EPFL
École polytechnique fédérale de Lausanne

Neuro X Institute

CHEMINA
Laboratory of Chemical Nanotechnology

Applications
Lesson 13

MSE 304

Nako Nakatsuka

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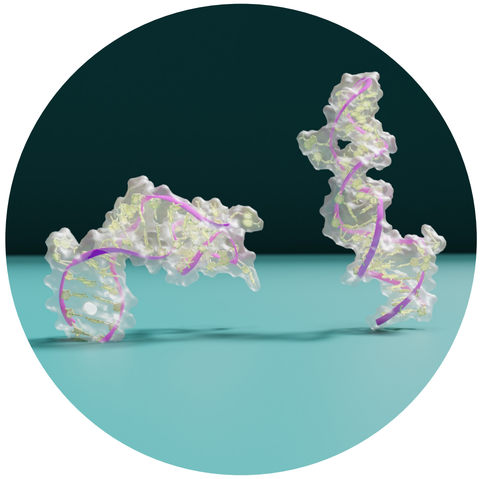

December 13th 2024

Recap of Last Week's Class on Applications

- Biosensors – molecular recognition and sensing parameters
- Clark Electrode for Oxygen Sensing – recap on electrochemistry
- Glucose Sensor – recap on electrolysis and why it's is successful
- Remaining Challenges of Biosensors – COVID-19 rapid test

What We Cover in Today's Class

- Glucose Biosensor –Raman spectroscopy for non-invasive monitoring
- Recap on Challenges of Biosensors – remaining technological gaps
- Strategies to Overcome Challenges – aptamer biosensors and Debye lengths
- Catalysis – how surfaces serve as catalysts/review of molecular orbital theory
- Optimization of Catalysts – balancing act of performance metrics

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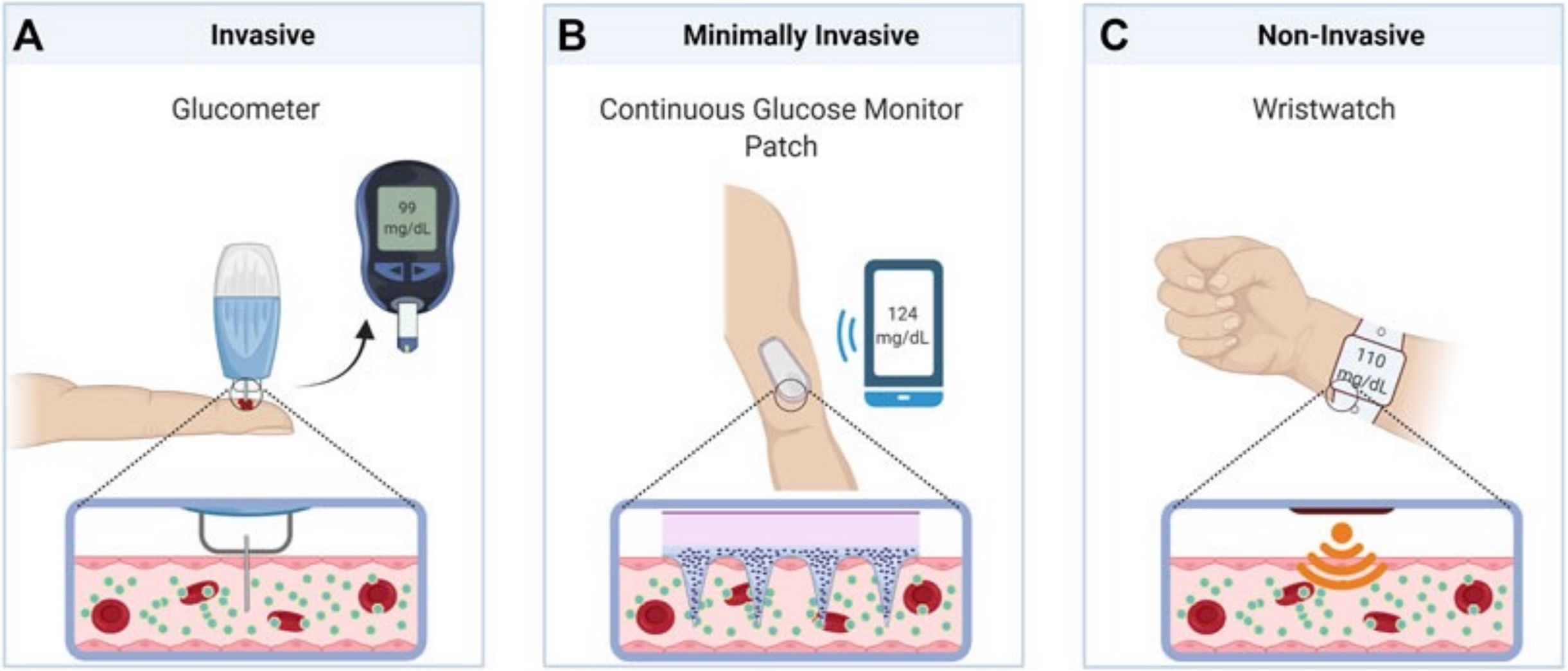
Glucose Biosensor – Transformative for Human Health



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

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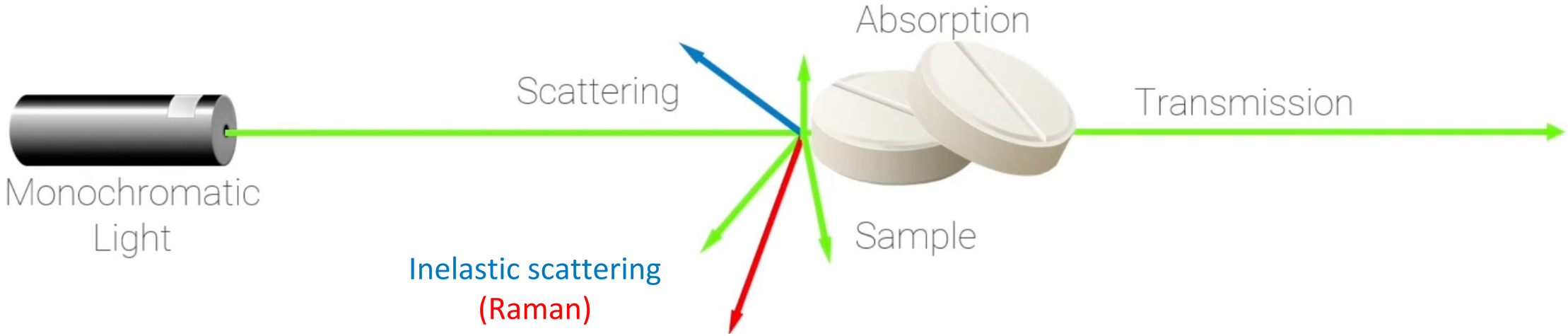
Raman Spectroscopy for Non-Invasive Glucose Detection

Chandrasekhara Venkata Raman

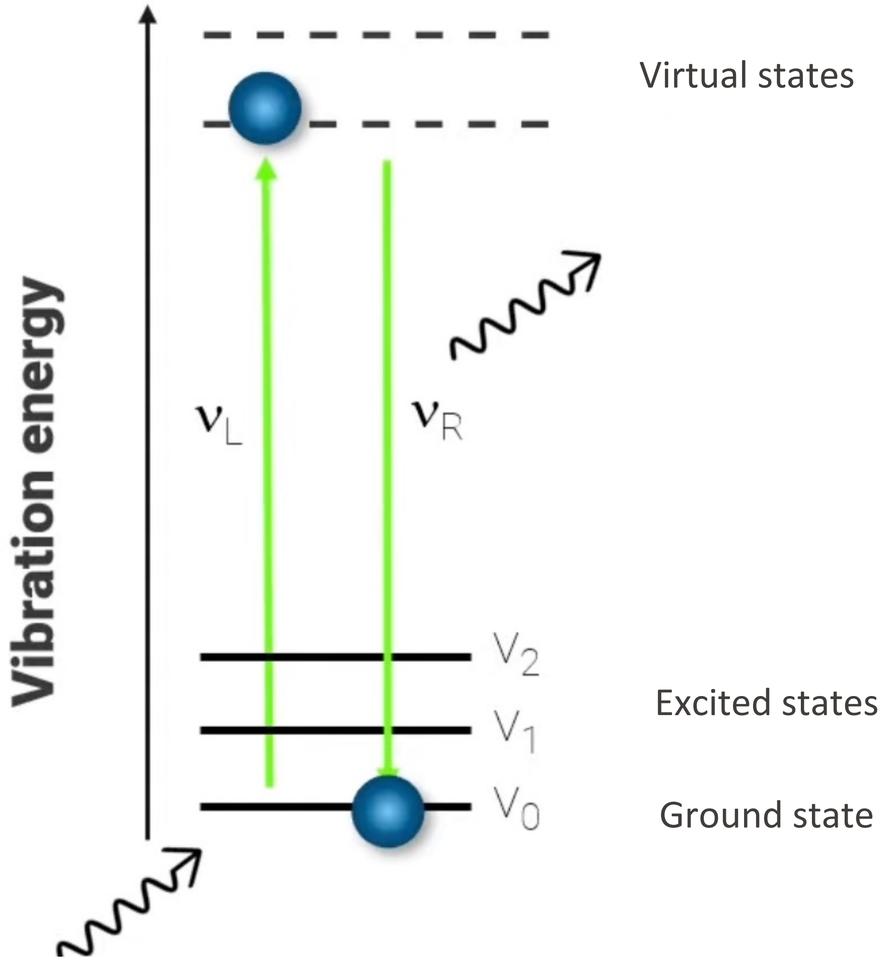
Nobel Prize in Physics (1930)



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

Raleigh Scattering: Molecule Falls to Ground State

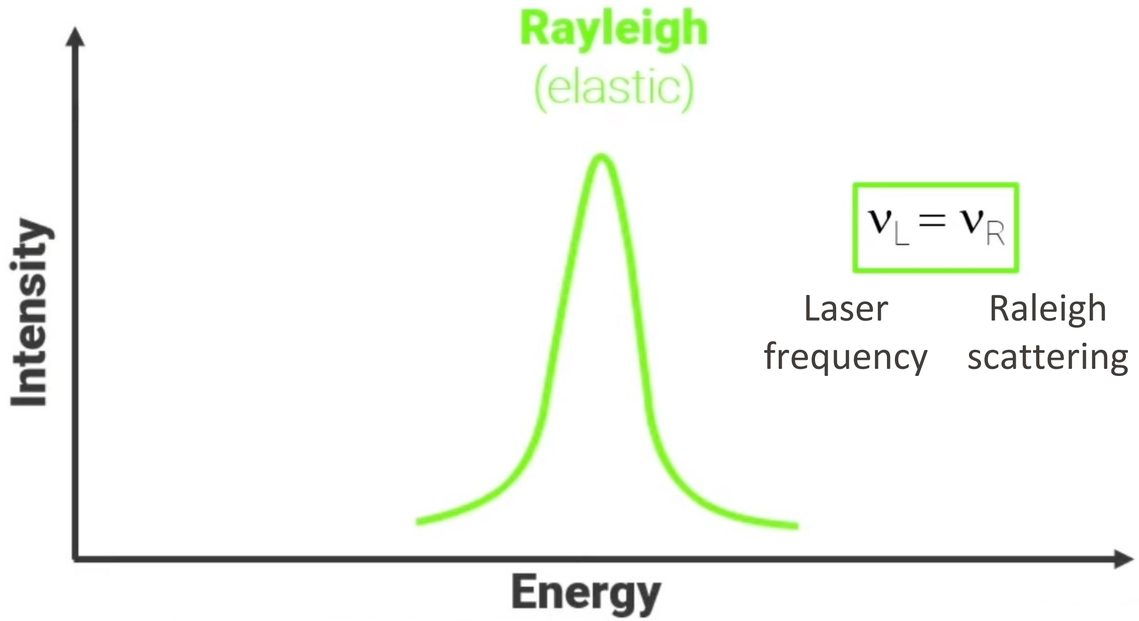
Elastic scattering (Raleigh)



Virtual states

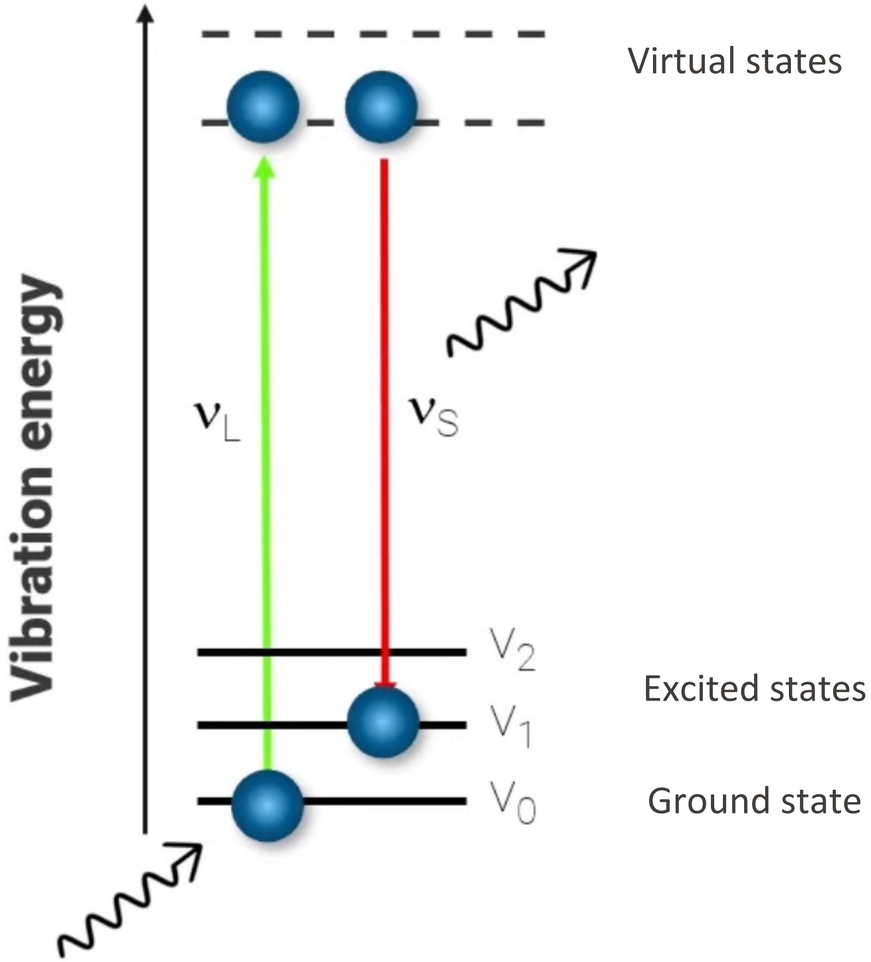
Excited states

Ground state



Raman Scattering = Molecule Falls to Excited State

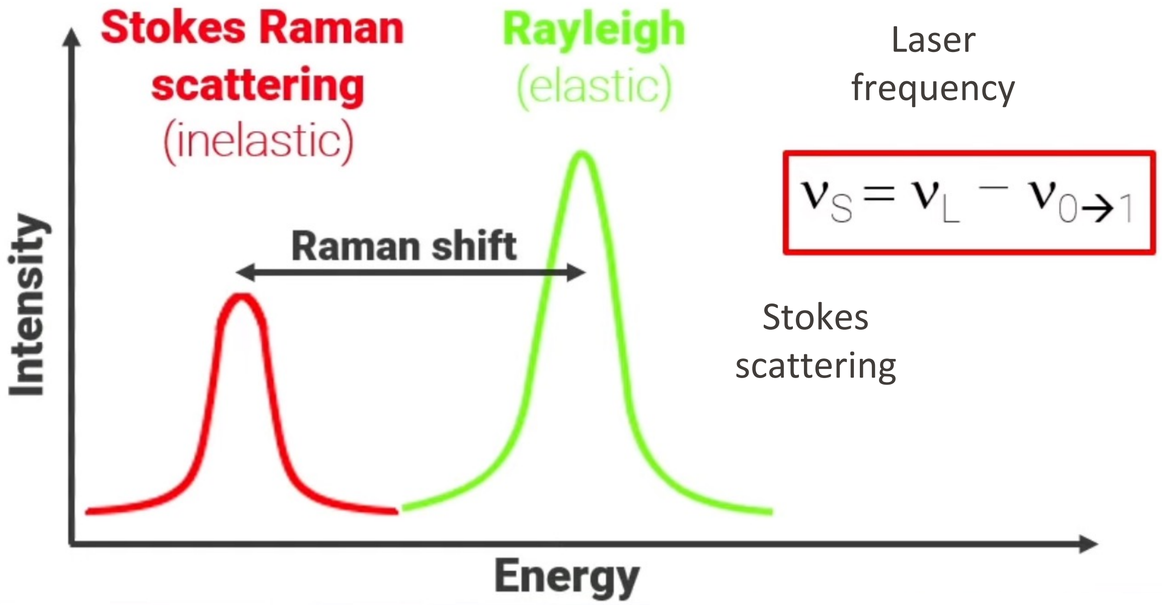
Inelastic scattering (Raman)



Virtual states

Excited states

Ground state



Laser frequency

$$\nu_S = \nu_L - \nu_{0\rightarrow 1}$$

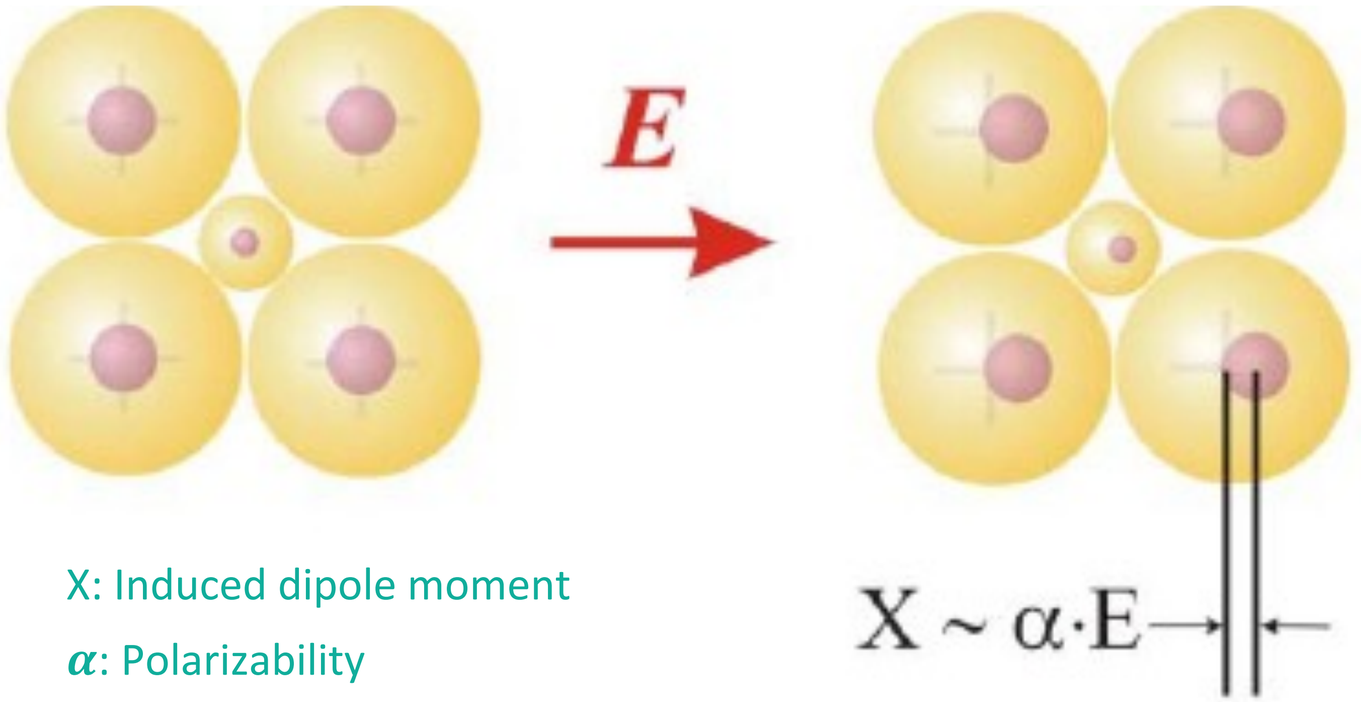
Stokes scattering

What is Polarizability?

Polarizability: The tendency of a substance to form a dipole moment when an electric field (light) is applied

Without electric field

With electric field



X: Induced dipole moment

α: Polarizability

E: Electric field

Claborn *et al.*, *CrystEngComm.*, *4*, 46, **2002**

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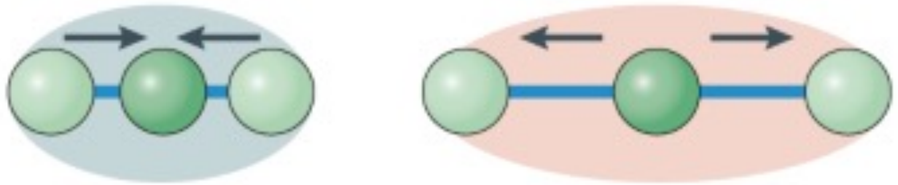
What Exactly is the Raman Shift? Frequency of Vibrations

Polarizability changes as the volume occupied by electrons changes

Symmetrical stretch

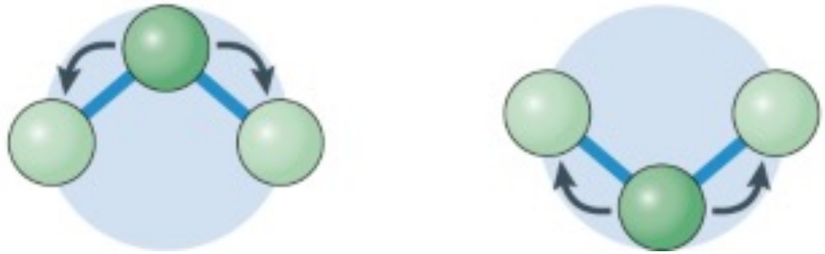


- Polarizability change during vibration
- **Raman active**
- Infrared inactive

Asymmetrical stretch

- Polarizability unchanged during vibration
- **Raman inactive**
- Infrared inactive

Bending



- Polarizability unchanged during vibration
- **Raman inactive**
- Infrared active

Raman active: change in polarizability

Infrared (IR) active: change in dipole moment

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

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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)

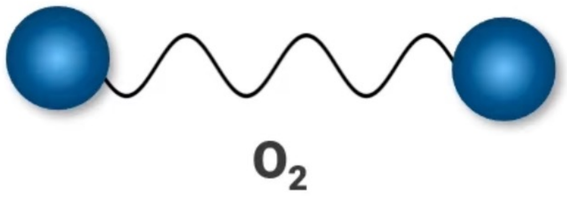
μ ← Reduced mass ($m_1m_2/(m_1+m_2)$)

Raman shift

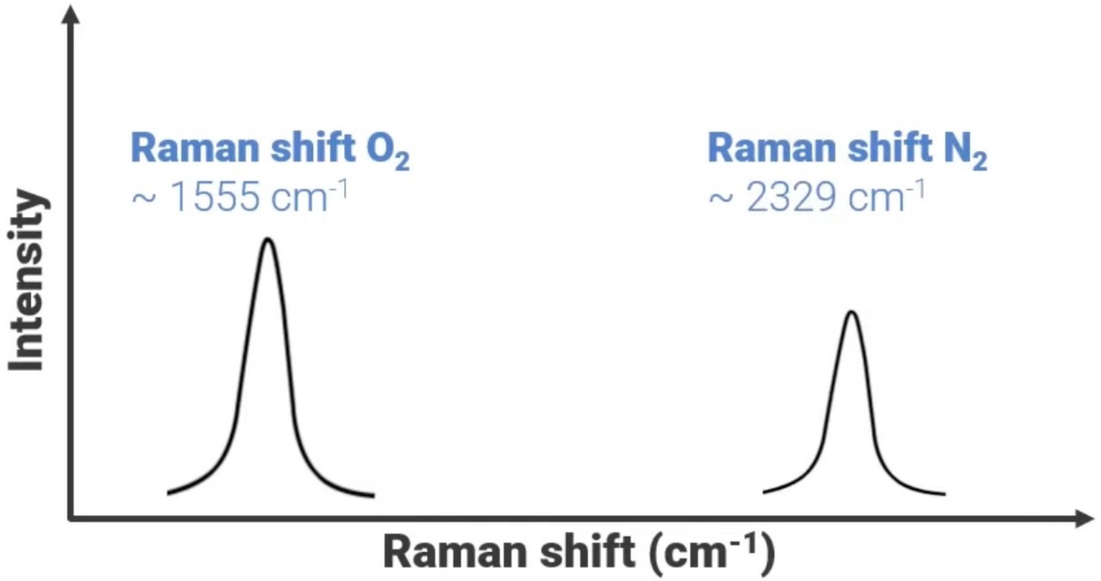
$$\Delta\nu = \nu_0 - \nu_v$$

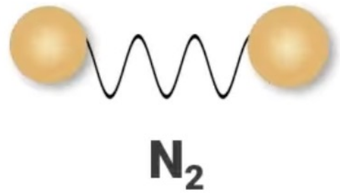
Vibrational frequency of molecule

Frequency of incident light



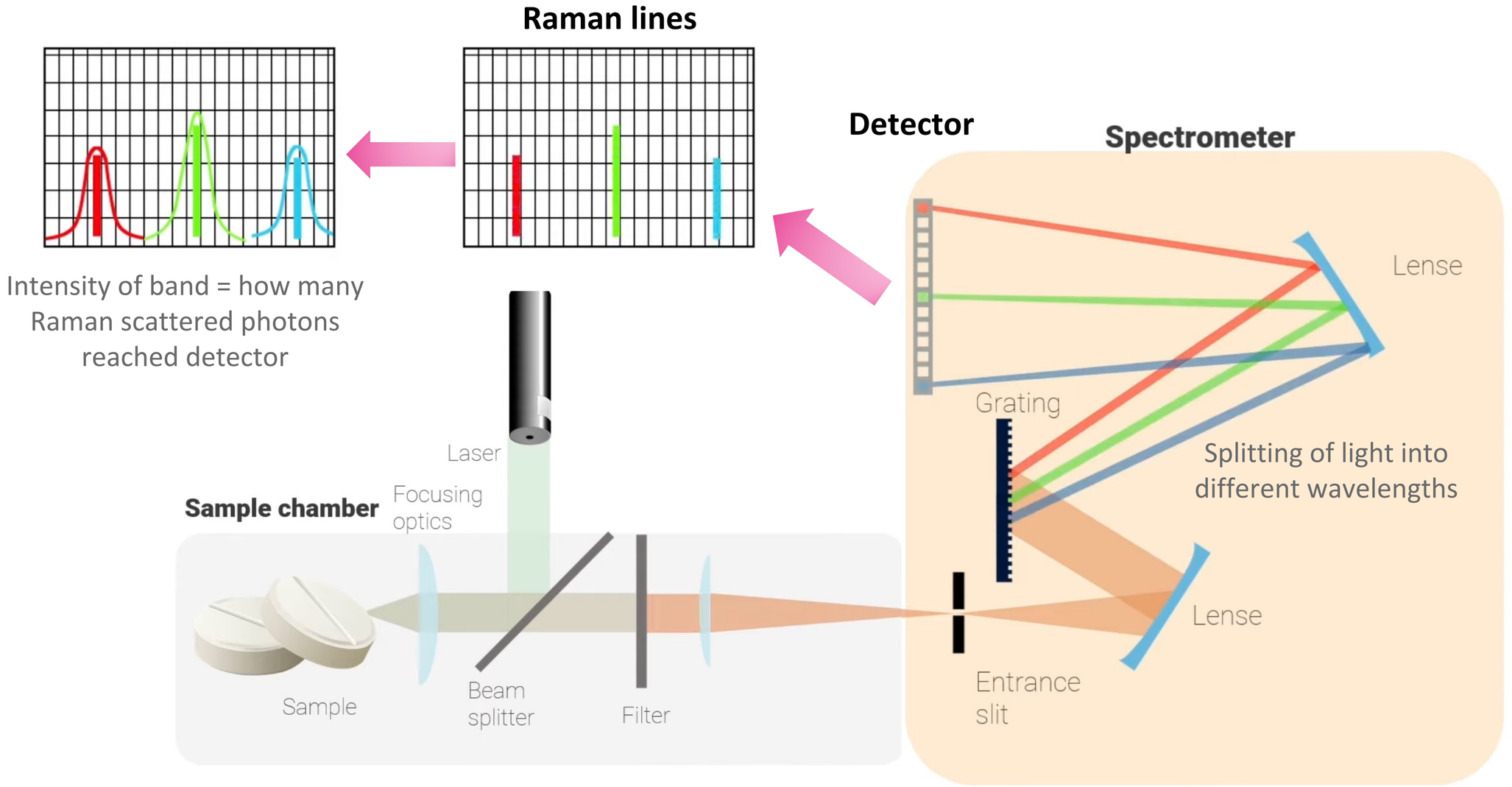
Heavier molecules have long wavelengths and low frequency





