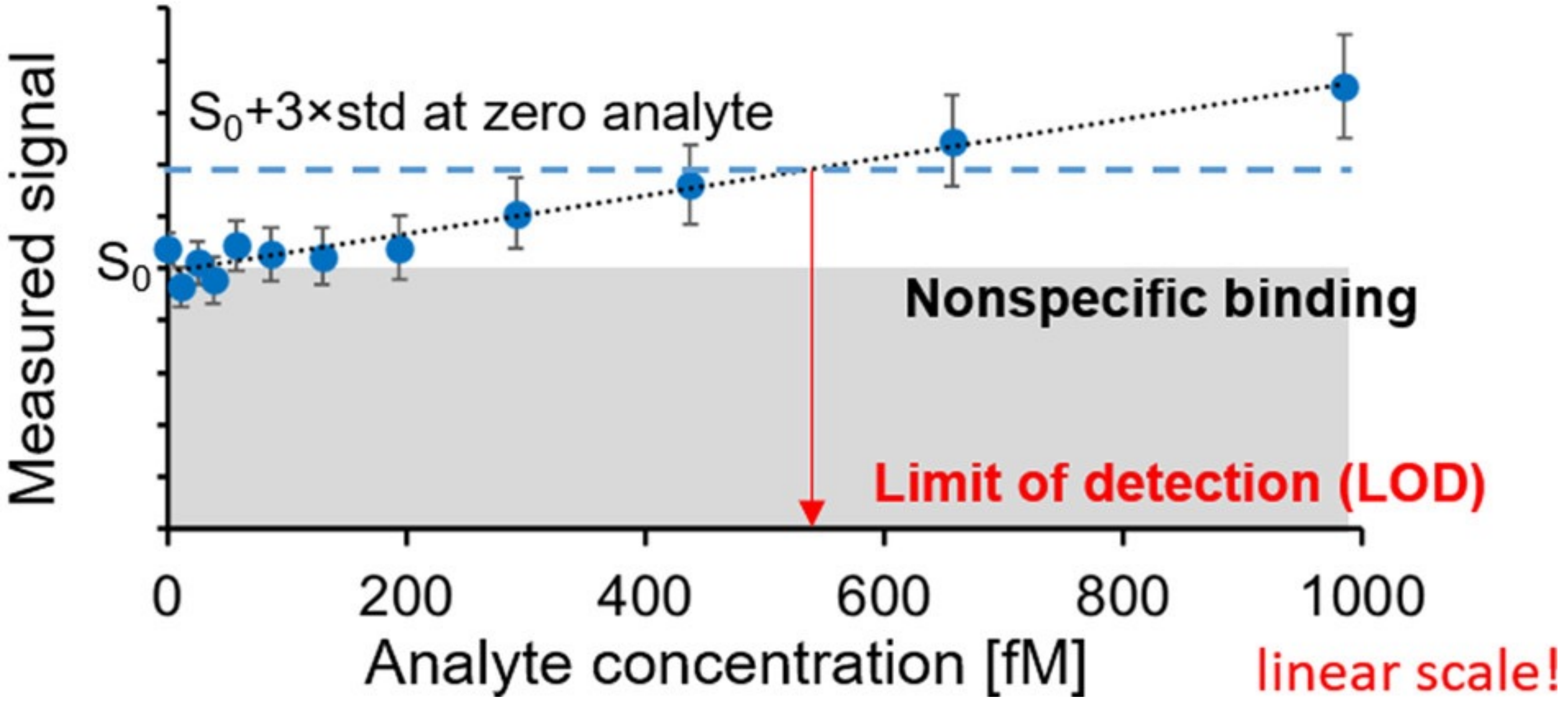
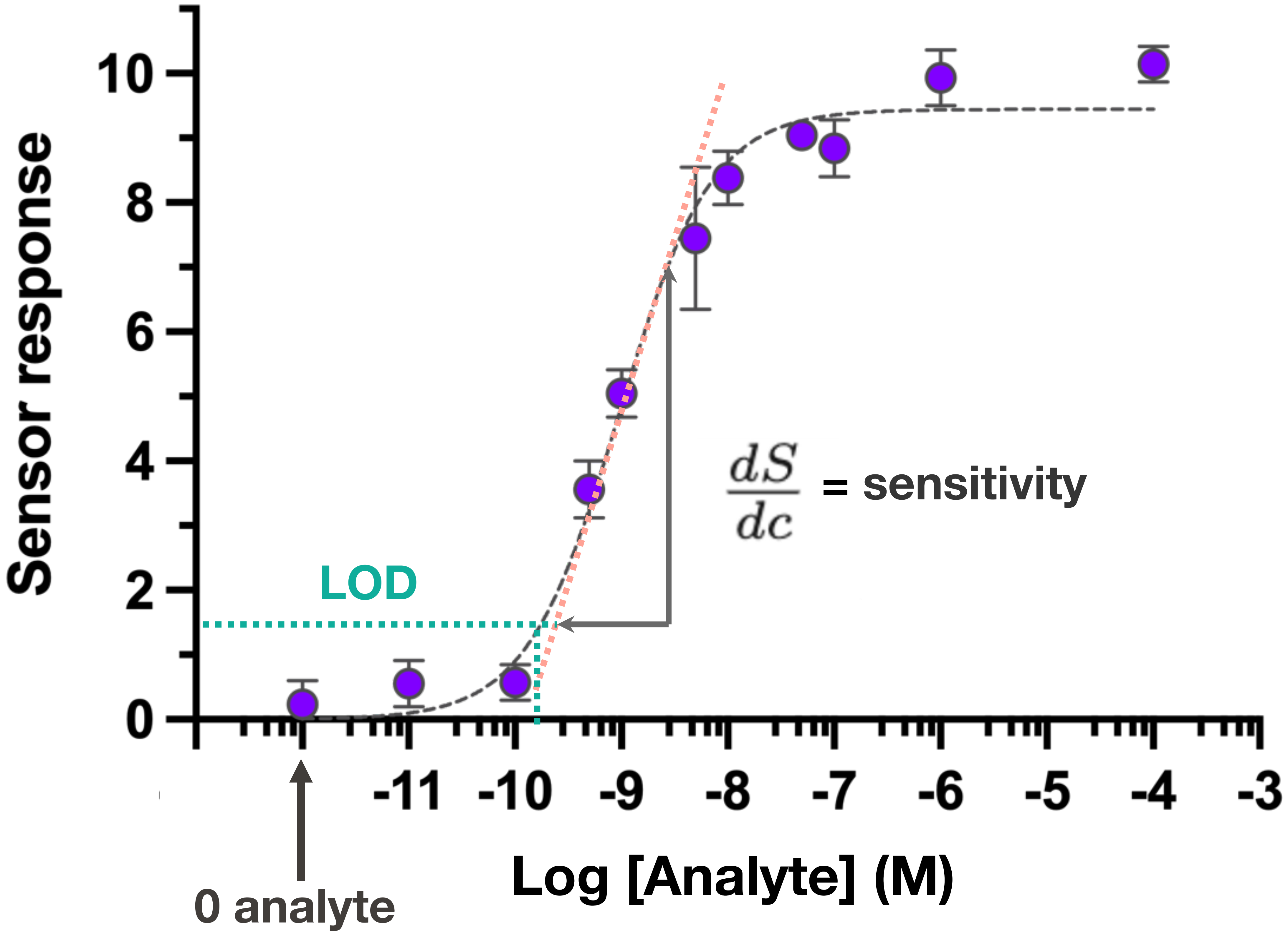
How to Calculate the Sensitivity and Limit of Detection (LOD)

$$\text{LOD} = \frac{3\sigma_{S_0}}{\frac{dS}{dc}}$$

3 x standard deviation of zero analyte signal

Sensitivity = Slope of the signal





Frutiger *et al.*, *Chem. Rev.*, *121*, 8095, **2021**

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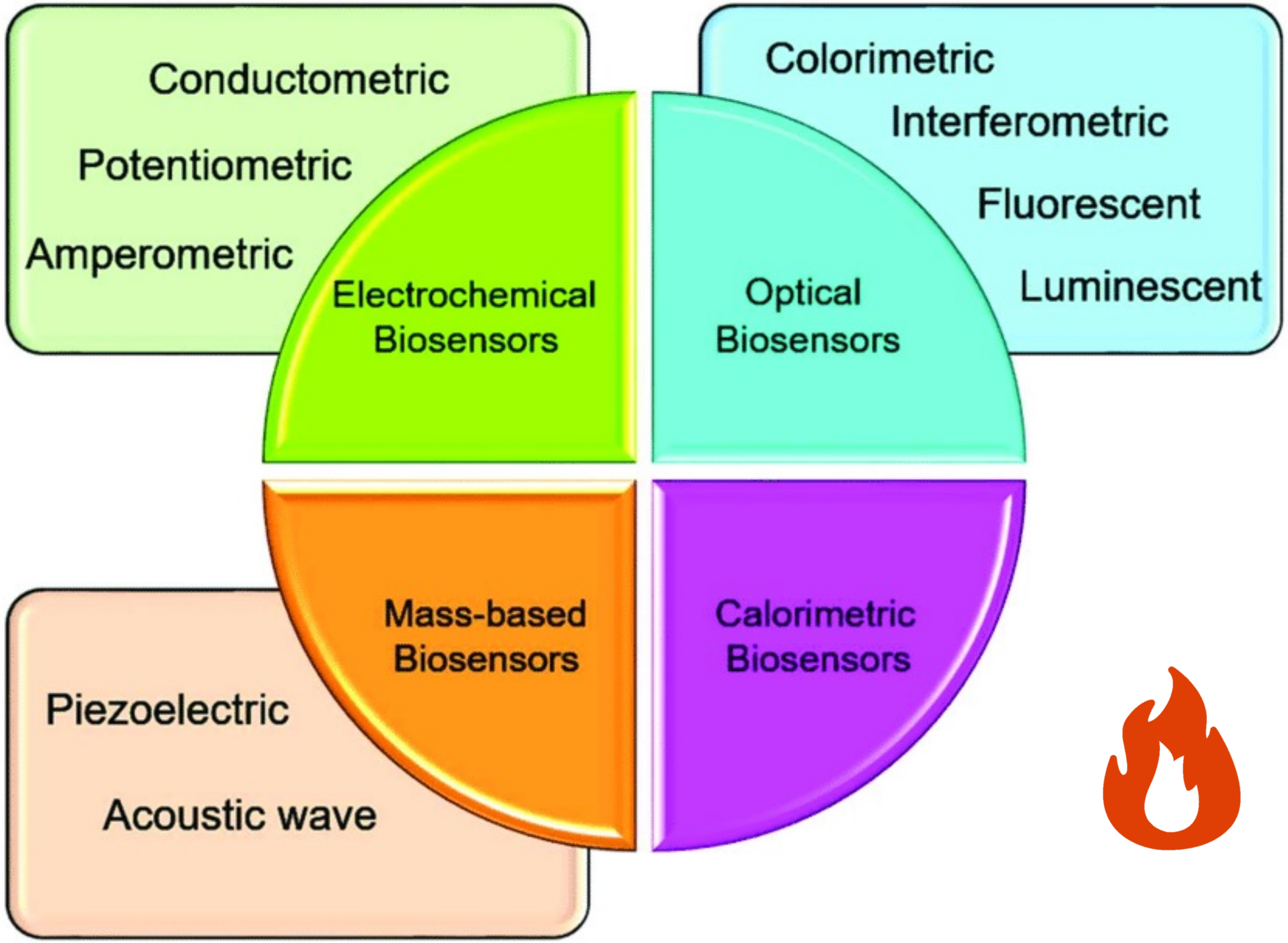
Different Signal Transduction Mechanisms of Biosensors

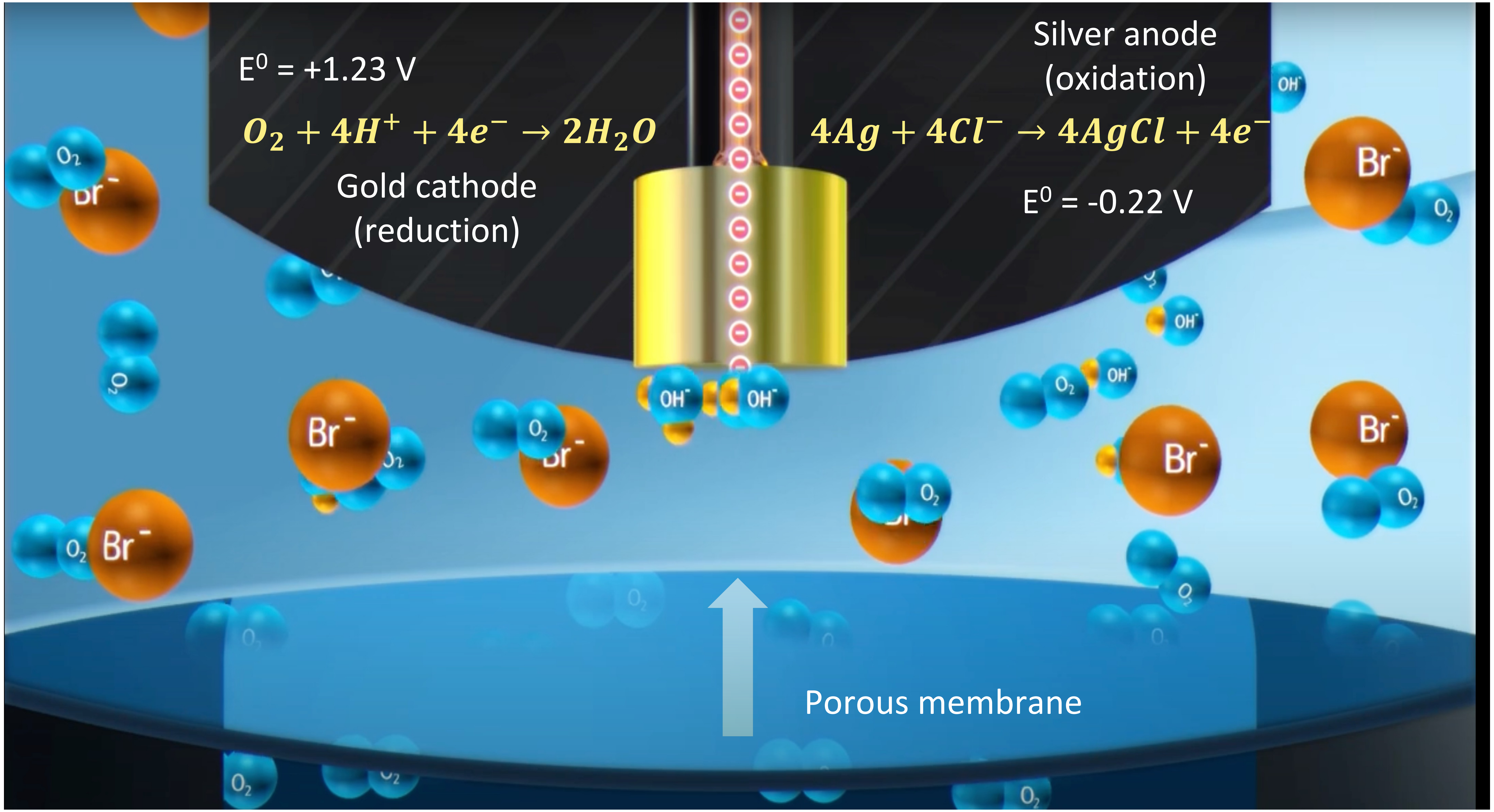


Vargas, *et al.*, *Biosensors*, *8*, 2, **2018**

Clark Electrode Measures Ambient Oxygen Partial Pressure

Redox processes are highly favorable so spontaneous process

Electron flow between electrodes generates current directly proportional to the partial pressure of oxygen in the sample



This work became the basis for the first glucose sensor

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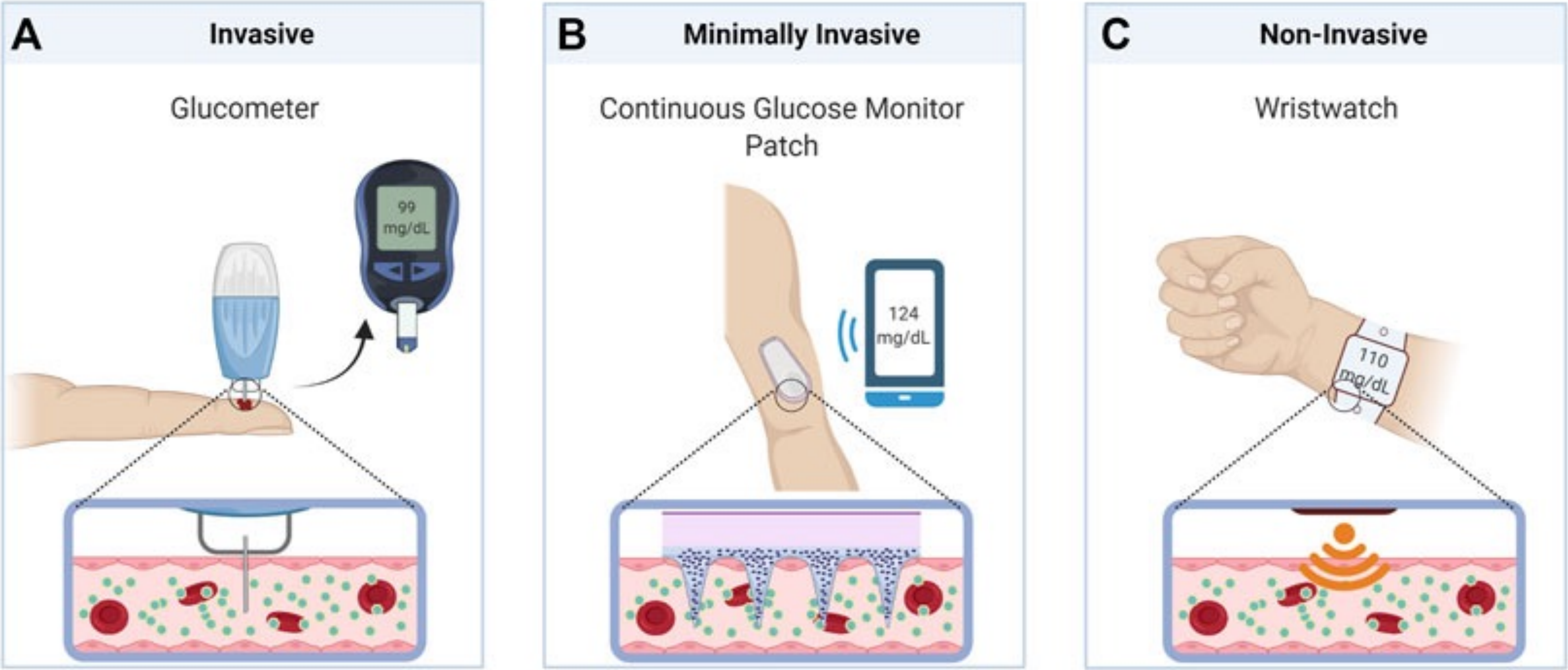
Glucose Biosensor – Transformative for Human Health



Todaro *et al.*, *Front. Chem.*, *10*, **2022**

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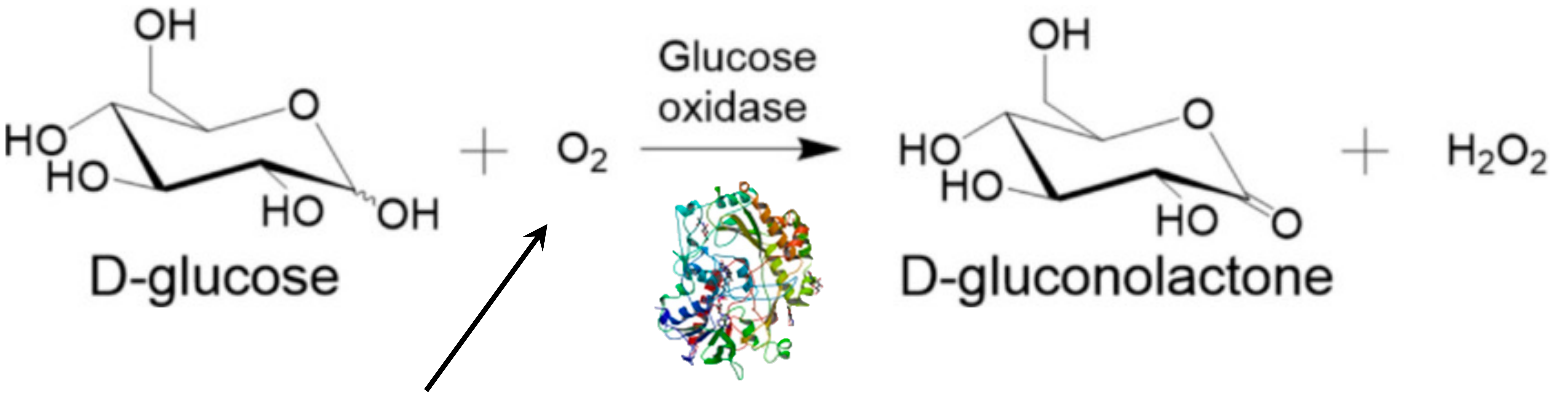
Glucose Sensor – Detection of Hydrogen Peroxide as Readout



Monitor decrease in O_2 as proxy for glucose

Monitor increase in H_2O_2 as proxy for glucose

Lack of **sensitivity** – small signal change since O_2 levels high in biofluids

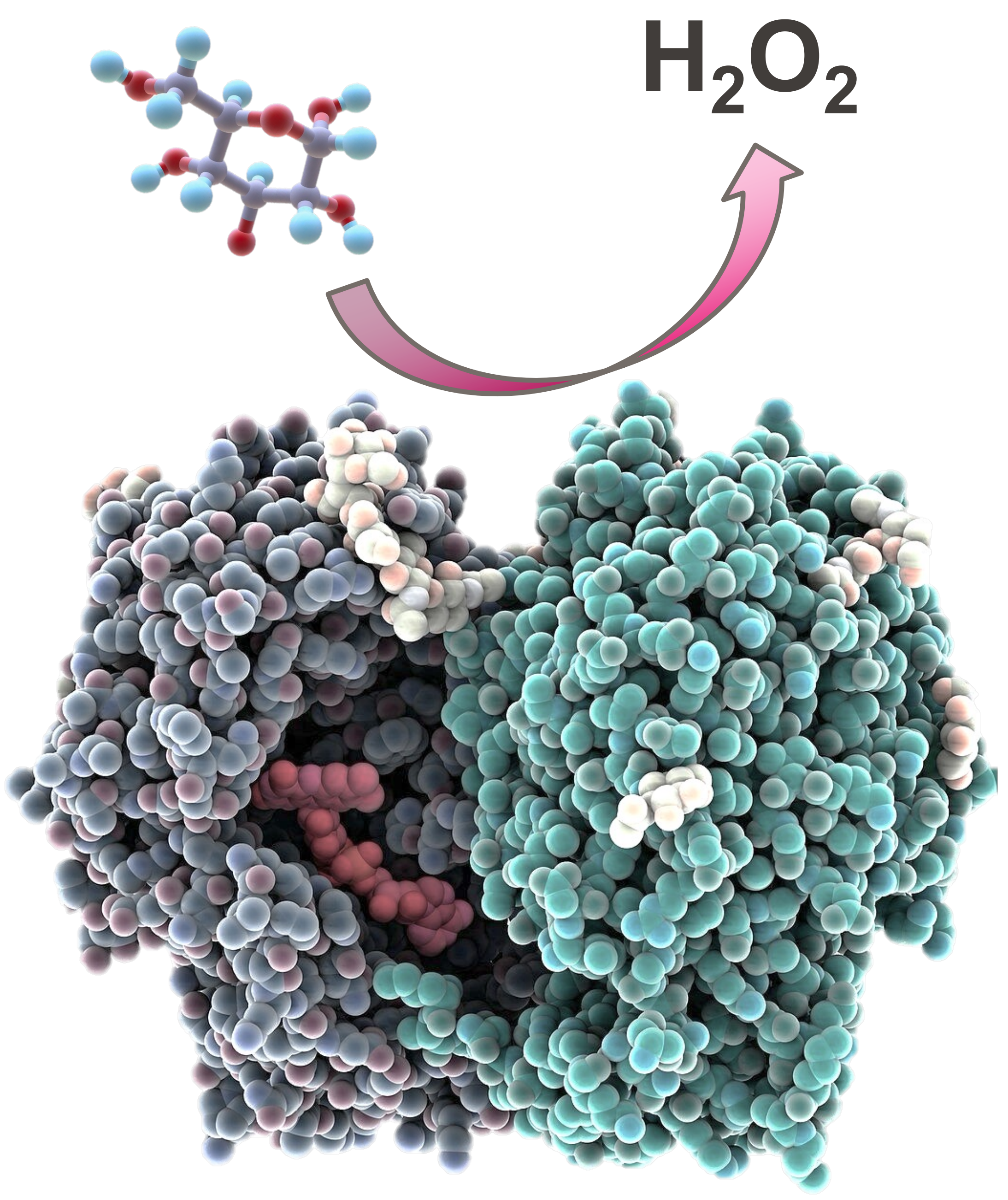
Higher **sensitivity** – H_2O_2 not abundant in the sample prior to enzymatic reaction

$$S = \frac{\Delta \text{Signal}}{\Delta \text{Concentration}}$$

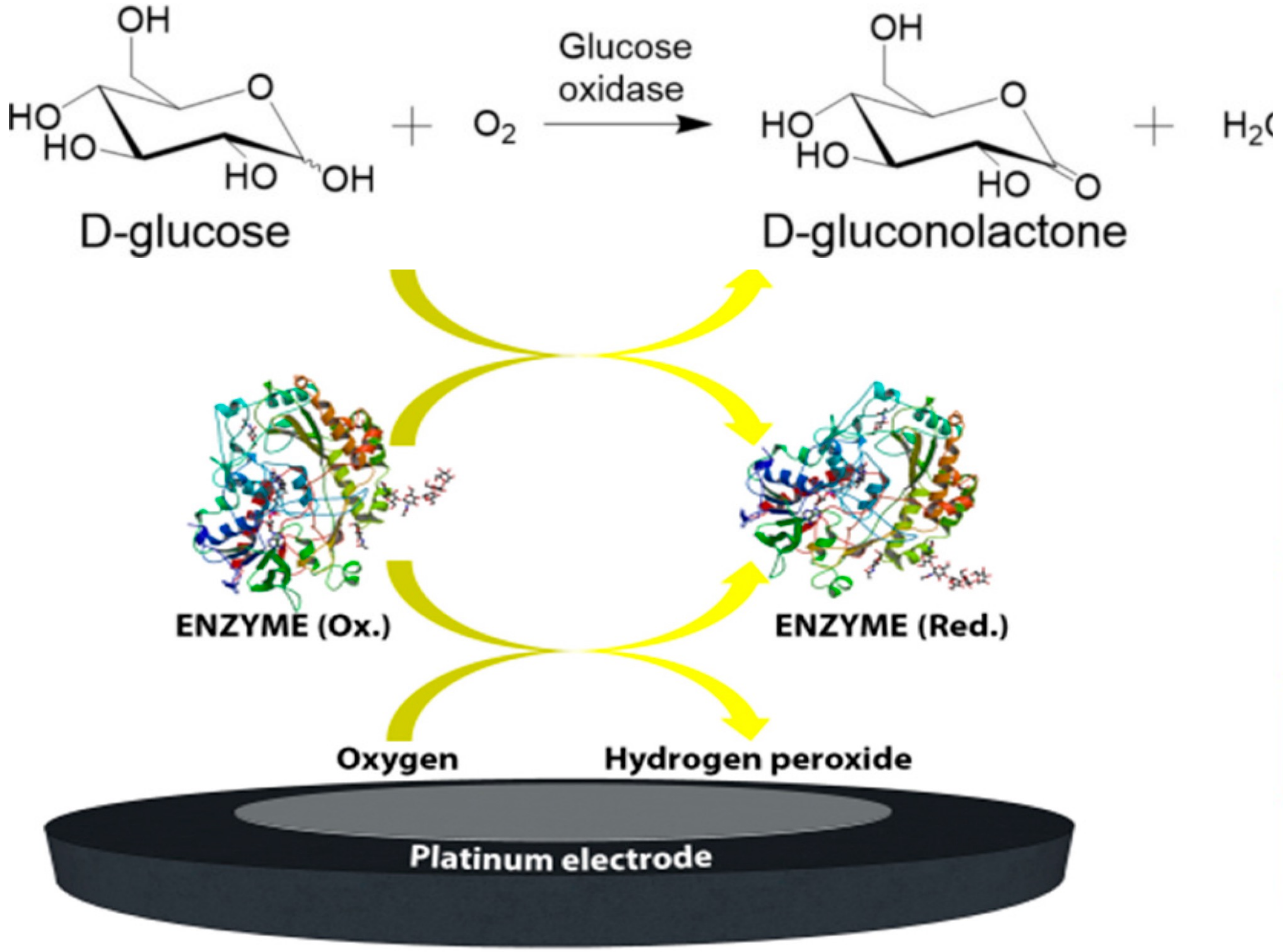
Lack of **specificity** – O_2 sensors influenced by changes unrelated to glucose (respiratory, temperature)