Lighter molecules have short wavelengths and high frequency

Raman Spectroscopy for Non-Invasive Glucose Detection



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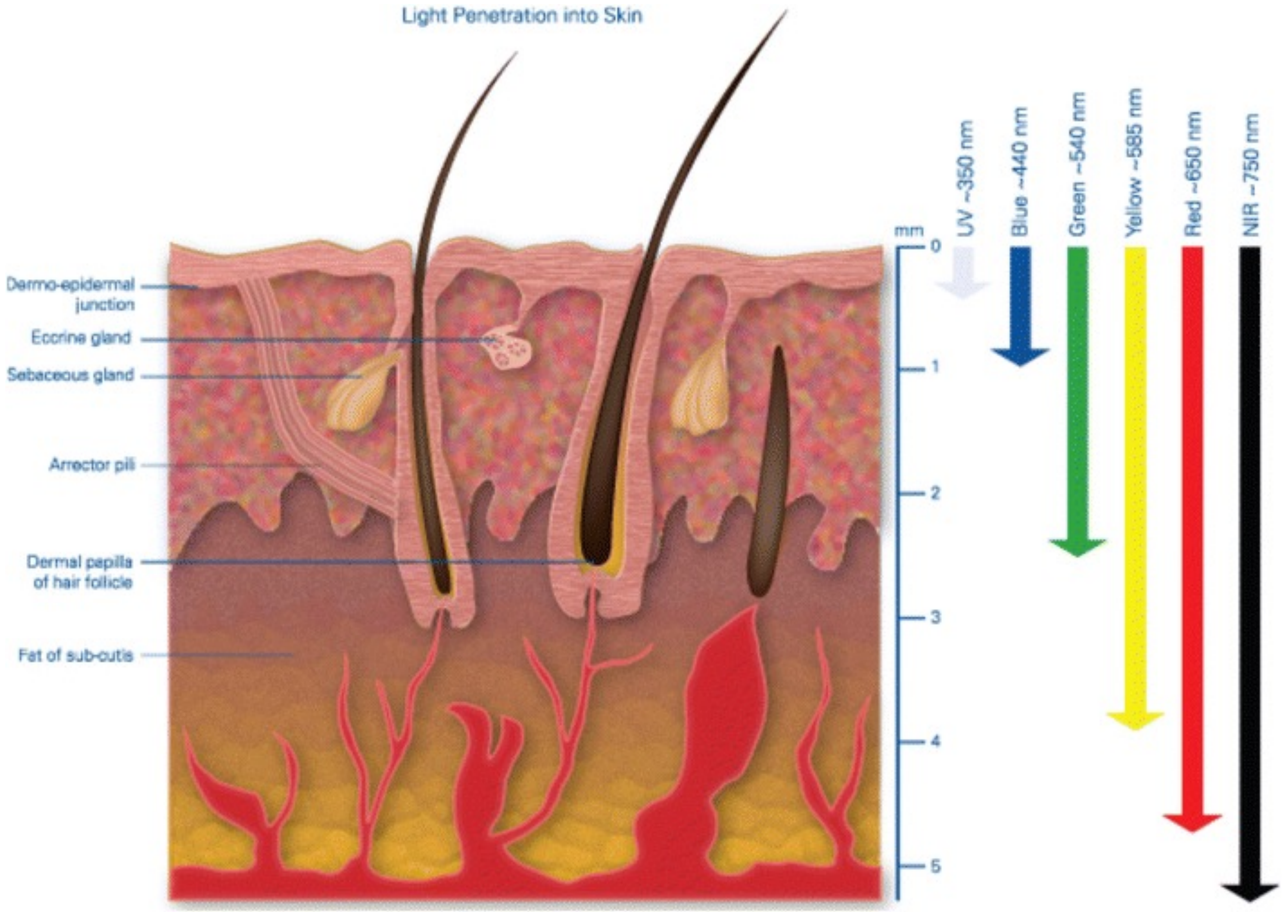
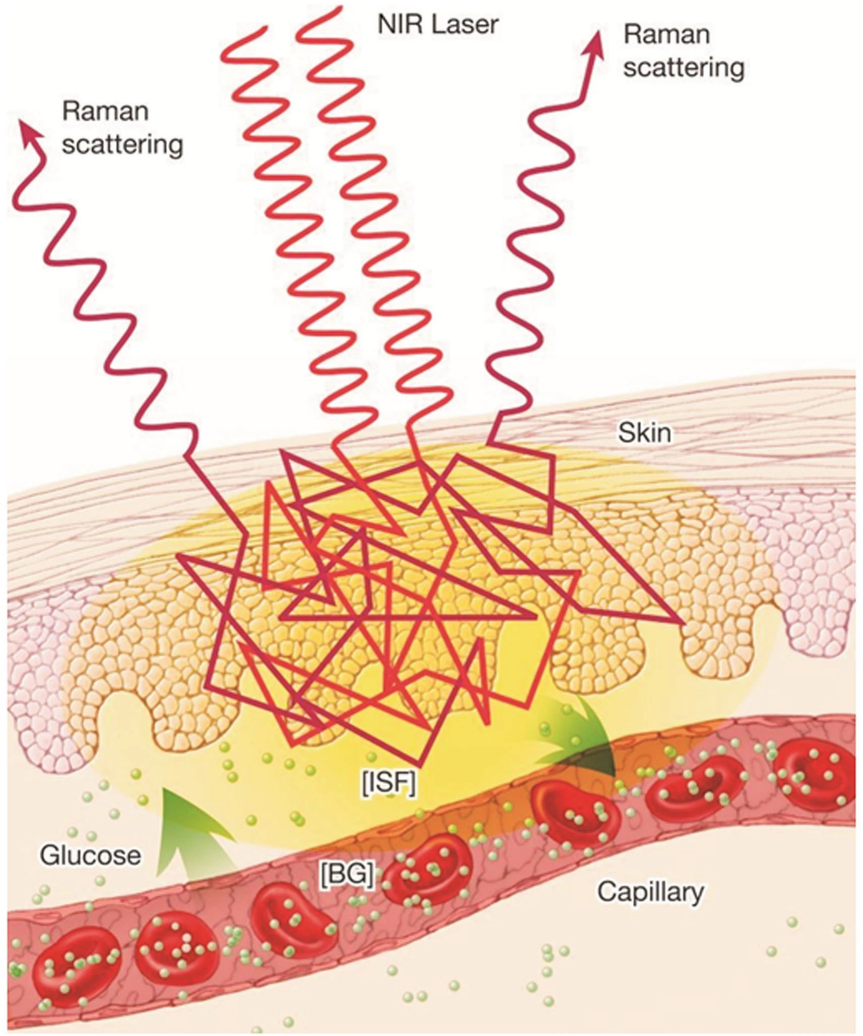
Tissue Penetration using Near-IR Laser



Ash *et al.*, *Las. Med. Sci.*, *32*, 4, **2017**



Spegazzini *et al.*, *Sci. Rep.*, *4*, 7013, **2014**

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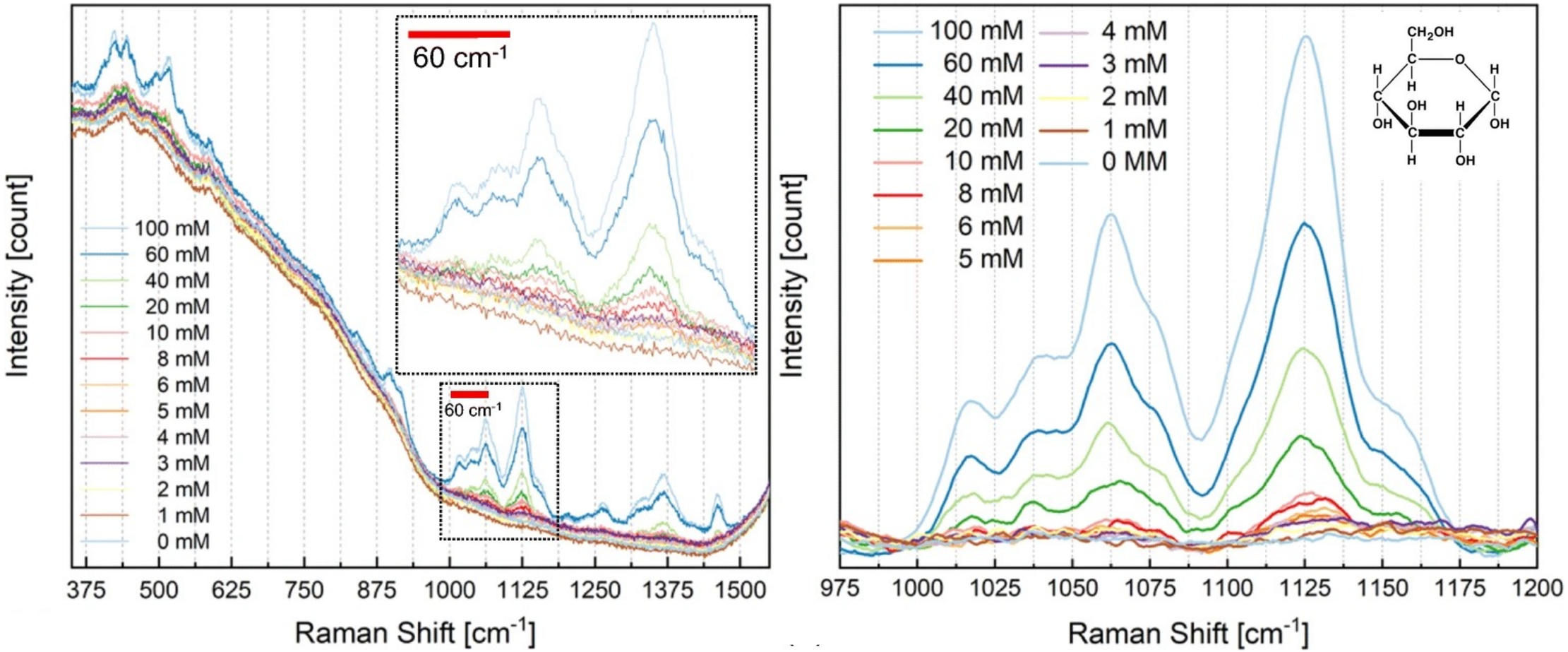
Raman Spectroscopy for Non-Invasive Glucose Detection

Complex molecules have more vibrational modes

Raman Fingerprint: Target of Raman is the material specific pattern of the spectrum



Golparvar *et al.*, *BioNanoScience, 11*, 871, **2021**

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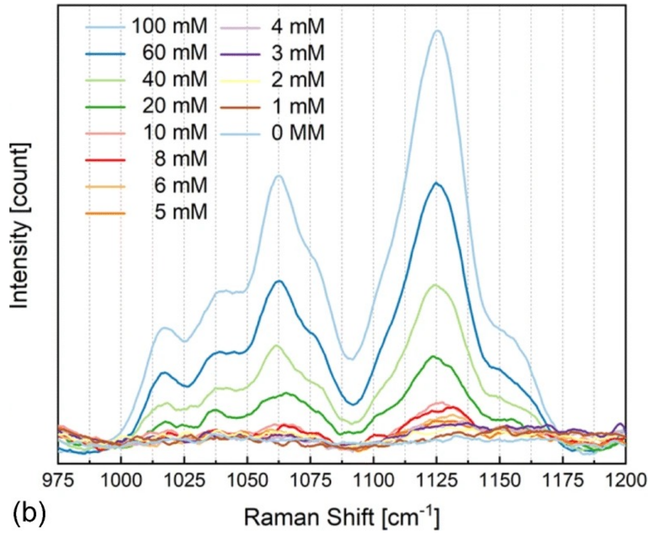
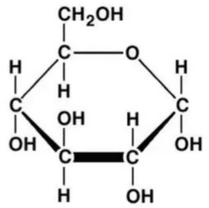
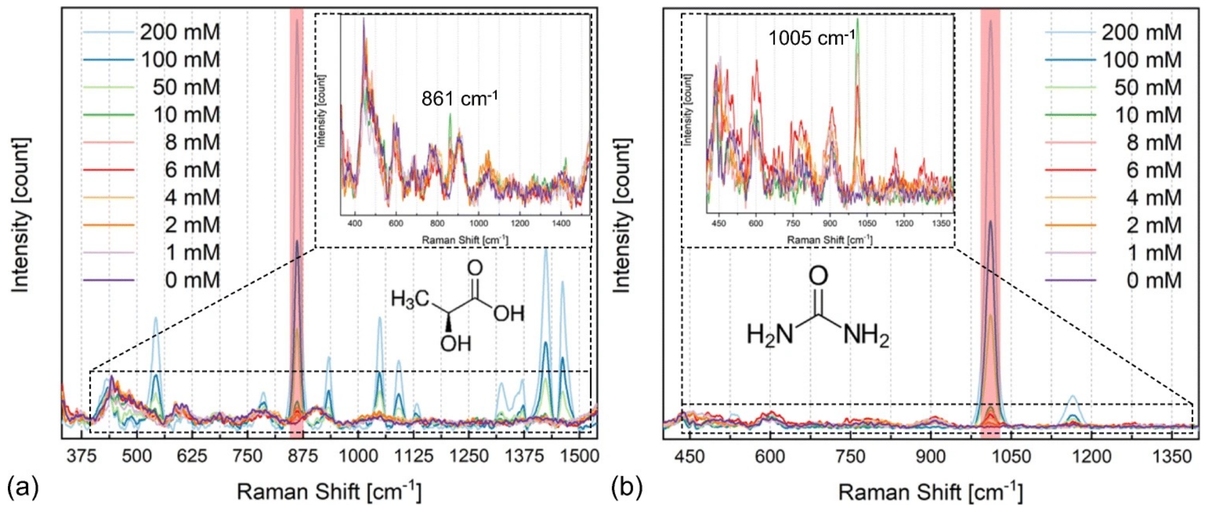
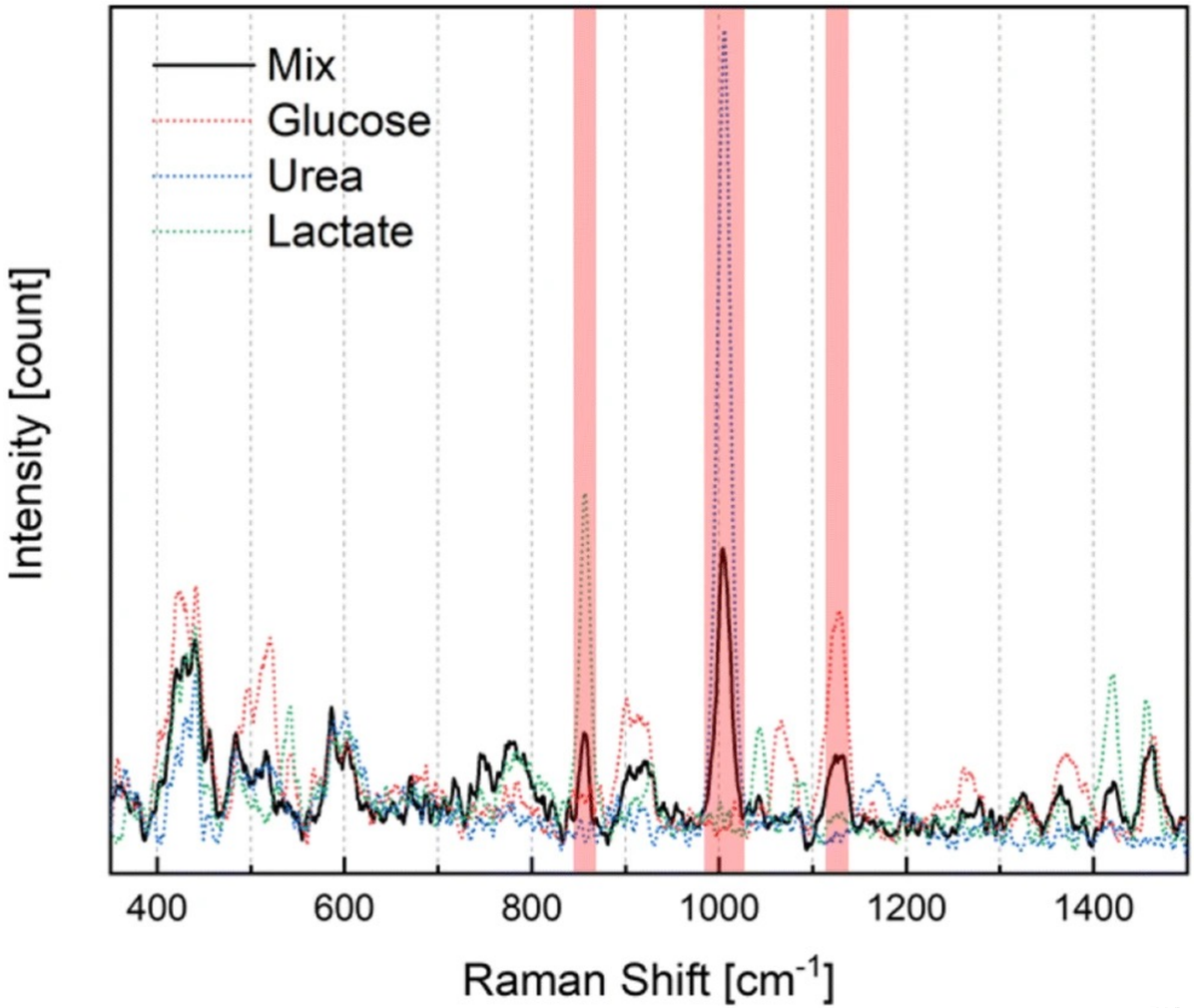
Raman Spectroscopy for Non-Invasive Glucose Detection









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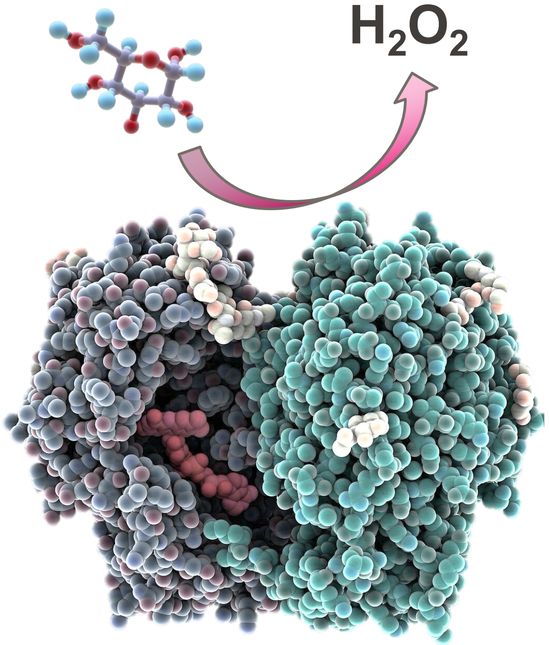
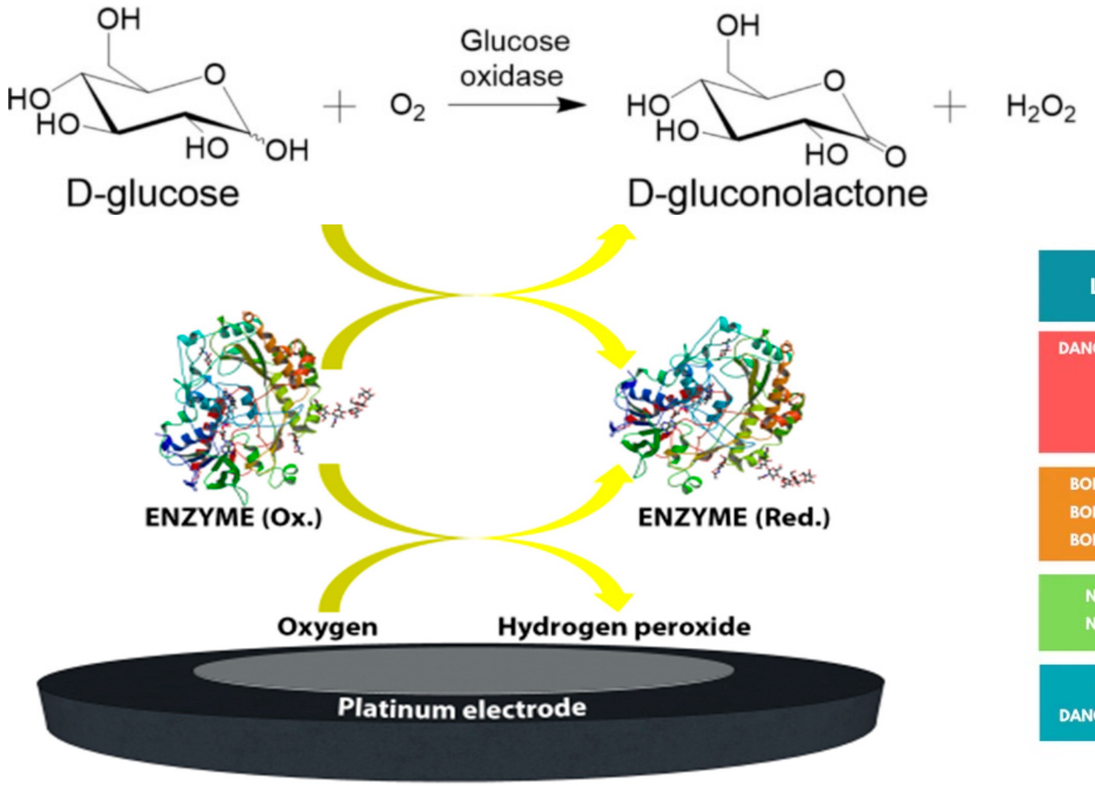
Success of the Glucose Biosensor – Robust System



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)

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Success of the Glucose Biosensor – Concentration Range