Higher **specificity** – H_2O_2 is direct product of enzymatic reaction

Success of the Glucose Biosensor – Robust System



Highly specific and robust enzyme



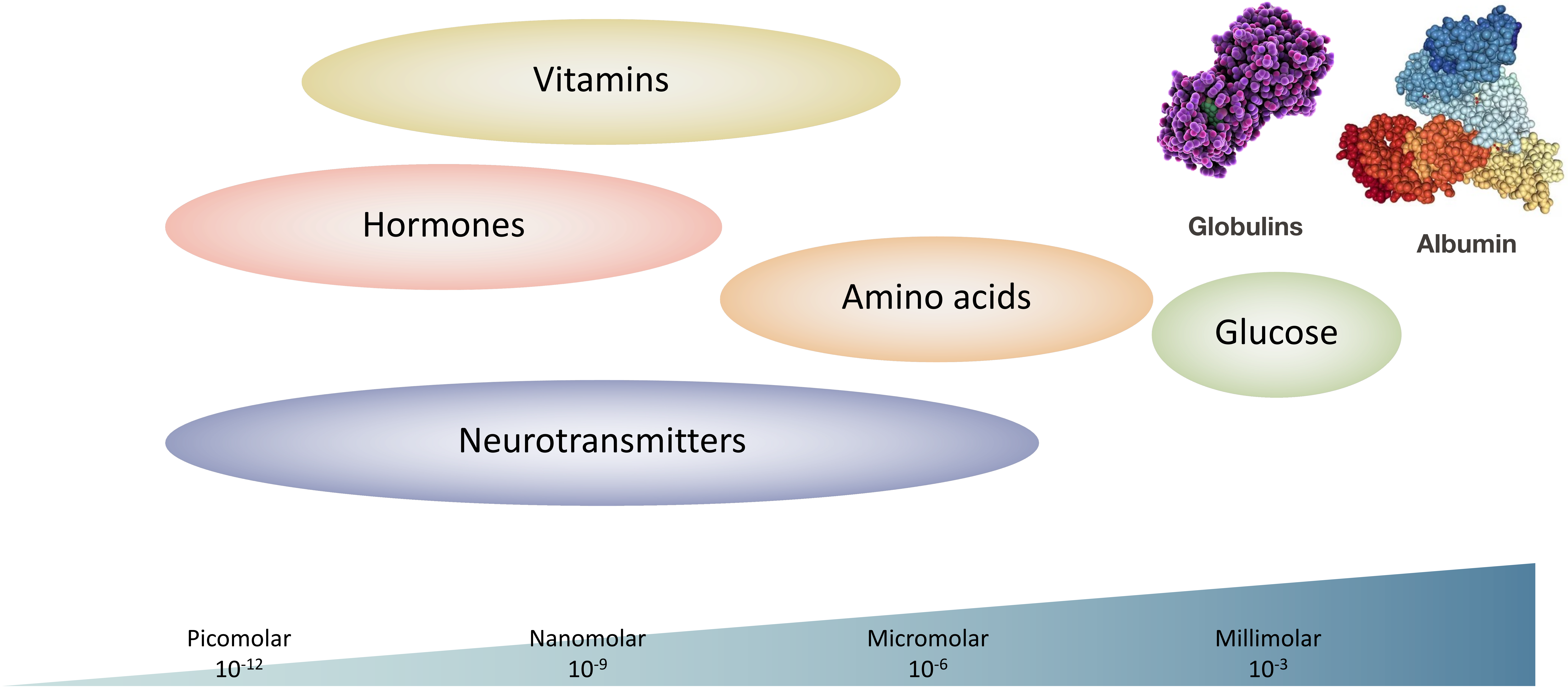
Detection window for H_2O_2 doesn't overlap with other species in blood

BLOOD GLUCOSE LEVELS CHART

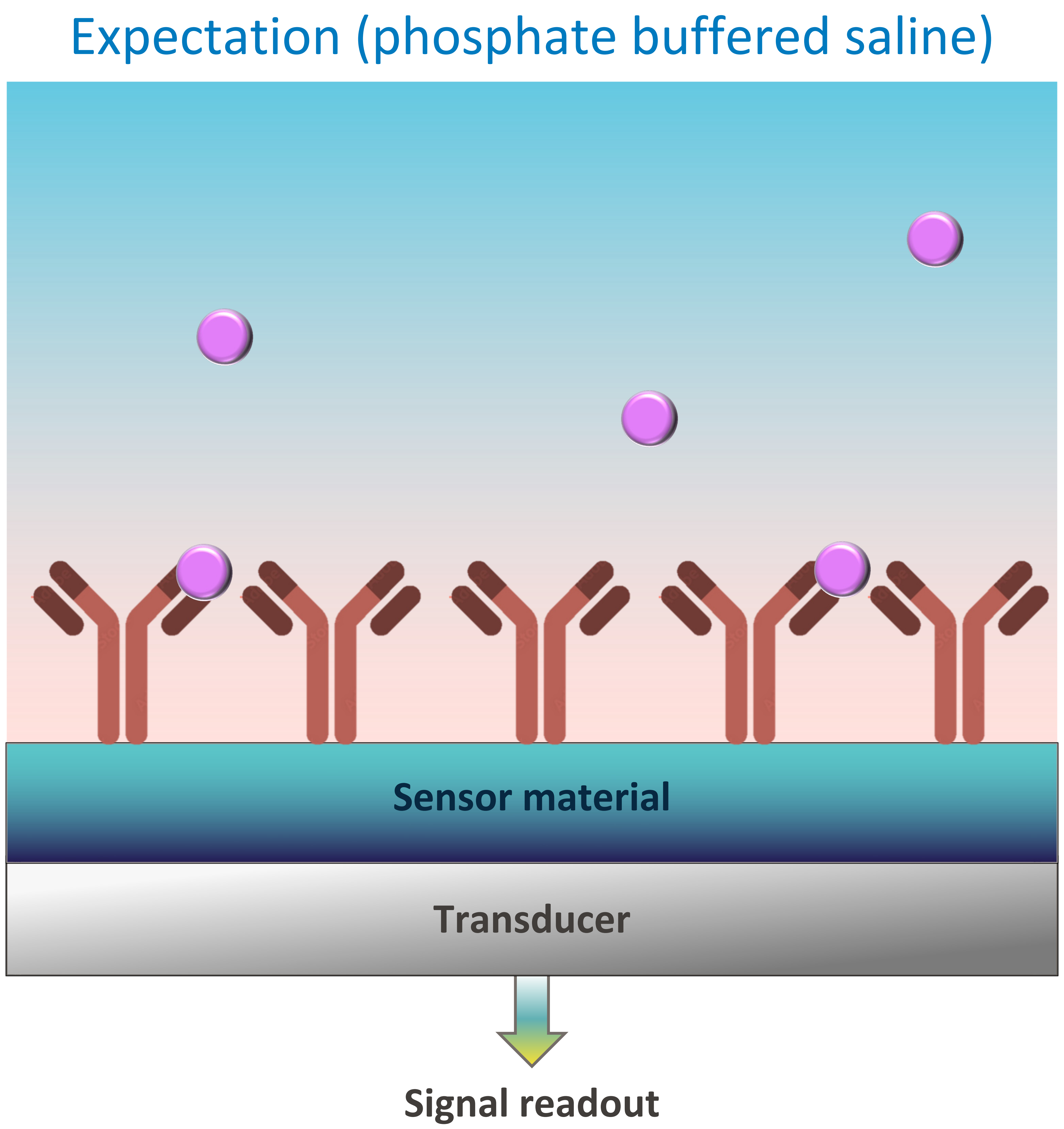
LEVEL	mg/dl	mmol/L	RISK	SUGGESTED ACTION
DANGER - HIGH	315+	17.4	VERY HIGH	MEDICAL ATTENTION
HIGH	280	15.6	HIGH	MEDICAL ATTENTION
HIGH	250	13.7	HIGH	MEDICAL ATTENTION
HIGH	215	11	HIGH	MEDICAL ATTENTION
BORDERLINE	180	10	MEDIUM	CONSULT DOCTOR
BORDERLINE	150	8.2	MEDIUM	CONSULT DOCTOR
BORDERLINE	120	7	MEDIUM	CONSULT DOCTOR
NORMAL	108	6	NO RISK	NO ACTION NEEDED
NORMAL	72	4	NO RISK	NO ACTION NEEDED
LOW	70	3.9	MEDIUM	CONSULT DOCTOR
DANGER - LOW	50	2.8	HIGH	MEDICAL ATTENTION

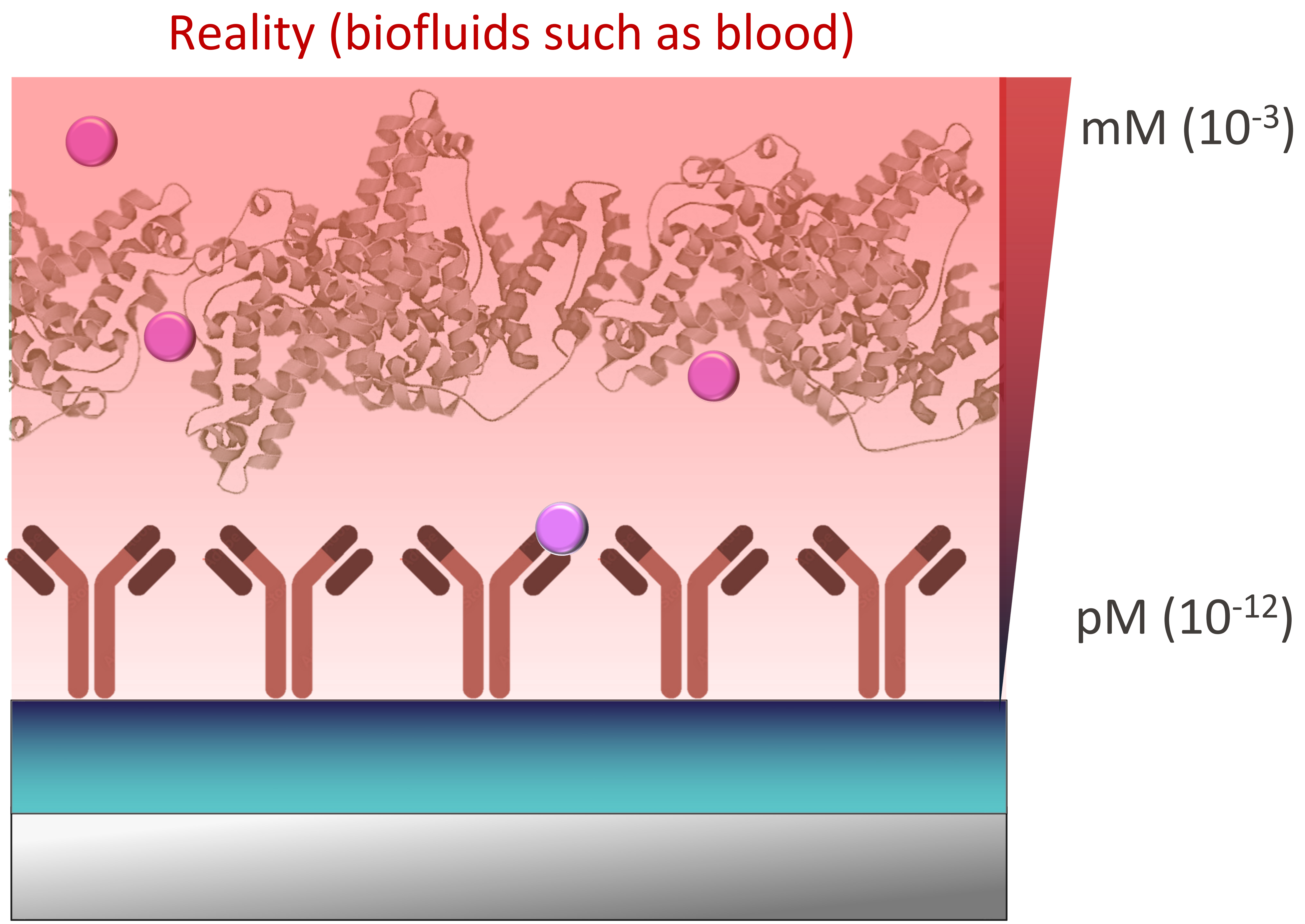
Clear values associated with healthy and disease states (diabetes)

Success of the Glucose Biosensor – Concentration Range



1. Nonspecific Binding (NSB) in Complex Environments

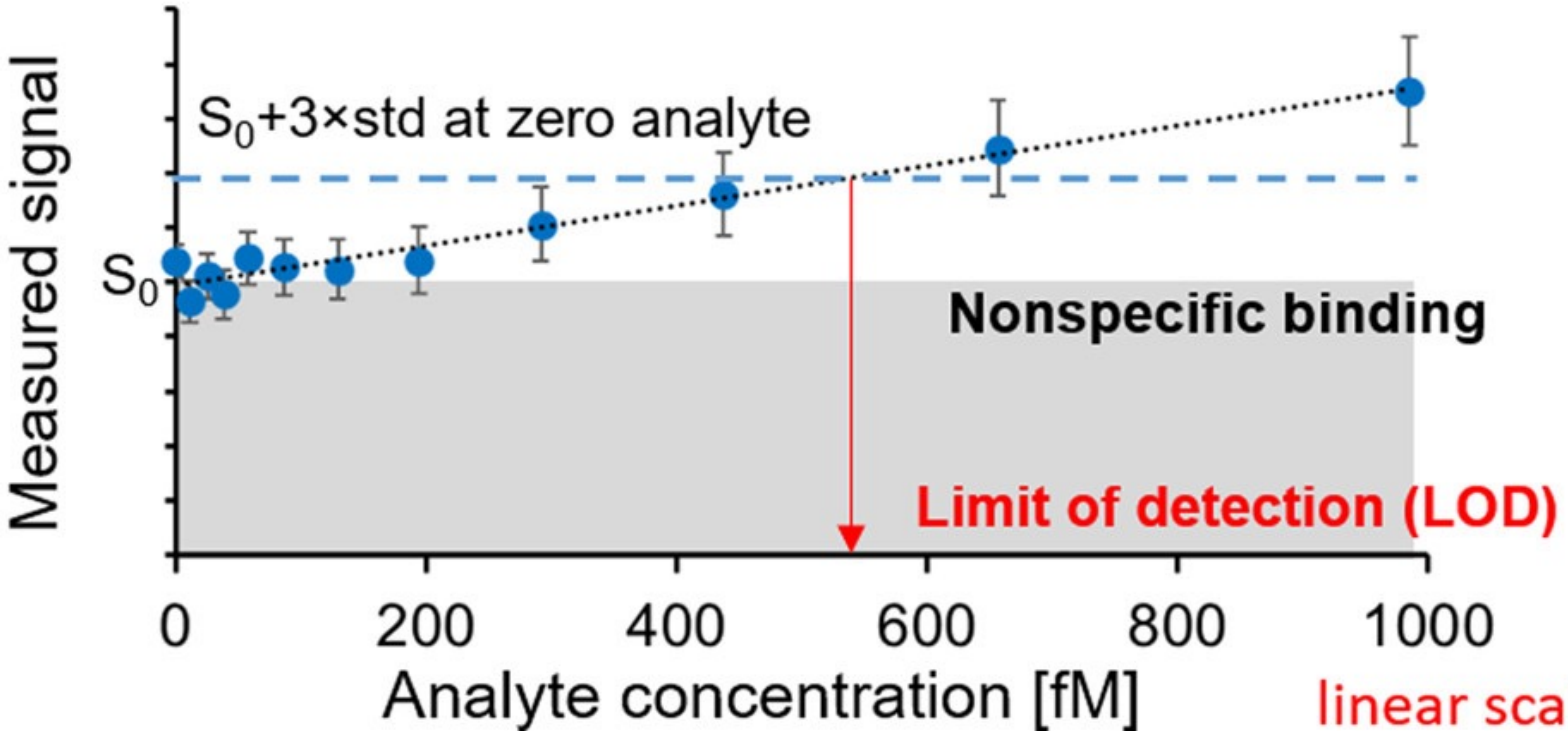




Frutiger *et al.*, *Chem. Rev.*, *121*, 8095, **2021**

Most Existing Diagnostics are Limited by Nonspecific Binding

Non-specific binding induced noise at low concentrations limits diagnostic biosensors

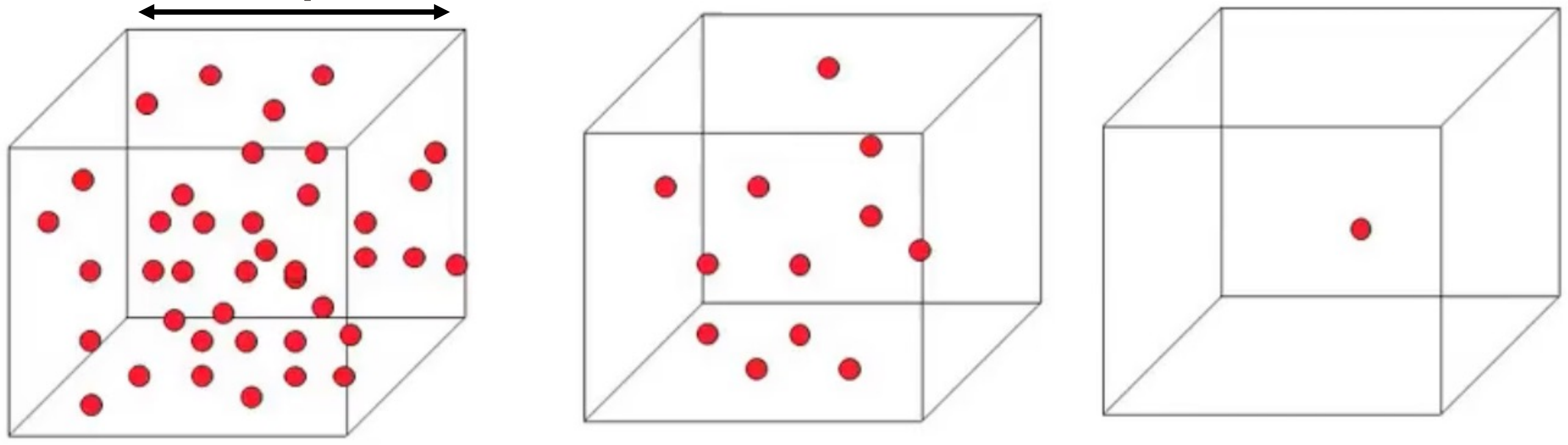


linear scale!

Frutiger *et al.*, *Chem. Rev.*, *121*, 8095, **2021**

2. Very Few Number of Molecules Within Sample Size

Stochastic process – probability of the biosensor seeing such a low concentration of target diffusing to the surface?

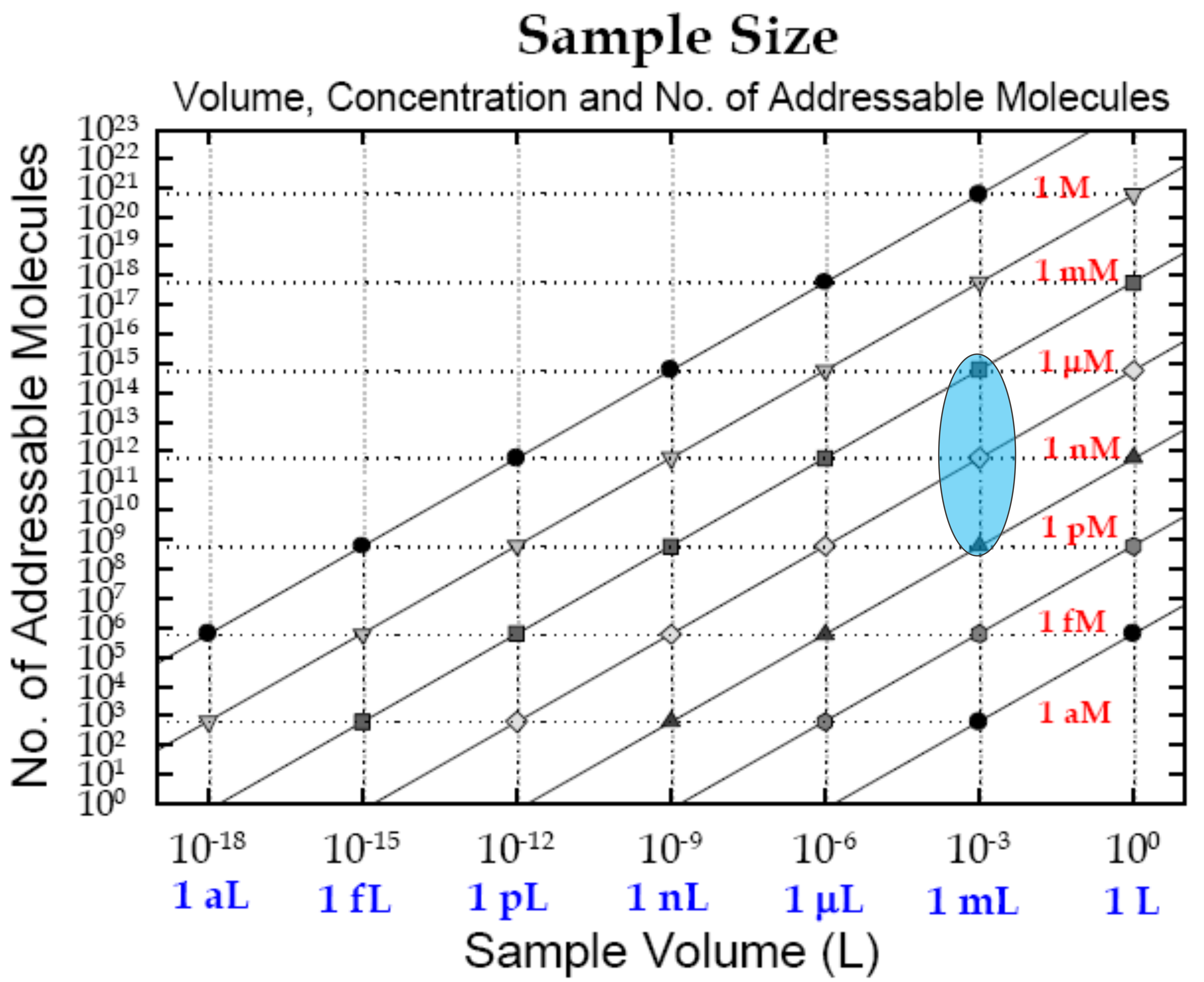


1 μM ~1 billion

1 pM ~1000

1 fM ~1

Single molecule of salt in several Olympic-sized swimming pools!



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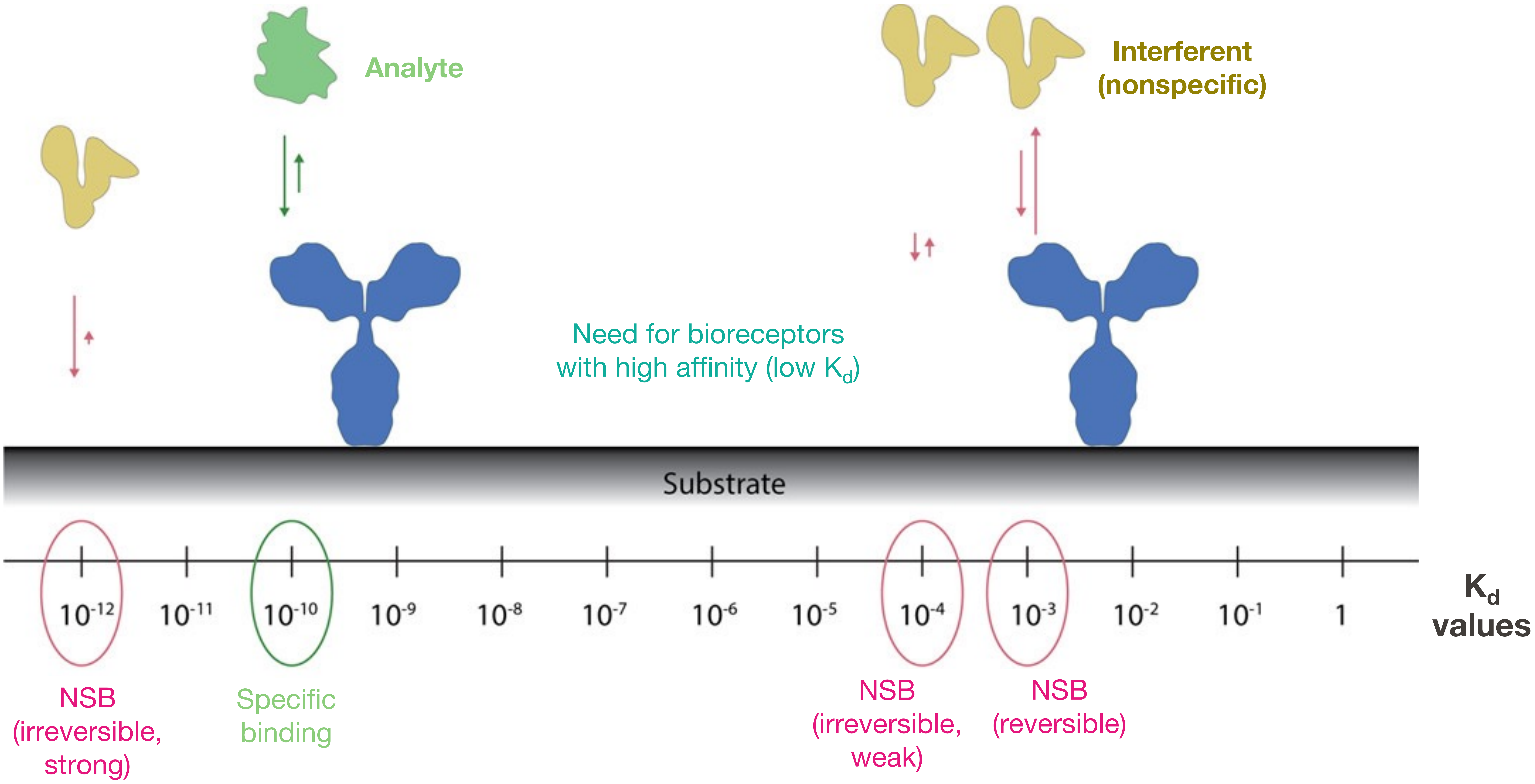
3. Challenges of Bioreceptor Specificity in Addition to NSB



Frutiger *et al.*, *Chem. Rev.*, *121*, 8095, **2021**

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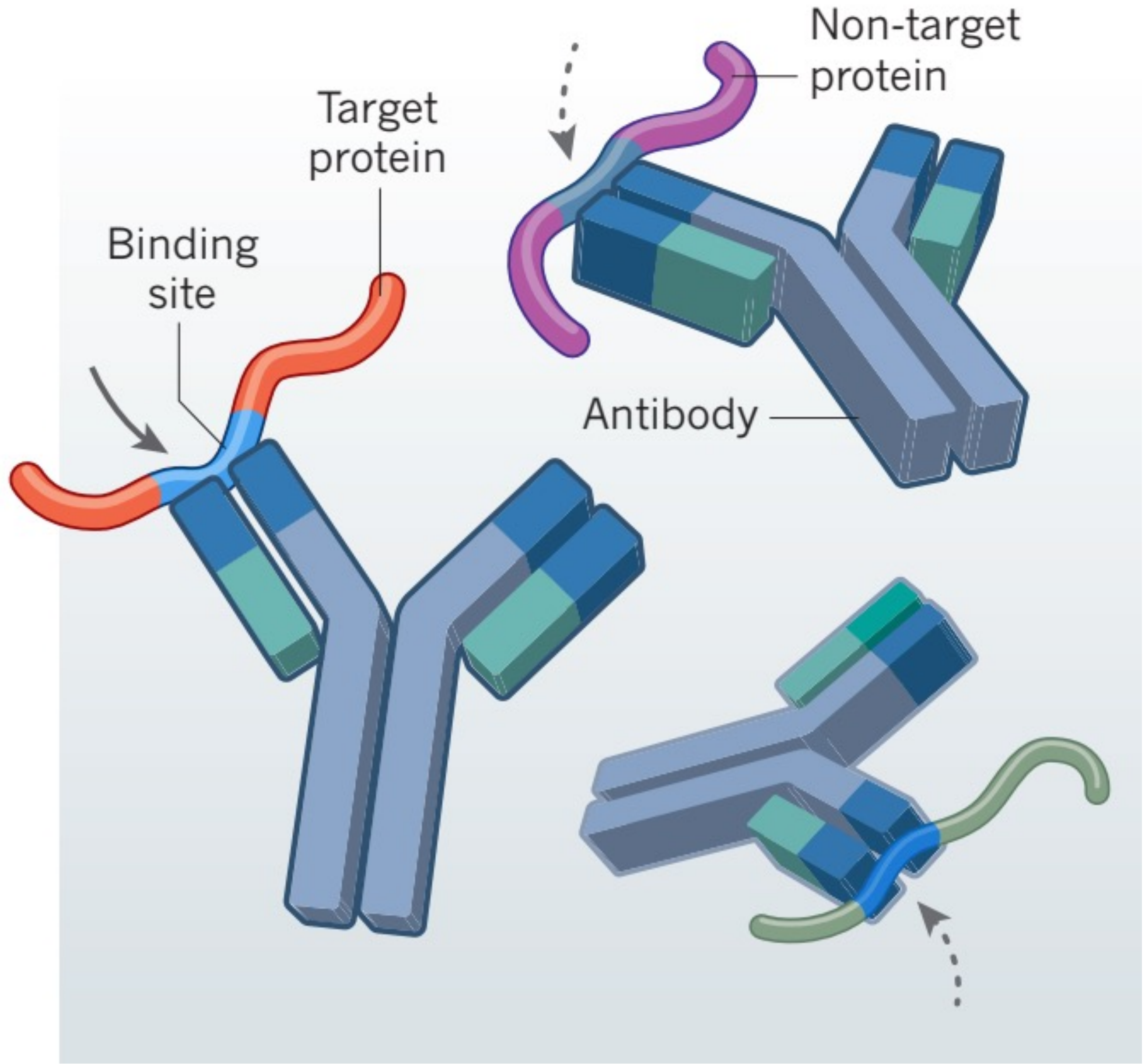
Bioreceptors Can be Cross-Reactive to Nonspecific Molecules