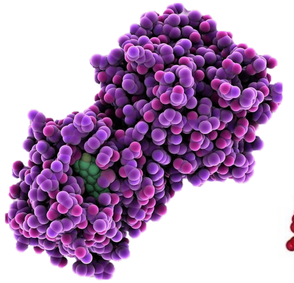
Vitamins

Hormones

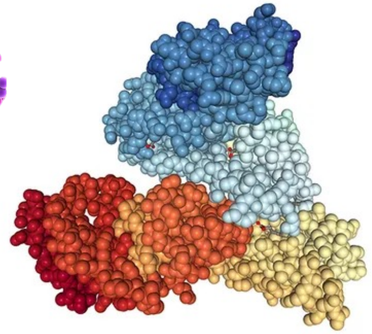
Amino acids

Glucose

Neurotransmitters



Globulins



Albumin

Picomolar
10^{-12}

Nanomolar
10^{-9}

Micromolar
10^{-6}

Millimolar
10^{-3}

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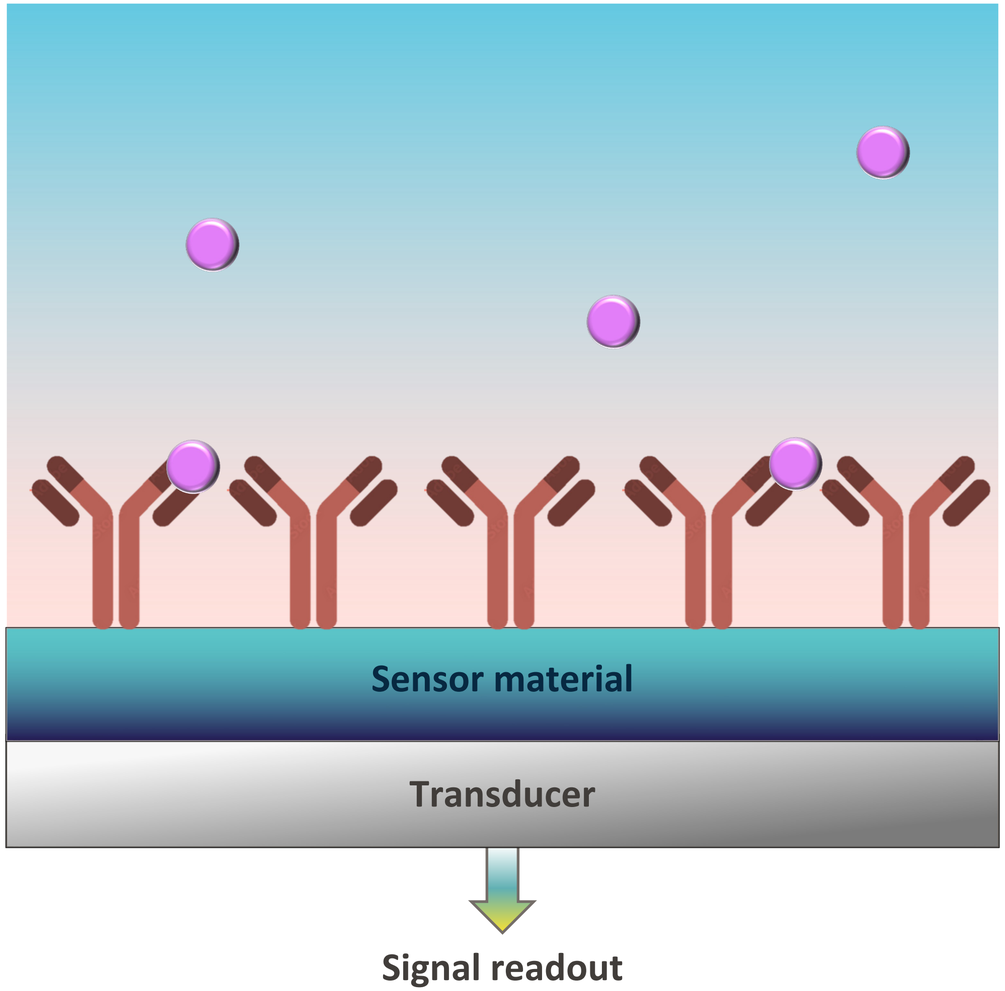
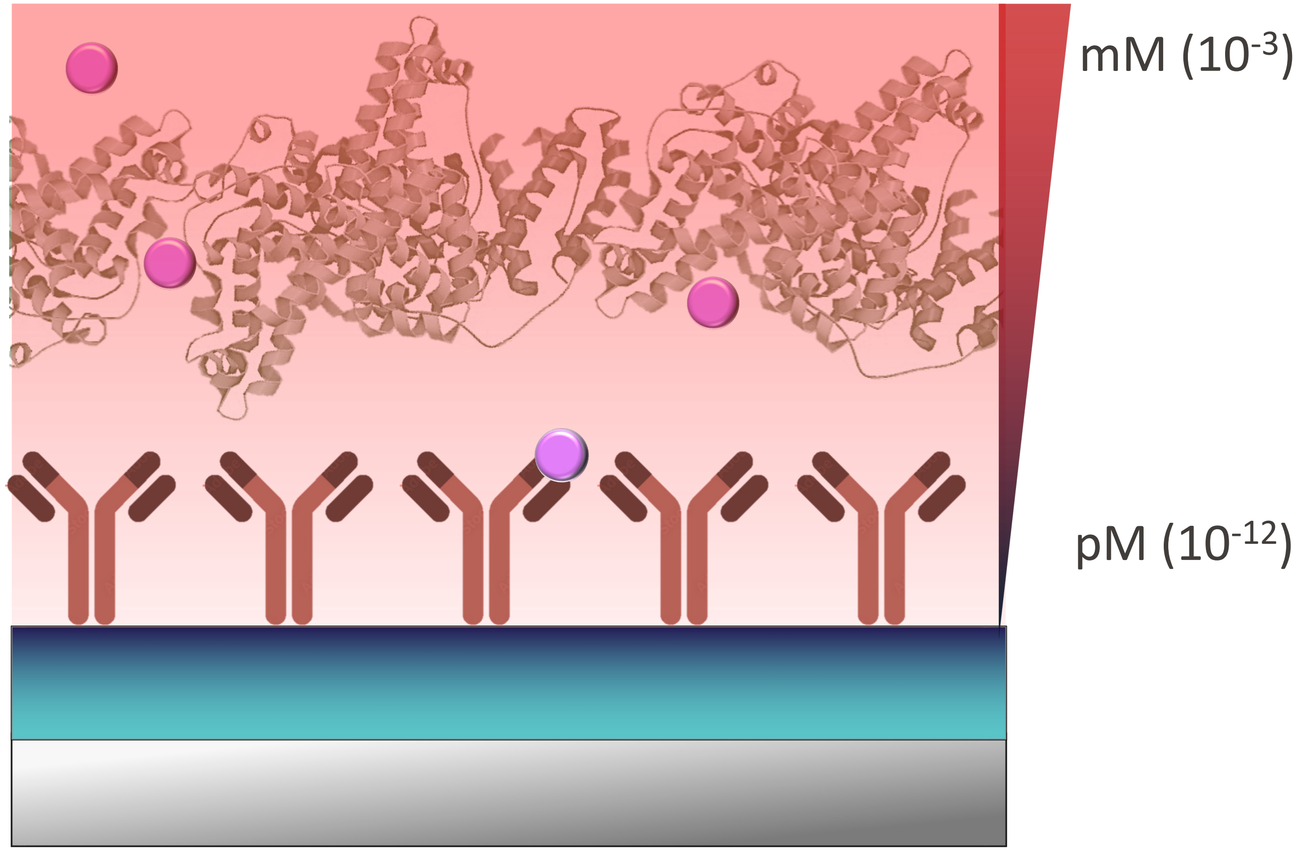
1. Nonspecific Binding (NSB) in Complex Environments

Expectation (phosphate buffered saline)



Reality (biofluids such as blood)



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

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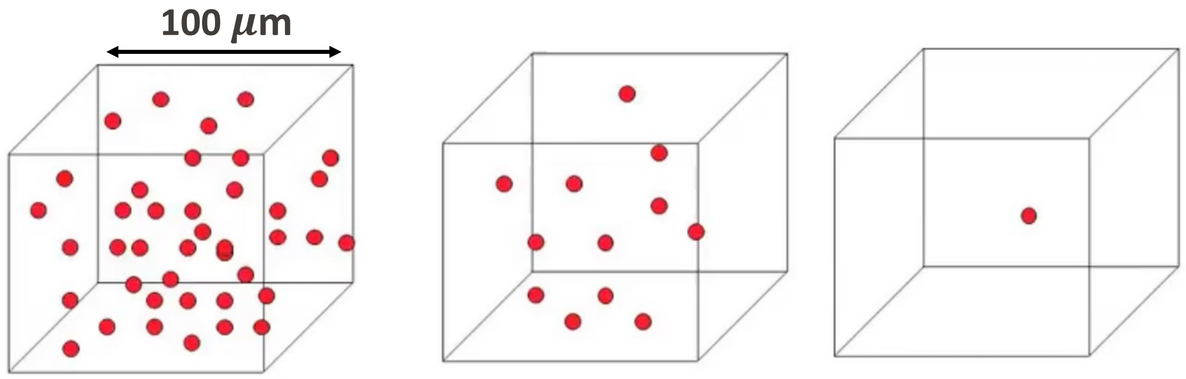
2. Very Few Number of Molecules Within Sample Size

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

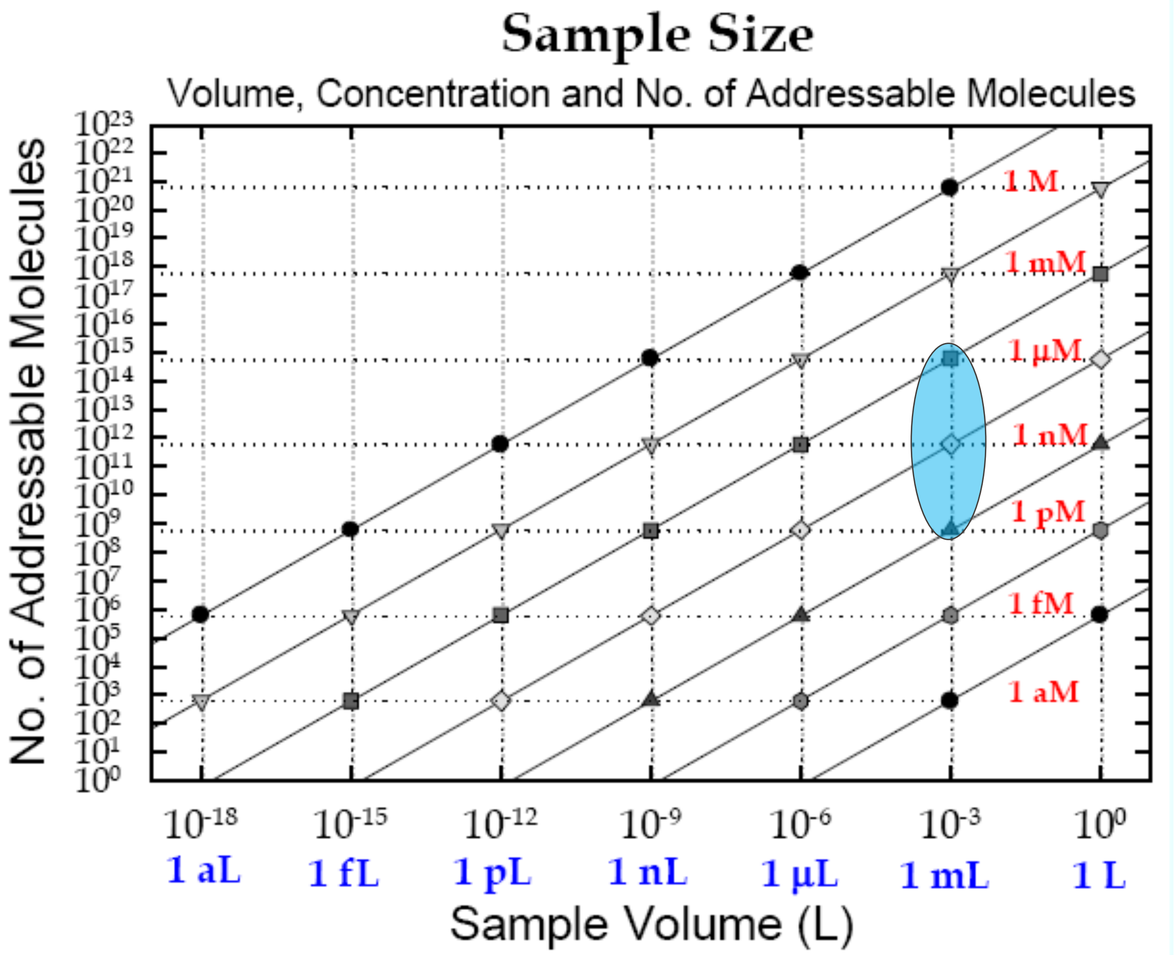


1 μM ~1 billion

1 pM ~1000

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

1 fM ~1



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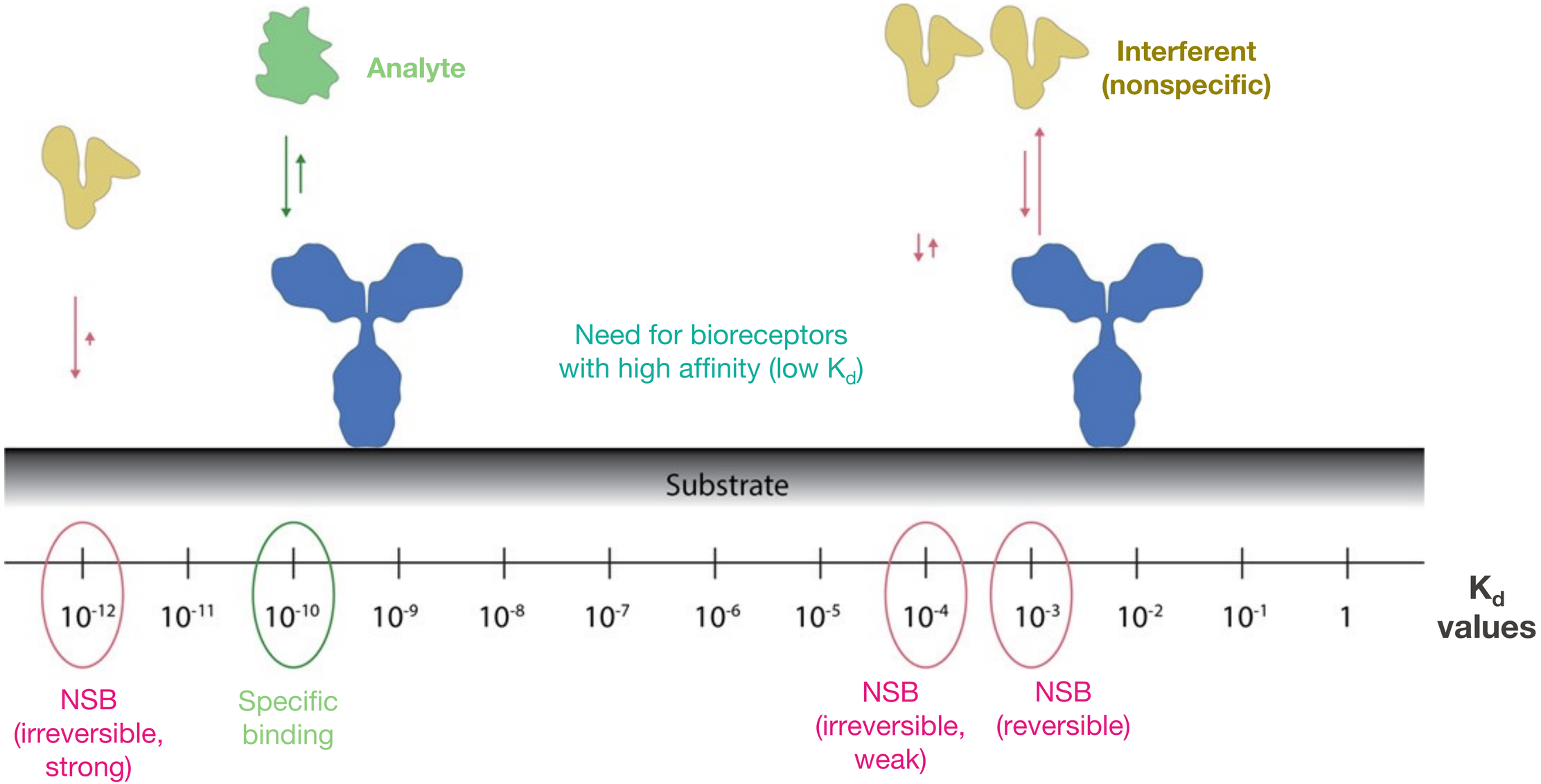
3. Challenges of Bioreceptor Specificity in Addition to NSB



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

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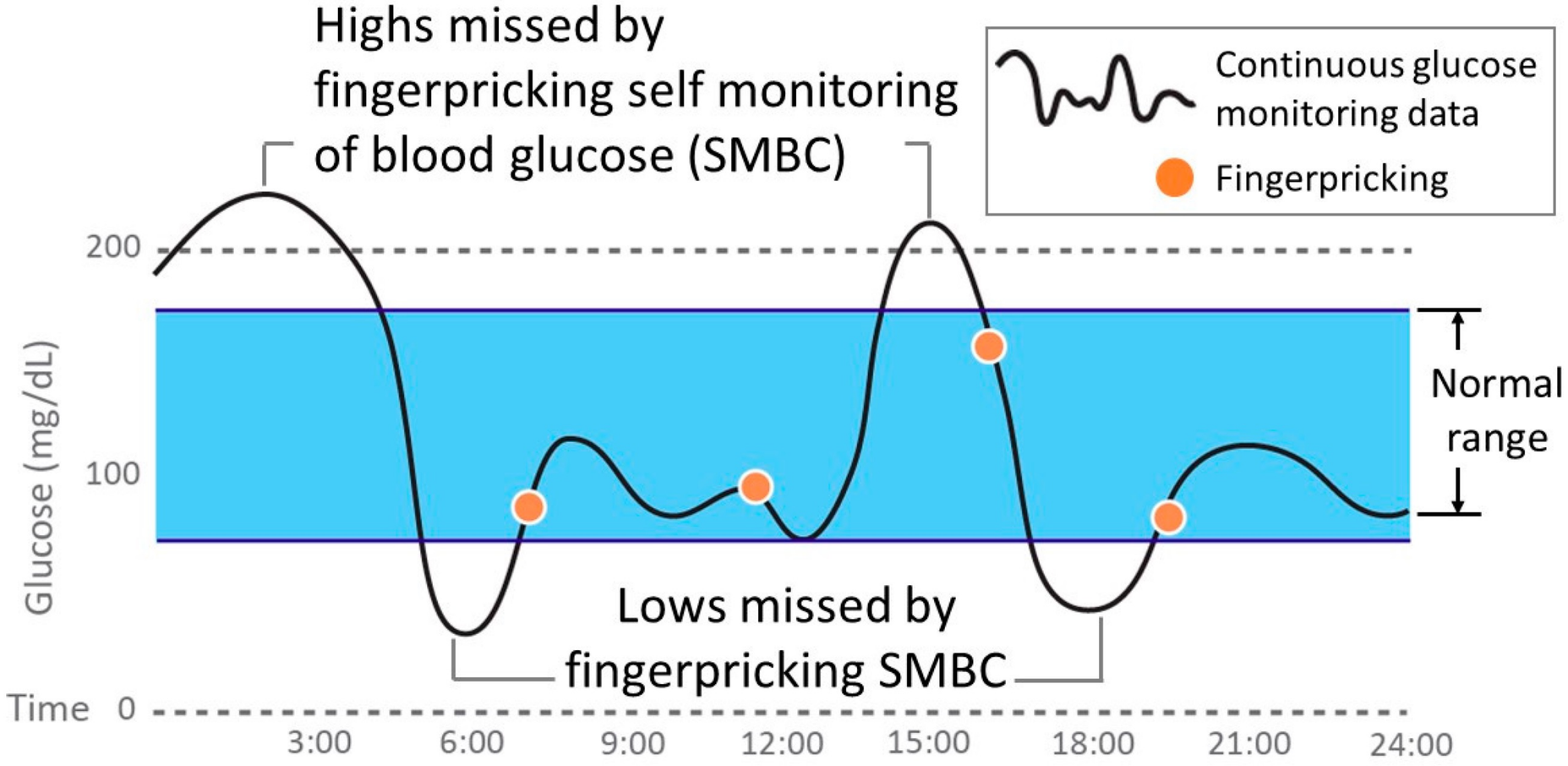
4. Challenges of Continuous Monitoring



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

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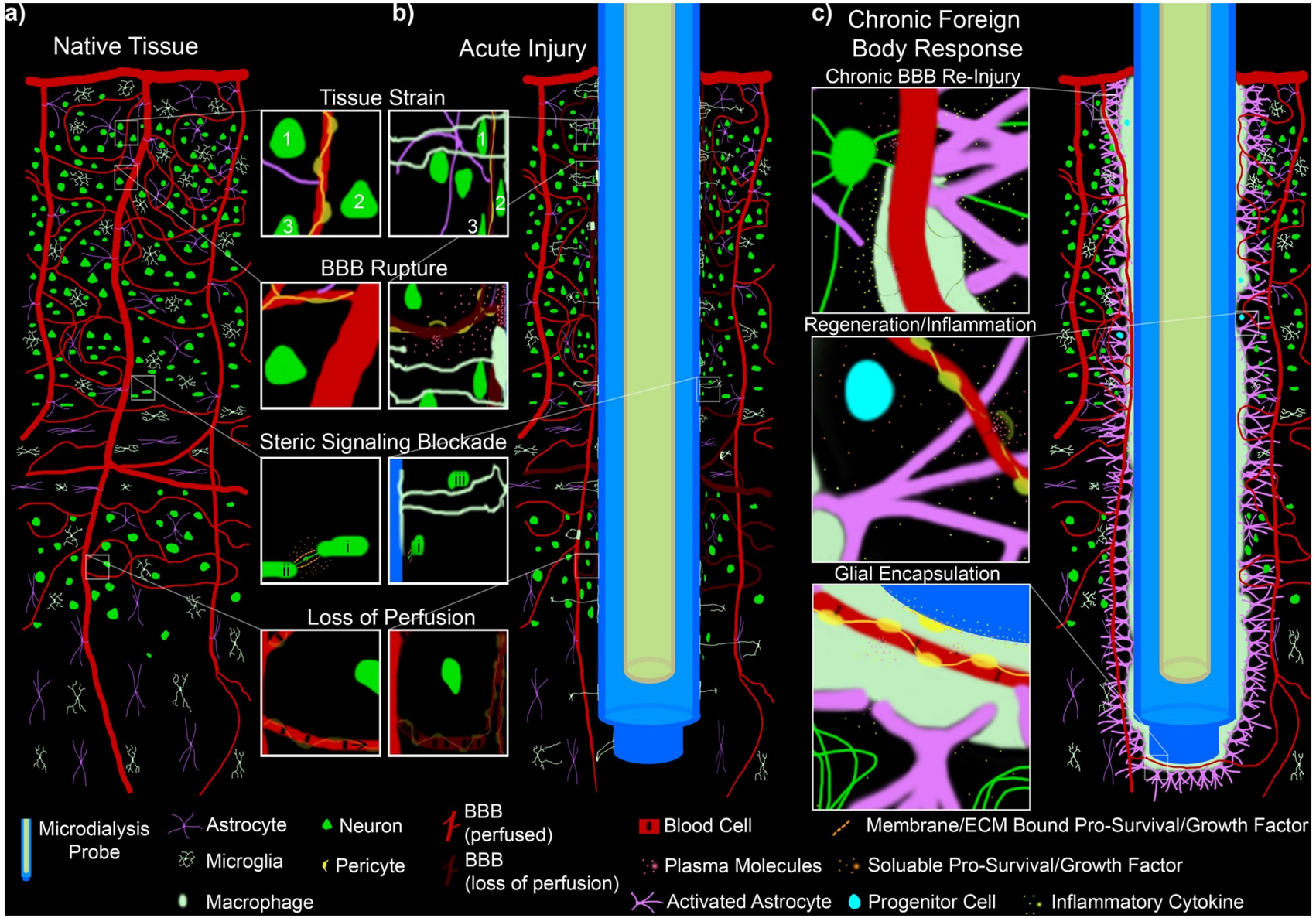
5. Tissue Response to Implanted Sensors Prevents Long-Term Use



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

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Alternative DNA-Based Bioreceptors for Improved Selectivity

Reproducibility crisis

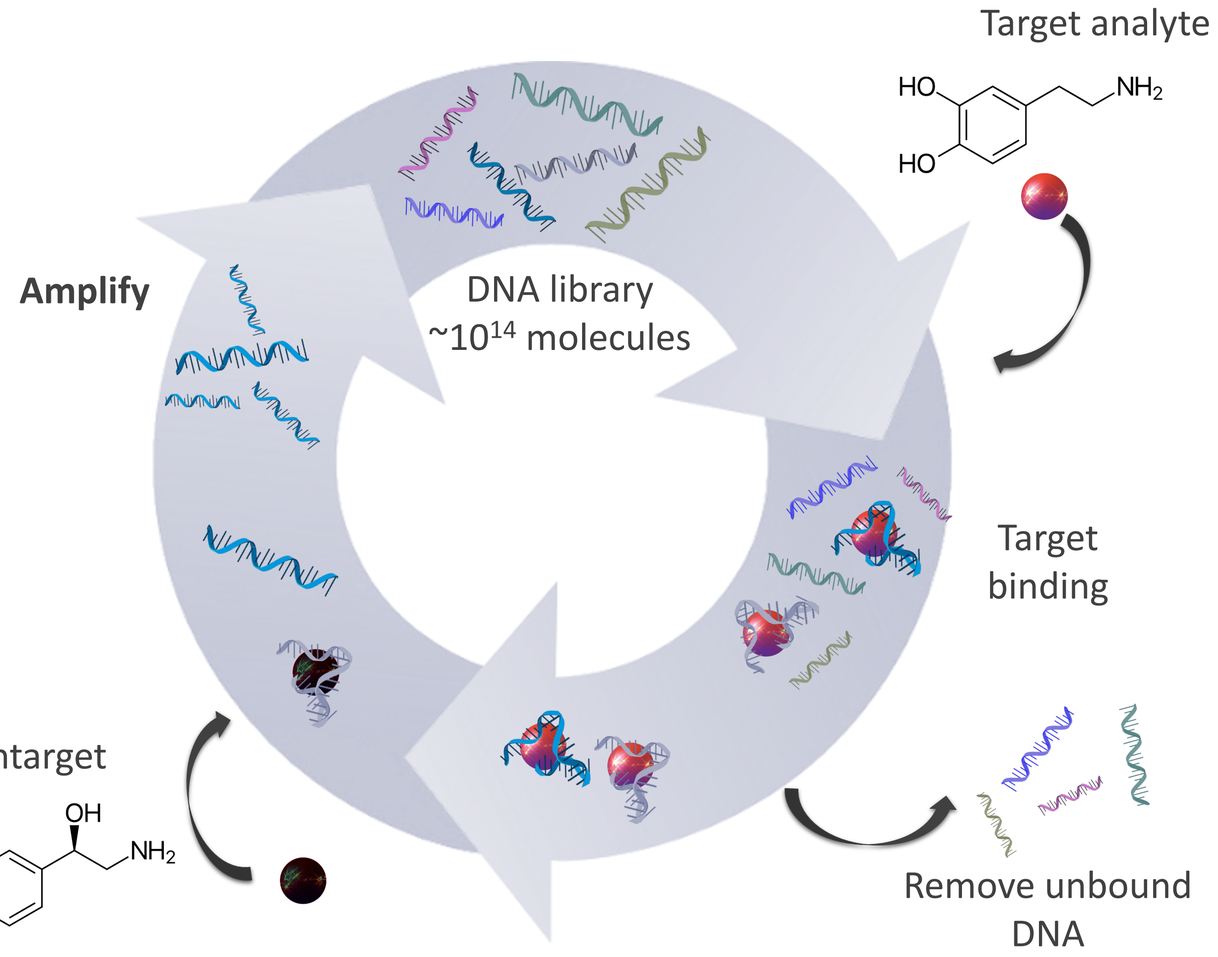
Monya Baker

Nature **521**, 274–276 (2015)

BLAME IT ON THE ANTIBODIES

Antibodies are the workhorses of biological experiments, but they are littering the field with false findings. A few evangelists are pushing for change.

BY MONYA BAKER



Nakatsuka *et al.*, *Science*, *362*, 319, **2018**

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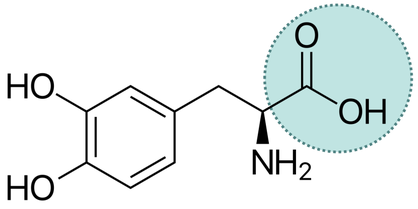
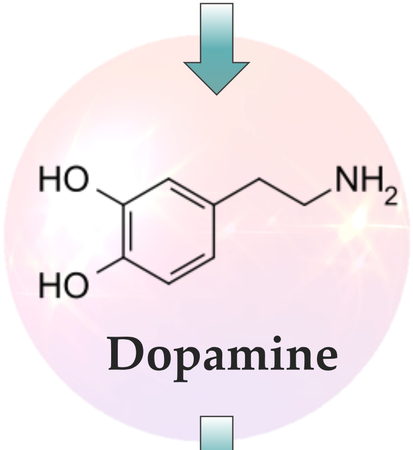
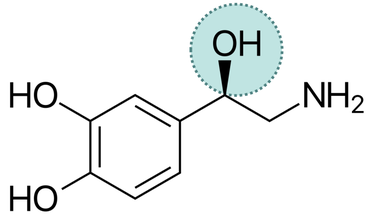
Using Aptamers to Differentiate Structurally Similar Chemicals in the Brain



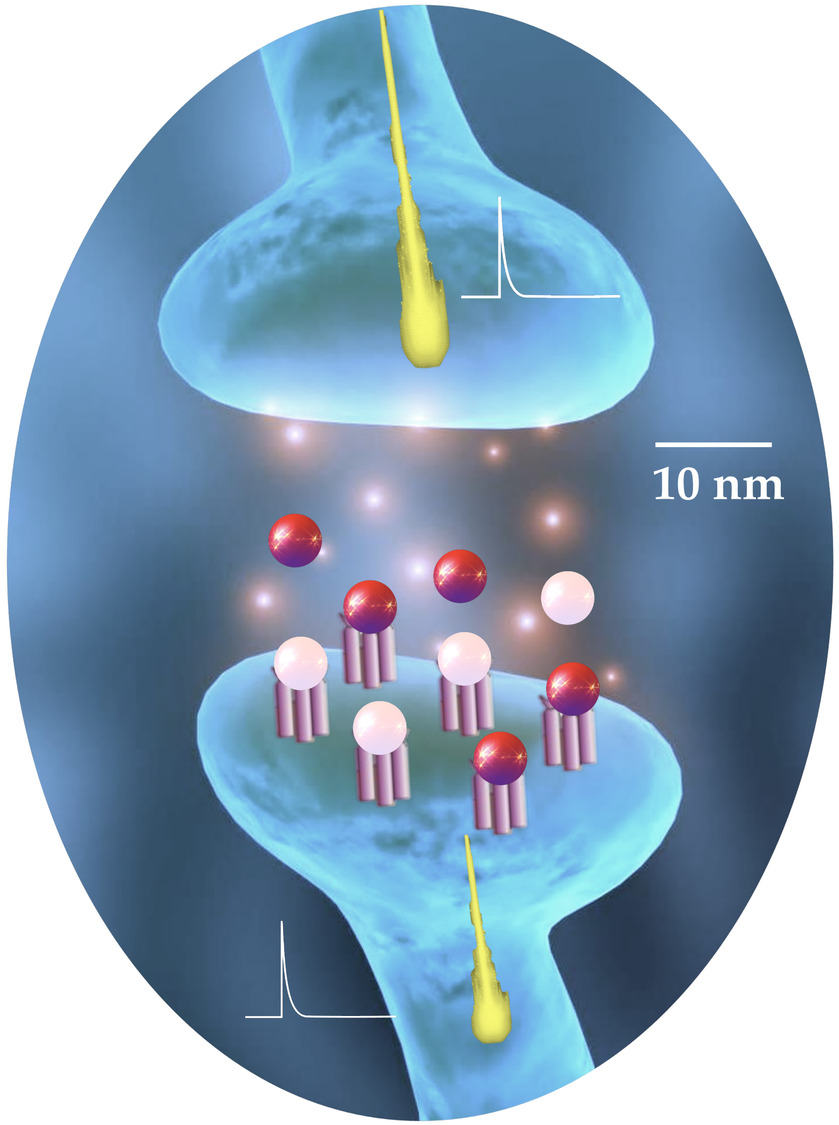
Levodopa

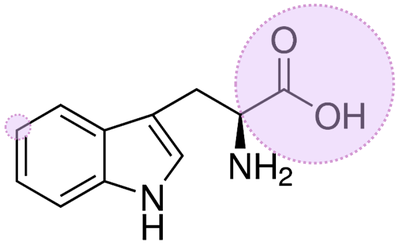


Dopamine

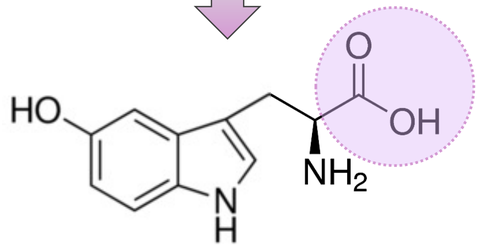


Norepinephrine

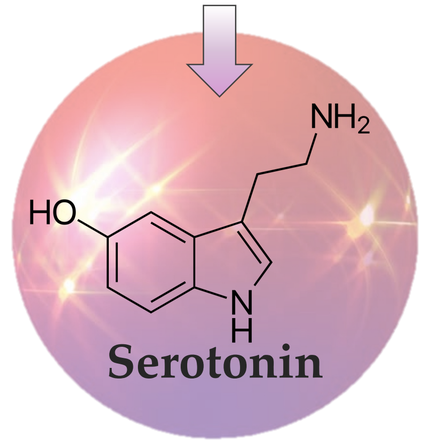




Tryptophan

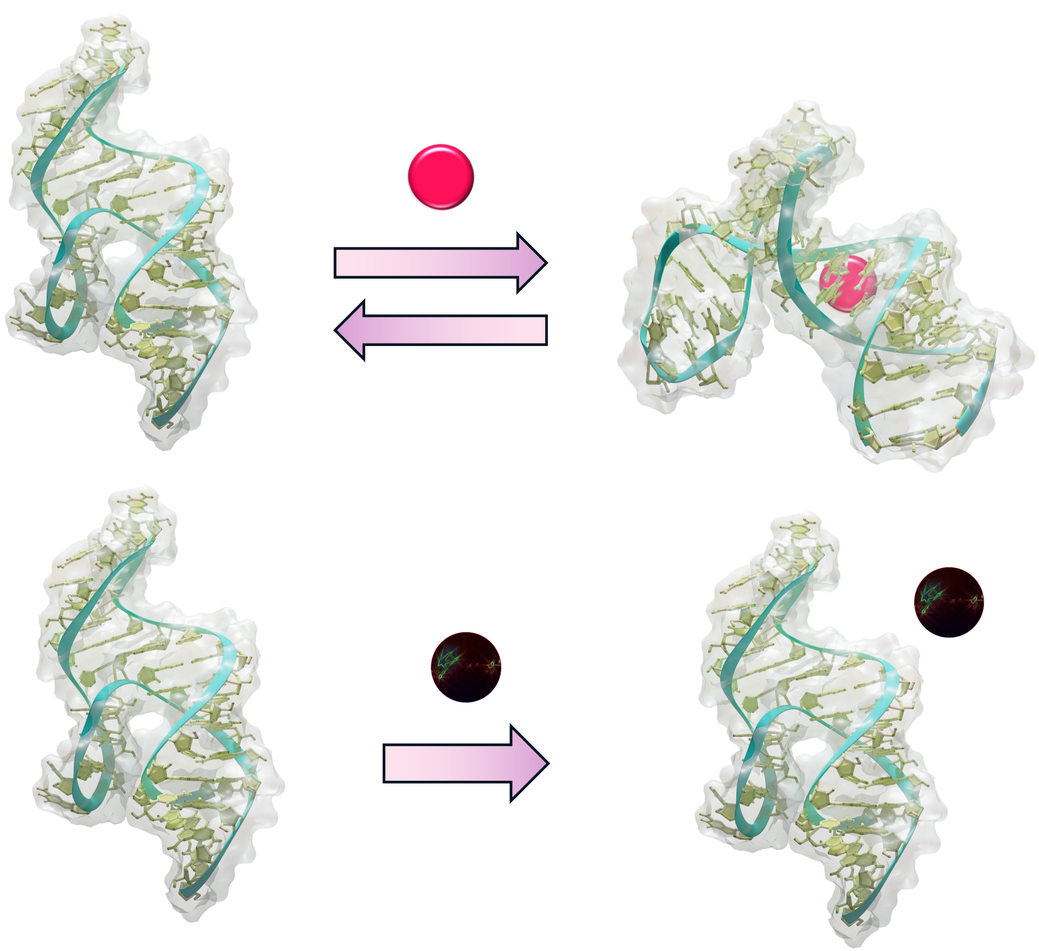


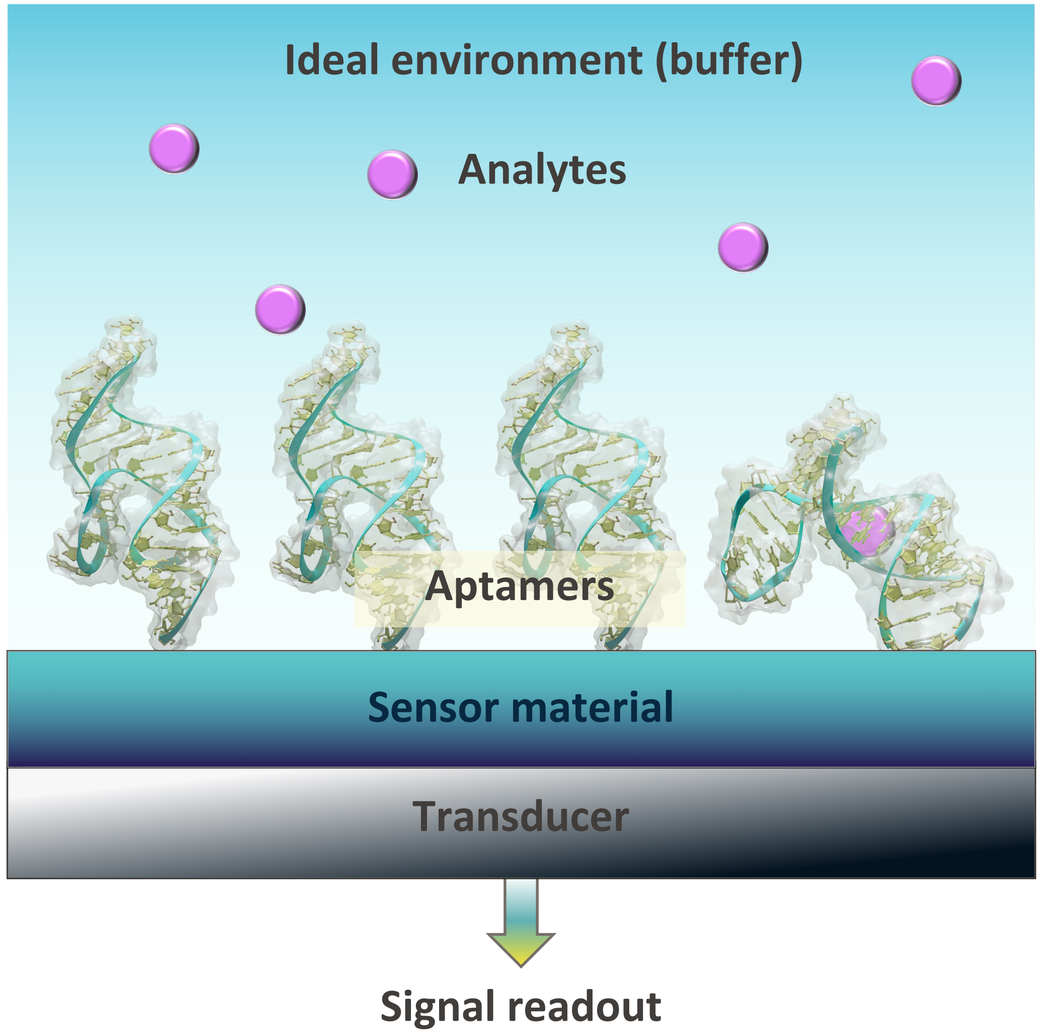
5-hydroxytryptophan



Serotonin

DNA Aptamer Structure Switching for Improved Selectivity





Nakatsuka *et al.*, *Science*, *362*, 319, **2018**

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

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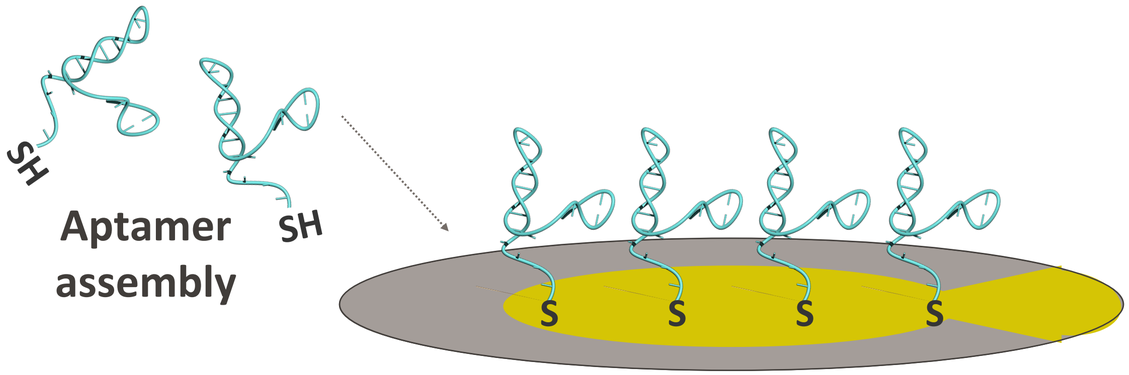
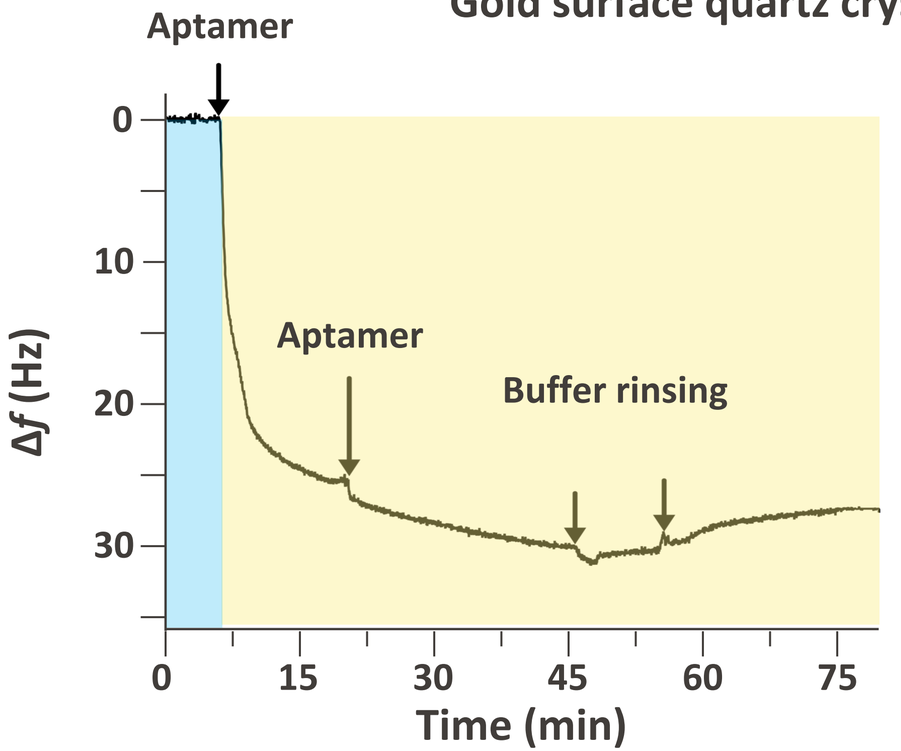
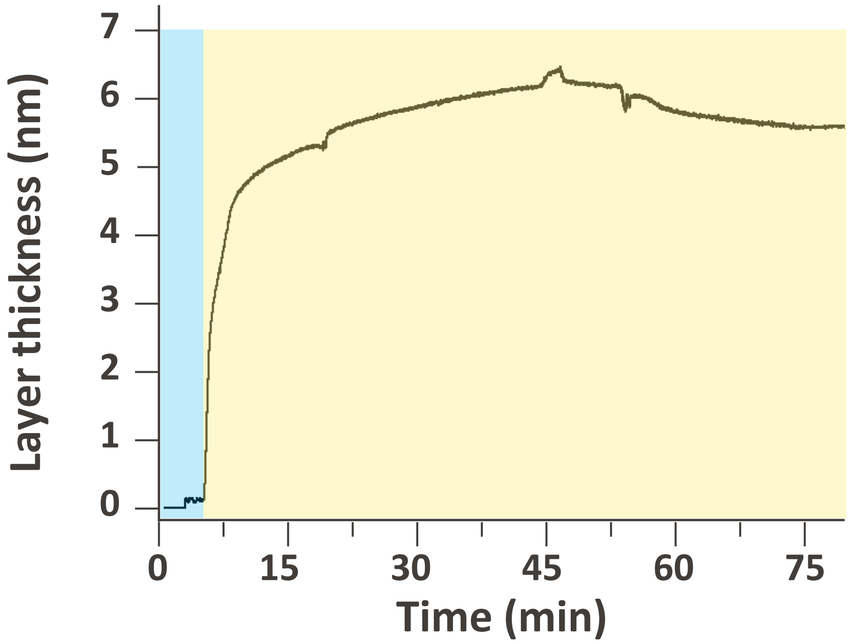
Monitoring the Assembly of Aptamers on Surfaces







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

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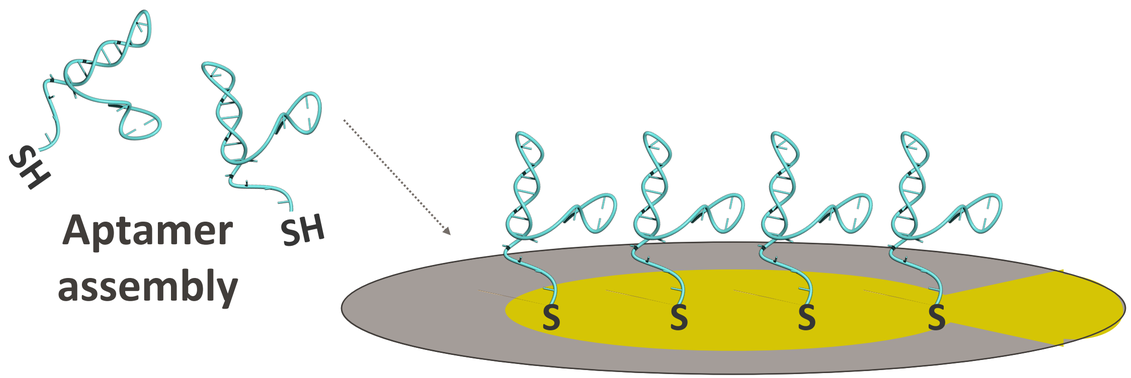
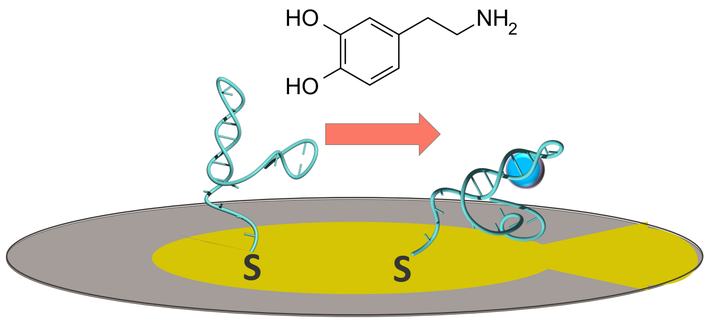
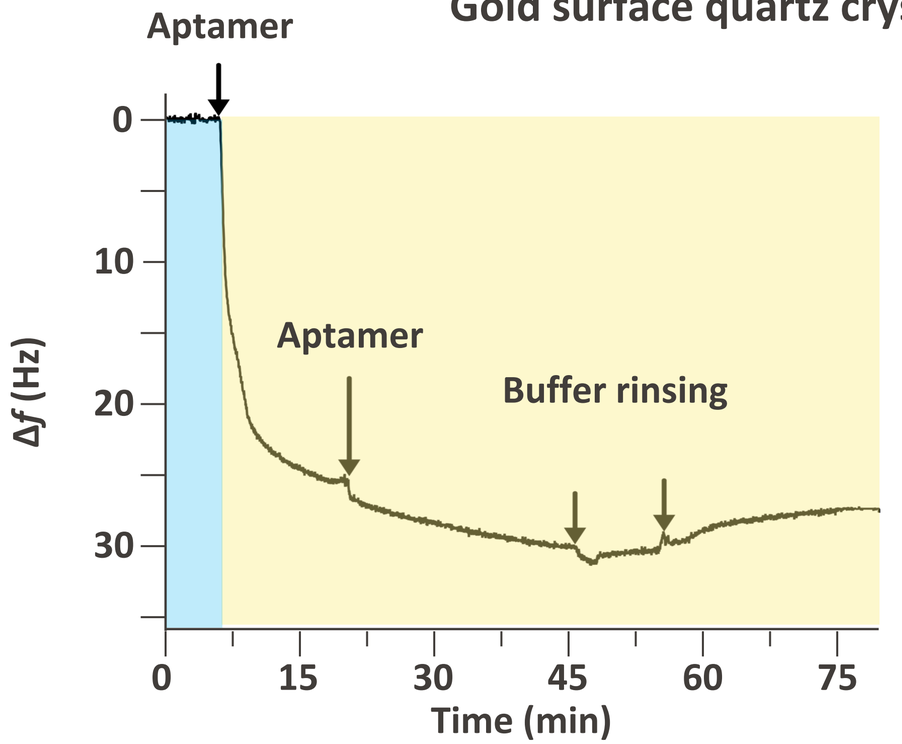
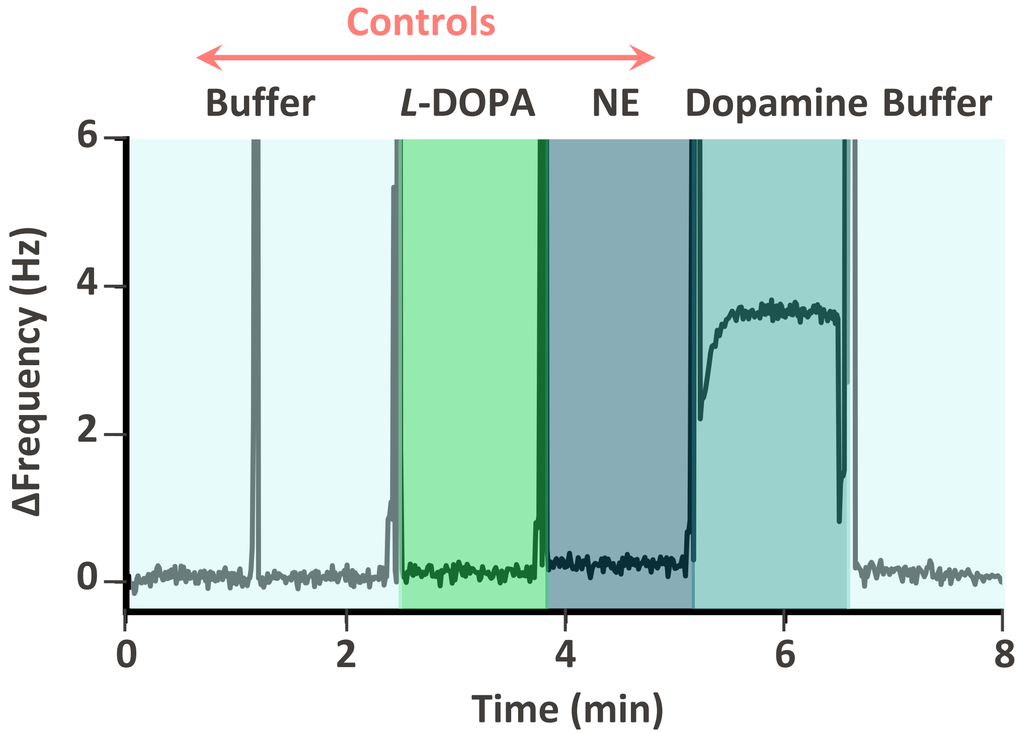
DNA Aptamer SAMs for Biosensing Applications









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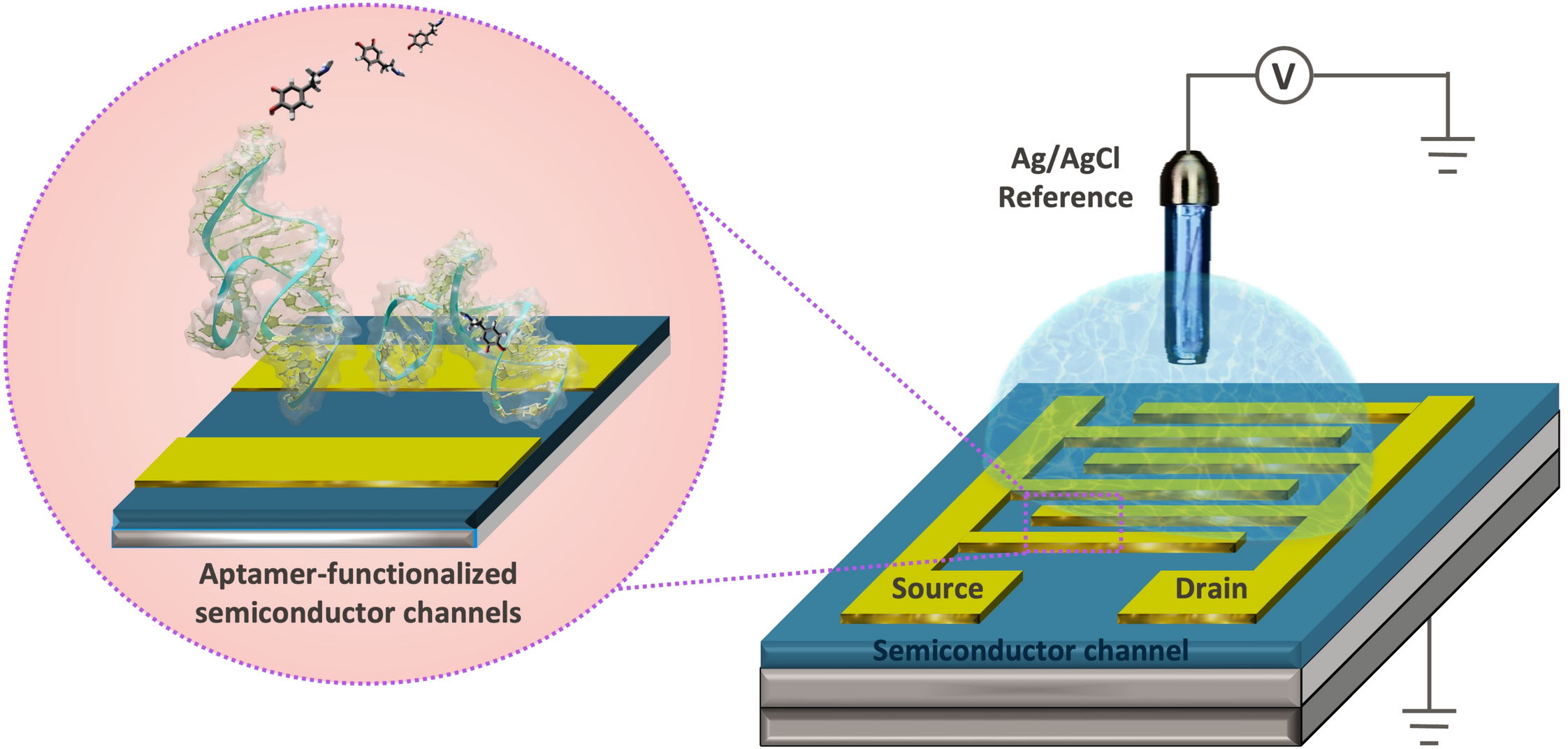
Using DNA Aptamers for Biosensing on Semiconductors