Reproducibility crisis: Blame it on the antibodies

Monya Baker

Nature **521**, 274–276 (2015) | Cite this article



Cross-reactivity: binding to other non-targets

Batch-to-batch variability

Sensitivity to environment

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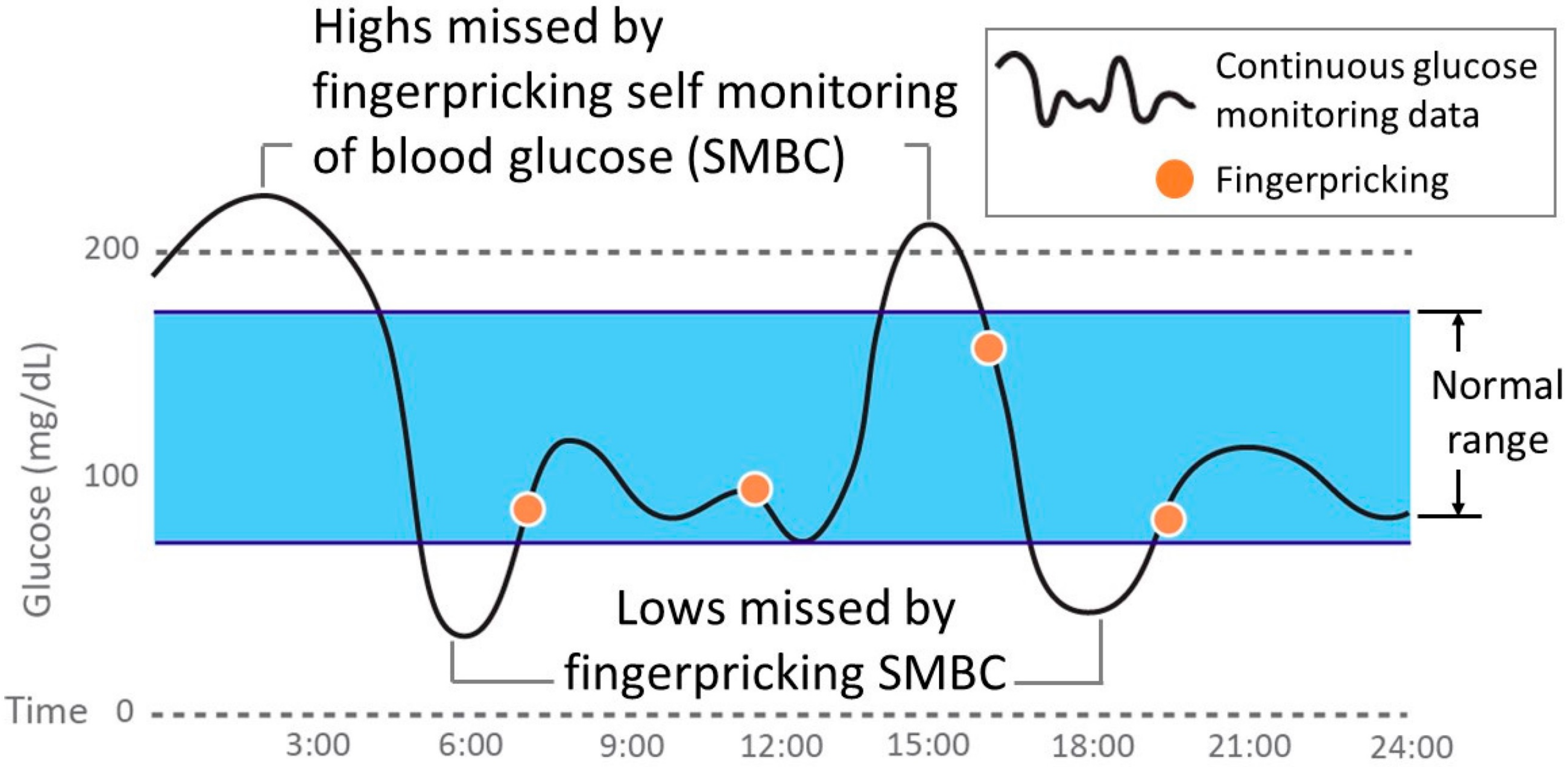
4. Challenges of Continuous Monitoring



Heo & Kim, *Appl. Sci.*, *9*, 10, **2019**

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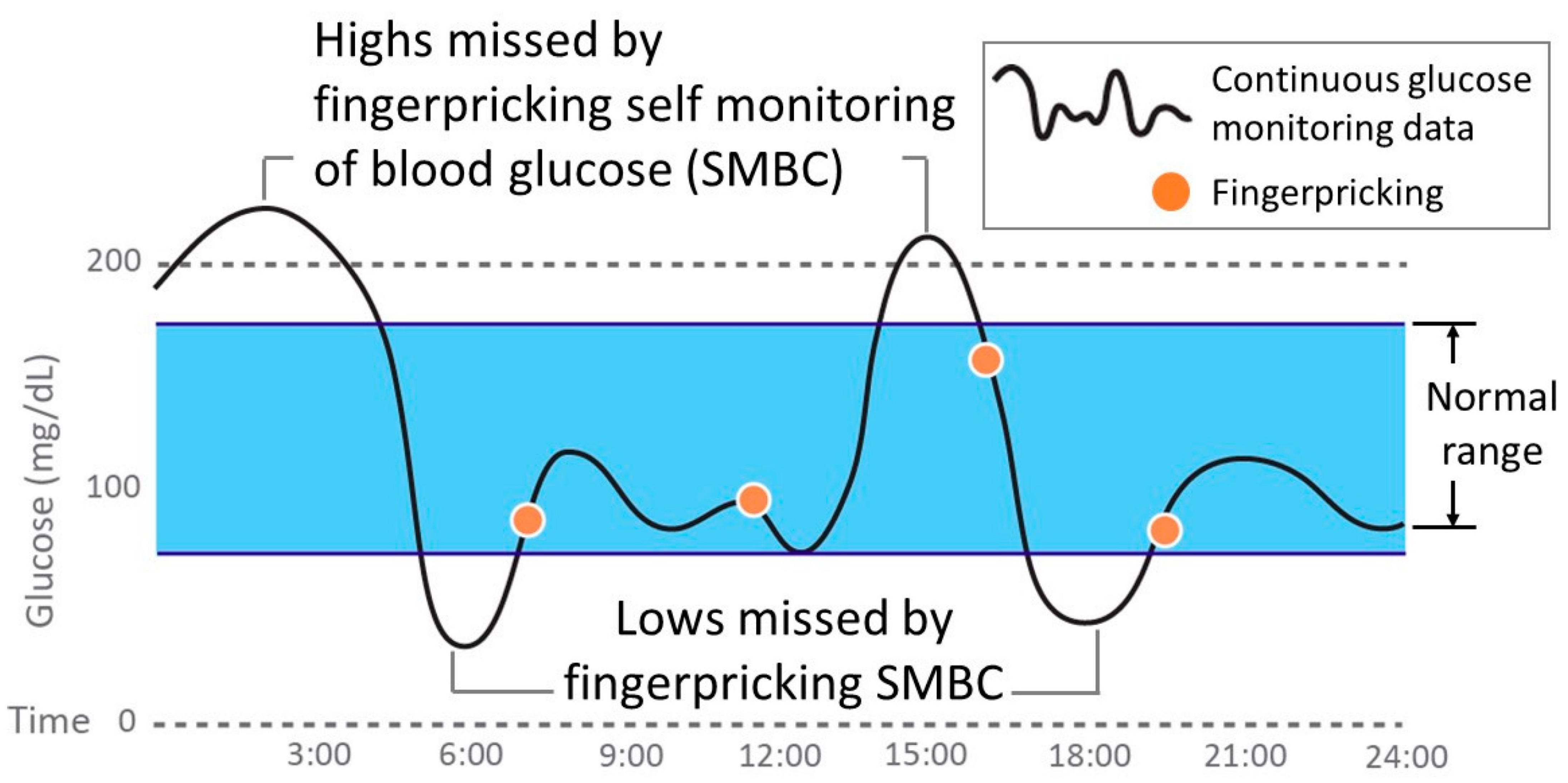
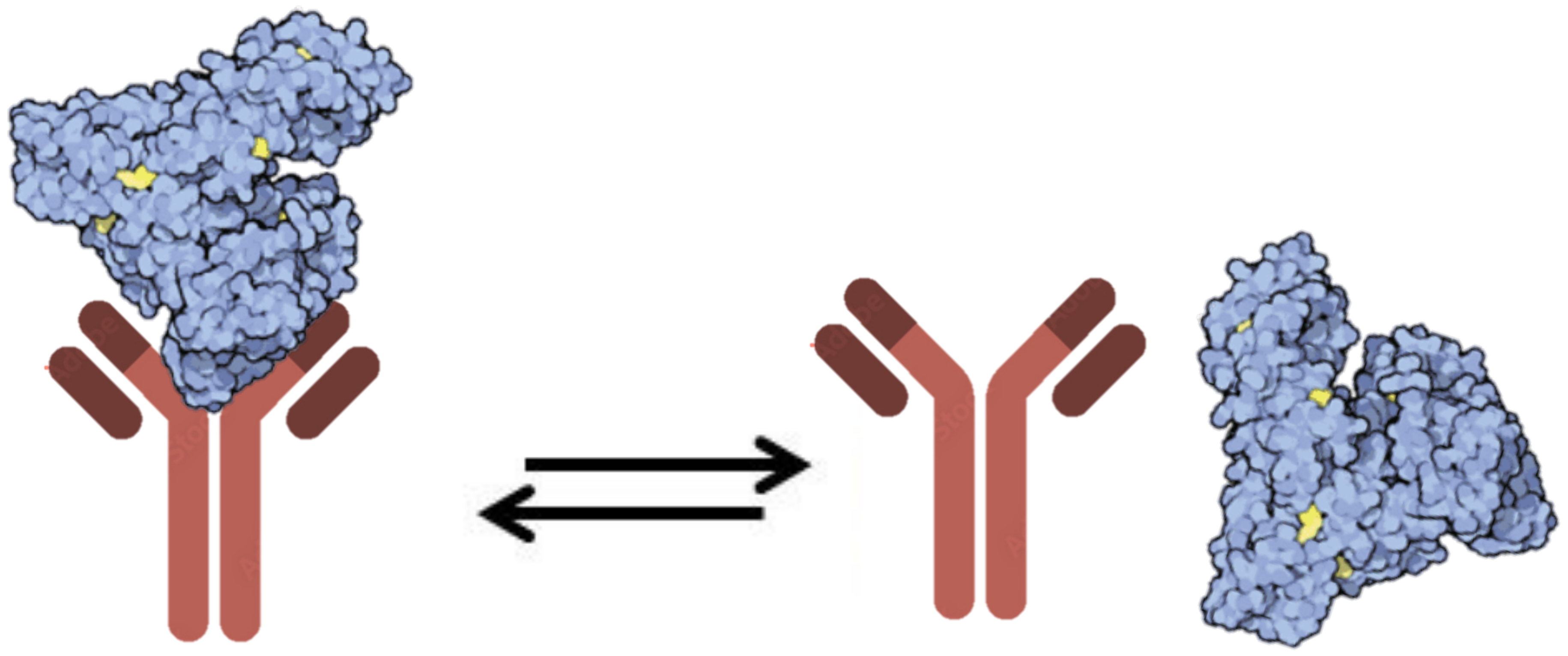
Continuous Measurements: Reversible Binding to Bioreceptors





$$AR \underset{k_a}{\overset{k_d}{\rightleftharpoons}} A + R$$

We need strong binding (low K_d)

To detect analytes at low concentrations

We need fast kinetics (high k_d)

$$K_d = \frac{[A][R]}{[AR]} = \frac{k_d}{k_a} = \frac{1}{K_a}$$

We need to engineer/redesign bioreceptors to overcome this mismatch

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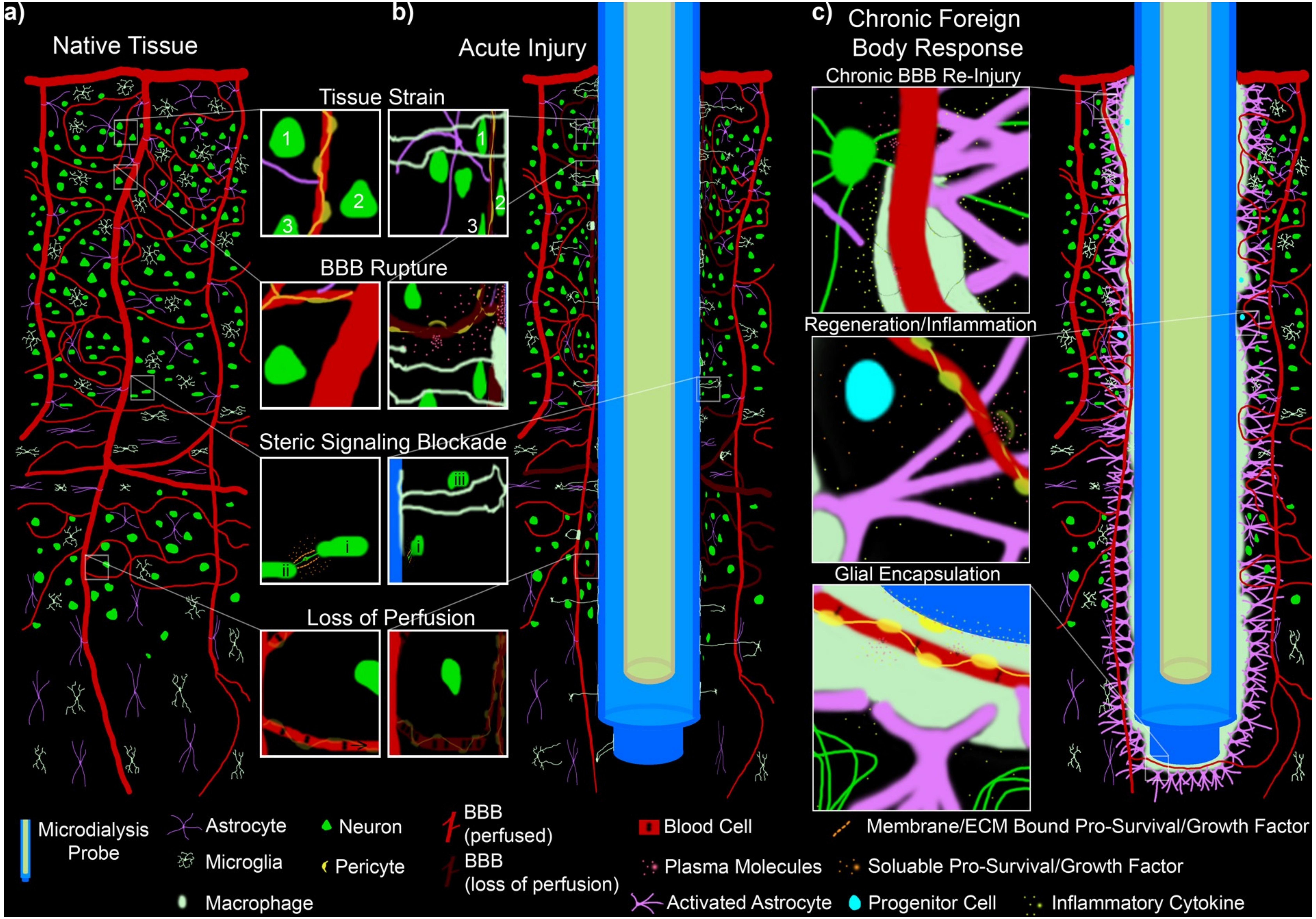
5. Tissue Response to Implanted Sensors Prevents Long-Term Use



Kozai, *ACS Chem. Neurosci.*, *6*, 1, **2014**

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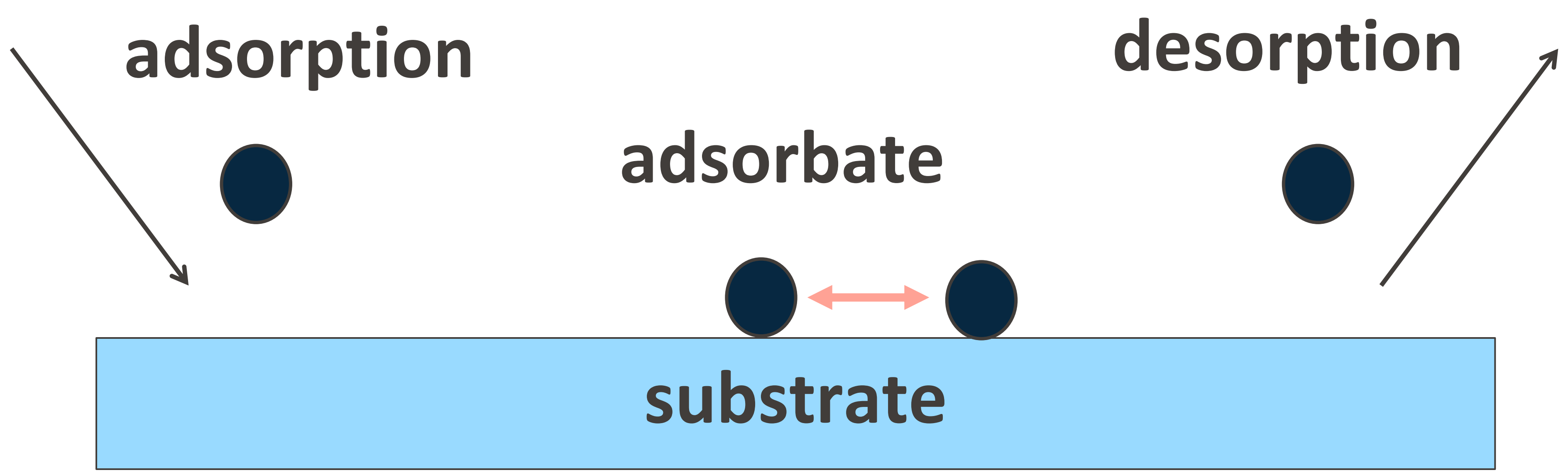
Different Interactions on Surfaces Influence Catalysis



Electrostatic interactions
Direct absorbate interactions
Local induced surface pertubations

Interaction between adsorbate and surface depends on coverage (**θ**):

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

θ = 0 clean surface

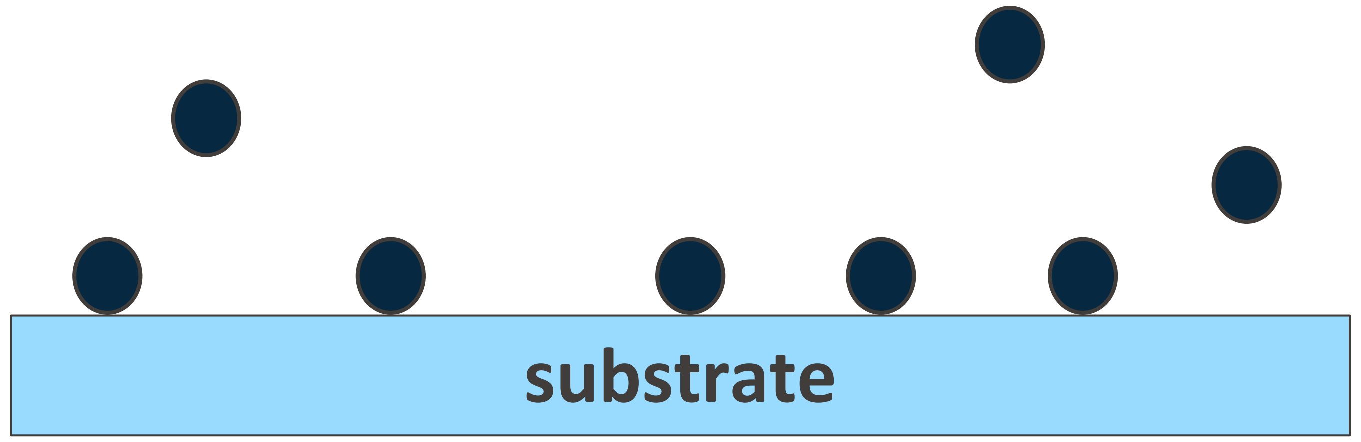
θ = 1 monolayer

Adsorption = Physisorption

Electrostatic interaction (charge transfer)

non-specific and weak

multilayer growth possible

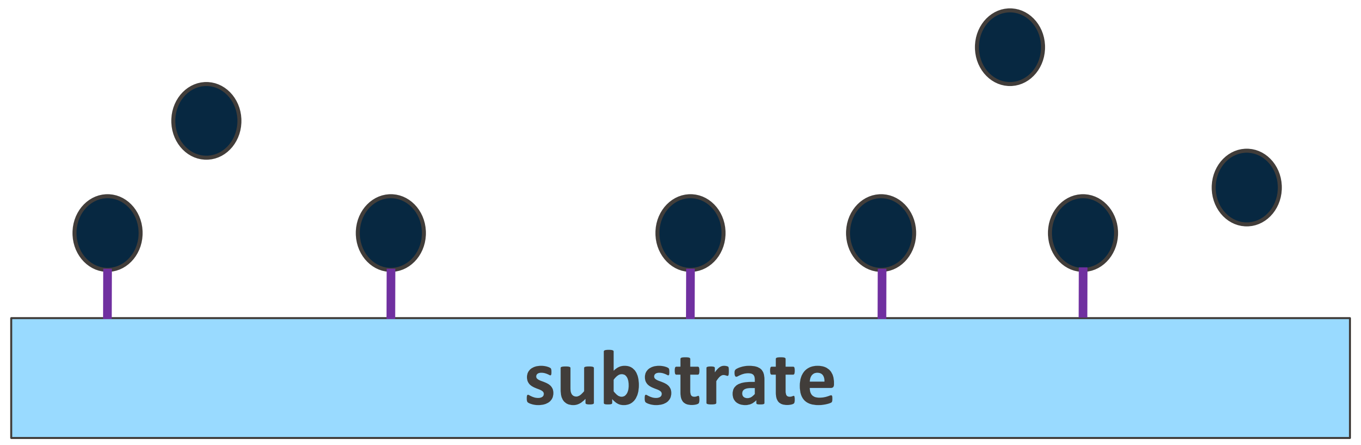


Absorption = Chemisorption

Geometrically defined interaction

Chemical bond between adsorbate and substrate

maximum coverage is 1 monolayer (θ = 1)



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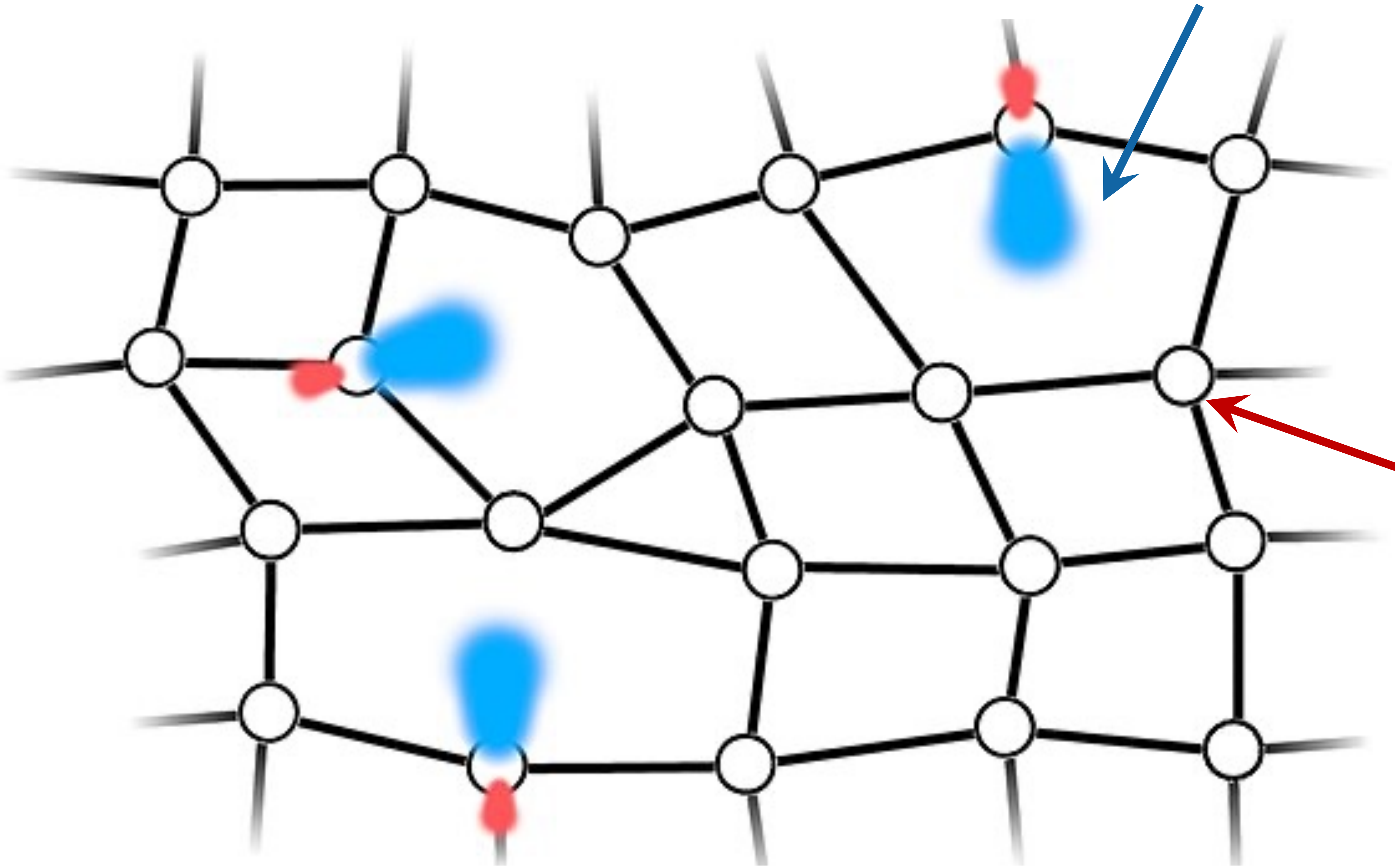
Catalysis Basics: Surfaces Are Intrinsically Dipolar