Nakatsuka *et al.*, *Science*, *362*, 319, **2018**

Nakatsuka, *Aptamer Technology Edition, Methods Mol. Biol.*, *2570*, 187, **2022**

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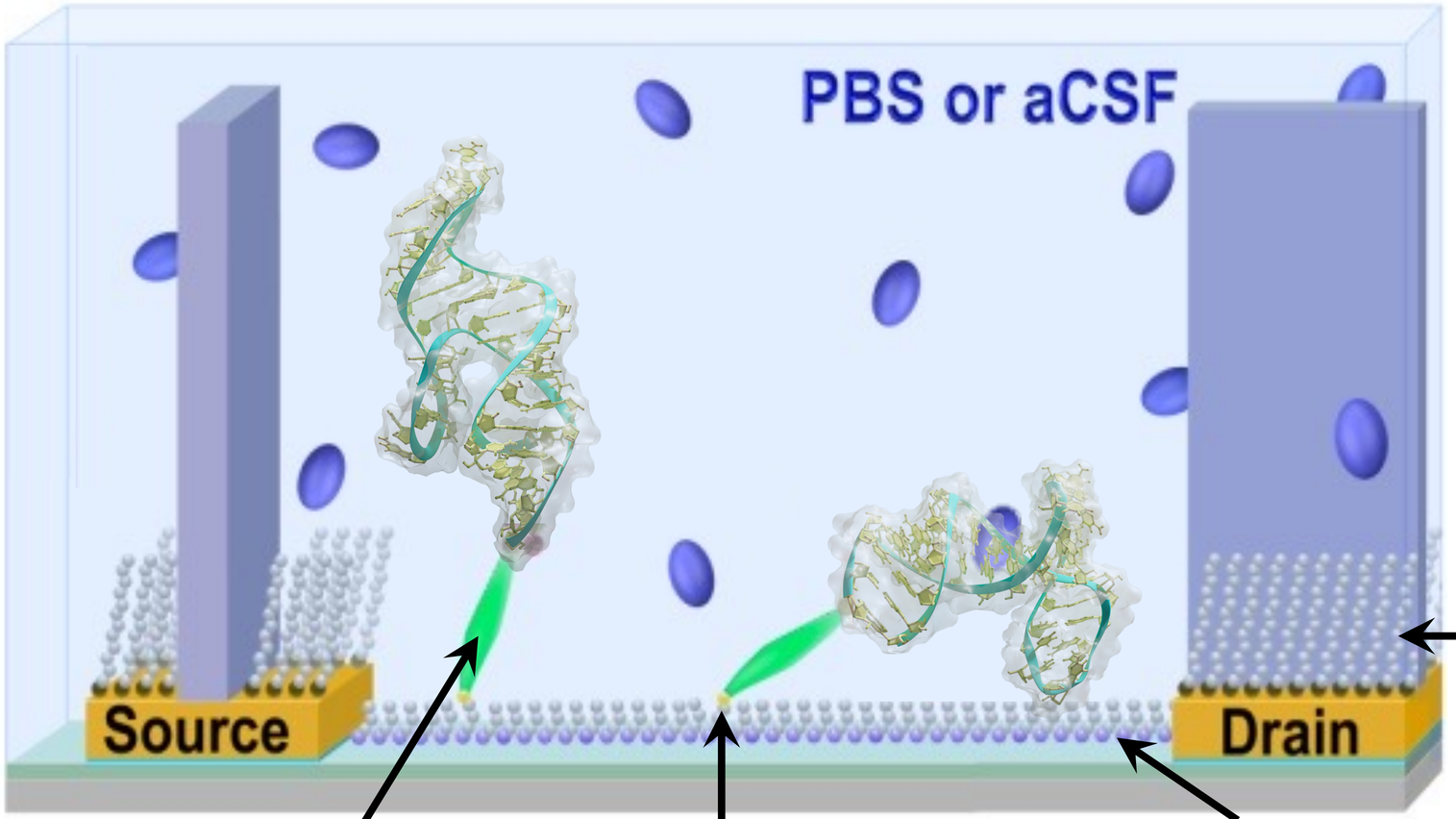
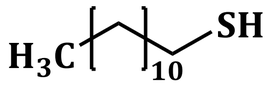
Various Surface Chemistries Enable Biosensor Configuration

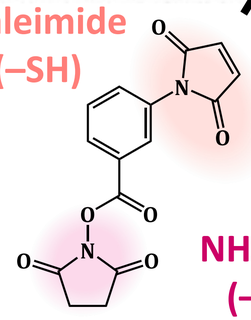


Au (30 nm)	Conductive electrodes
Ti (10 nm)	Adhesive layer
In_2O_3 (4 nm)	Semiconductor
SiO_2 (100 nm)	Dielectric layer
Si Wafer (500 μm)	Substrate

Dodecanethiol

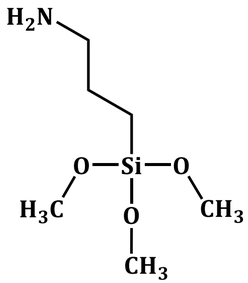


Maleimide (–SH)

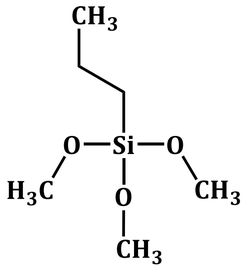


NHS ester ($–NH_2$)

3-Aminopropyltrimethoxysilane



Propyltrimethoxysilane



Nakatsuka *et al.*, *Science*, *362*, 319, **2018**

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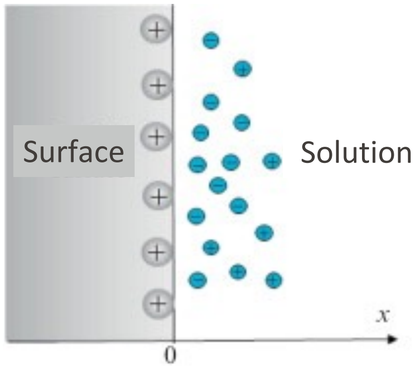
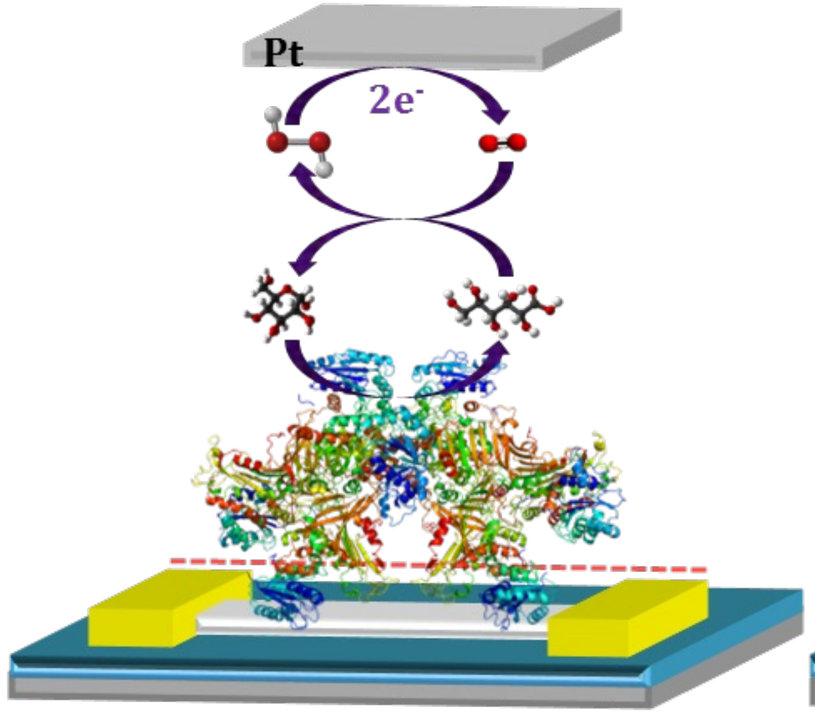
The Debye Screening Length Complicates Sensitive Detection

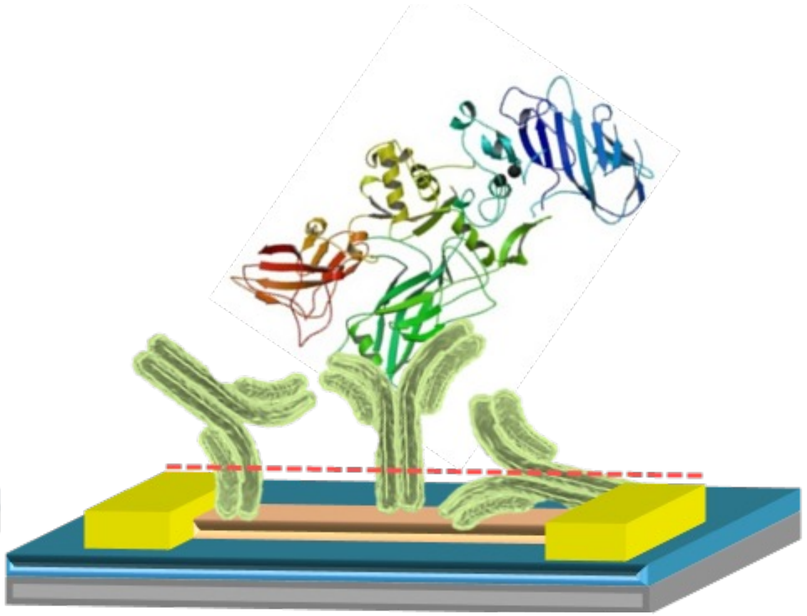
$$\lambda_D = \sqrt{\frac{\varepsilon_r \varepsilon_0 k_B T}{2 N_A e^2 I}}$$

Buffer strength	Ionic strength (I)	Debye length (λ_D)
1.0 x	163 mM	0.75 nm
0.1 x	16.3 mM	2.38 nm
0.01 x	1.63 mM	7.53 nm

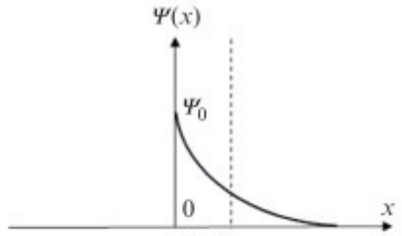


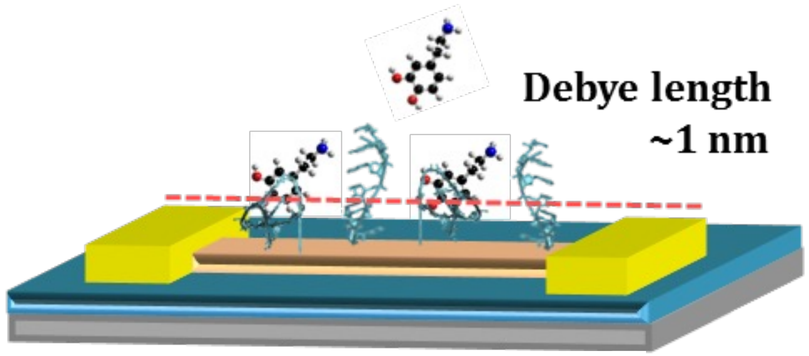


Enzyme transistors



Antibody transistors





Aptamer transistors

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The Debye Screening Length Complicates Sensitive Detection

$$\lambda_D = \sqrt{\frac{\varepsilon_r \varepsilon_0 k_B T}{2 N_A e^2 I}}$$

Buffer strength	Ionic strength (I)	Debye length (λ_D)
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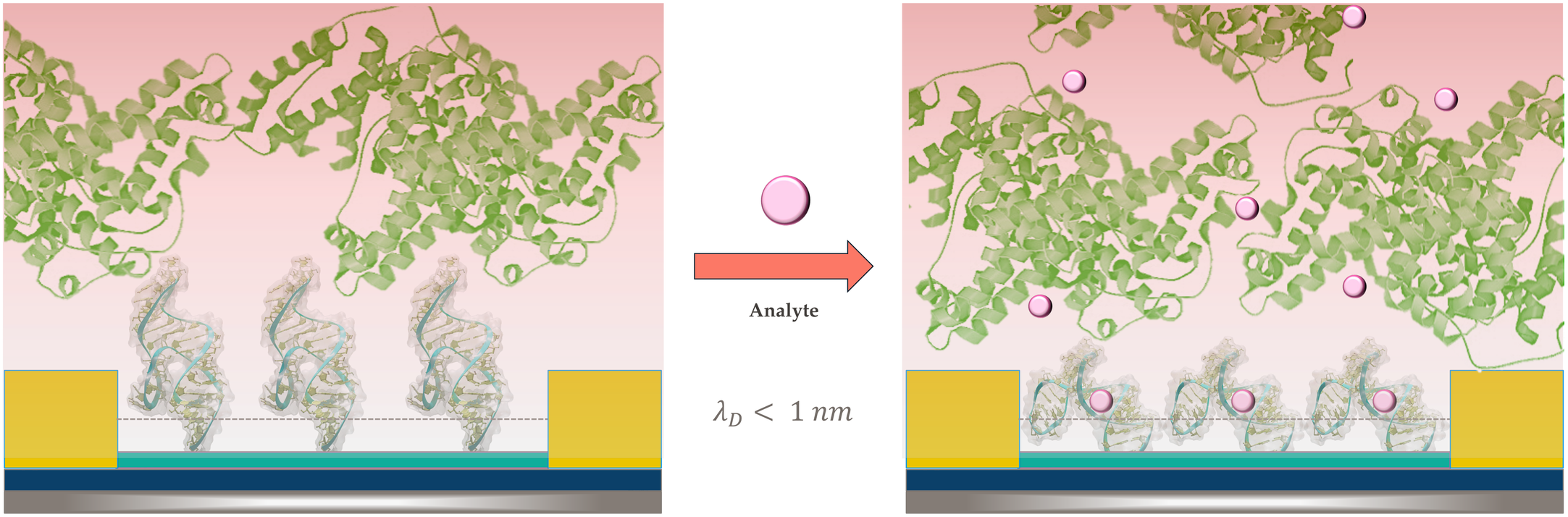

Nakatsuka *et al.*, *Science*, *362*, 319, **2018**

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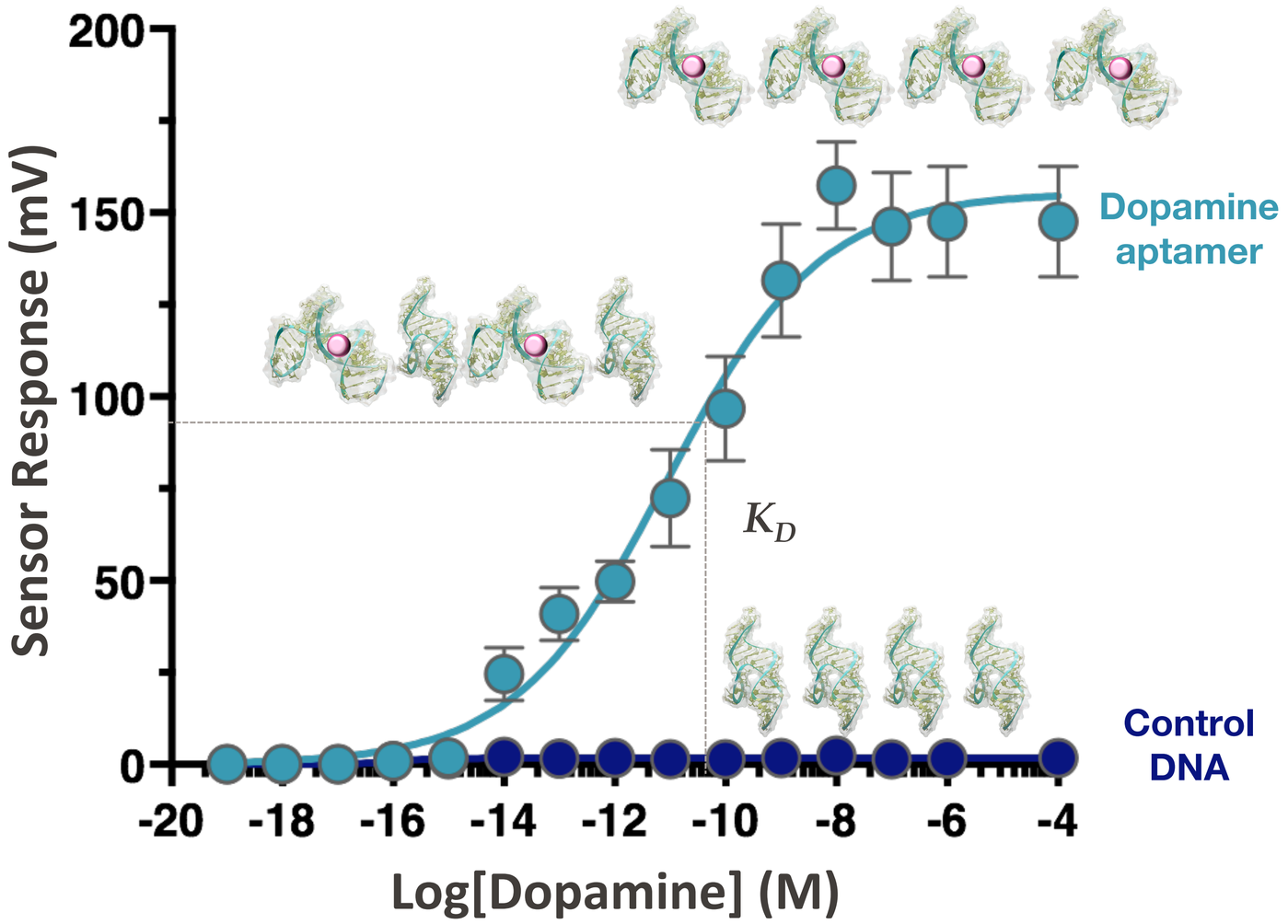
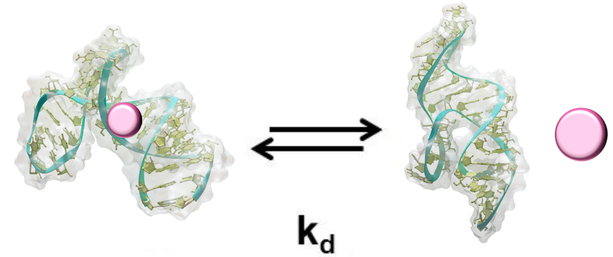
Biosensor Response Follows a Langmuir Isotherm



$$\theta = \frac{[A]K}{1 + [A]K}$$

Fractional occupation



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

Nakatsuka *et al.*, *Science*, *362*, 319, **2018**

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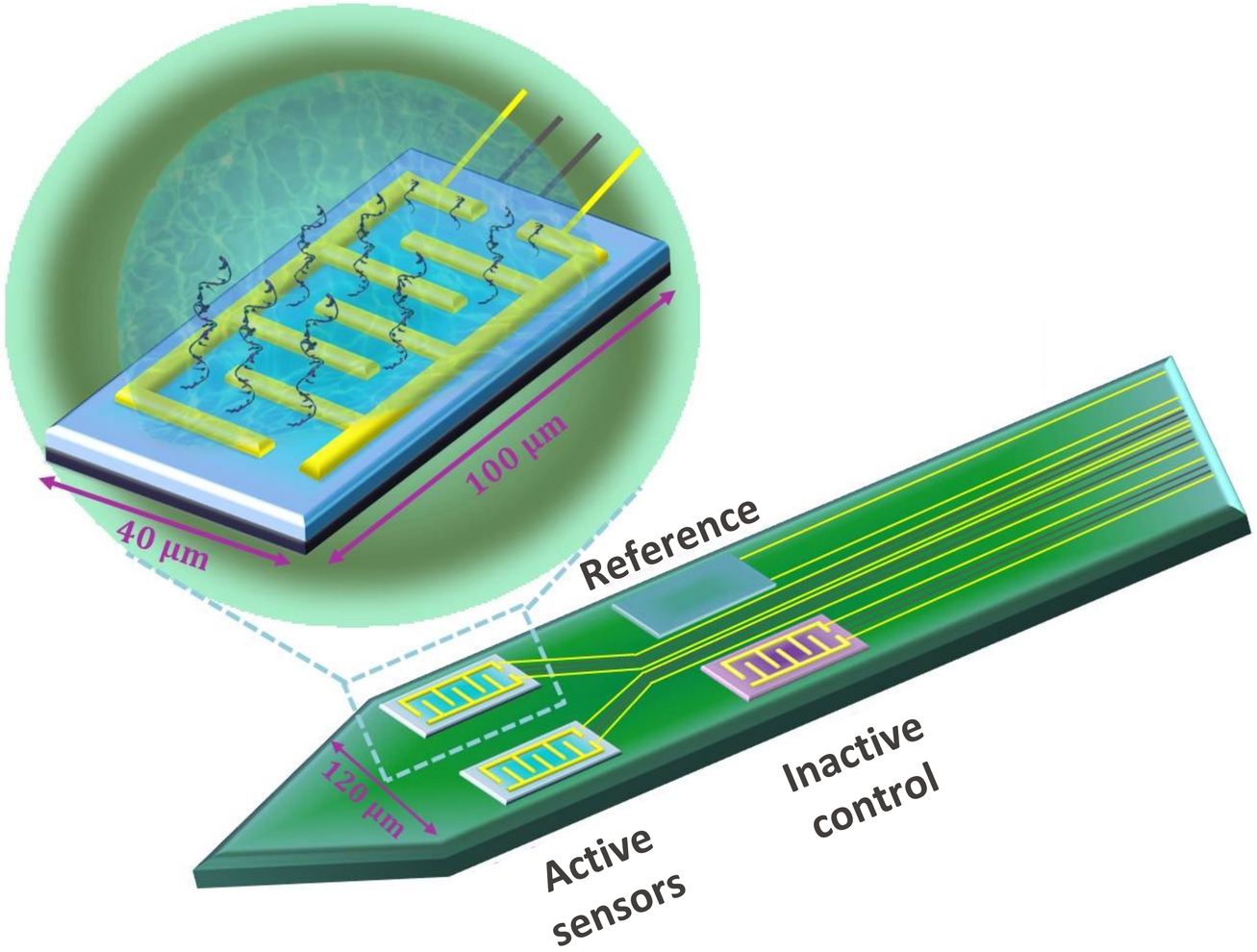
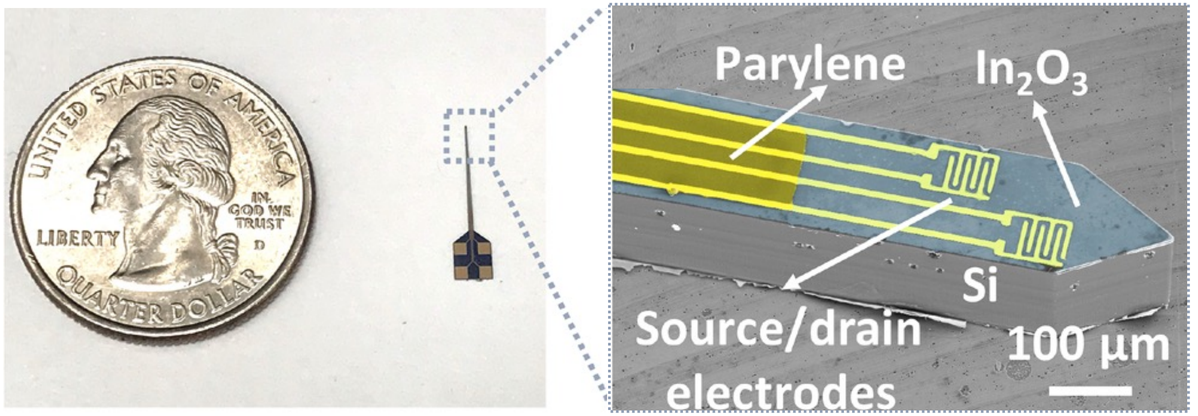
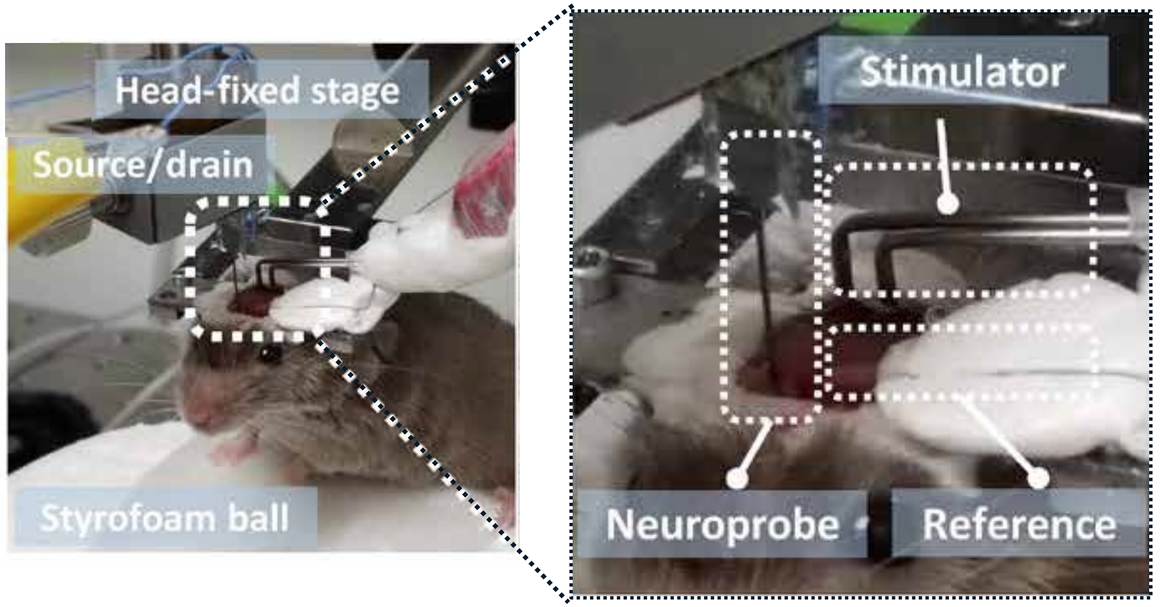
Applications of Aptamer-Based Biosensors for Neuroscience