Unpaired valence electrons

Involved in bond formation

Z^+ nucleus – Z^- core electrons

Core of a crystal:
Nuclei in crystallographic positions
Core electrons

Since they are dipolar ➔ form bond ➔ driver for absorption

Yasemi *et al.*, *Processes*, *9*, **2021**

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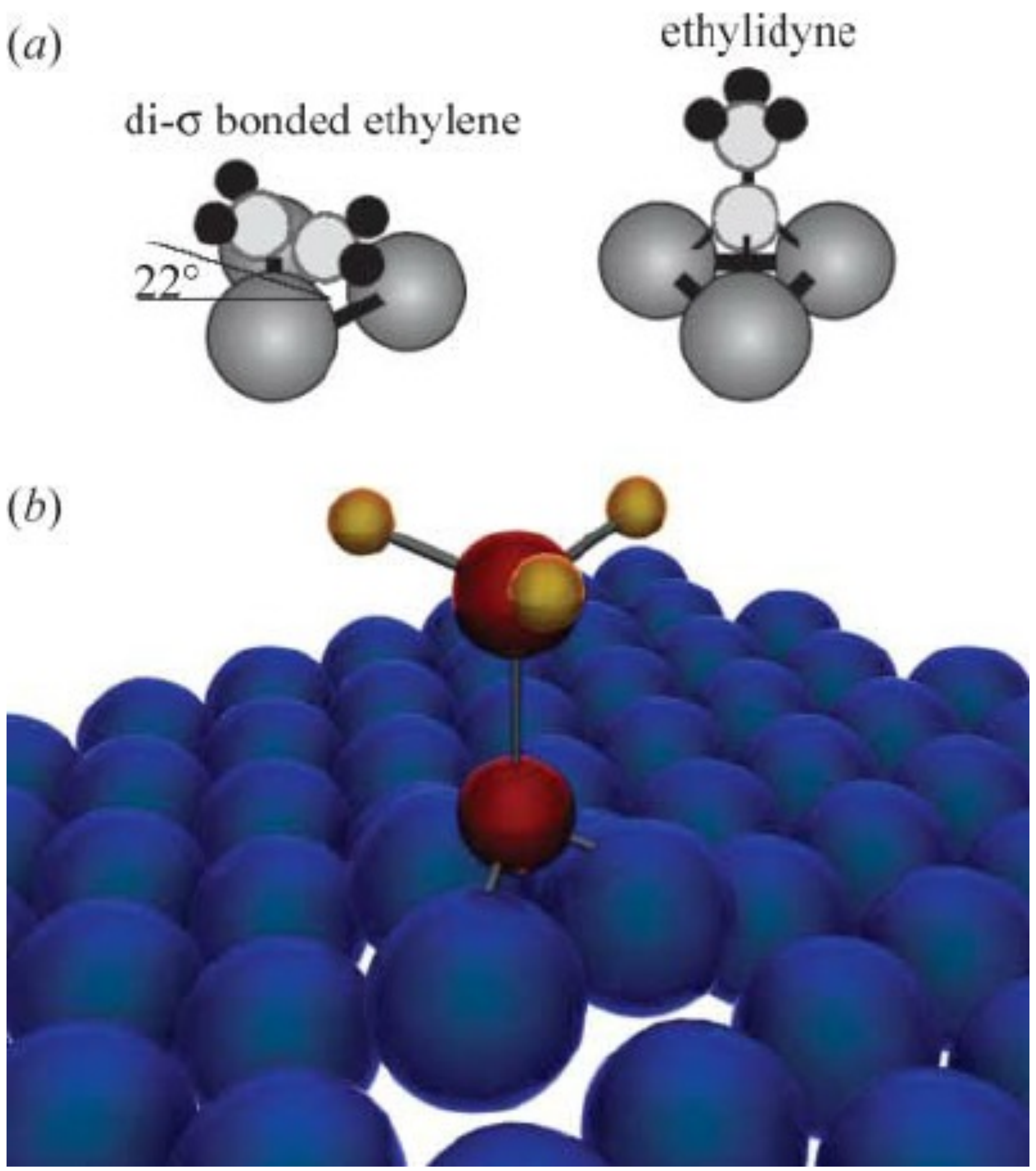
Chemical Bonds of Molecules Rely on Symmetry and Geometry



Pt (111)

Somorjai & Marsh, *Phil. Trans. A, 363,* **2005**

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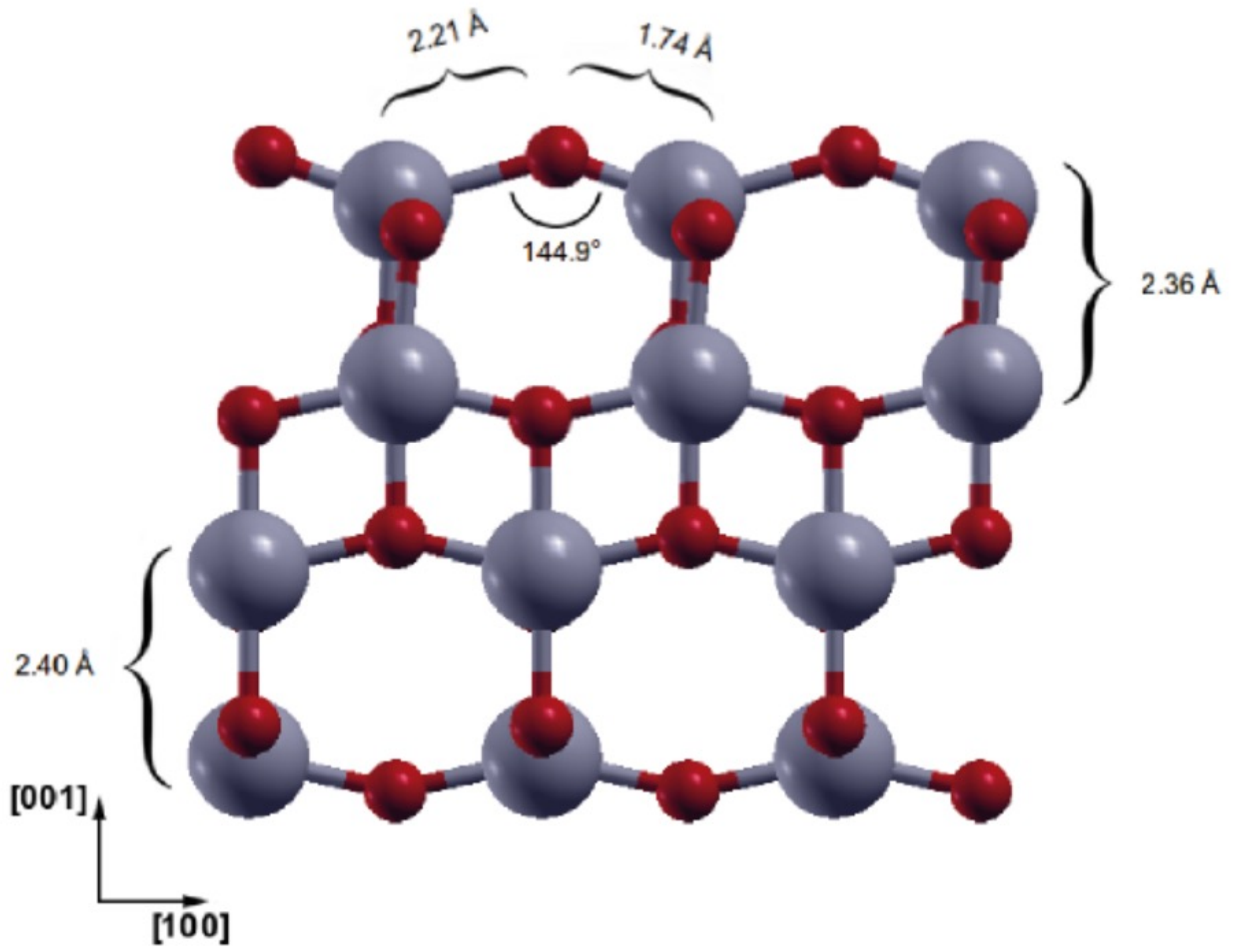
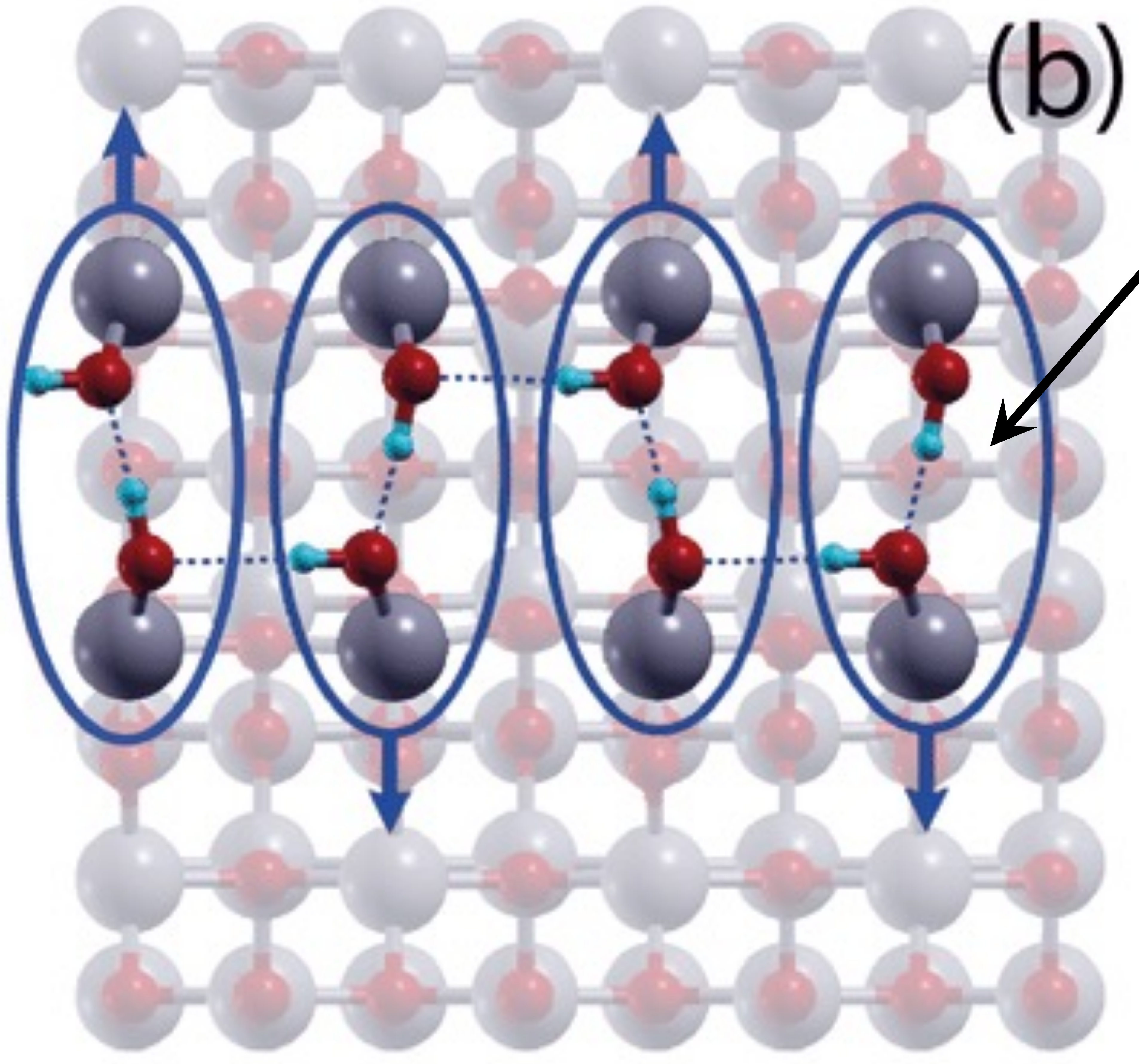
Reconstruction of “Soft” Surfaces Due to Absorption

Molecules that induce surface reconstructuring ➔ **change the surface band structure of the material**



TiO_2 surface



Absorb on surface and pull the surface based on intermolecular forces

H_2O-induced reconstruction

Interaction different from facet to facet (ledge vs. kink. vs. terrace)

Zollo & Vitale, *Appl. Sci.*, *8,* 12, **2018**

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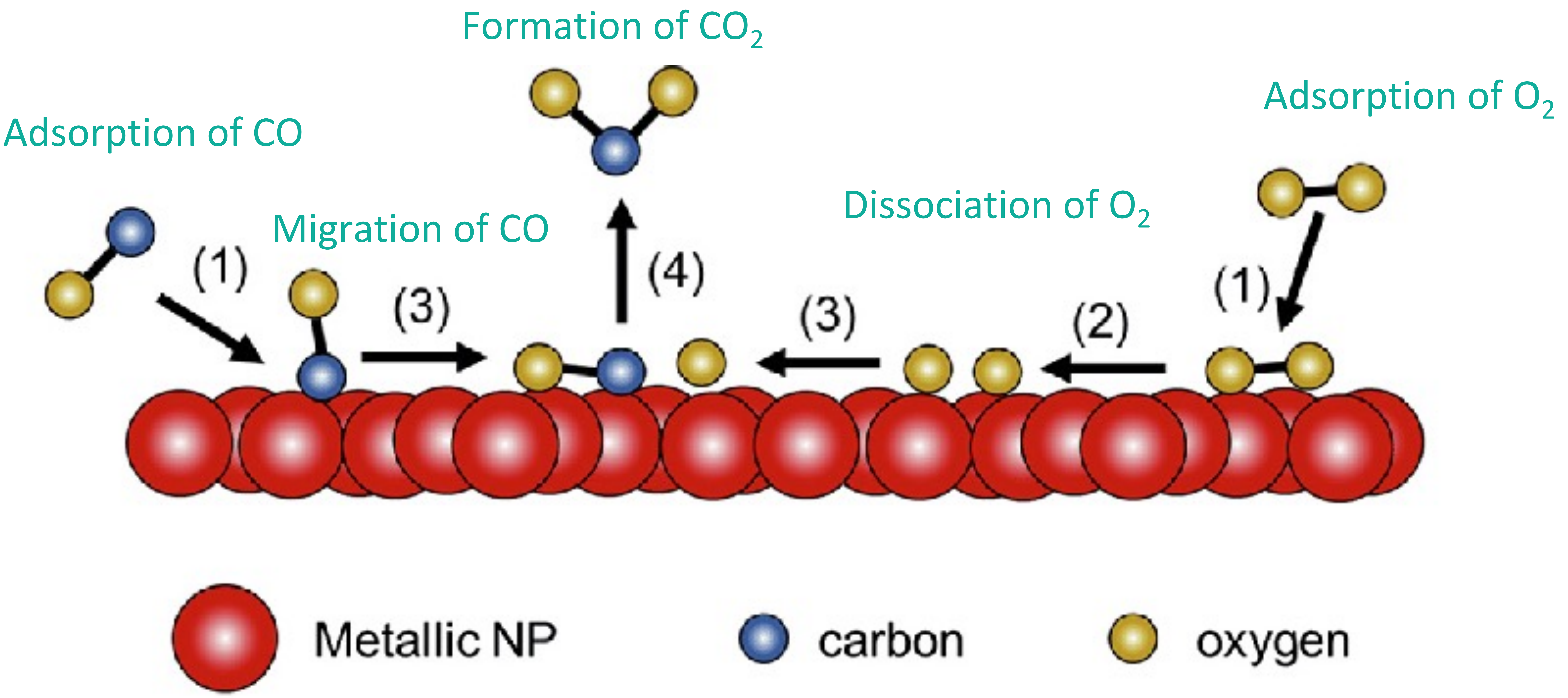
How Surfaces Serve as Catalysts: Adsorption + Dissociation



Gueye *et al.*, *J. Catalysis*, *380*, **2019**

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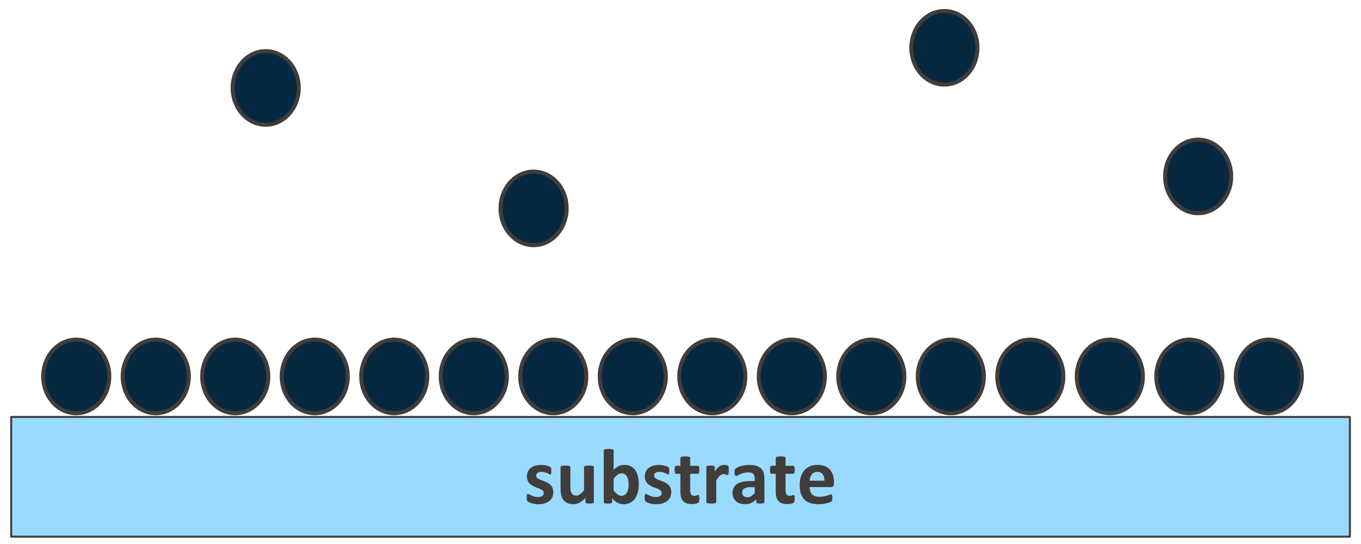
How can Surfaces Serve as Catalysts?

1. Locally enhance the concentration of reactants

Physisorption

Van der Waals interactions between adsorbate and substrate (non-specific and weak)



$C_R^{Surface} >> C_R^{Solution}$

$$P(t) = K_a \times C_R$$

Rate of product formation over time (mol L^{-1} s^{-1})

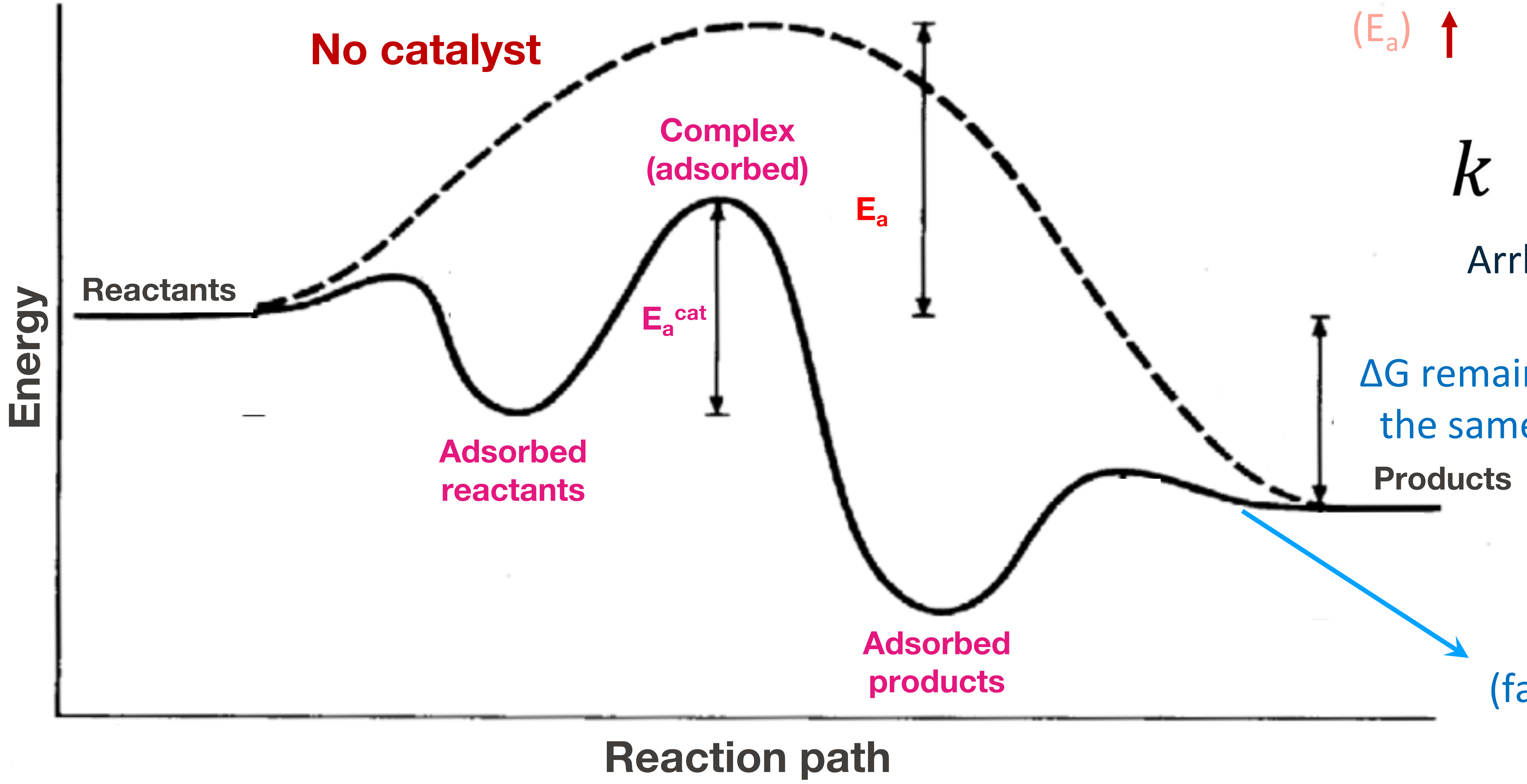
Rate of adsorption (s^{-1})

Concentration of reactant (mol L^{-1})

How can Surfaces Serve as Catalysts?

2. Surface bonds can change the energy landcape of the reaction, lowering activation energy

Rate of catalysed reaction: function of E_a, T, number of active sites on catalyst surface, surface concentration of reagents



Activation energy (E_a) ↑ → Rate of reaction (k_a) ↓

$$k = Ae^{\frac{-E_a}{RT}}$$

Arrhenius Equation

ΔG remains the same

Surface route has lower E_a (faster and happens at lower T)

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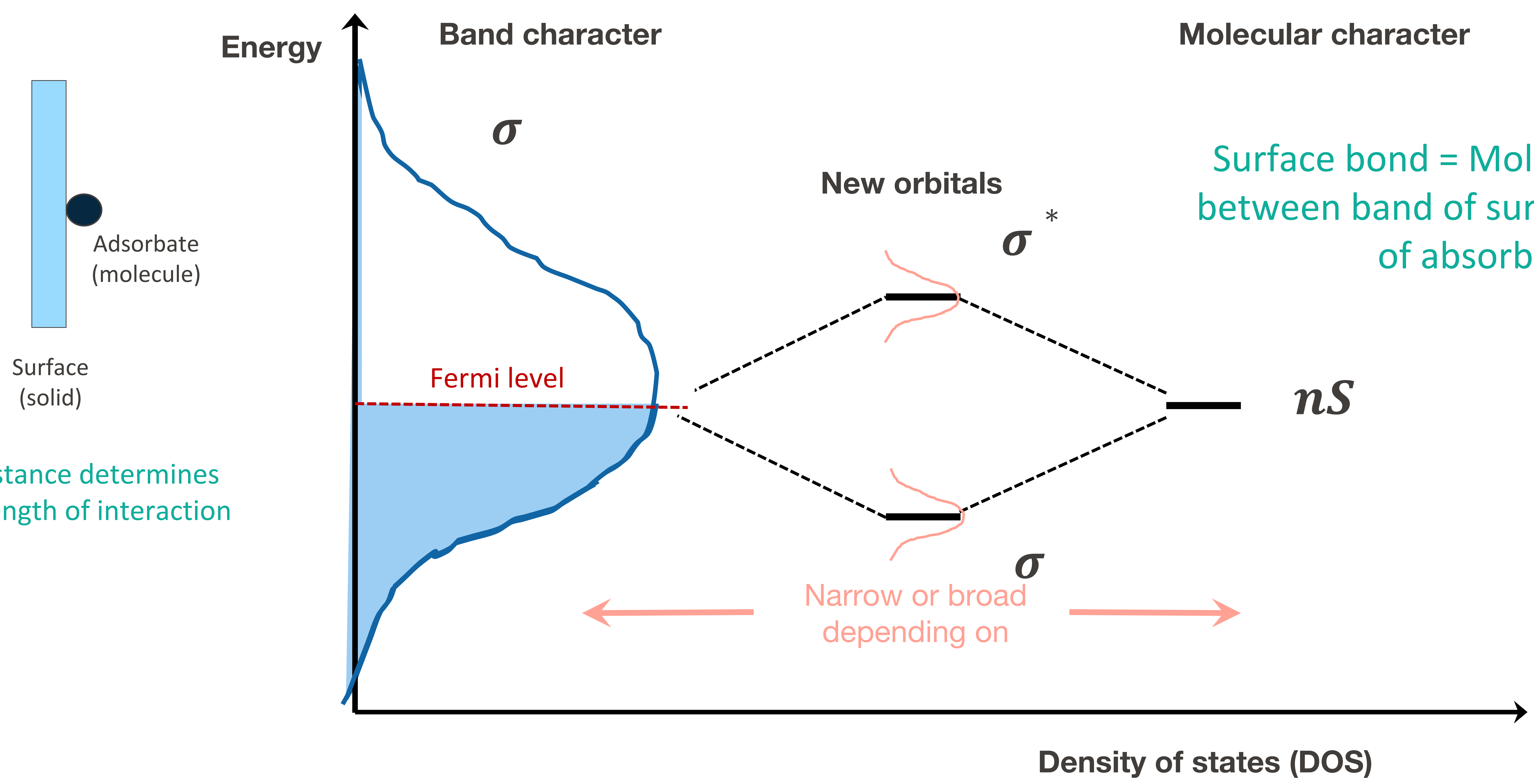
How can Surfaces Serve as Catalysts?