Nakatsuka & Andrews, *Neuropsychopharmacology, 41,* 378, **2016**





Zhao *et al.*, *Sci. Adv.*, *7*, 1, **2021**

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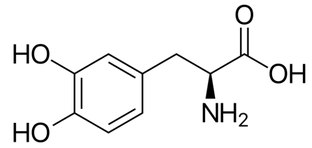
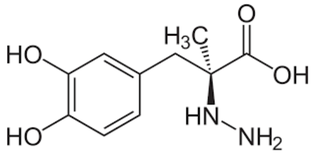
Applications of Aptamer-Based Biosensors for Humans

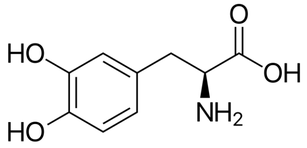


L-DOPA

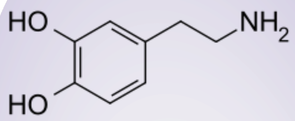
+



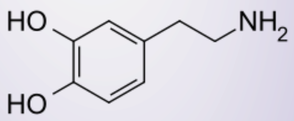
Inhibitor



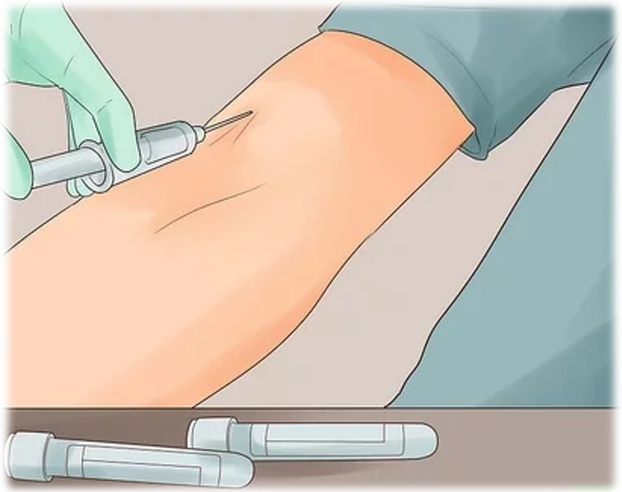
L-DOPA



Dopamine



Dopamine



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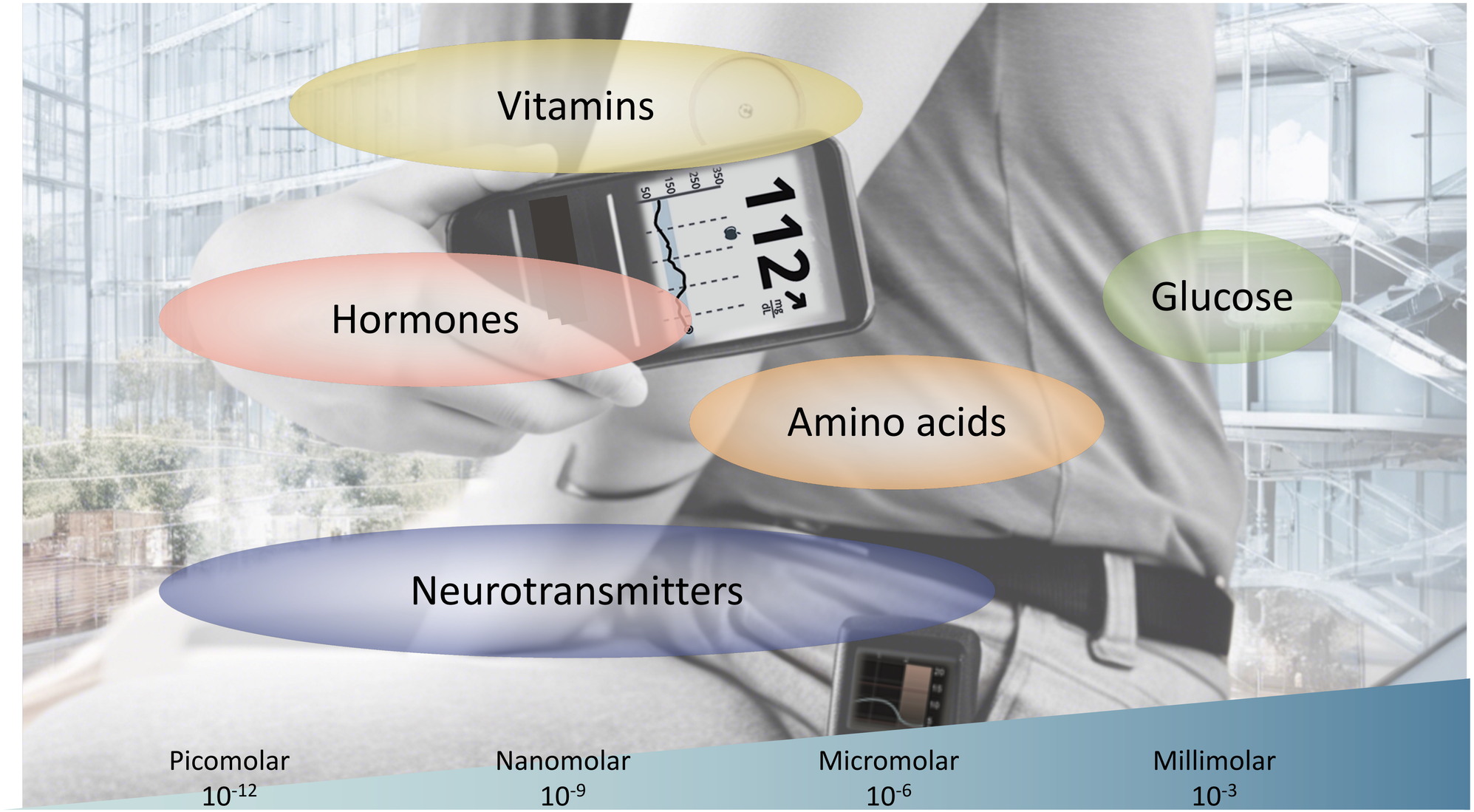
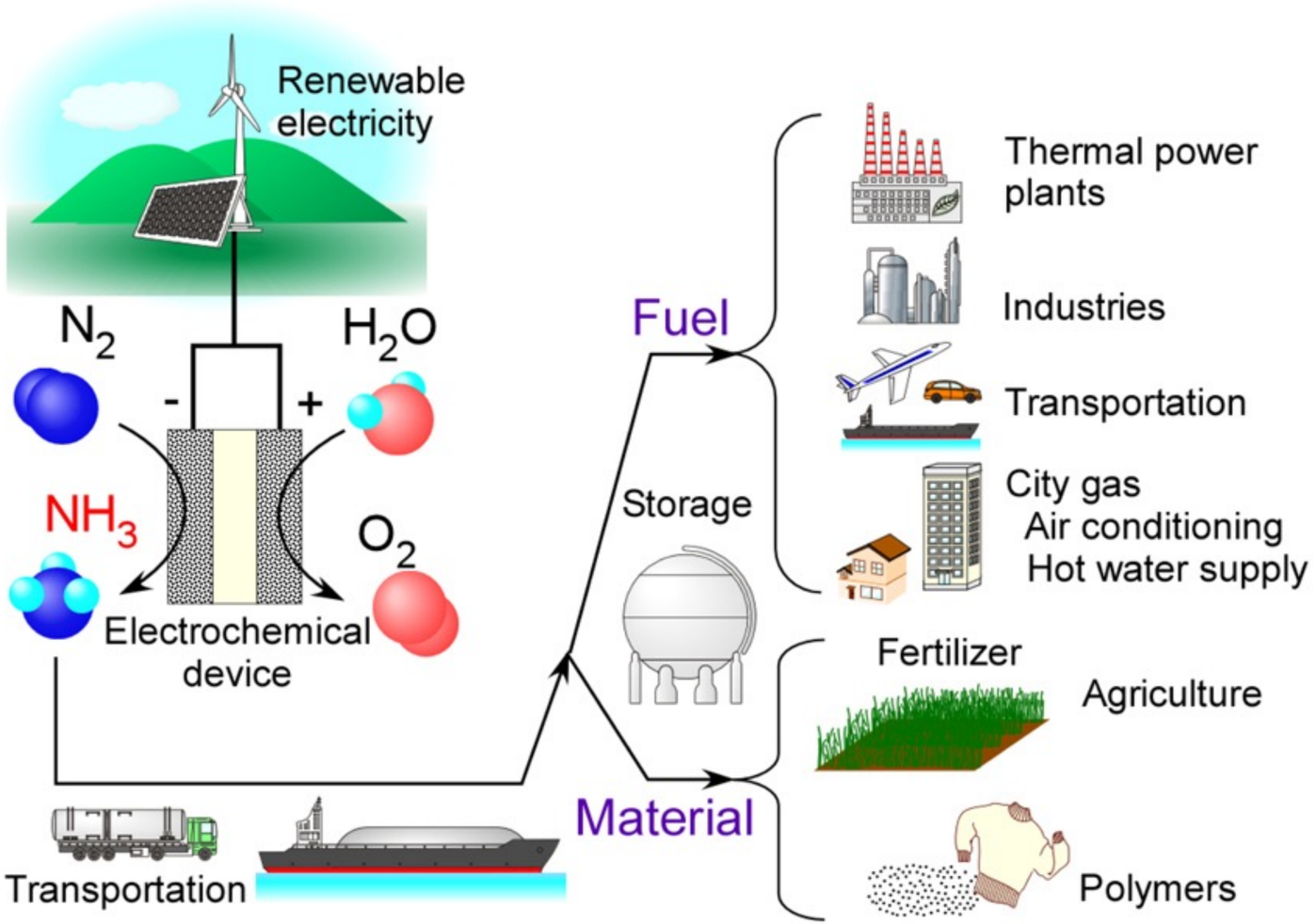
Future of Biosensing for Human Health?

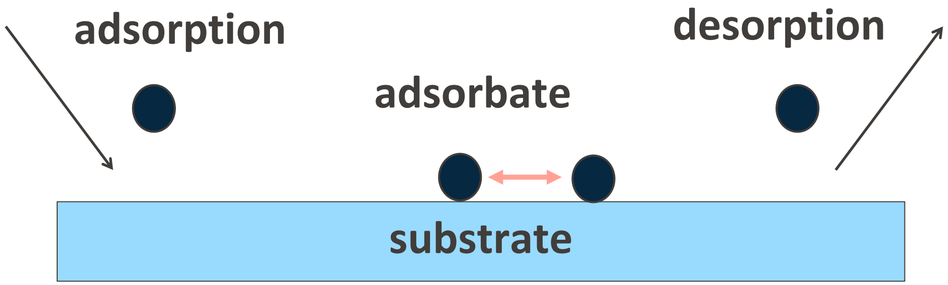


Importance of Catalysis: Sustainable Ammonia Synthesis

Catalysis is the increase in rate of a chemical reaction due to an added substance known as a **catalyst.** Catalysts are not consumed by the reaction and remain unchanged after it.



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

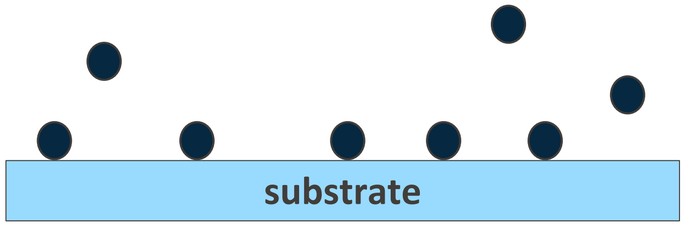
θ = 1 monolayer

Adsorption = Physisorption

Electrostatic interaction (charge transfer)

non-specific and weak

multilayer growth possible

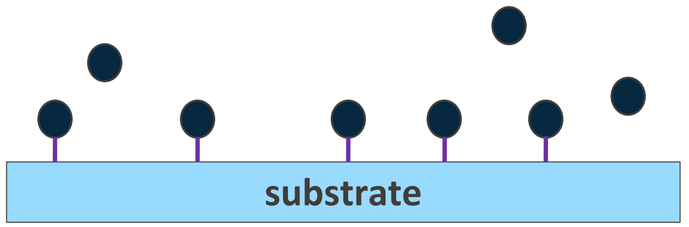


Absorption = Chemisorption

Geometrically defined interaction

Chemical bond between adsorbate and substrate

maximum coverage is 1 monolayer (θ = 1)



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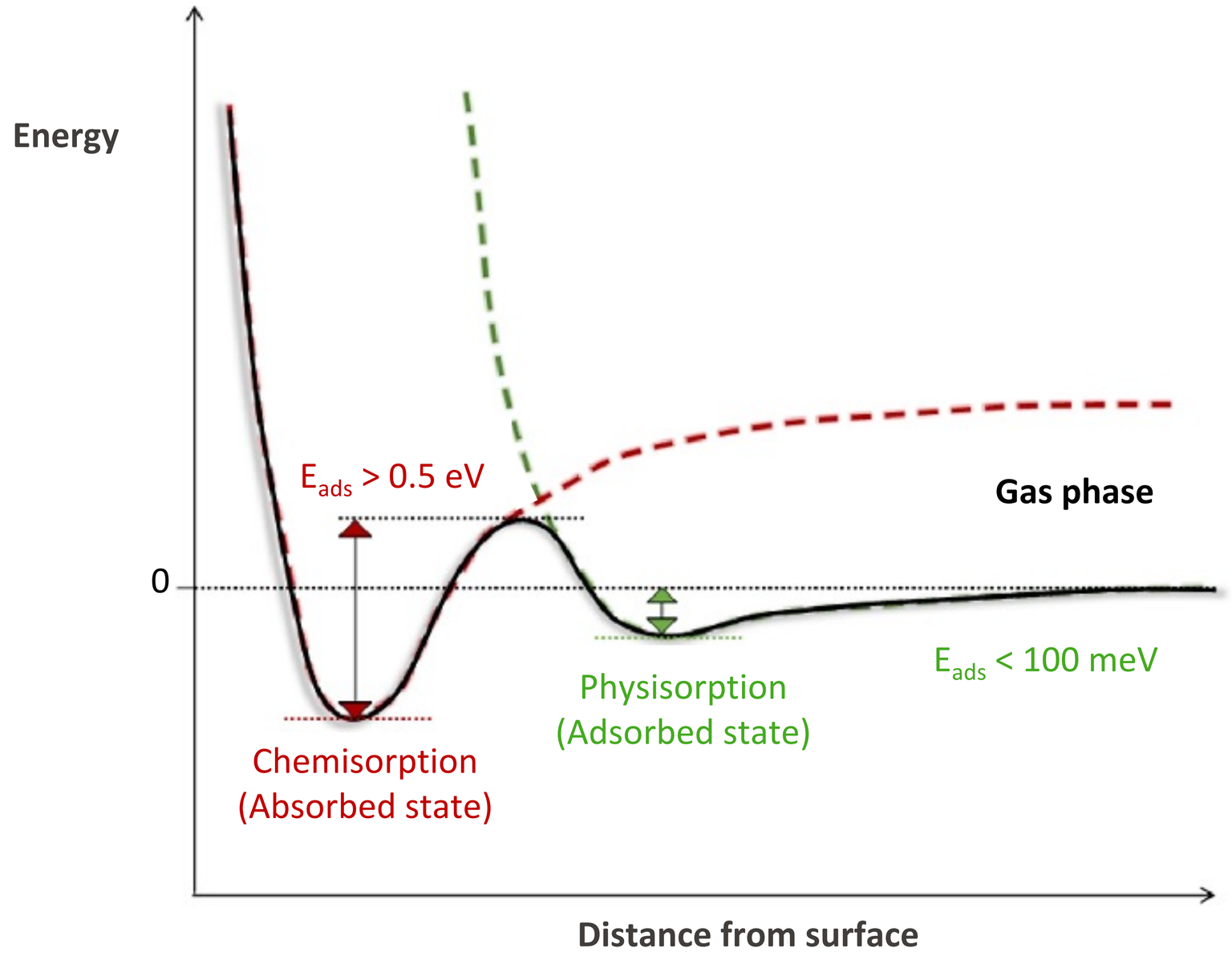
Energy Profiles of Chemisorption *vs.* Physisorption



Lennard-Jones Potential

$$V(r) = 4\varepsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} \right]$$

V(r): potential energy as function of distance

ε: depth of potential well (interaction strength)

σ: distance at which potential = 0

r: distance between two particles

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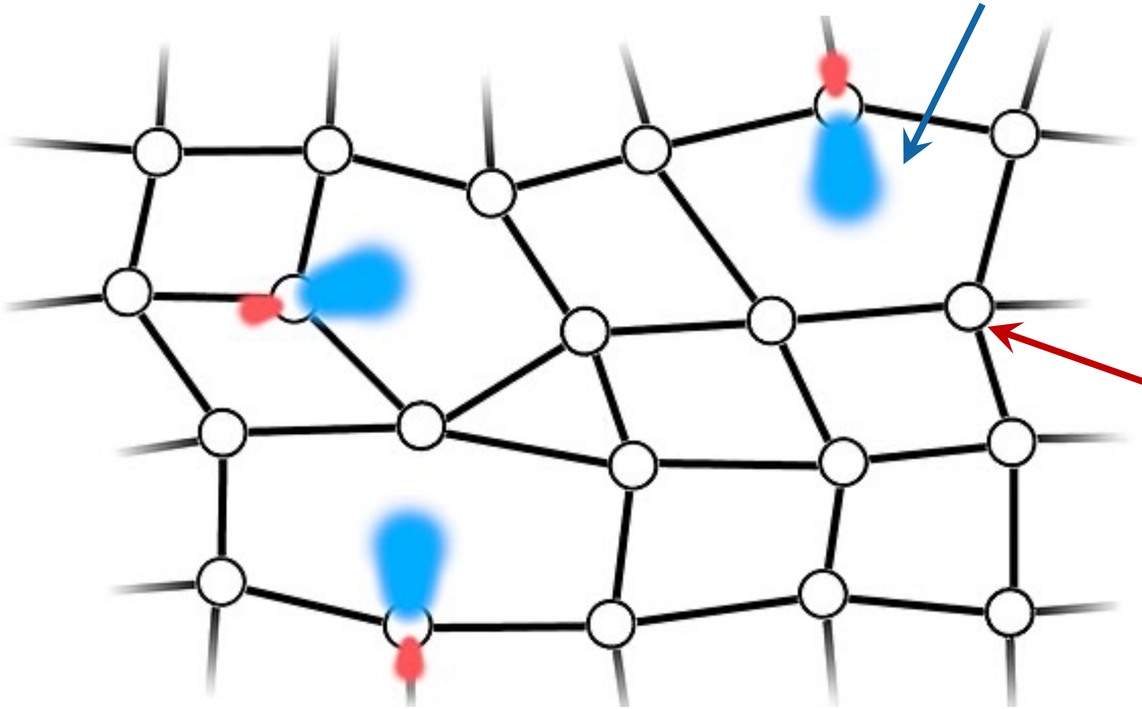
Catalysis Basics: Surfaces Are Intrinsically Dipolar



Unpaired valence electrons

Involved in bond formation

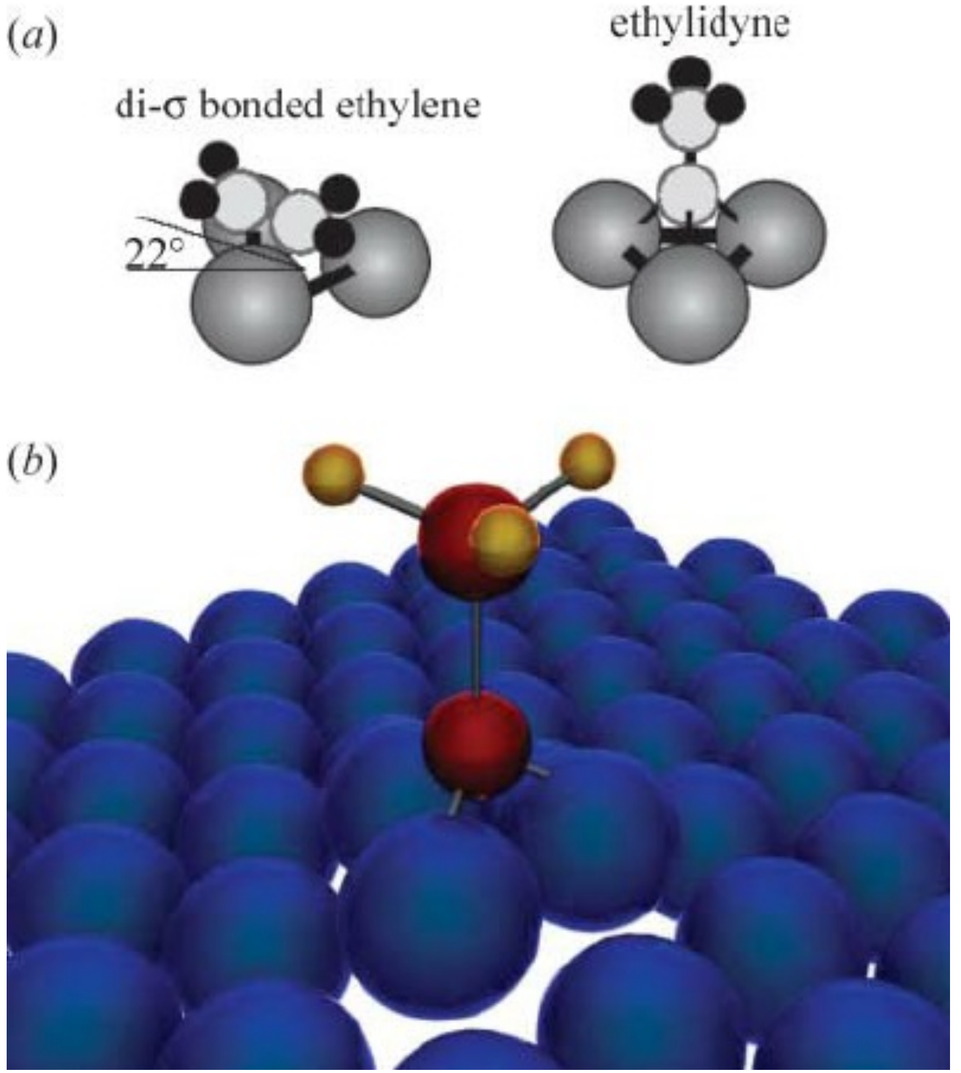
Z^+ nucleus – Z^- core electrons

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**

Chemical Bonds of Molecules Rely on Symmetry and Geometry



Pt (111)

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

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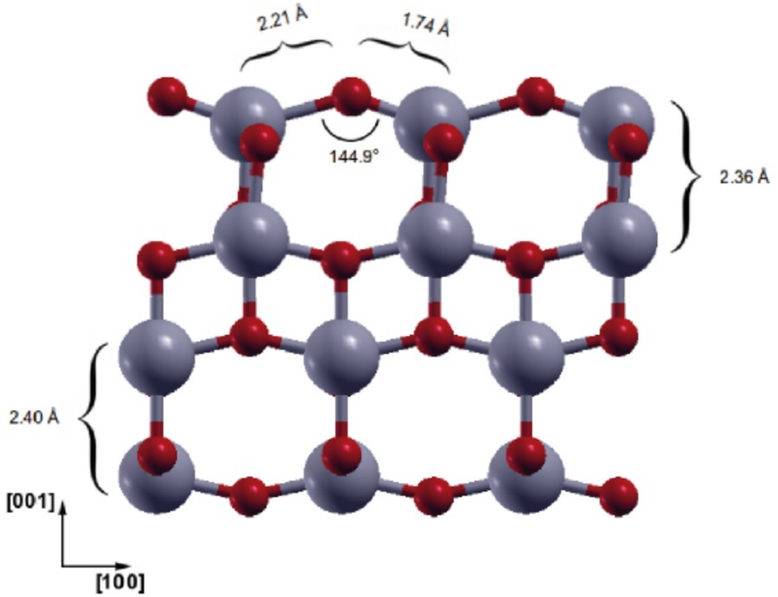
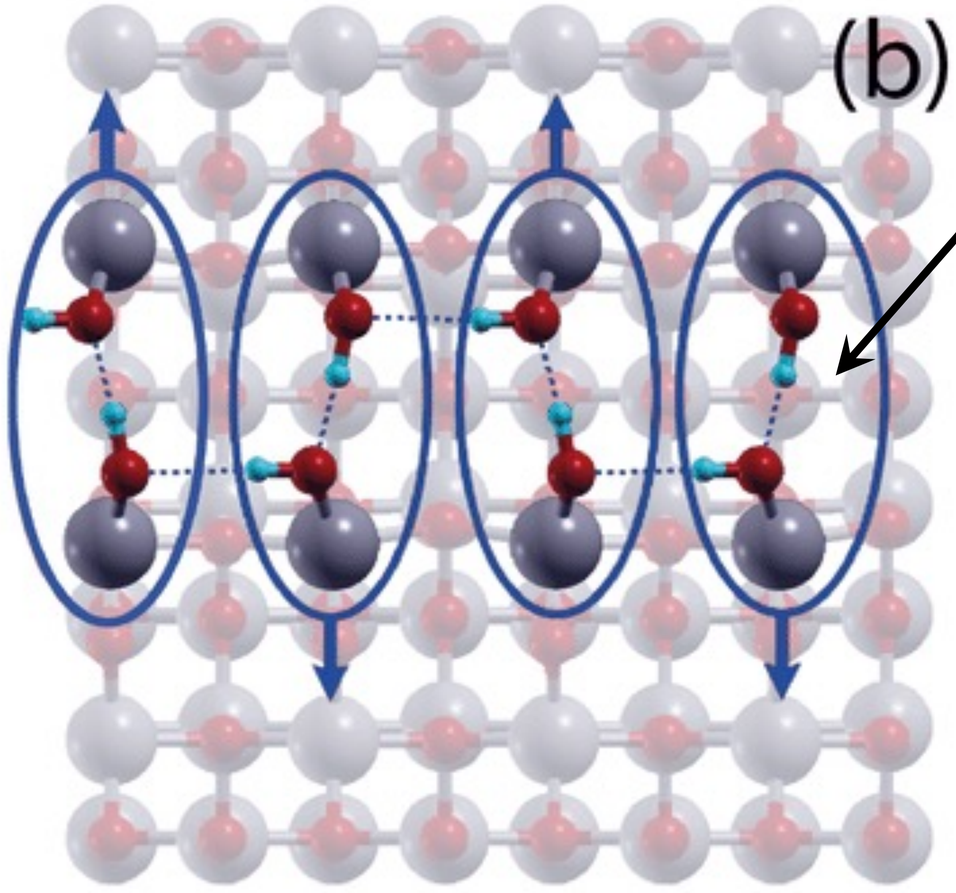
Reconstruction of “Soft” Surfaces Due to Absorption