3. Induce one-step reaction (molecular orbital theory)



Distance determines strength of interaction

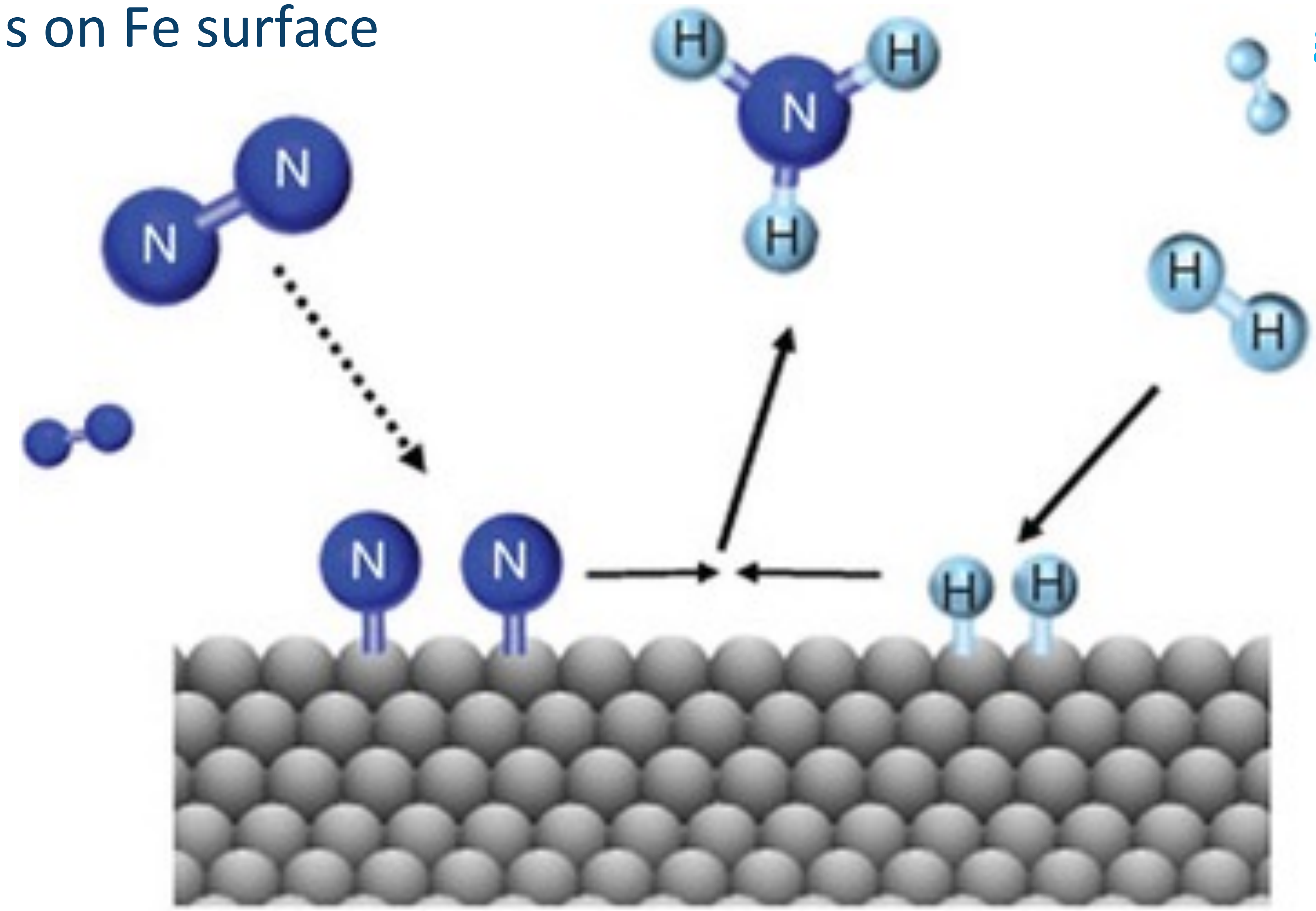
Surface bond = Molecular orbital between band of surface + orbitals of absorbate

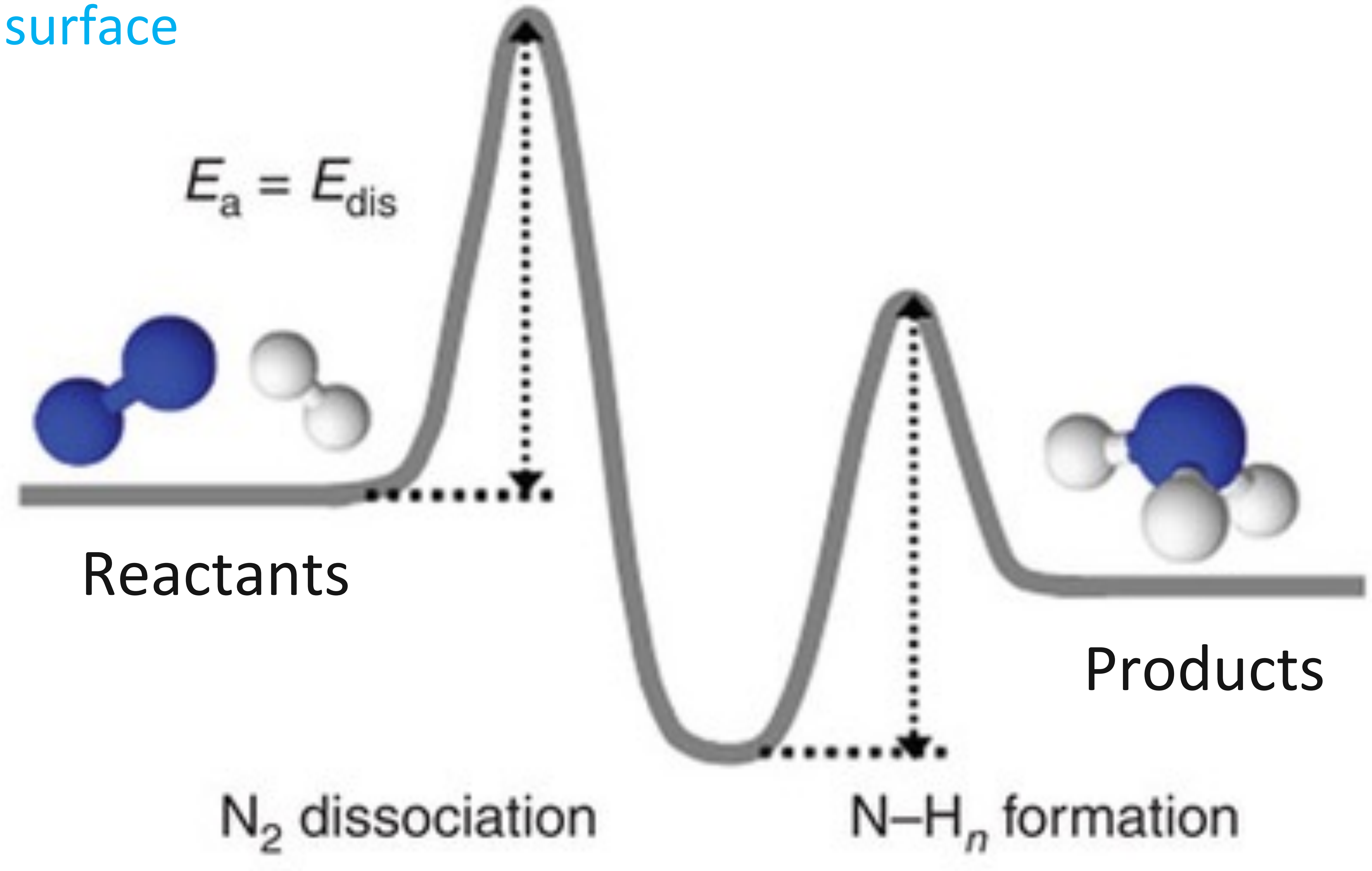
Example of Important Catalyzed Reaction: Ammonia Synthesis

Adsorption of N_2 gas on Fe surface

Ammonia desorption

Adsorption of H_2 gas on Fe surface





Fe catalyst provides active surface that adsorbs molecules, weakening their bonds

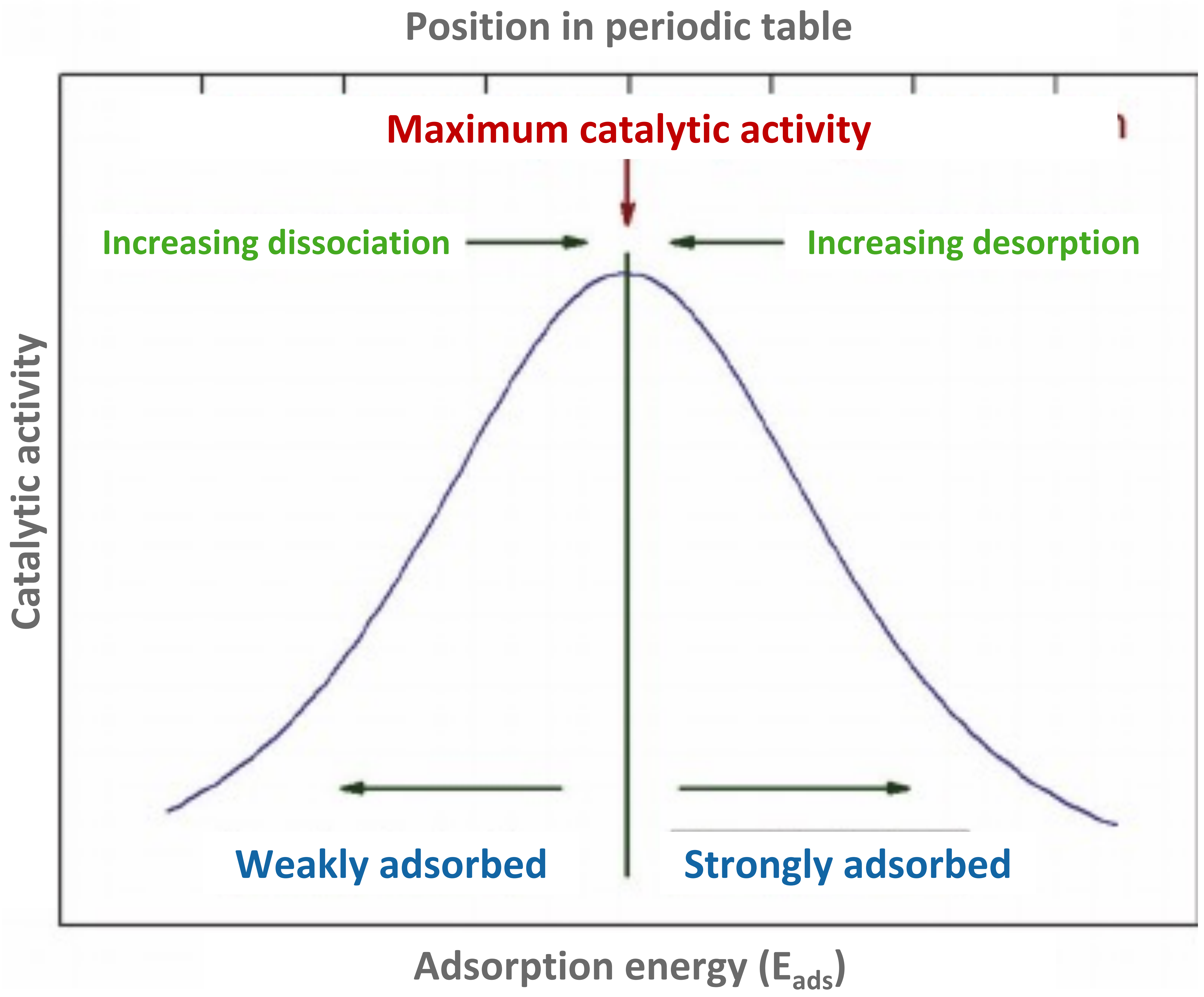
Nitrogen atoms easier to dissociate from the surface

Kitano, *et al., Nat. Comm. 6*, 1, **2015**

Catalysis Optimization – Trade-Offs of Adsorption Energy

Adsorption Energy (E_{ads}): energy change when a molecule binds to the catalyst surface

Low E_{ads} → Reactants do not adsorb → Low activity



High E_{ads} → Products cannot desorb → Surface sites are blocked → Low activity

How Can We Characterize Surfaces?

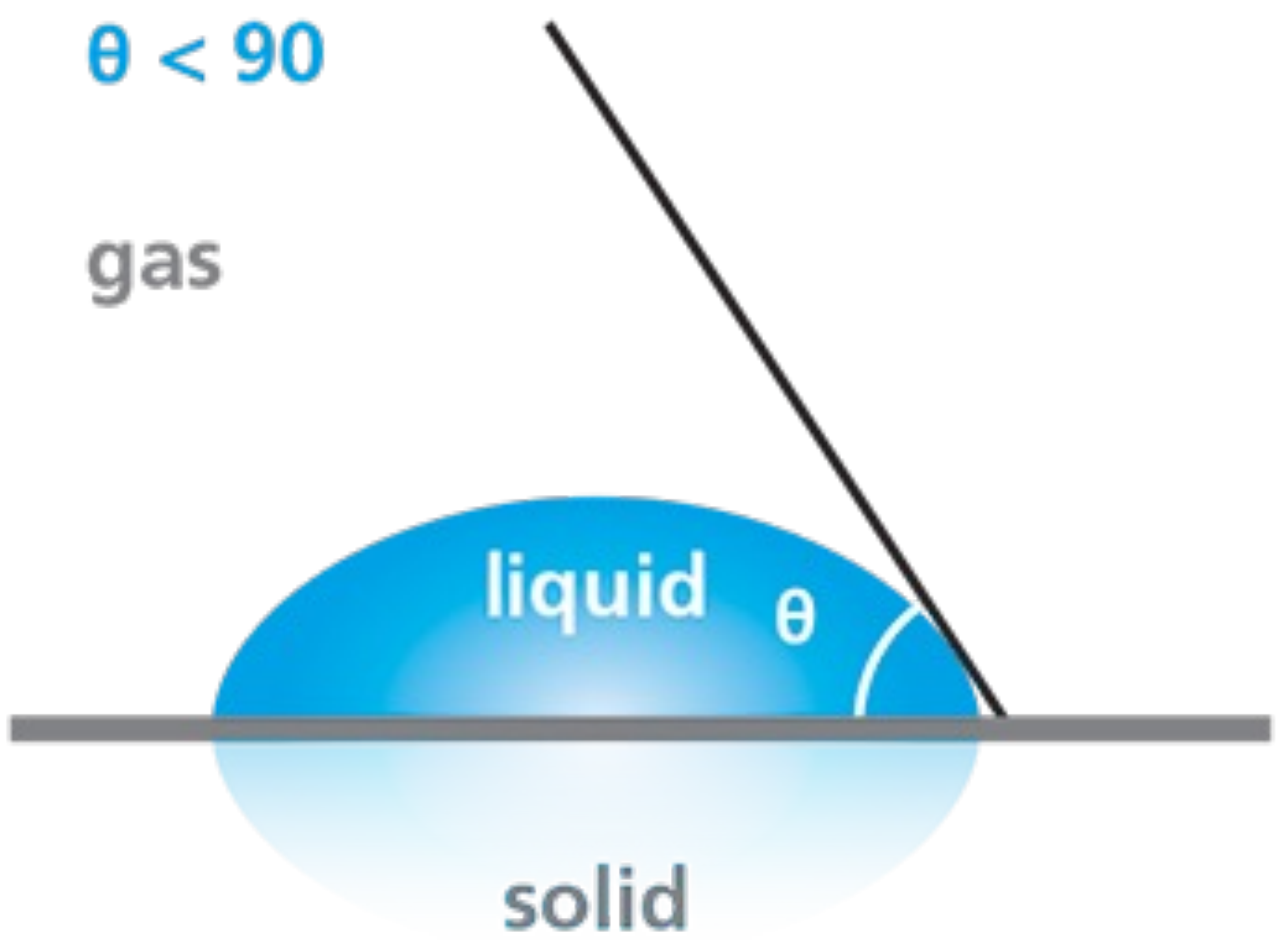
What are some techniques that we covered for monitoring/analyzing surface properties?

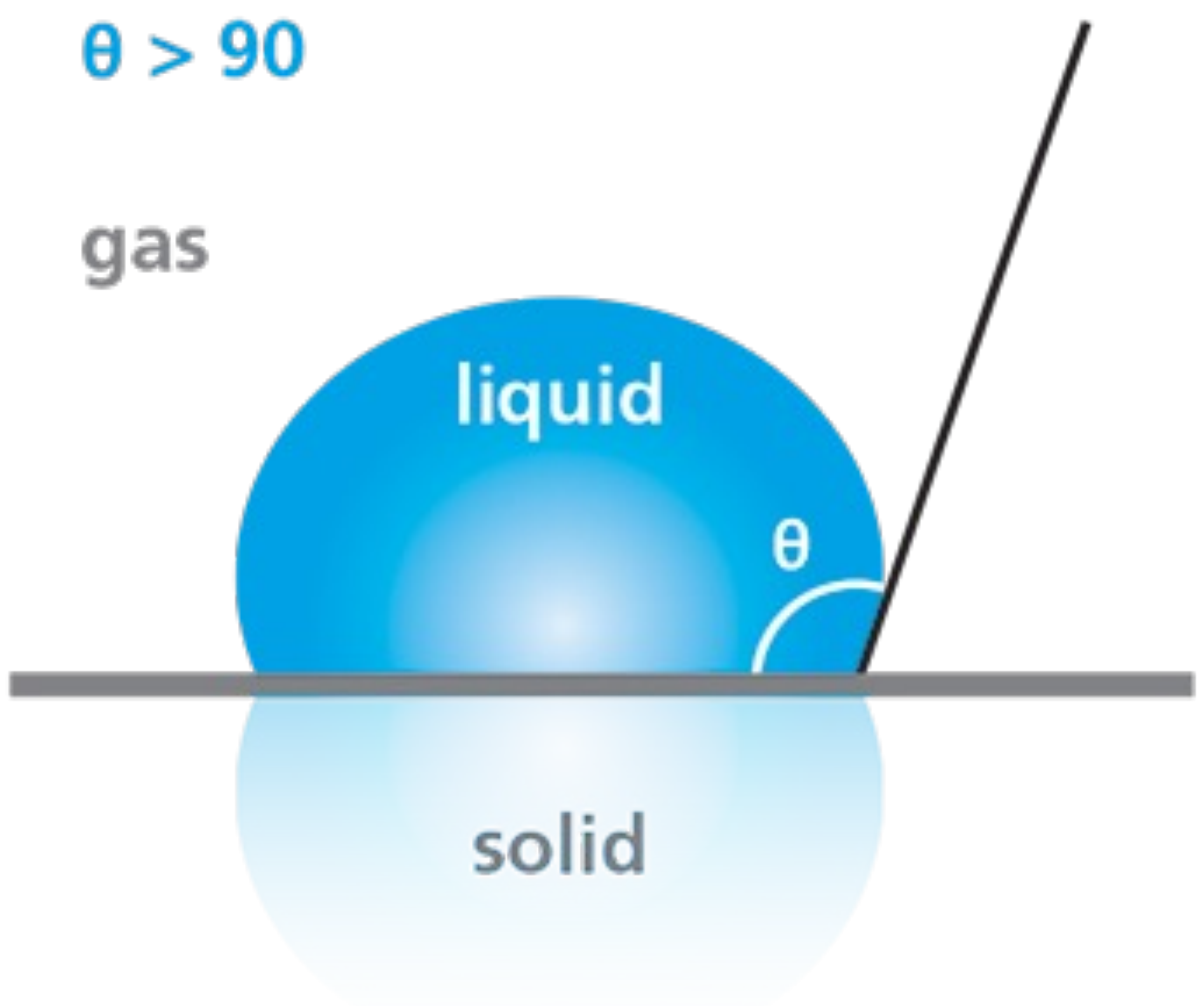
- Contact angle – hydrophilicity/hydrophobicity
- Quartz crystal microbalance – surface chemistry and viscoelastic properties
- X-ray photoelectron spectroscopy – elemental composition
- Raman spectroscopy – molecular signatures

Contact Angle Monitors Wettability of Surfaces

Hydrophilic

High wettability

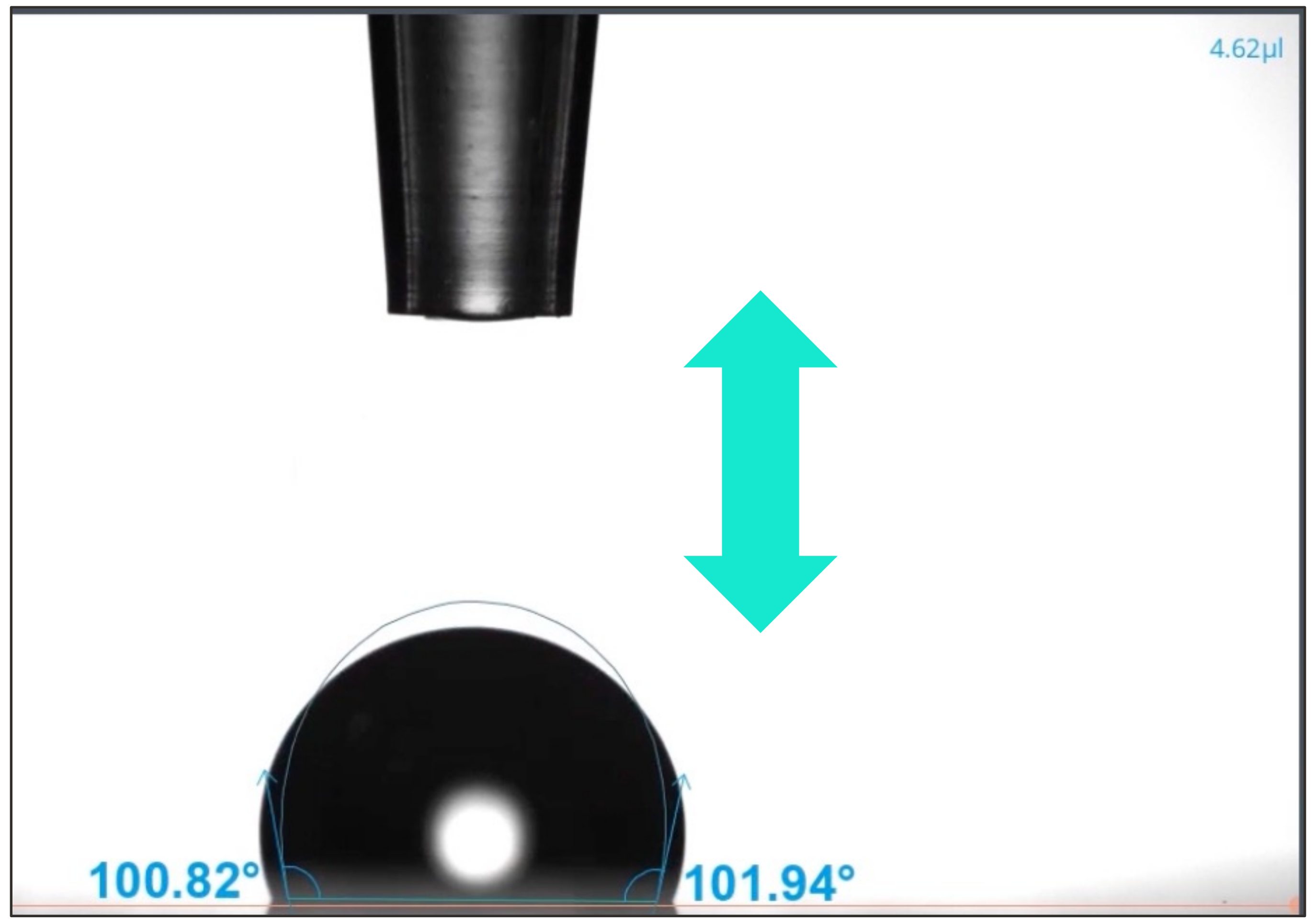


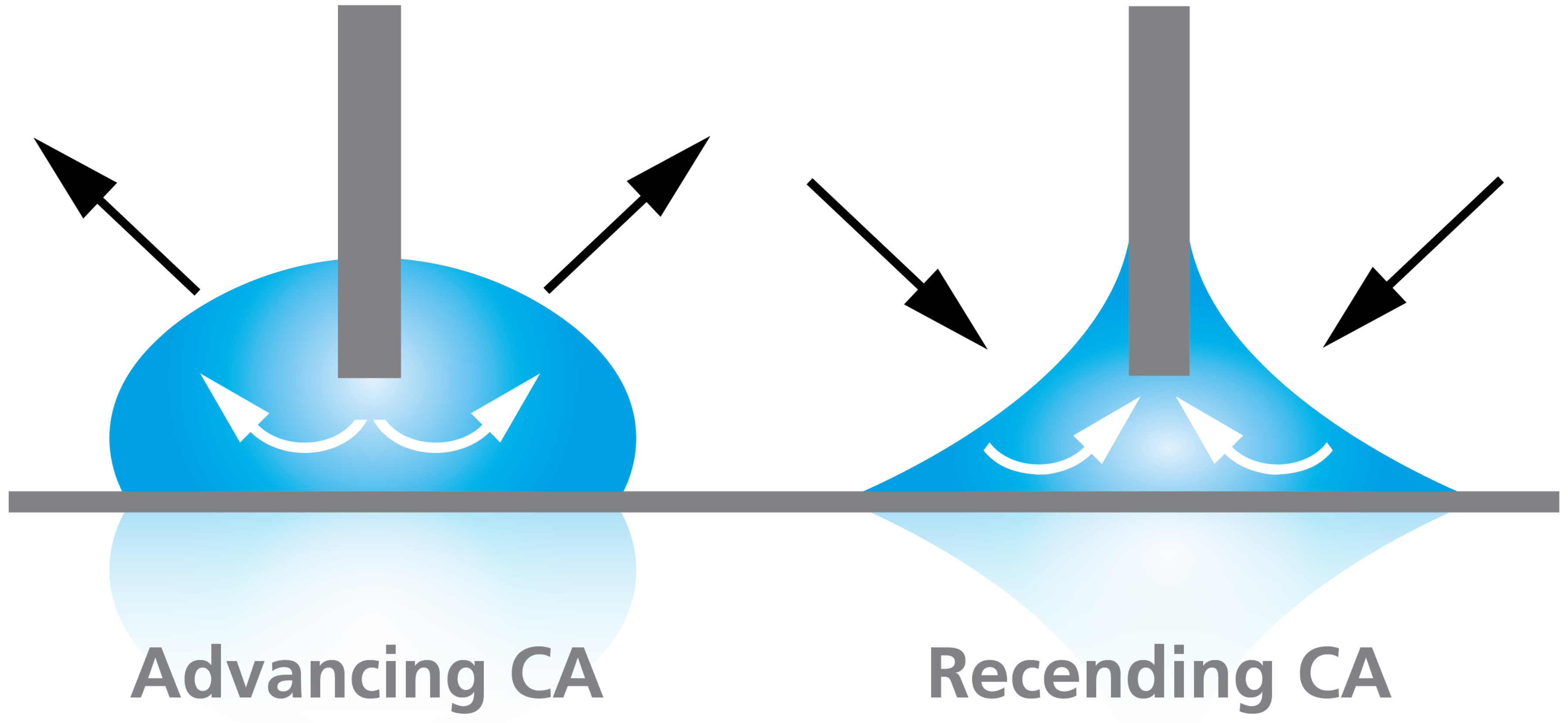


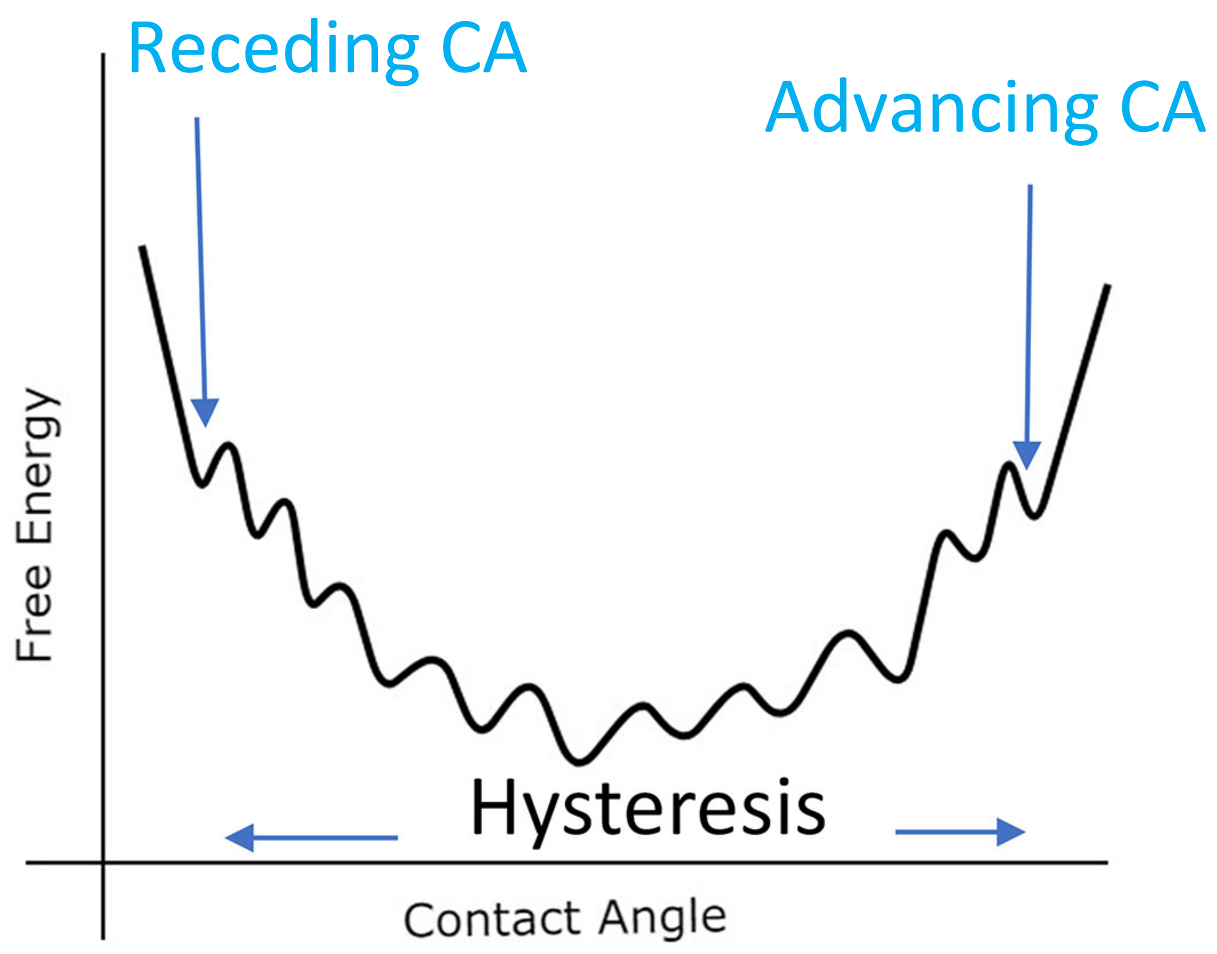
Hydrophobic

Low wettability

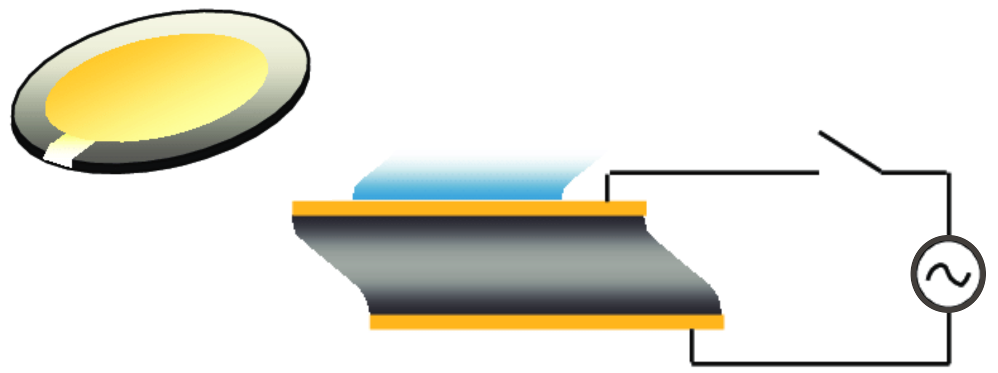
Static Contact Angle / Sessile Drop measured by an Optical Tensiometer