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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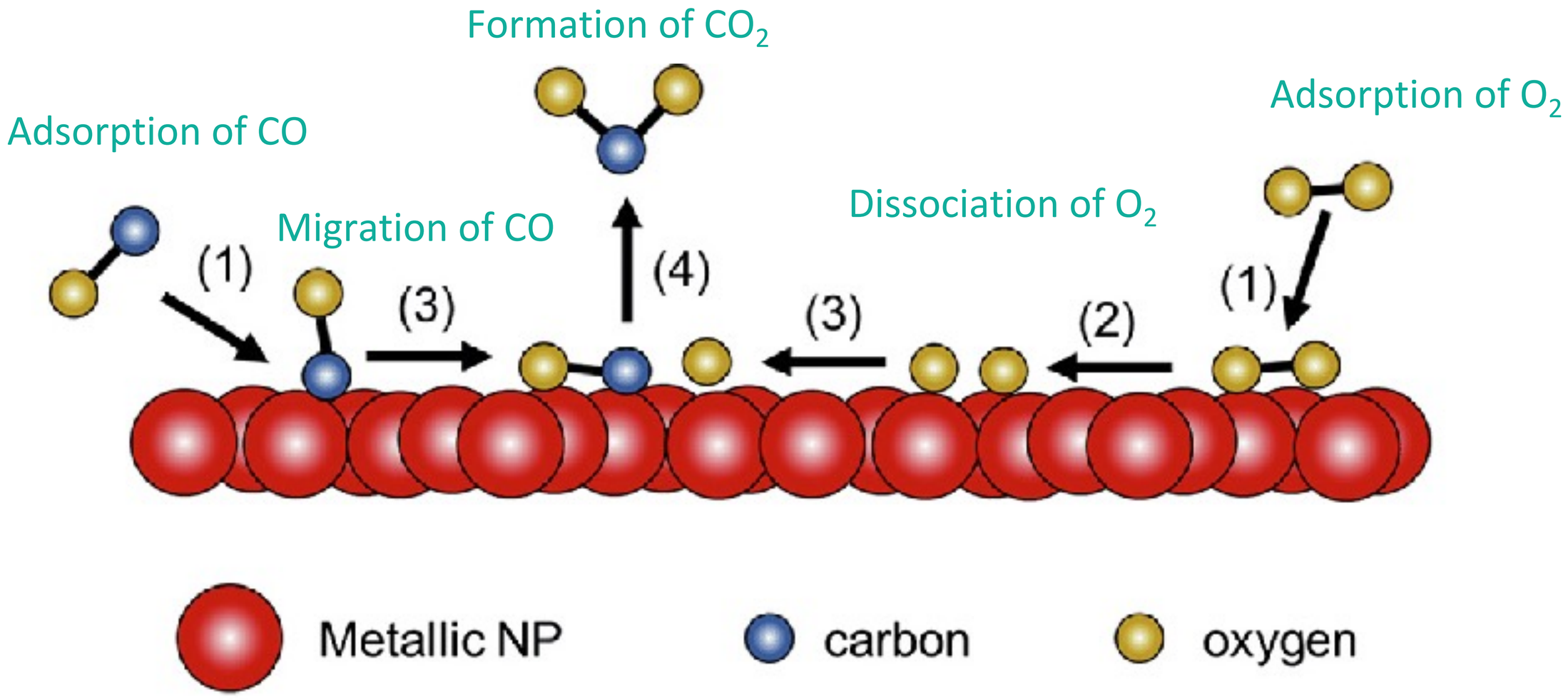
How Surfaces Serve as Catalysts: Adsorption + Dissociation



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

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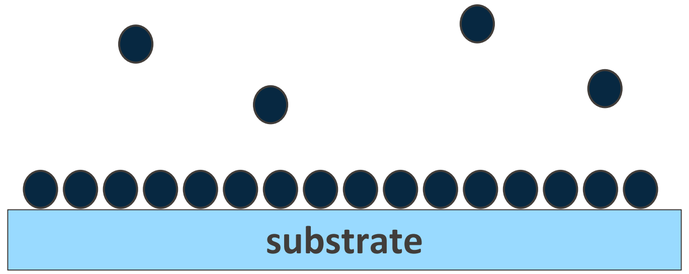
How can Surfaces Serve as Catalysts?

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})

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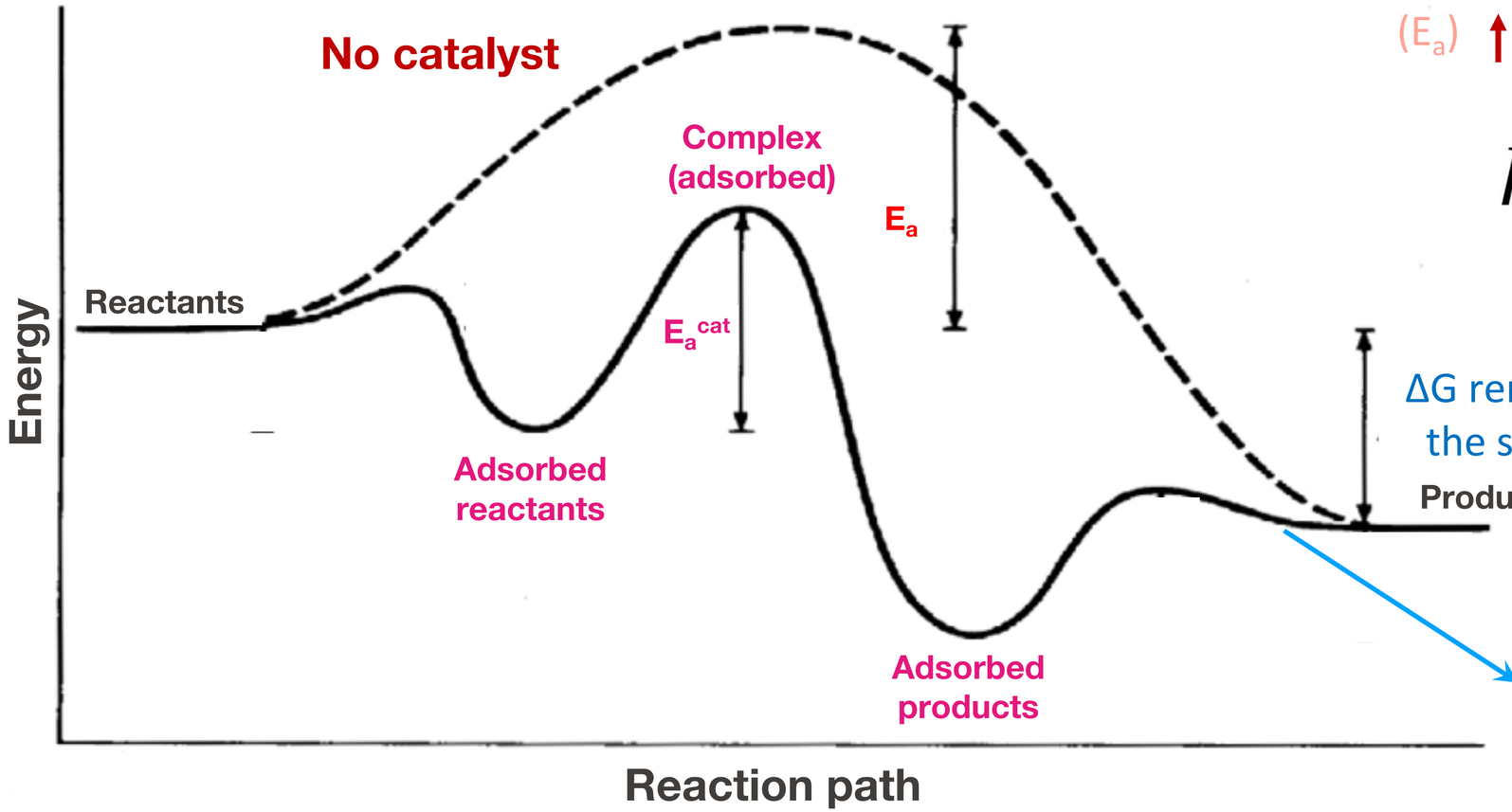
How can Surfaces Serve as Catalysts?

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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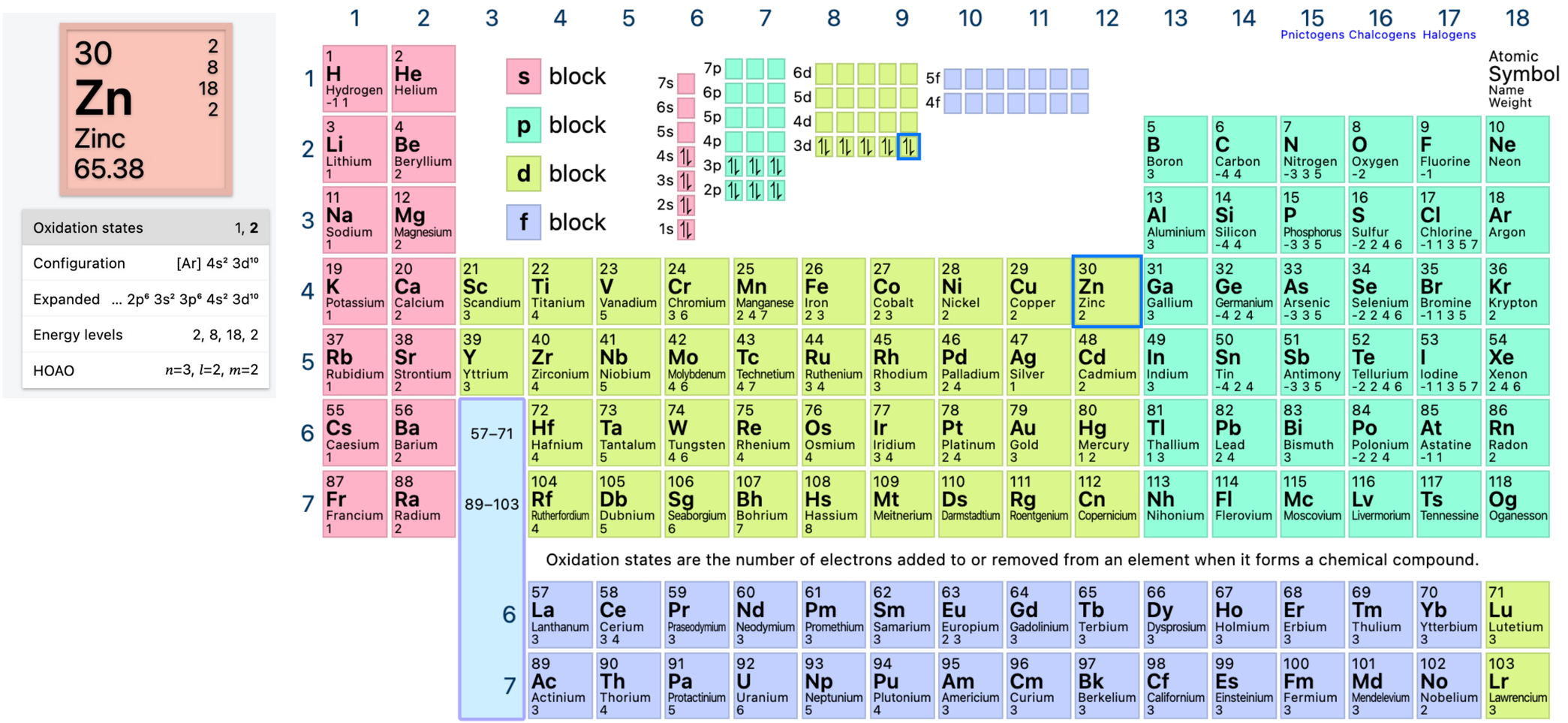
Electronic Configuration and Molecular Orbitals

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

Orbital: region in an atom or molecule where there is high probability of finding an electron



https://www.ptable.com

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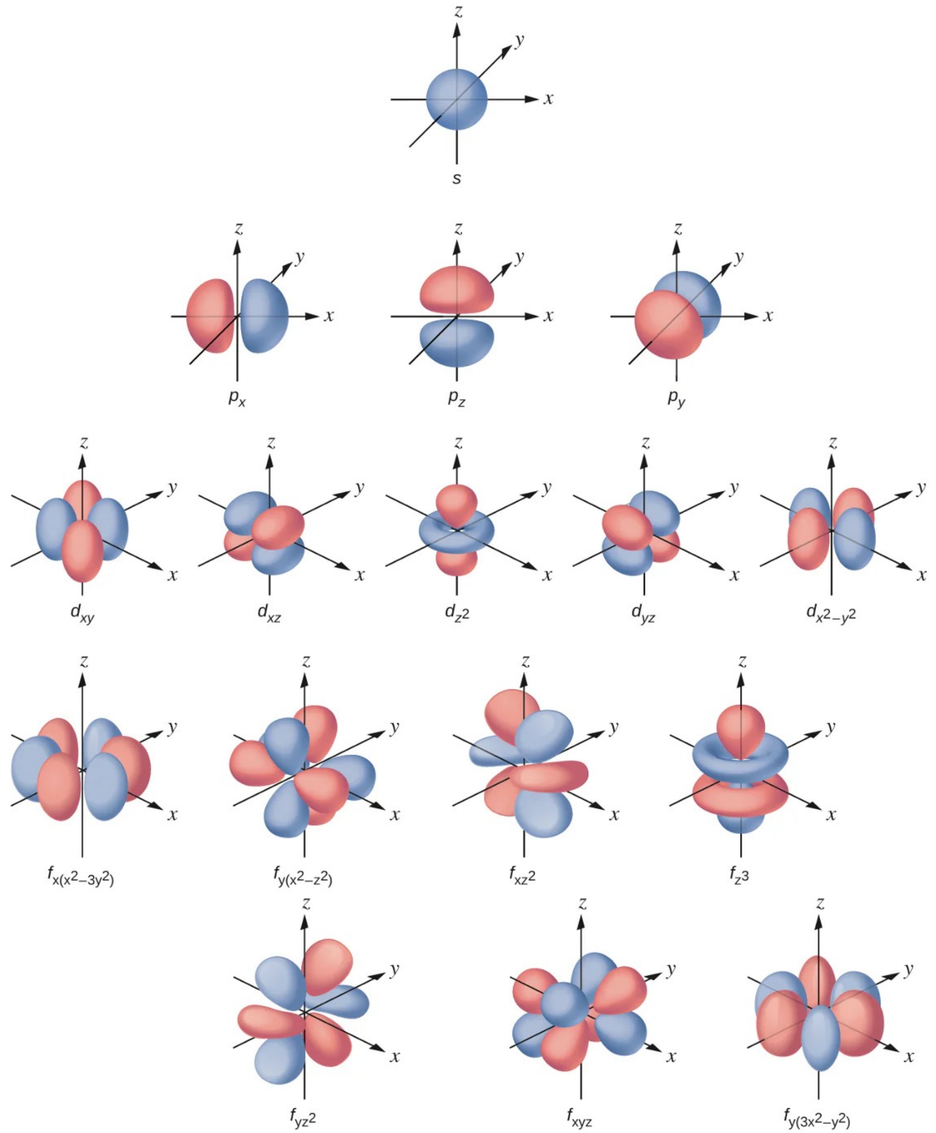
Electronic Configuration and Molecular Orbitals

Orbital: region in an atom or molecule where there is high probability of finding an electron

Energy



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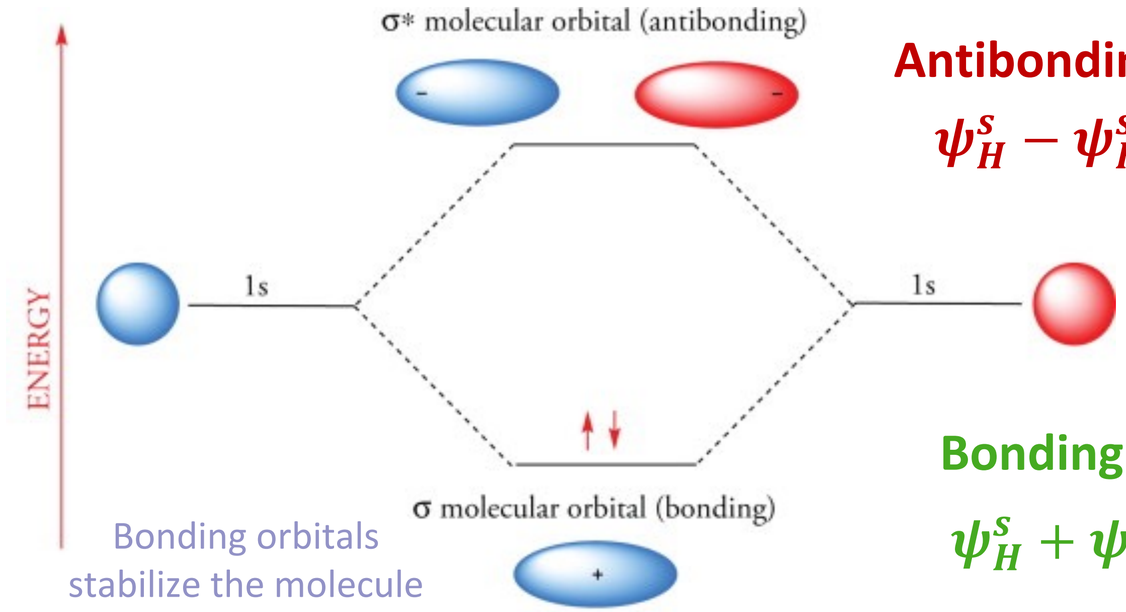
Molecular Orbital Diagrams and Bond Order



Bonding orbitals stabilize the molecule = stronger bonds

Antibonding state

$$\psi_H^S - \psi_H^S = \sigma^*$$

Bonding state

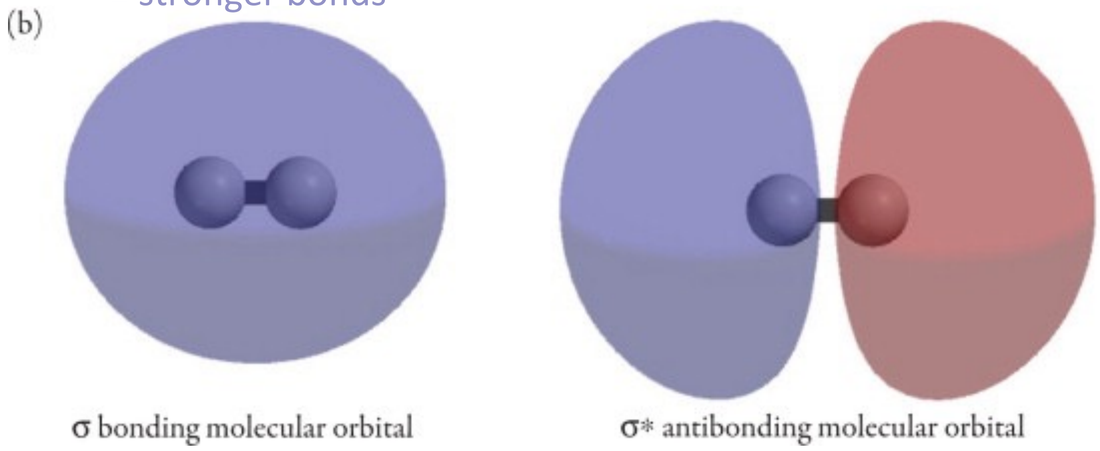
$$\psi_H^S + \psi_H^S = \sigma$$

*Don't forget the Pauli exclusion principle

$$\textbf{Bond Order} = \frac{\#\ \textbf{Bonding}\ e^- - \#\ \textbf{Antibonding}\ e^-}{2}$$

$$\textbf{Bond Order} = \frac{2 - 0}{2} = 1$$

H – H



Antibonding orbitals have electron density that pulls nuclei apart, destabilizing the molecule = weaker bonds

Ouellette & Rawn, *Org. Chem. Study Guide*, **2015**

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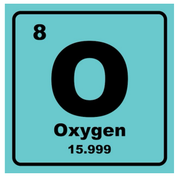
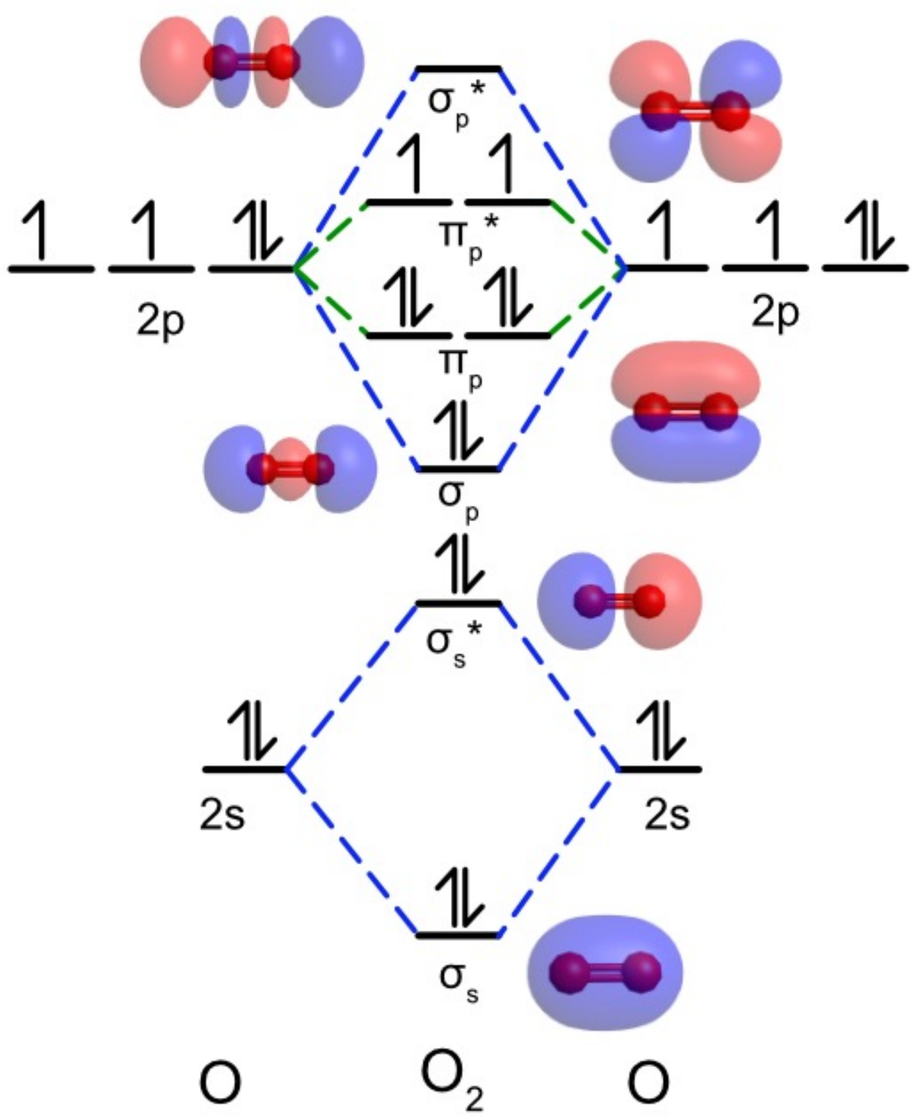
Molecular Orbital Diagrams and Bond Order





$$\textbf{Bond Order} = \frac{\#\ \textbf{Bonding}\ e^- - \#\ \textbf{Antibonding}\ e^-}{2}$$

$$\textbf{Bond Order} = \frac{10\ - 6}{2} = 2$$

O = O

Ouellette & Rawn, *Org. Chem. Study Guide*, **2015**

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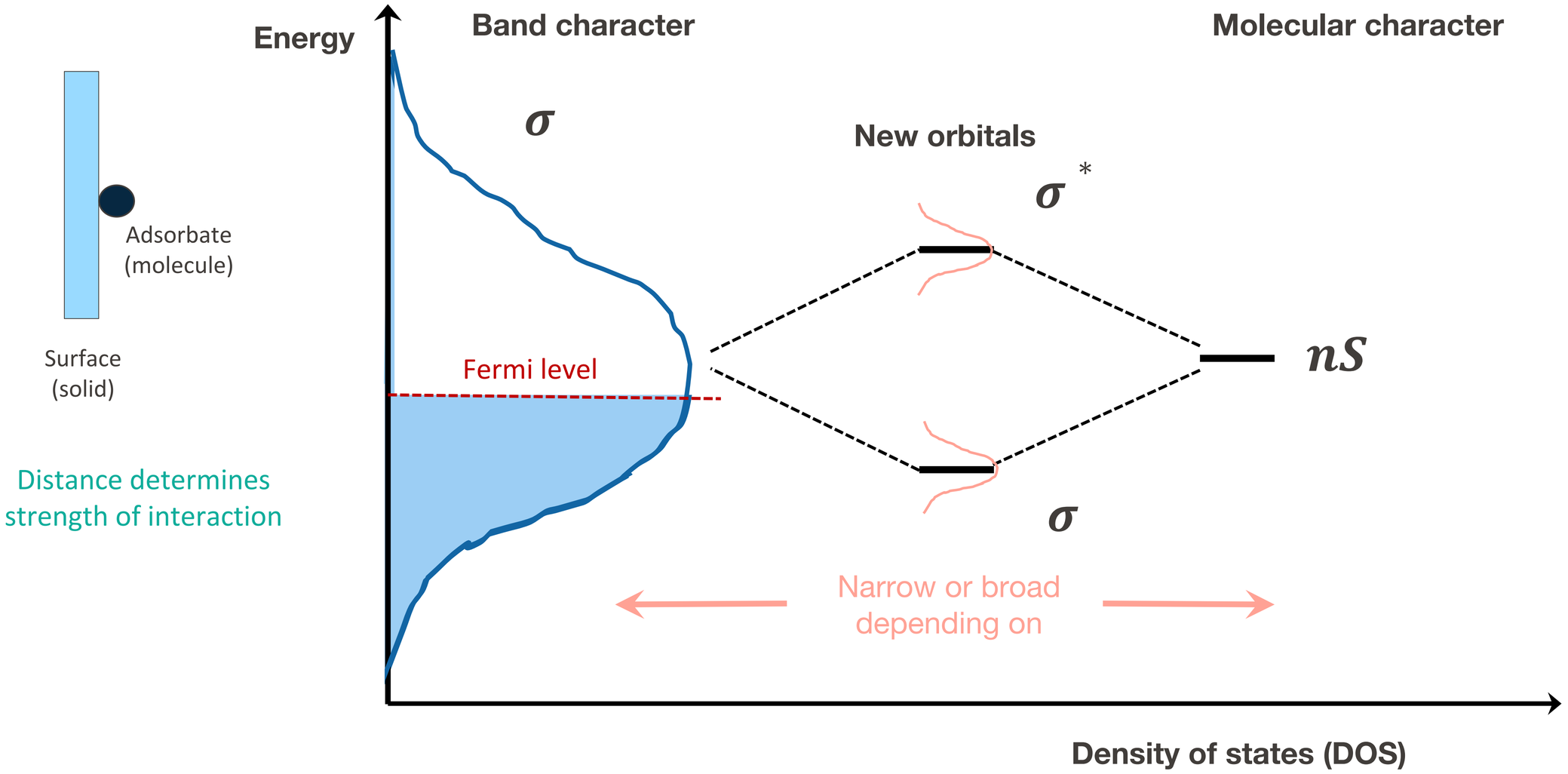
Bonding at Surfaces = Orbital Mixing