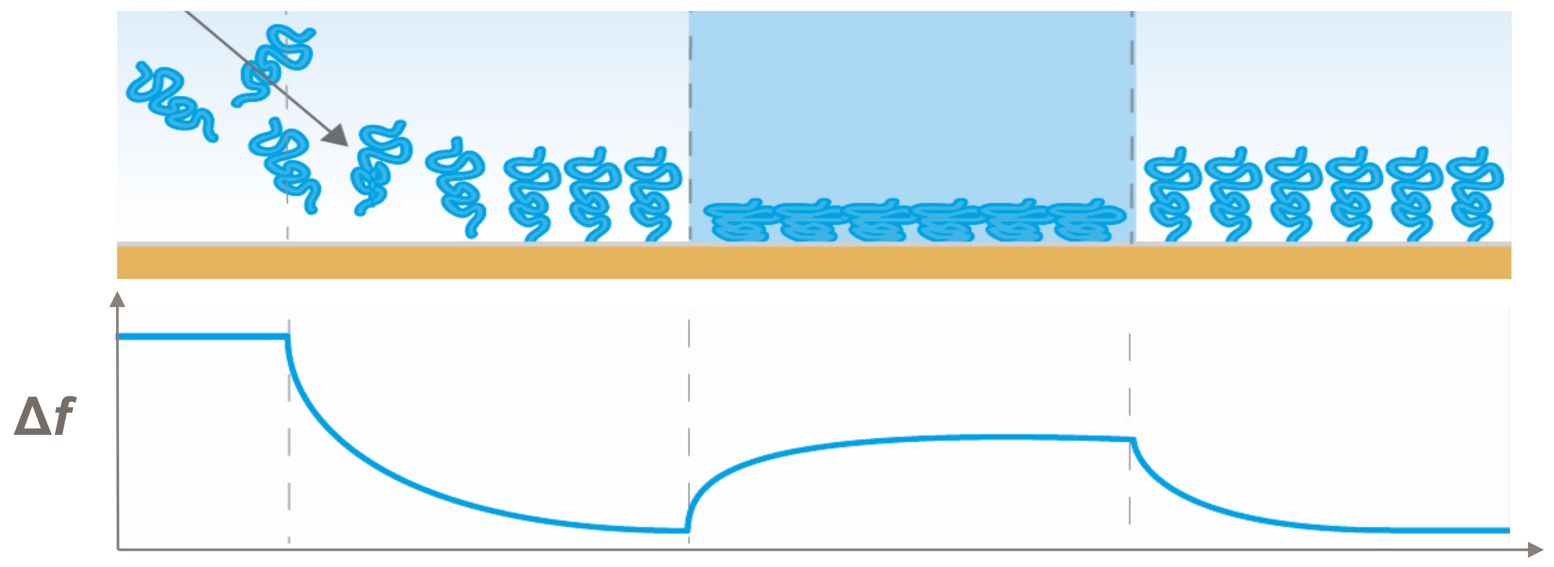


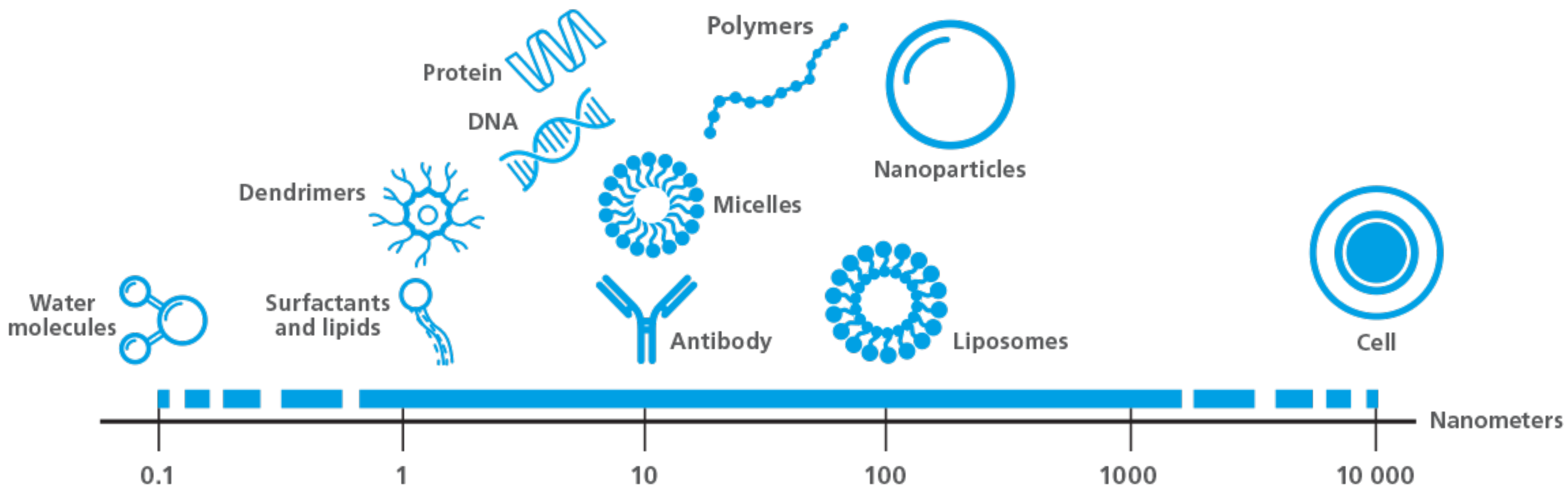




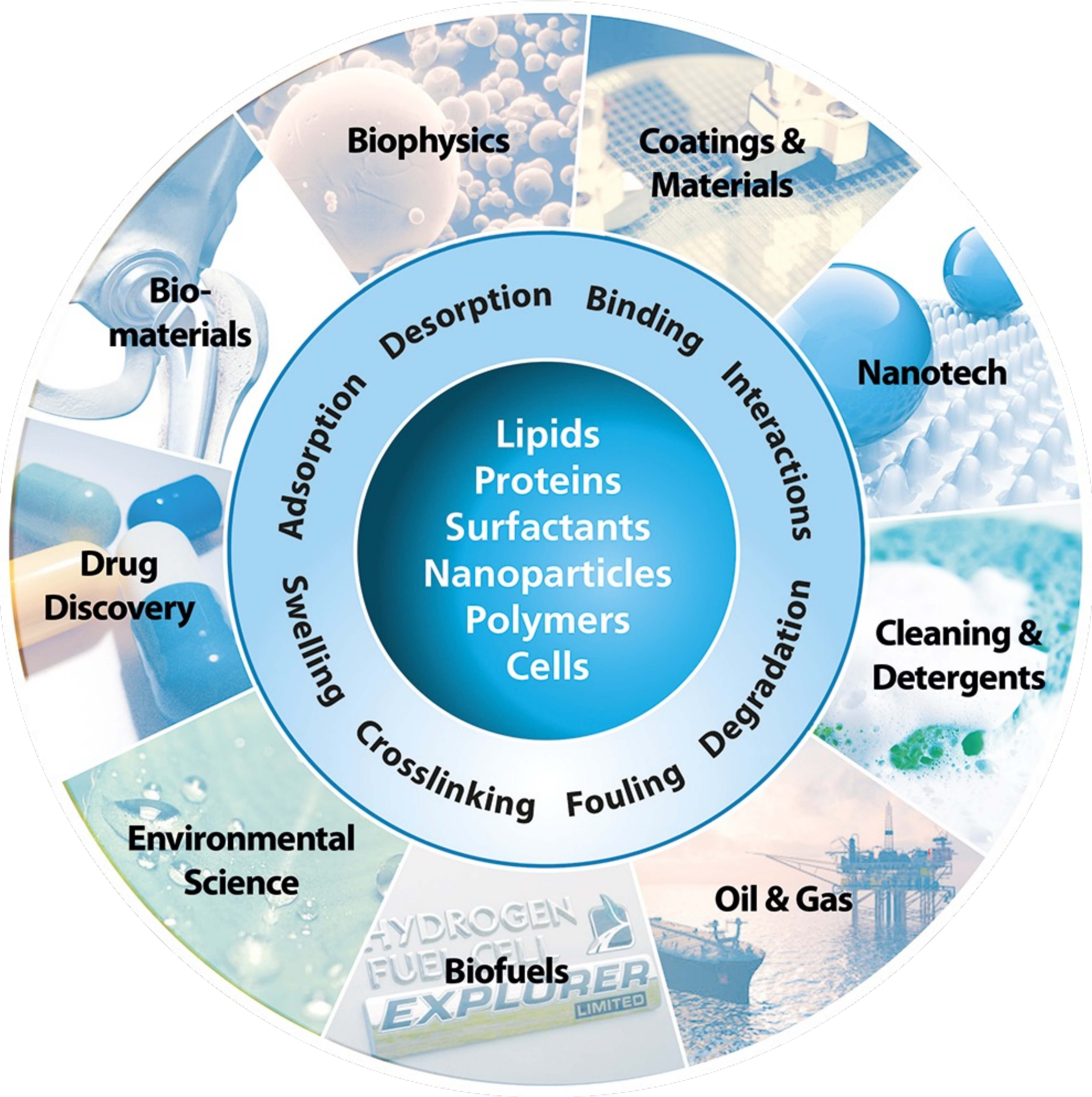
Quartz Crystal Microbalance Monitors Surface Chemistry







Detection range from 1 Å to 1 μM



Biolin Scientific

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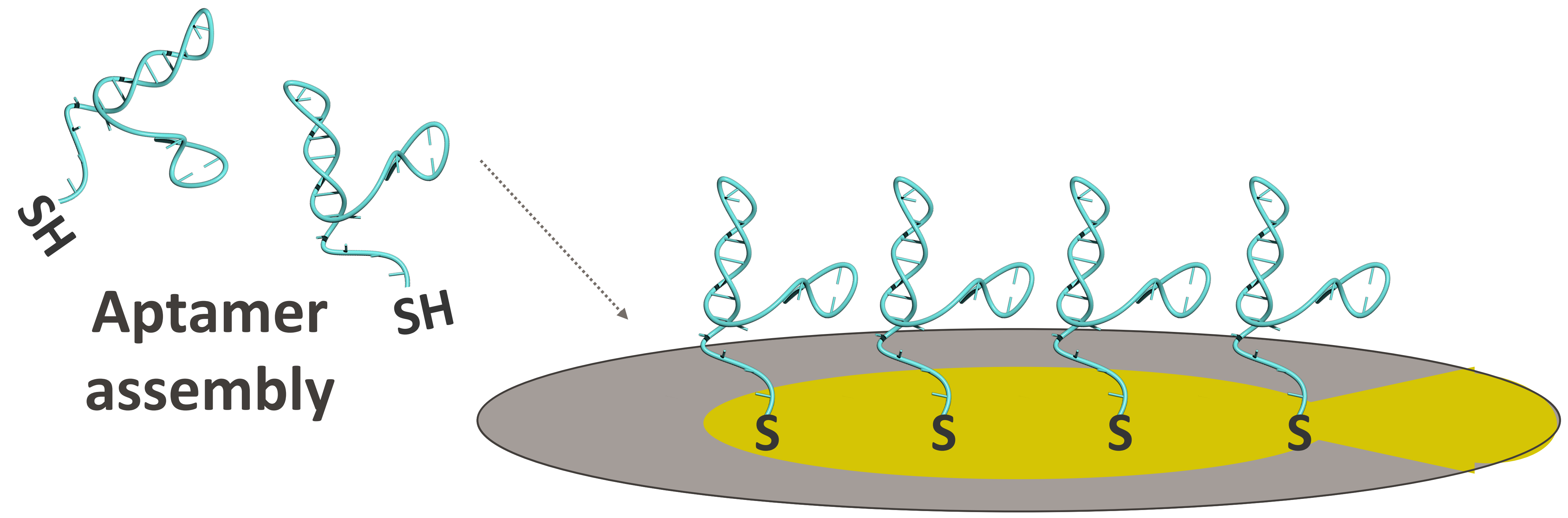
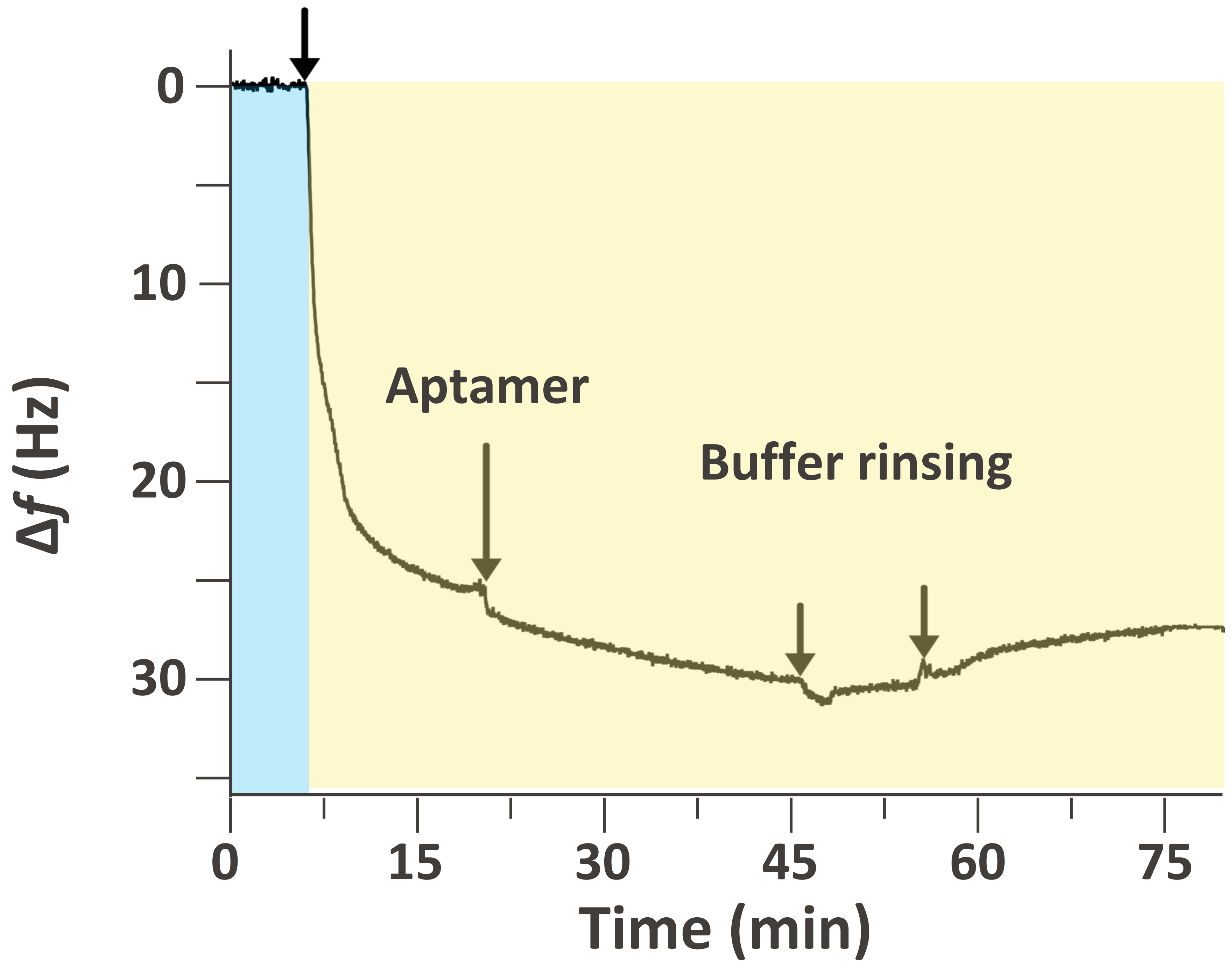
Monitoring the Assembly of Aptamers on Surfaces

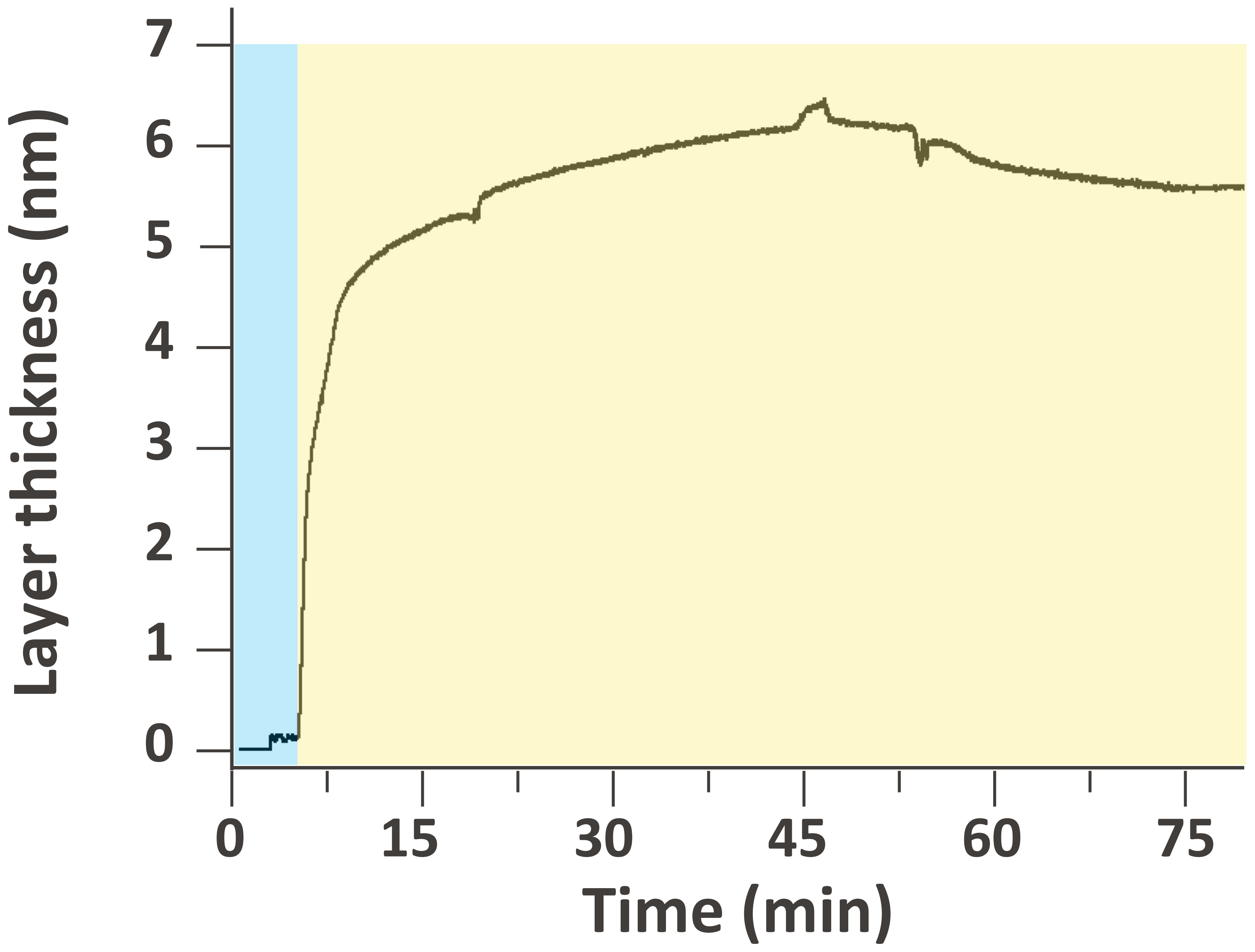


Gold surface quartz crystal



$$\Delta m = -C \cdot \frac{\Delta f}{n}$$

Mass sensitivity constant



Nakatsuka *et al.*, *Anal. Chem.*, *93*, 4033, **2021**

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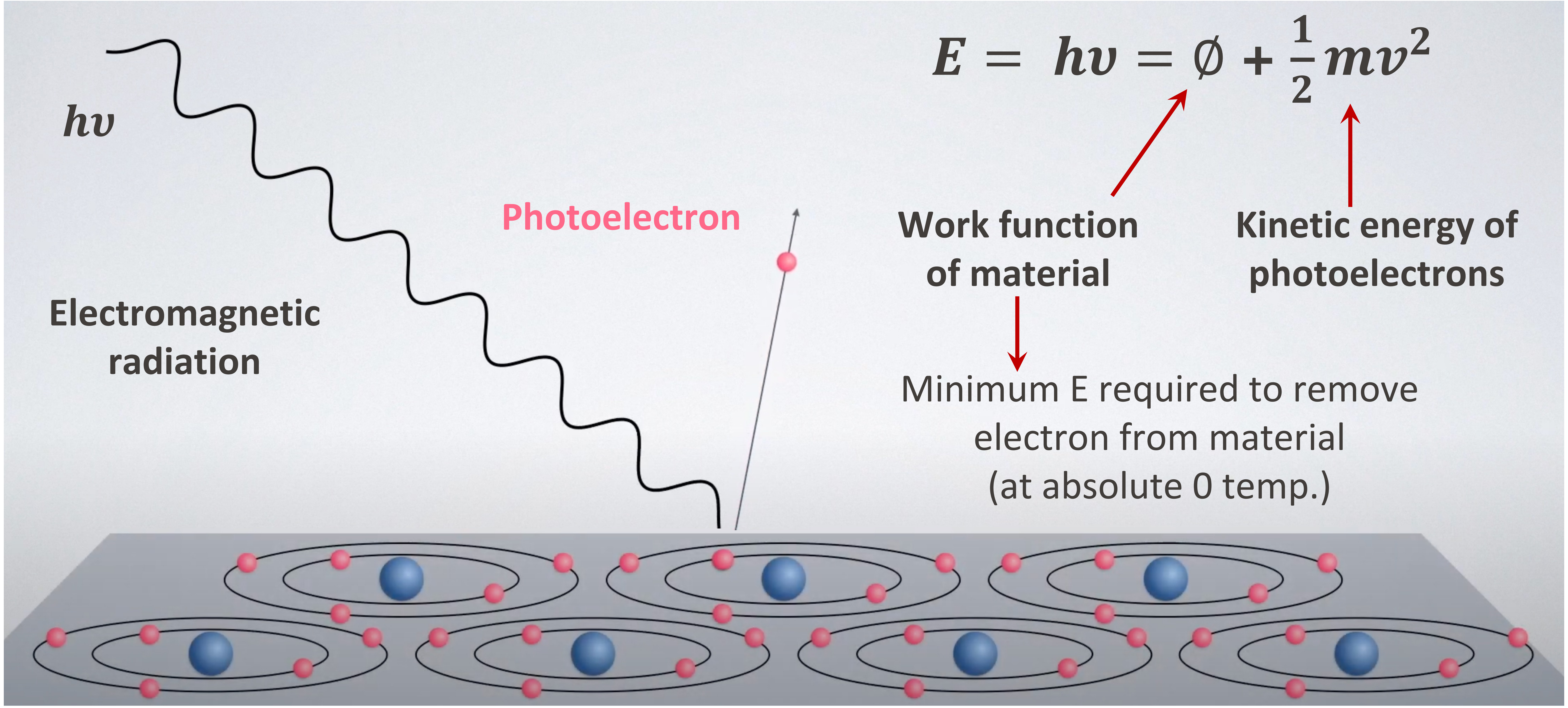
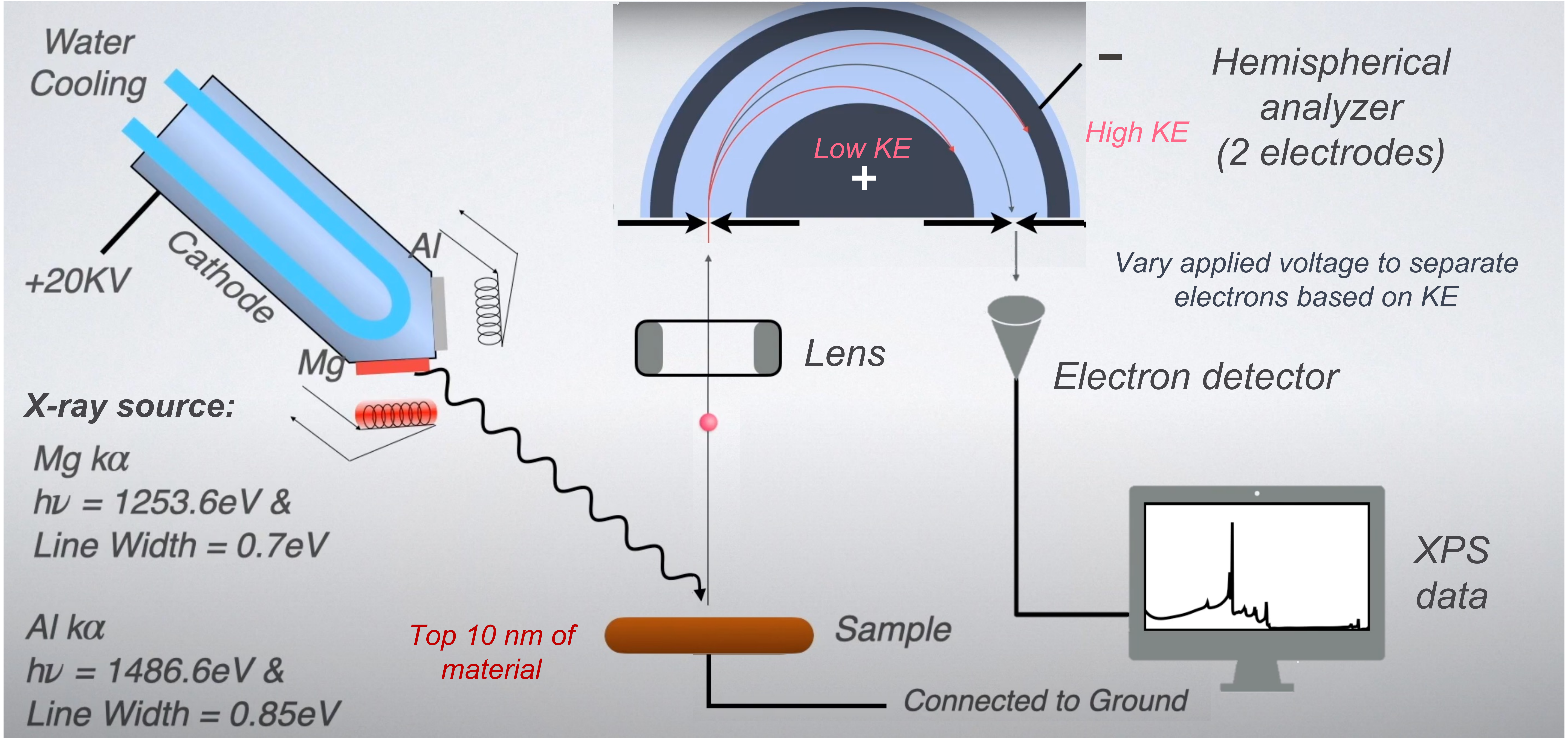
Electron Spectroscopy to Monitor Surface Species

X-ray Photoelectron Spectroscopy (XPS)



Surface of sample

How Does XPS Analyze Surface Elements?



*Counteract sample charging

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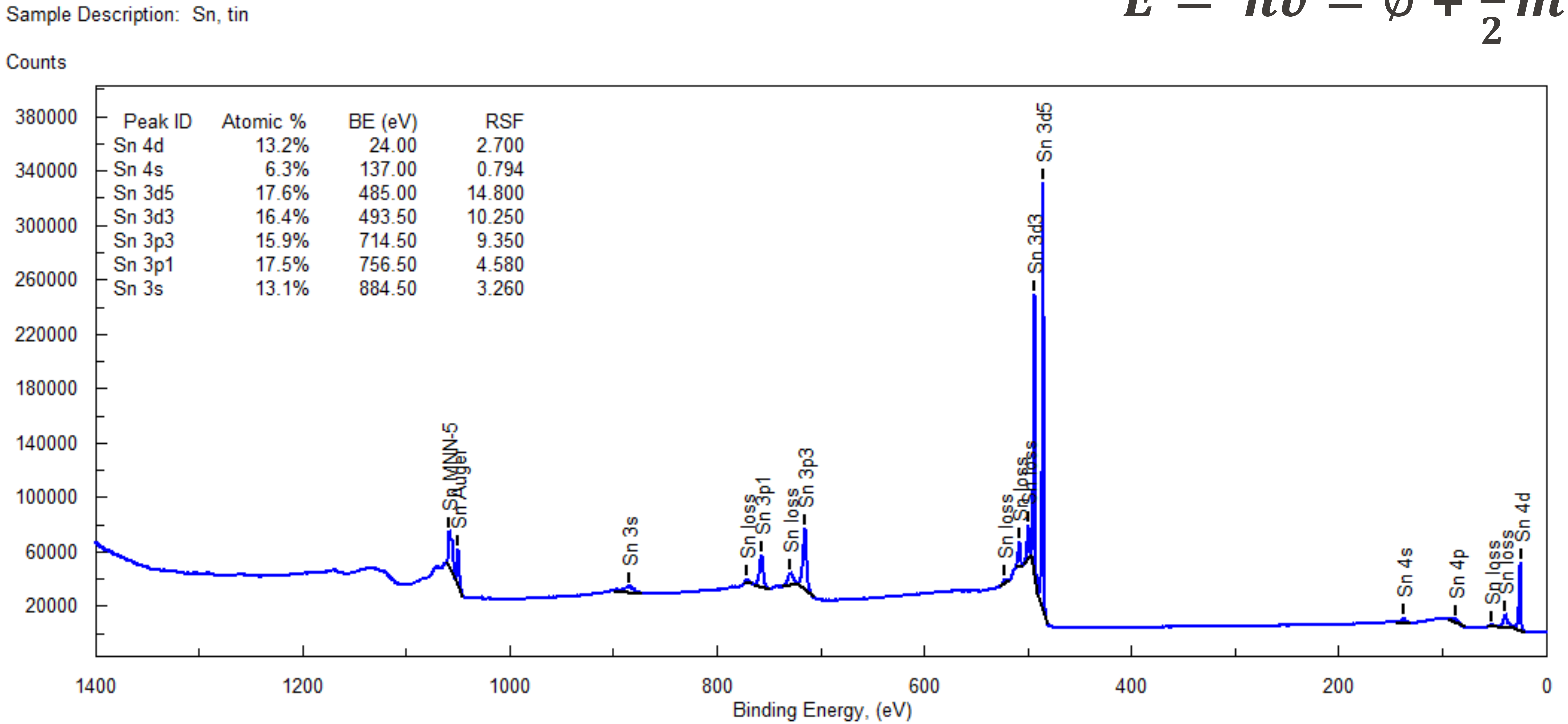
Binding Energy (eV) vs. Number of Electrons Counted

Kinetic energy of ejected electrons is related to the binding energy of the electron in the atom, which is unique to each element

$$E = hv = \emptyset + \frac{1}{2}mv^2$$

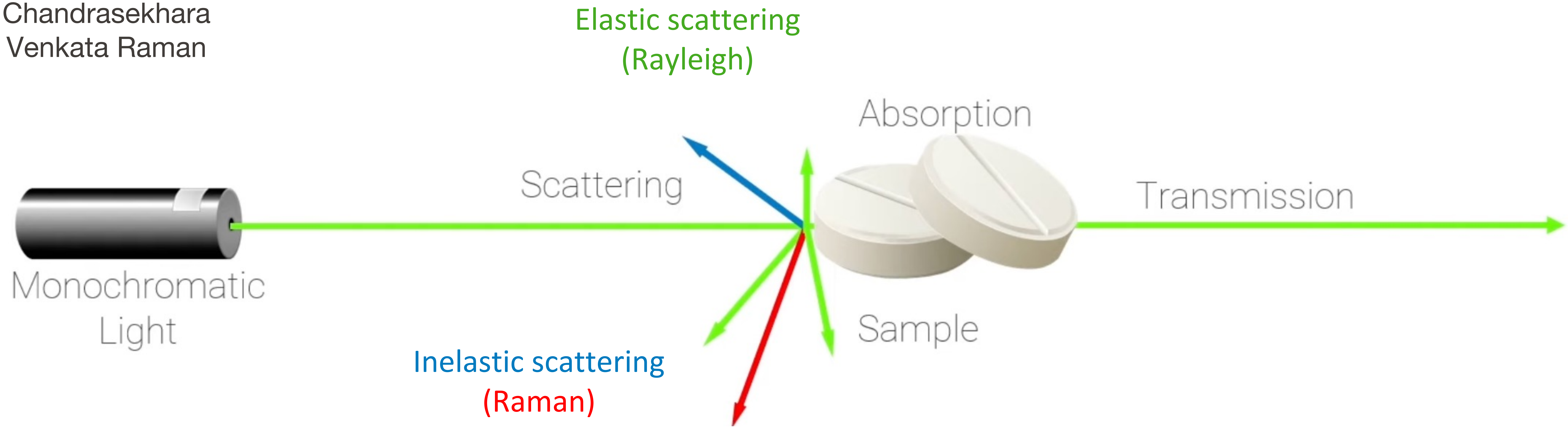


Peak ID	Atomic %	BE (eV)	RSF
Sn 4d	13.2%	24.00	2.700
Sn 4s	6.3%	137.00	0.794
Sn 3d5	17.6%	485.00	14.800
Sn 3d3	16.4%	493.50	10.250
Sn 3p3	15.9%	714.50	9.350
Sn 3p1	17.5%	756.50	4.580
Sn 3s	13.1%	884.50	3.260

Raman Spectroscopy for Identifying Molecules

Chandrasekhara Venkata Raman

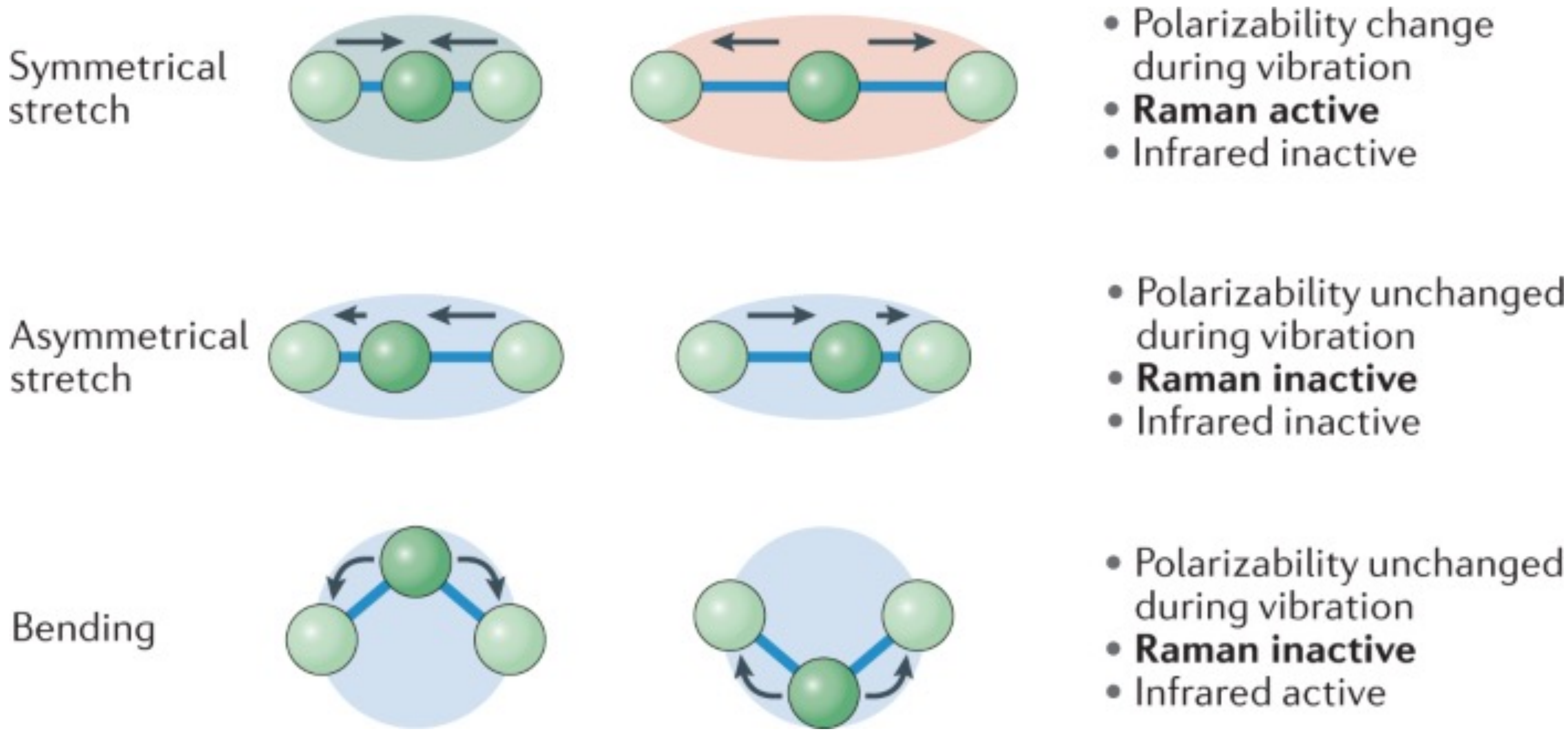
Nobel Prize in Physics (1930)



Todaro *et al.*, *Front. Chem.*, *10*, **2022**

What Exactly is the Raman Shift? Frequency of Vibrations

Polarizability changes as the volume occupied by electrons changes



Raman active: change in polarizability

Infrared (IR) active: change in dipole moment

Mosca *et al.*, *Nat. Rev. Methods Primers*, *1*, **2021**

What Exactly is the Raman Shift? Frequency of Vibrations

Raman shift depends on the vibrational frequencies of the molecule, which are determined by the mass of the atoms and the stiffness of the chemical bonds.

Vibrational frequency of molecule

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

k ← Bond force constant (stiffness)

μ ← Reduced mass ($m_1m_2/(m_1+m_2)$)

Raman shift

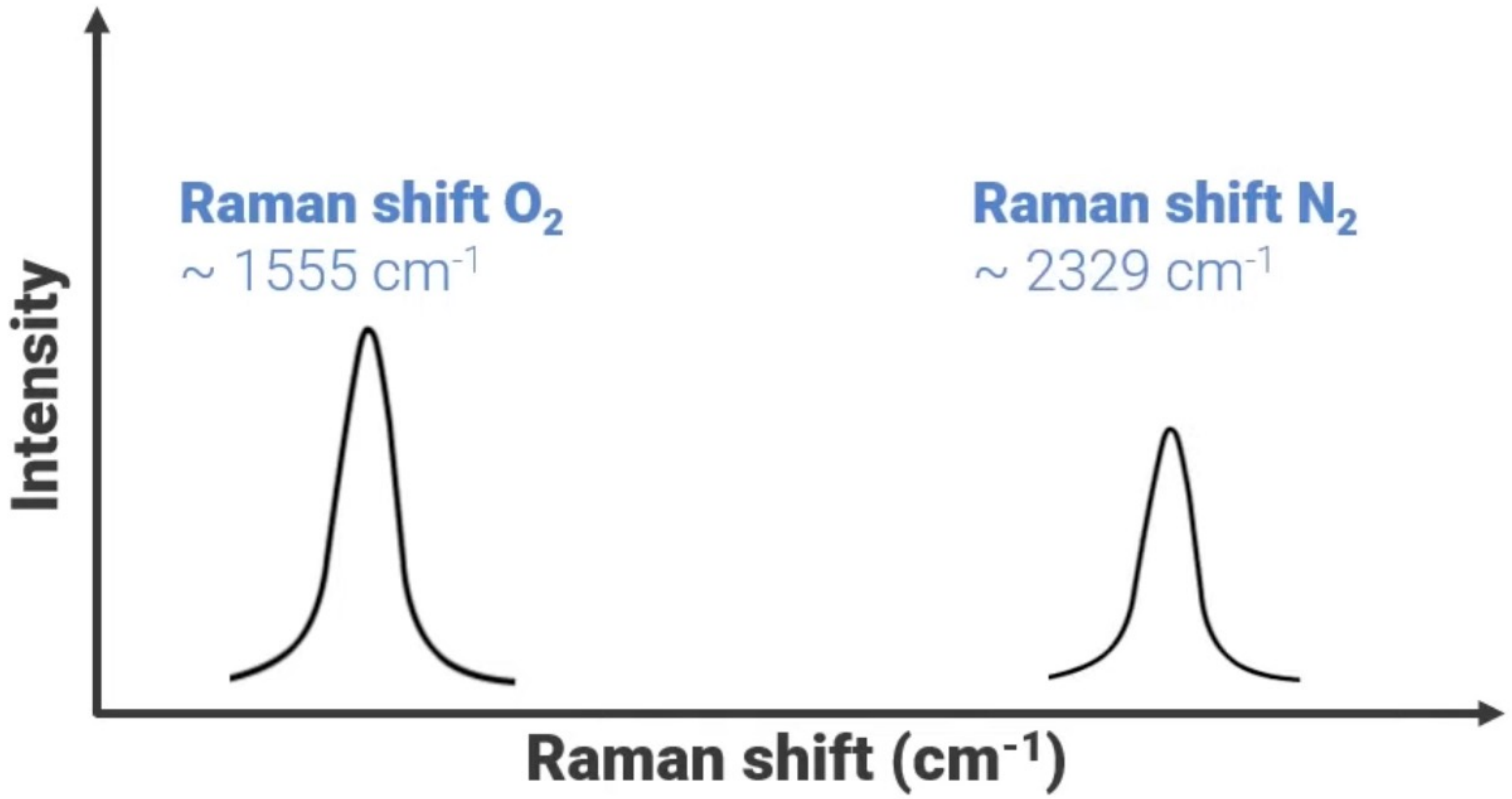
$$\Delta\nu = \nu_0 - \nu_v$$

Vibrational frequency of molecule

Frequency of incident light

O_2

Heavier molecules have long wavelengths and low frequency



N_2

Lighter molecules have short wavelengths and high frequency

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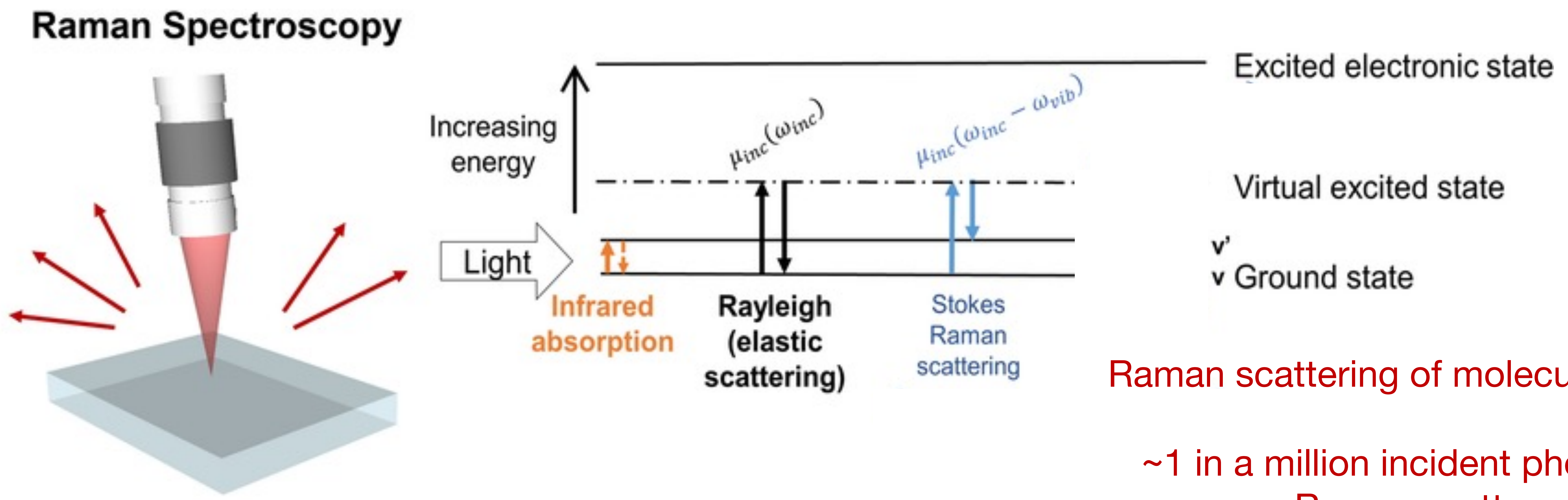
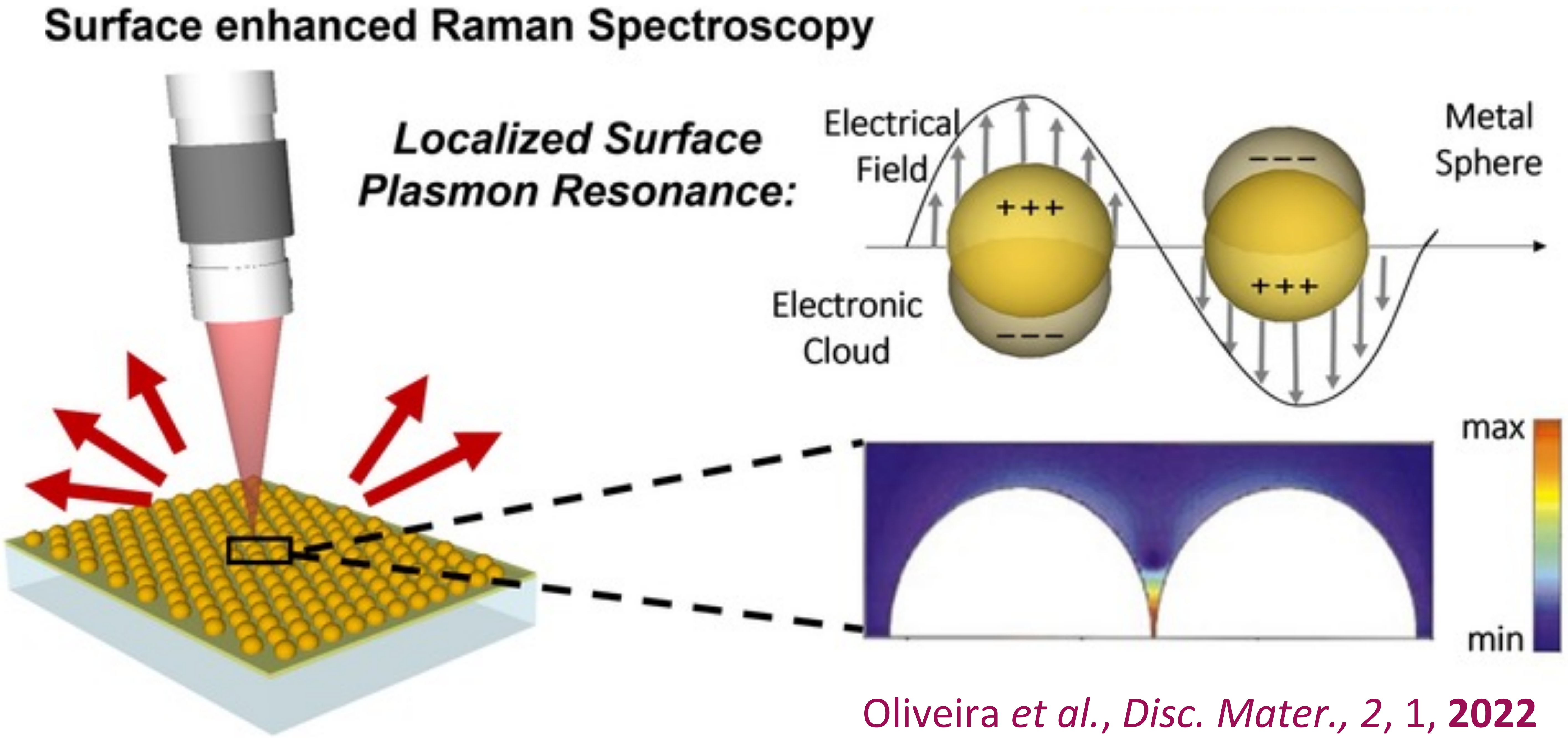
Raman Spectroscopy for Surface Analysis



Raman scattering of molecules is weak!

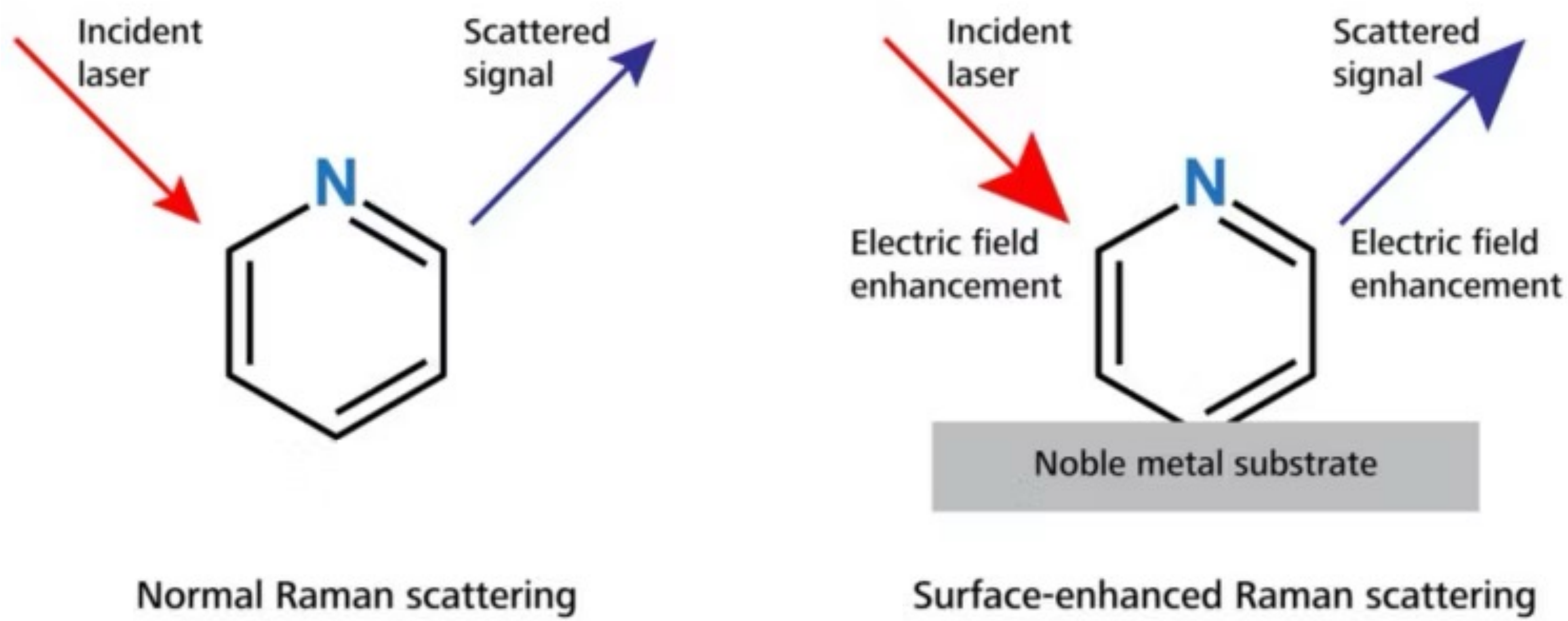
~1 in a million incident photoms are Raman scattered

Laser excites sample and drives localized surface plasmons into resonance



Oliveira *et al.*, *Disc. Mater.*, *2*, 1, **2022**

Raman *vs.* Surface-Enhanced Raman Scattering



Signal enhancement by factors as large as 10^{11}

Metrohm

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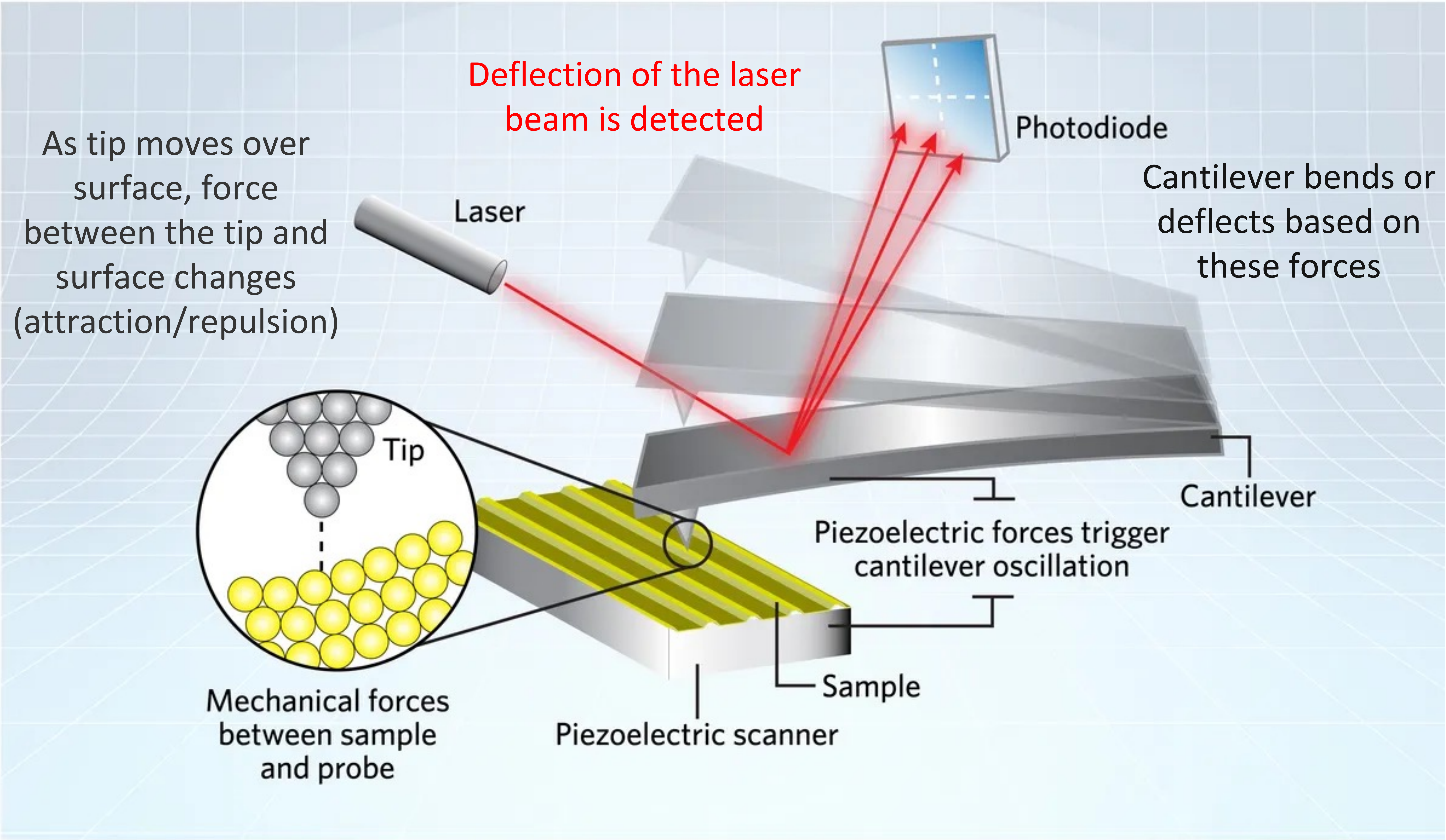
How Can We Characterize Surfaces?

What are some techniques that we covered for visualizing surfaces?

- Atomic force microscopy
- Scanning tunneling microscopy

How Can We "See" What is Happening on Surfaces?

Atomic Force Microscopy (AFM)



TheScientist

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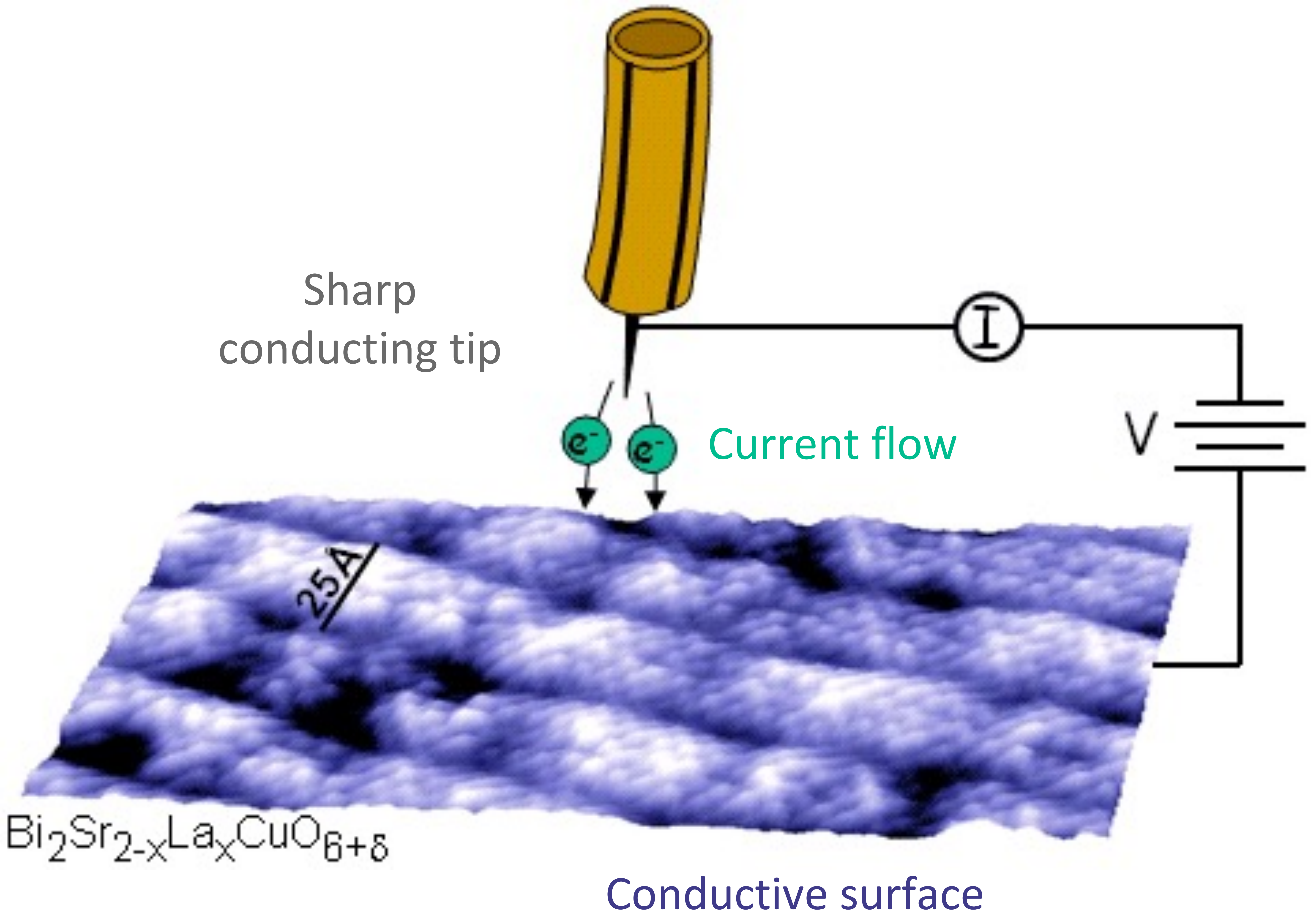
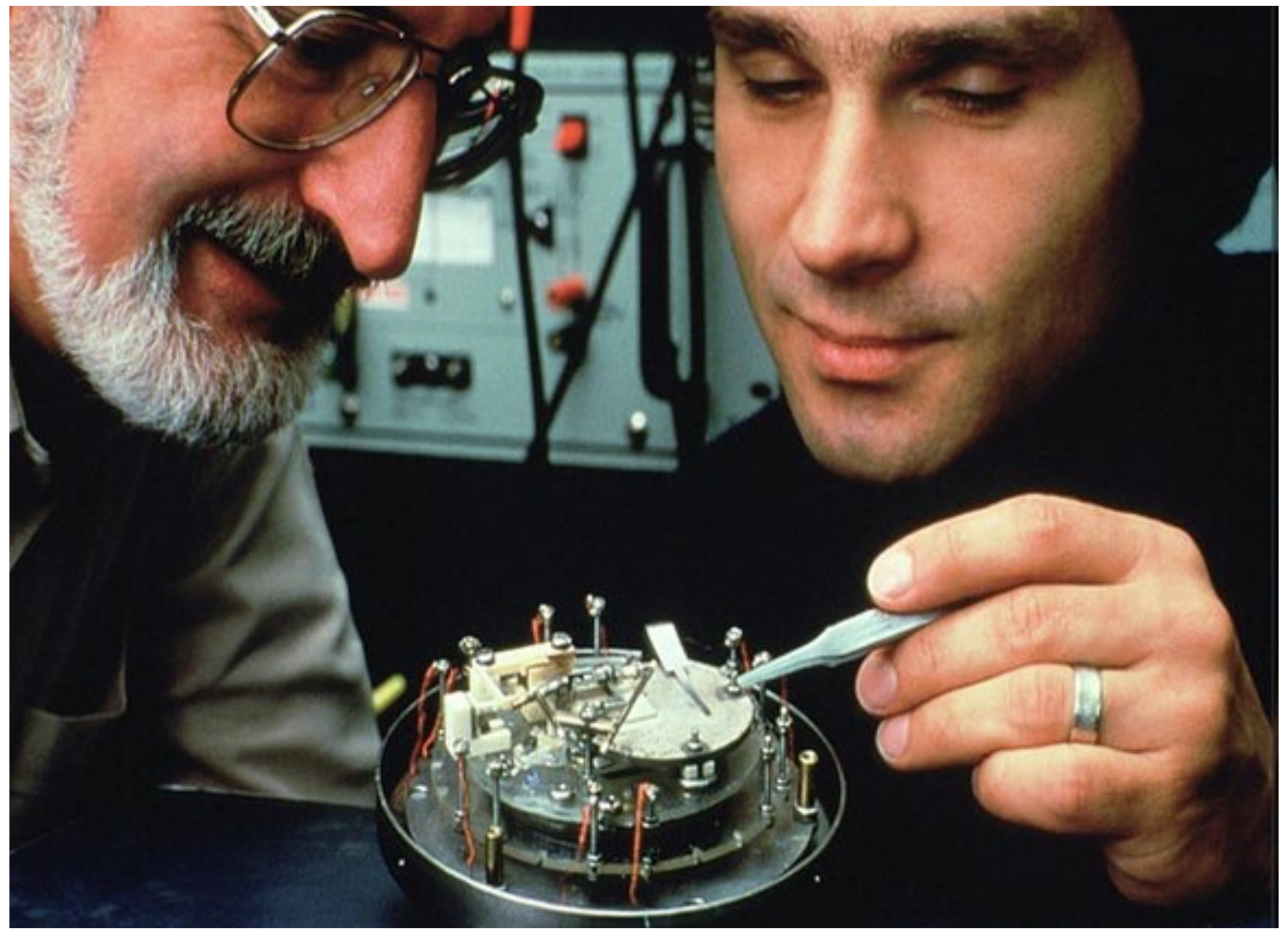
How Can We "See" Surfaces with Higher Resolution?

Scanning Tunneling Microscopy (STM)

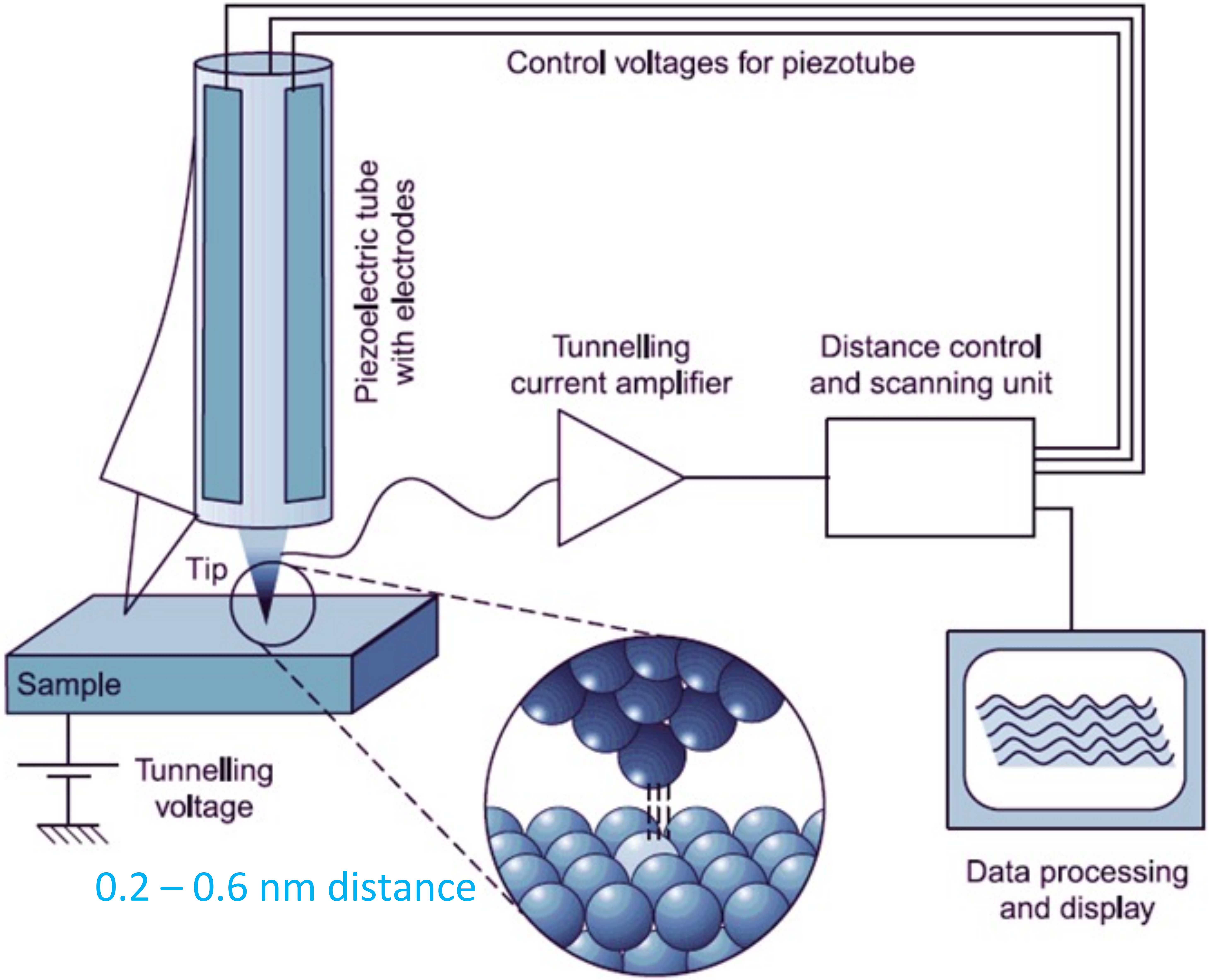


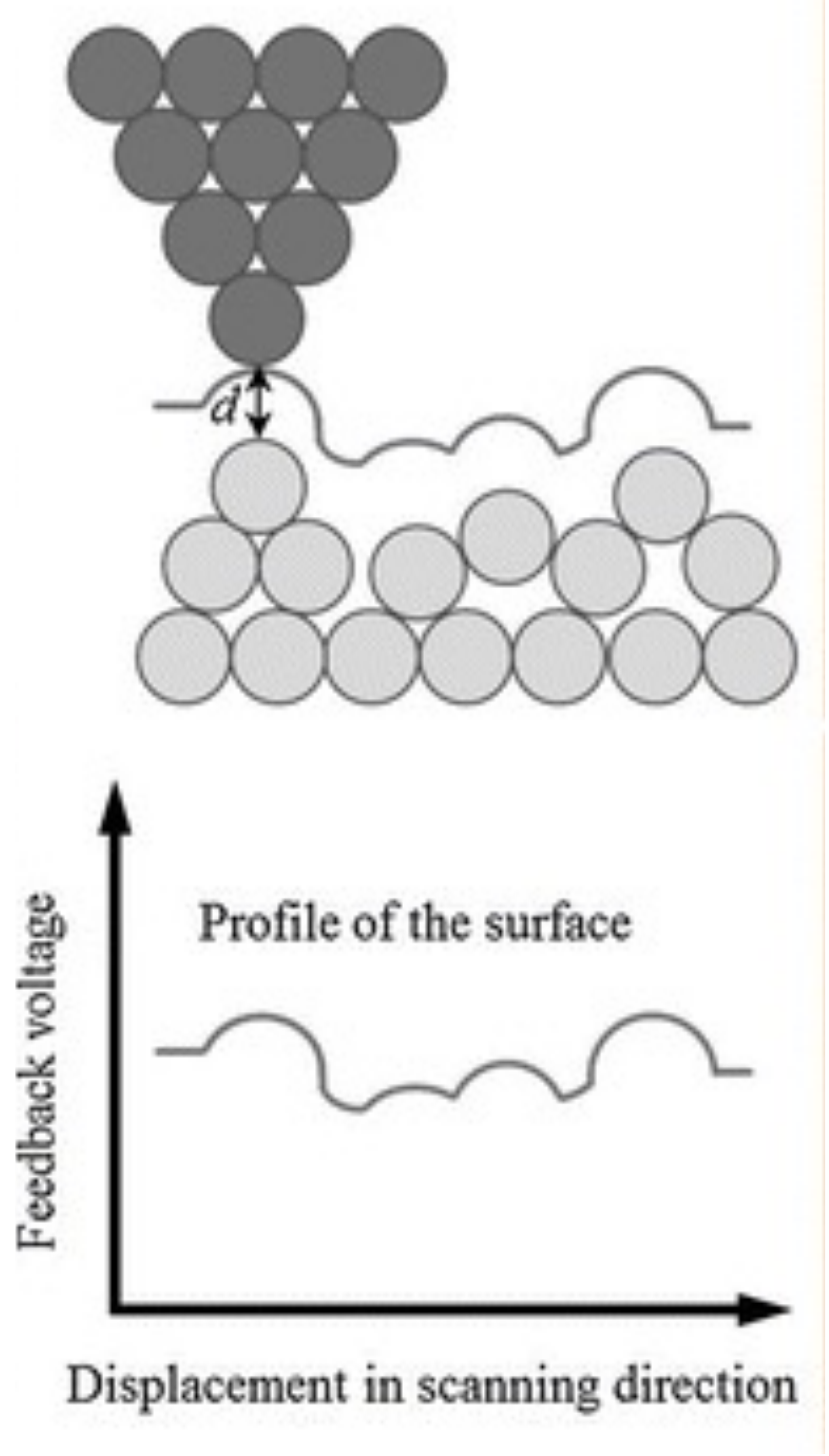


Heinrich Rohrer & Gerd Binnig

Nobel Prize in Physics for invention of STM (1986)

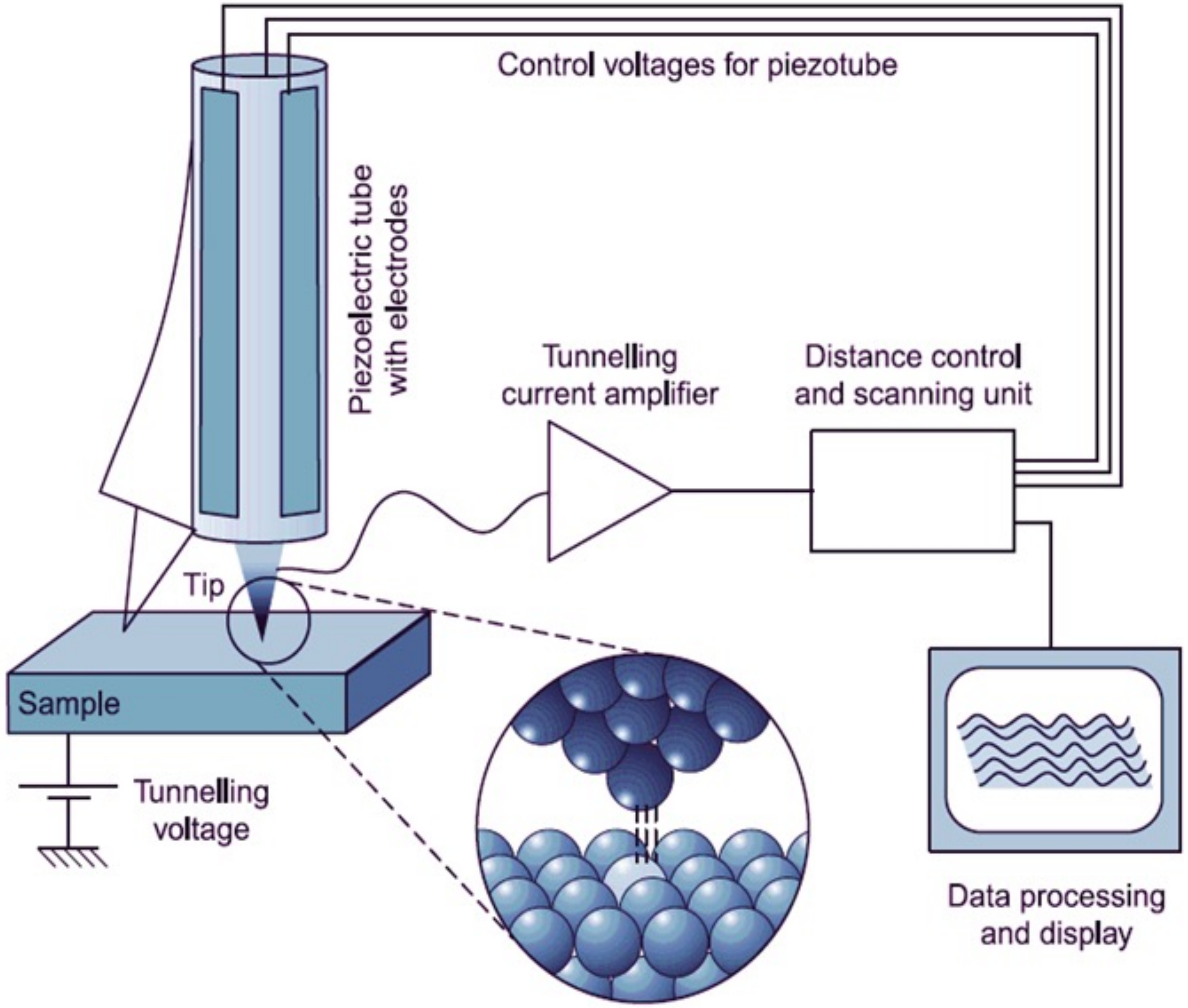
STM Uses a Tunneling Current to Map Atoms on Surfaces



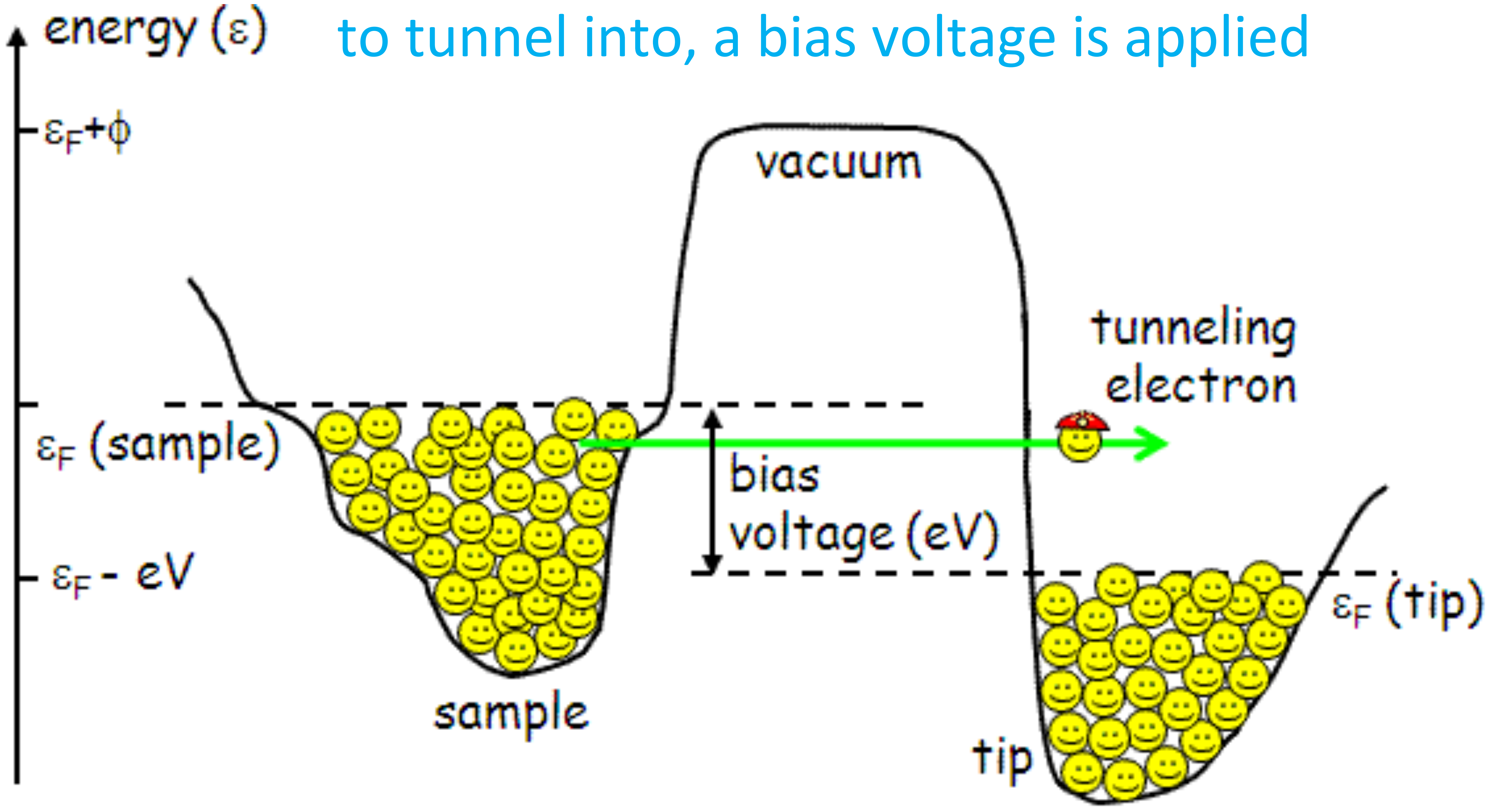


Wikipedia

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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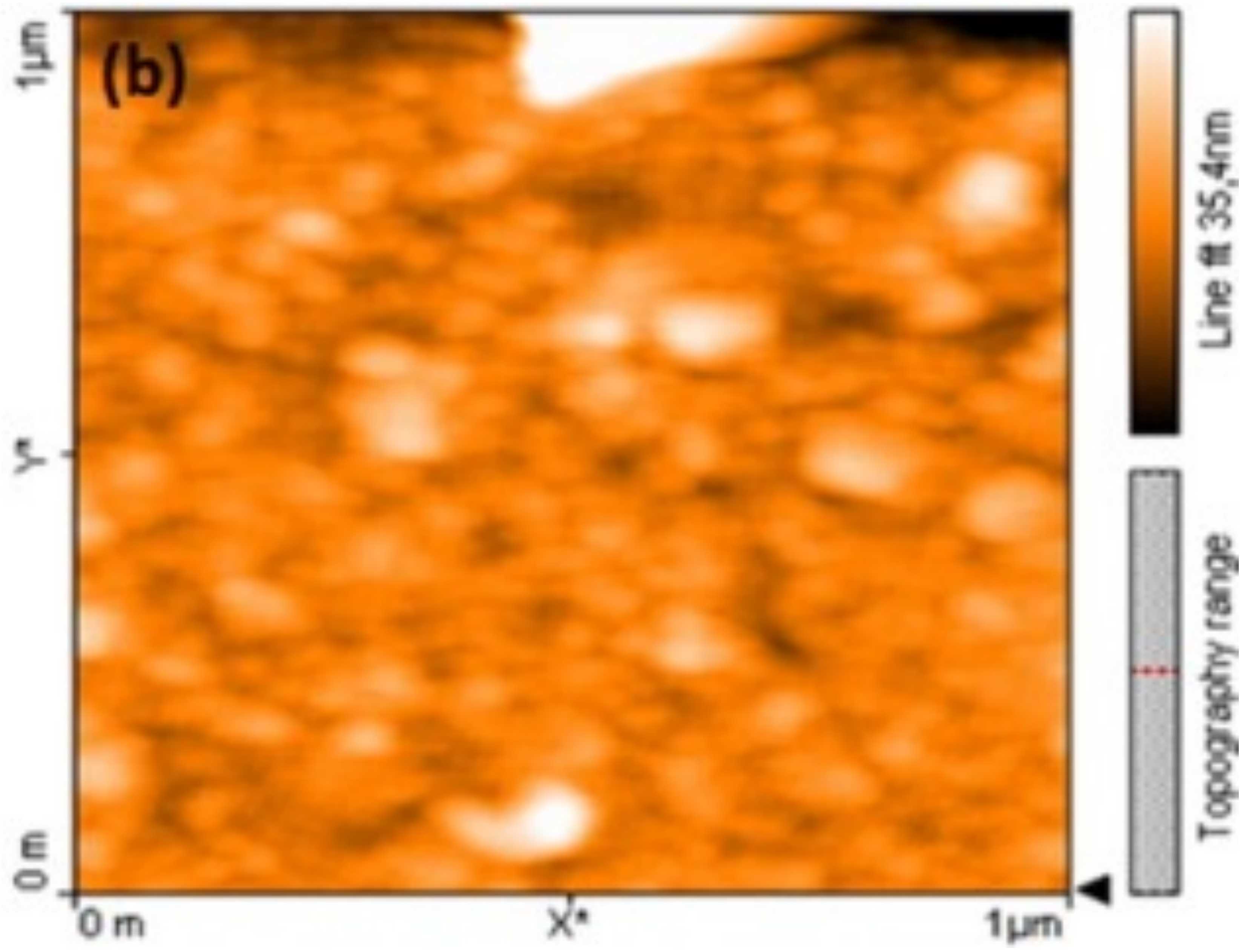
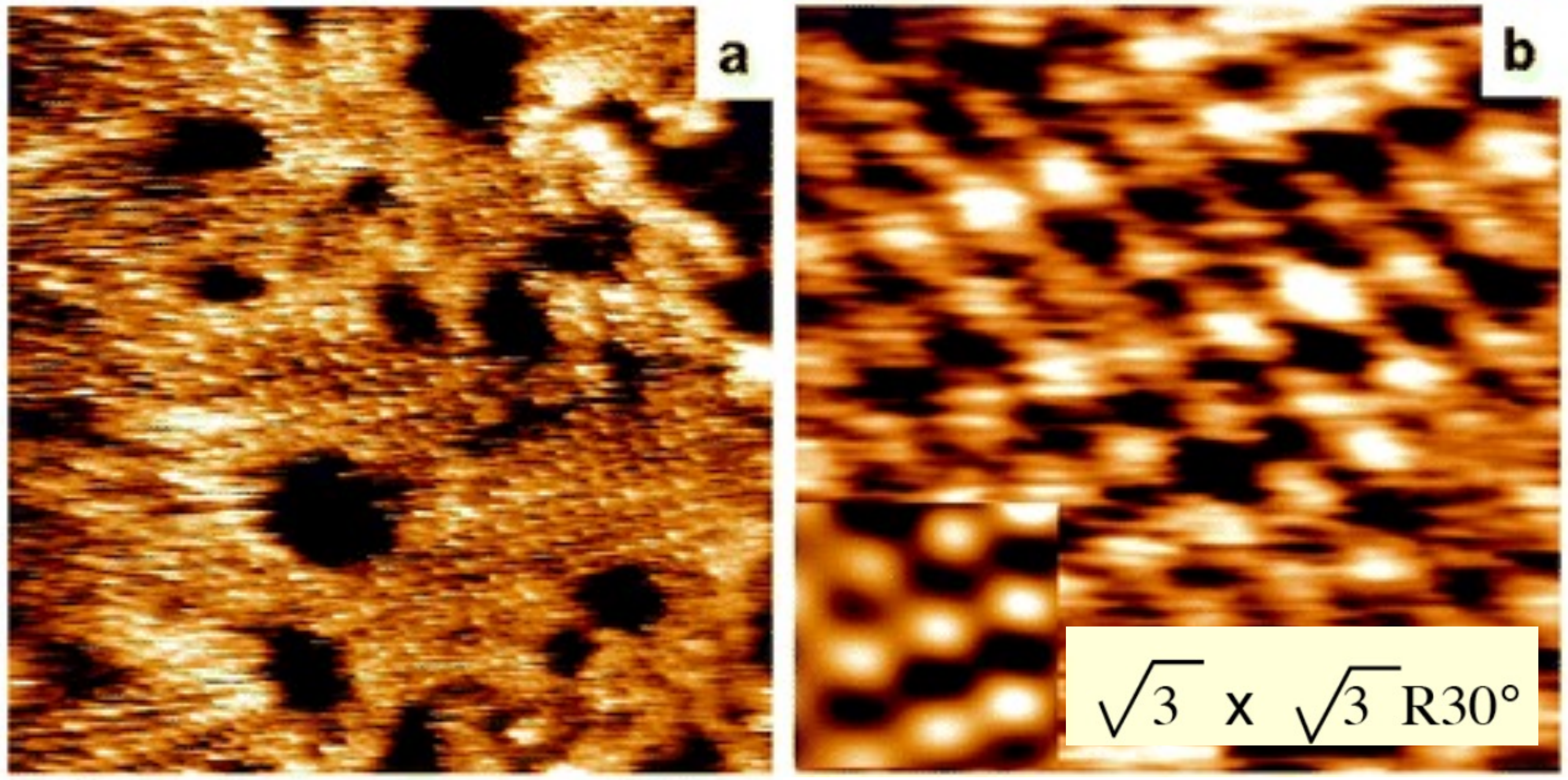
Resolution of AFM *vs.* STM – Hexadecanethiol (C16) on Au (111)





30 nm

4 nm

Simpler – works in air and liquids	More complex (requires UHV and low temp.)
Conducting/non-conducting surfaces	Only conducting surfaces
0.1-10 nm (0.1 is ultimate best equipment)	0.1 nm (0.01 nm in vertical direction)
Topography, force measurements, mechanical properties	Topography, electronic properties
Uddin, *Res. Phys.*, *7*, 2289, **2017**	Mendoza, *Langmuir*, *23*, 2, **2006**

Happy Holidays and See You in The New Year!

I hope you can apply what you learned about surfaces and interfaces while you are skiing over the holidays!

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