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



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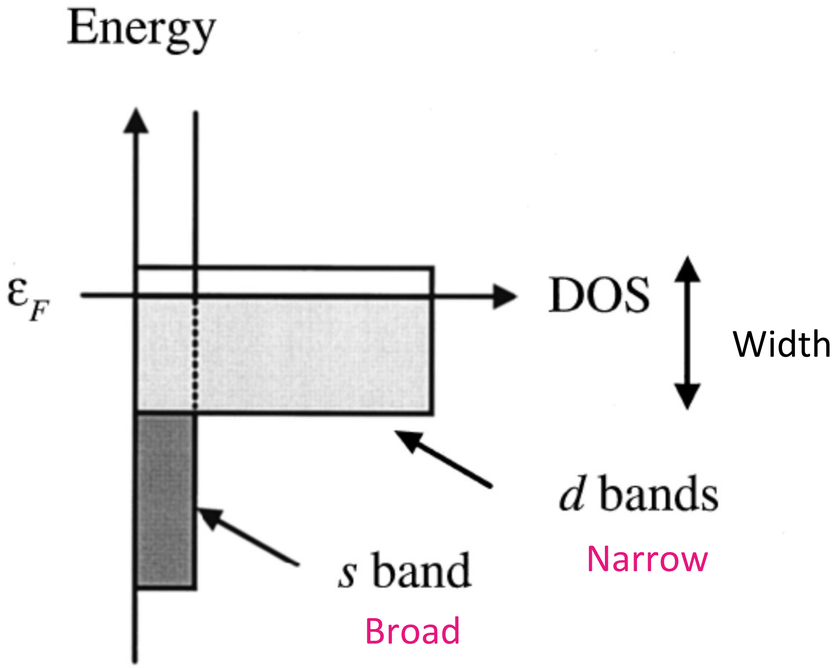
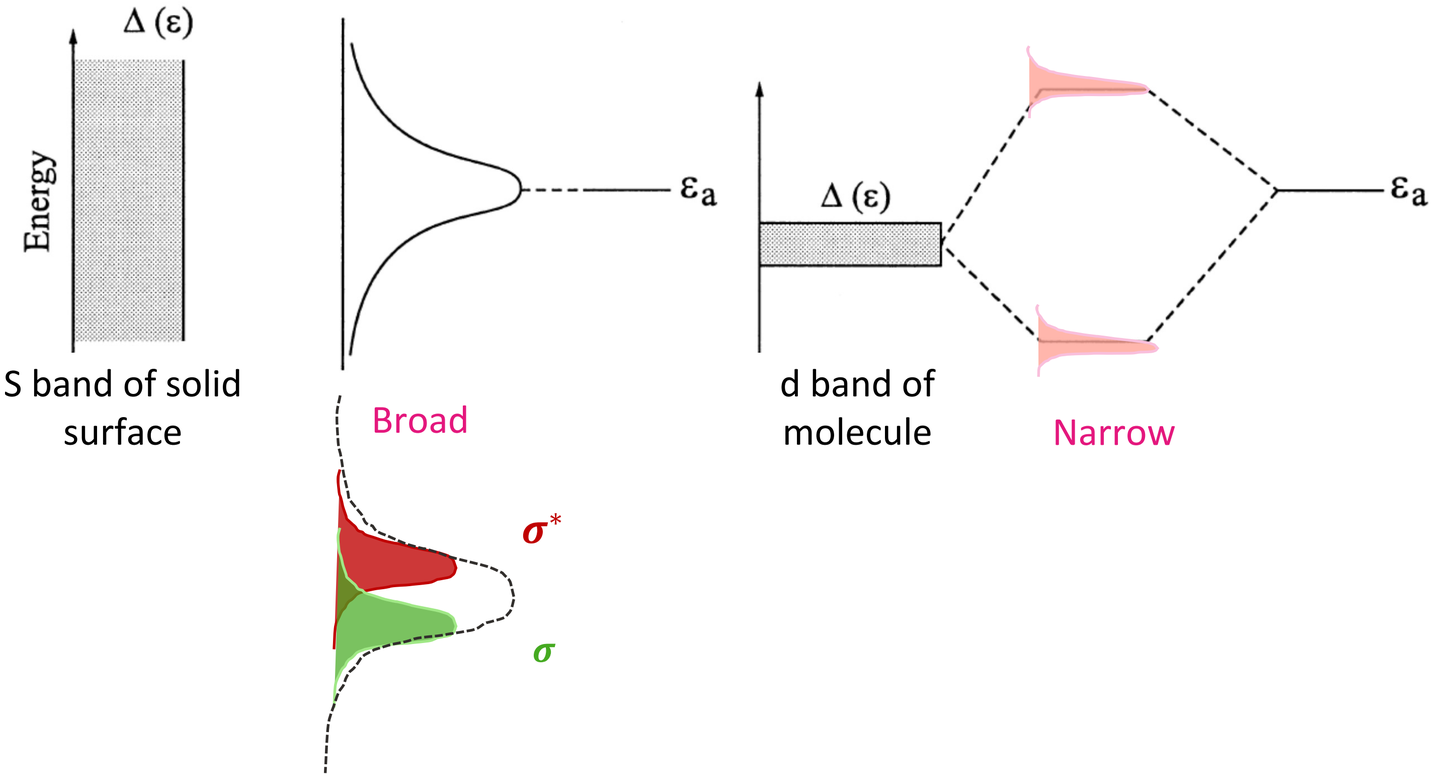
Bonding at Surfaces – DOS of Transition Metals

Transition metals have d-bands that play a critical role in catalysis by interacting with molecular orbitals.



Mixing molecular orbital with s band of solid surface



From Hammer & Nørskov

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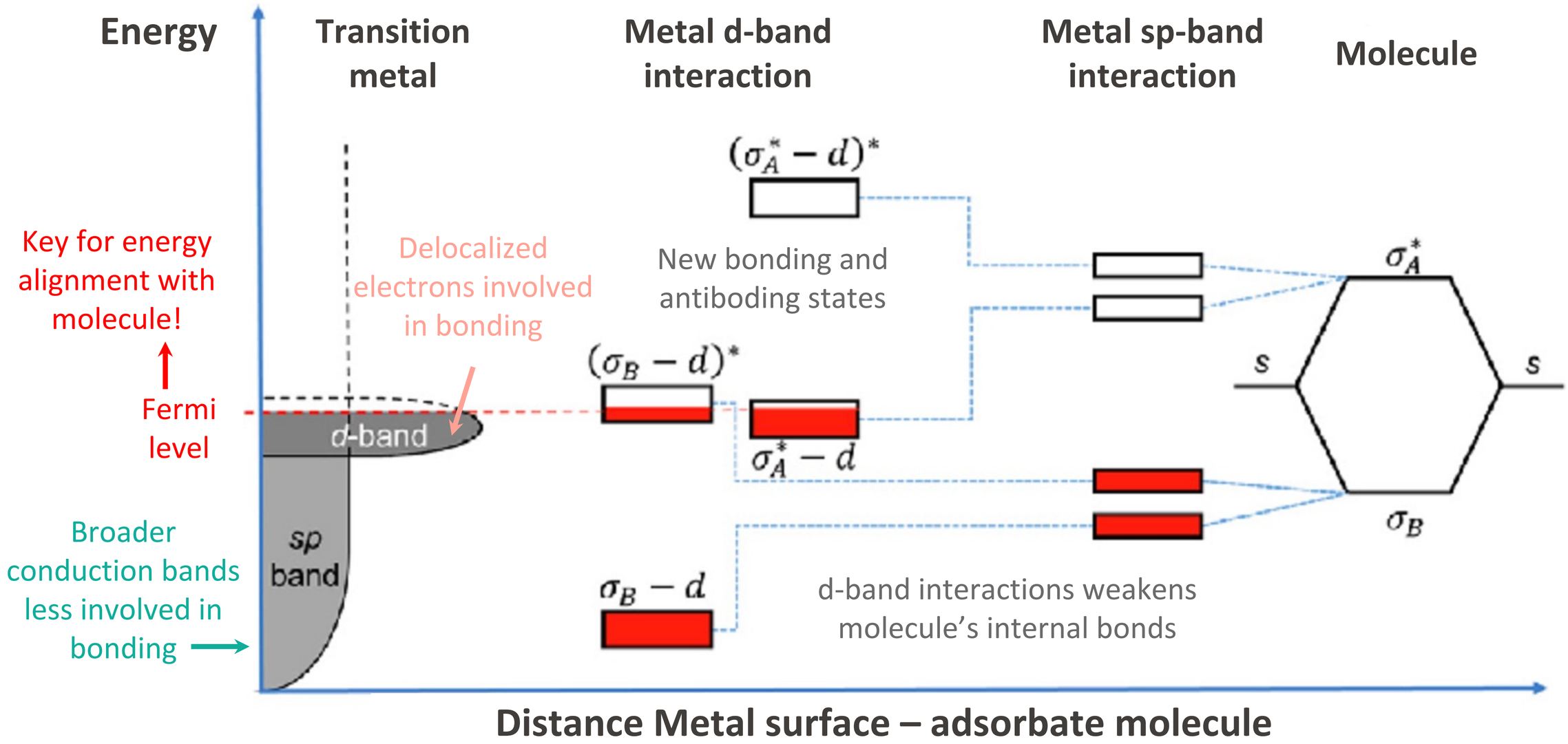
Molecular Orbital Interactions on Transition Metal Surfaces



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

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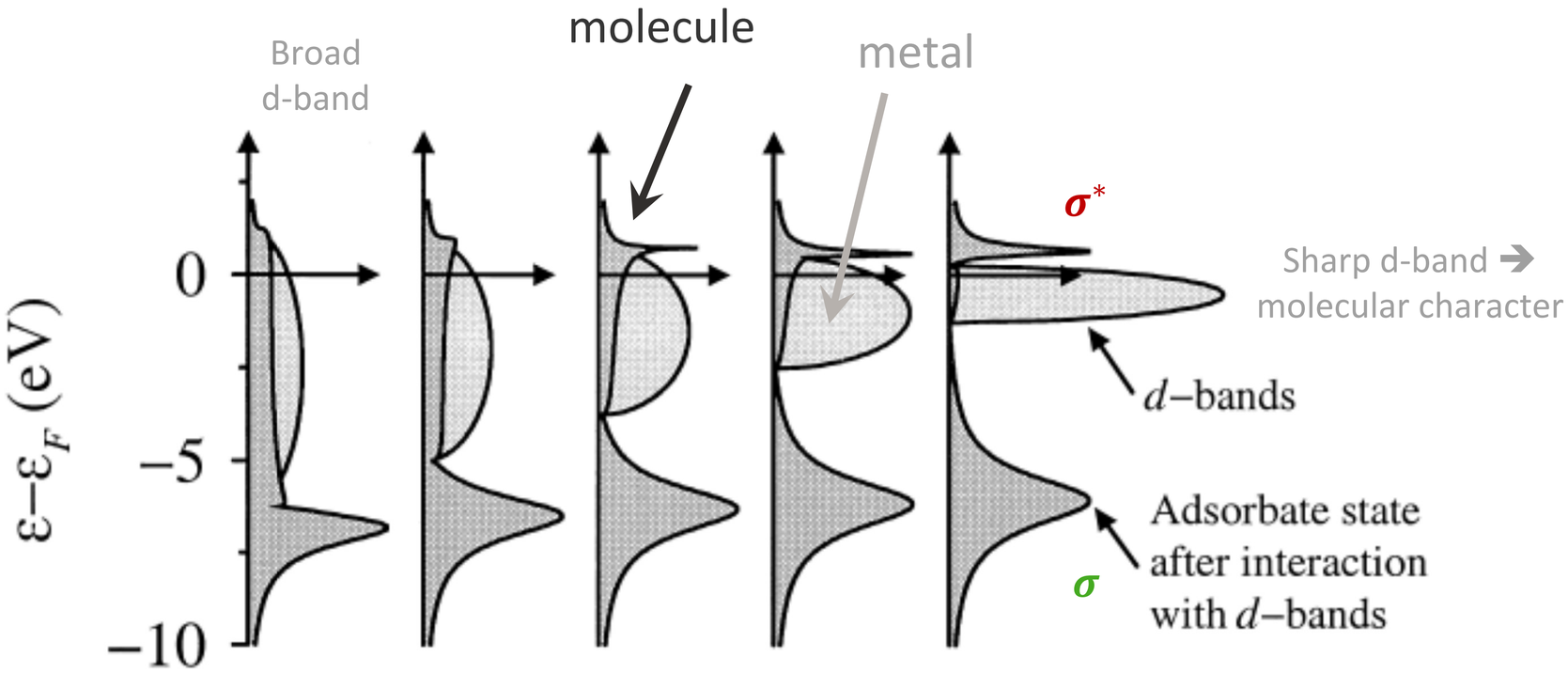
Strength of Bonding on Surfaces

Adsorption strength depends on orbital overlap—broad bands promote metallic character, while sharp bands retain molecular character

Oxygen on Pt(111)



Strong σ interaction

σ becomes broader ➔ metallic character

Weak chemisorption ⟵ ⟶ Strong chemisorption

From Hammer & Nørskov

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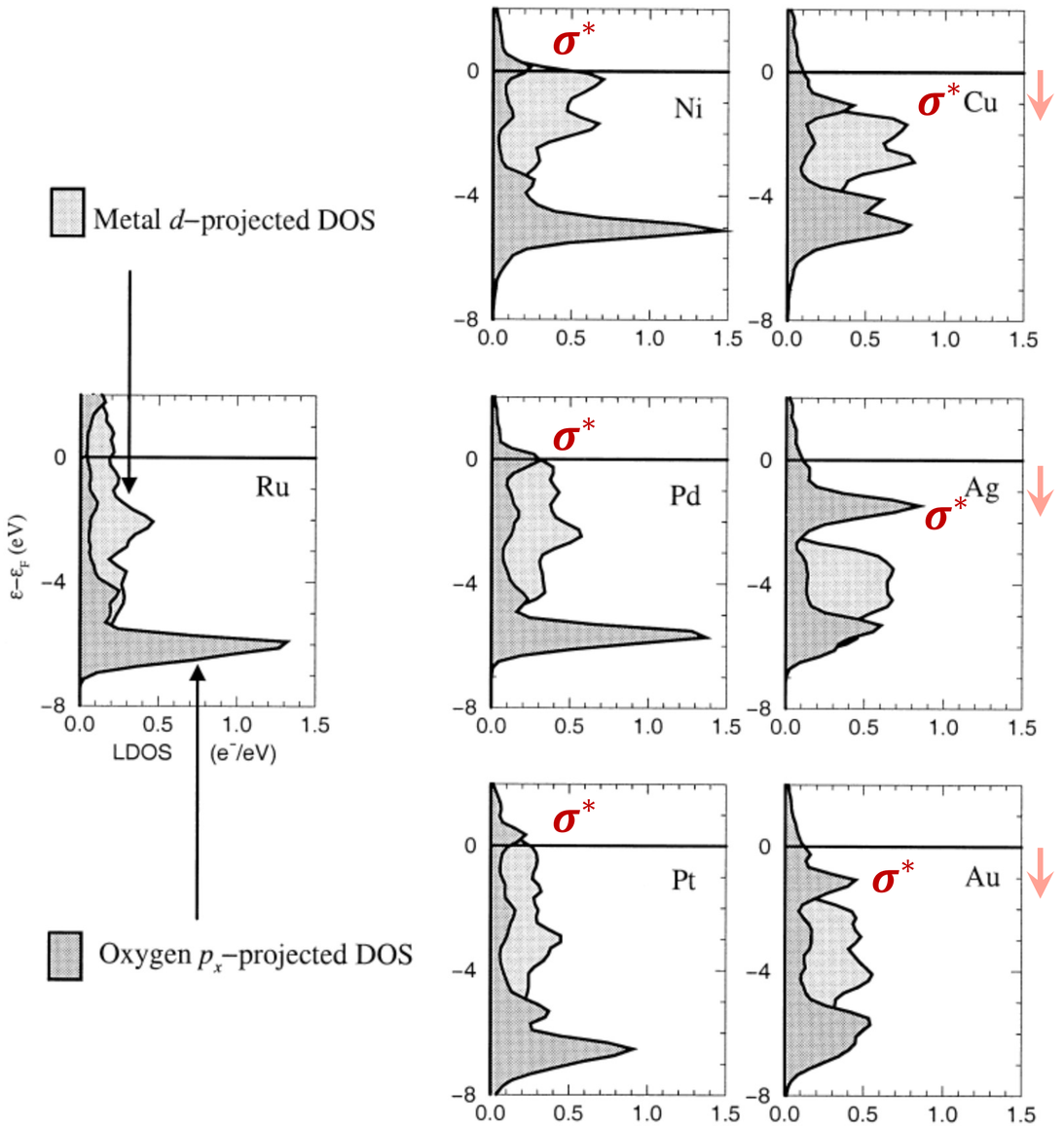
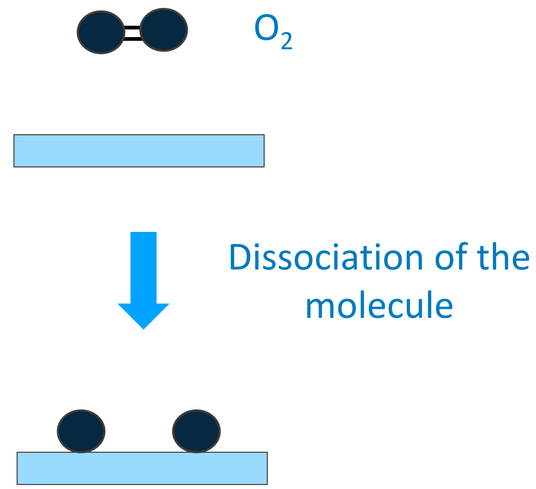
Facilitating Dissociation via Antibonding Orbitals

Strong adsorption is defined as clear peak of σ^* above the Fermi level

If σ∗ orbital remains unpopulated, O–O bond remains strong



Filled σ^* weakens O–O bond, promoting dissociation.



From Hammer & Nørskov

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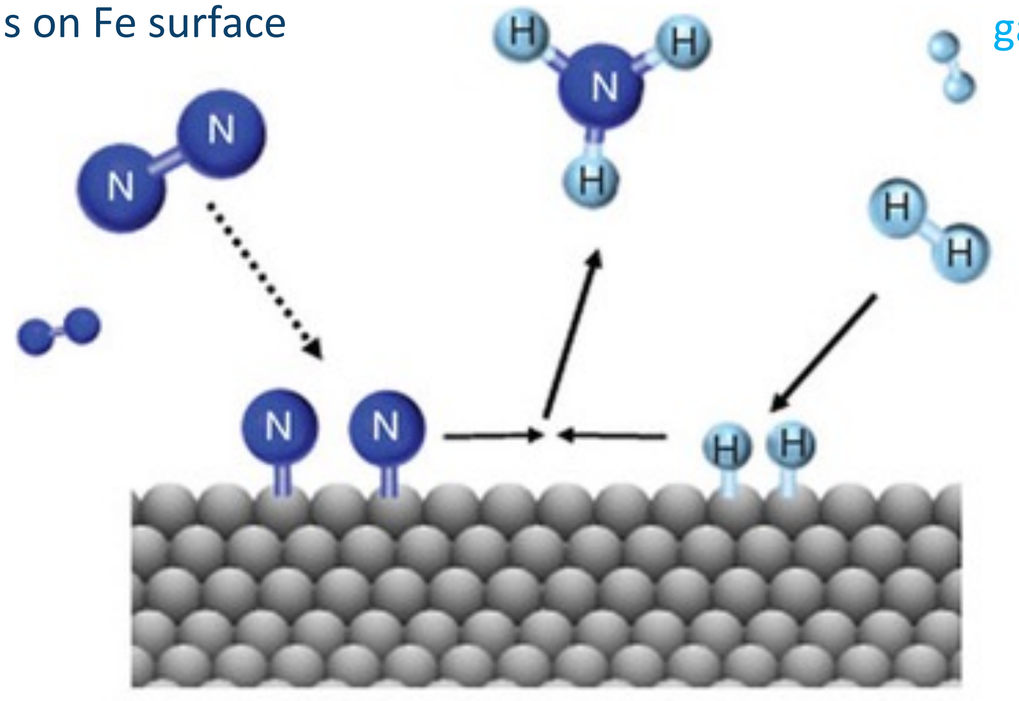
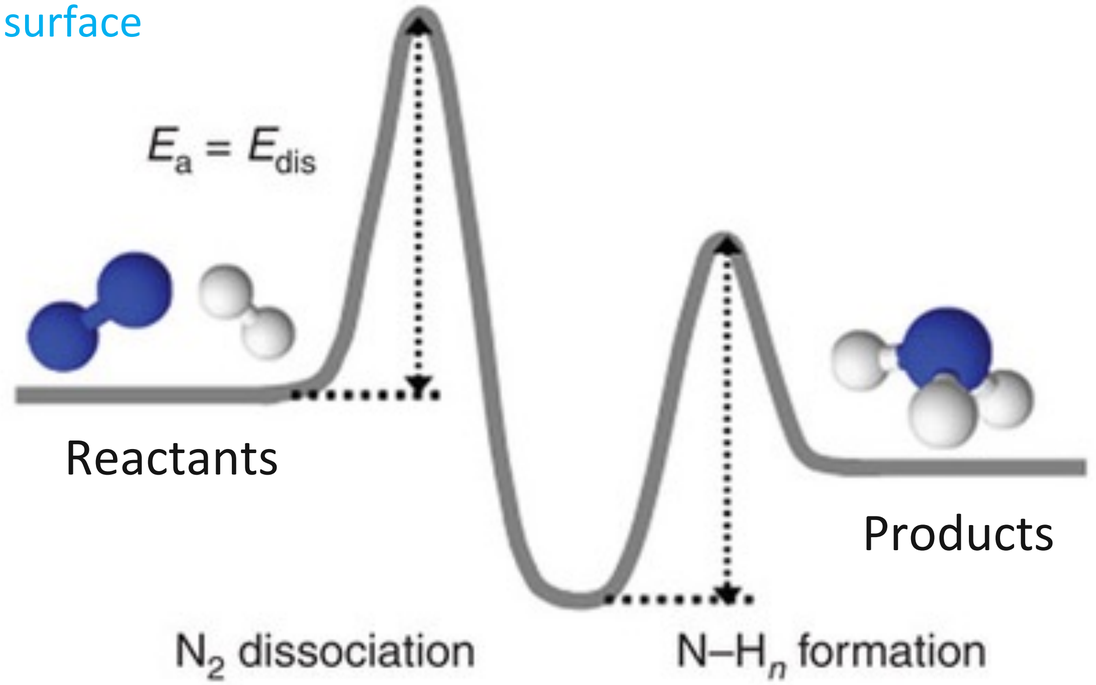
Example of Important Catalyzed Reaction: Ammonia Synthesis

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**

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Example of Important Catalyzed Reaction: Ammonia Synthesis

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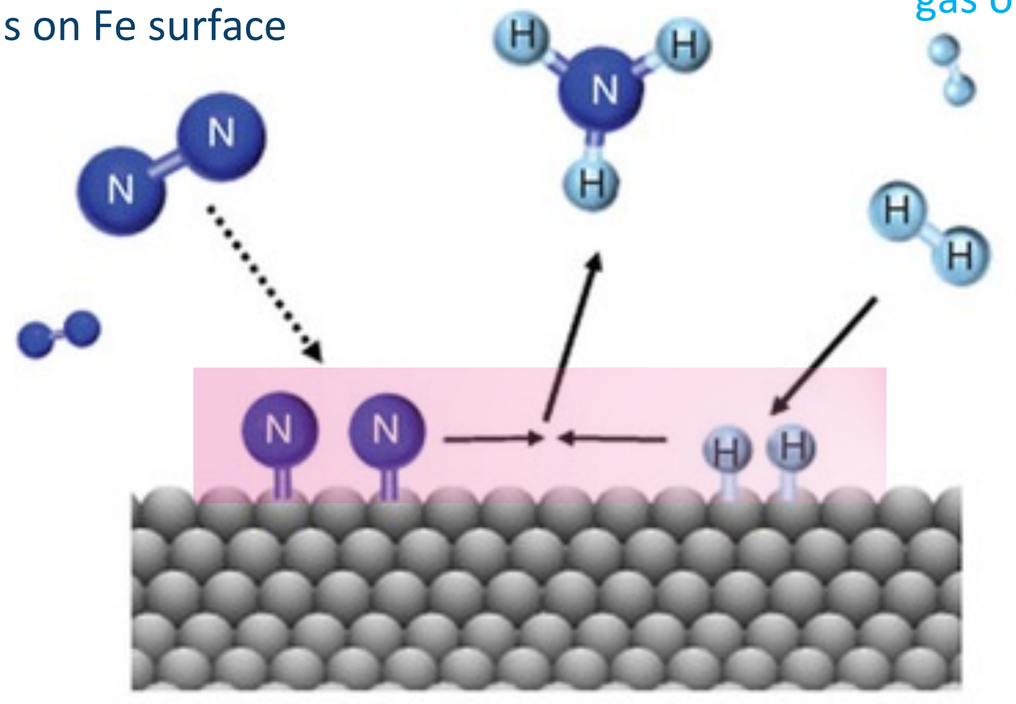

Fe catalyst provides active surface that adsorbs molecules, weakening their bonds

Nitrogen atoms easier to dissociate from the surface

Dissociated molecule (D) Molecule (M)

CO

Sc	Ti D	V	Cr	Mn	Fe D	Co	Ni M	Cu	3d
Y	Zr	Nb	Mo D	Tc	Ru M	Rh	Pd M	Ag	4d
La	Hf	Ta	W D+M	Re	Os	Ir M	Pt M	Au	5d

N_2

Sc	Ti (D)	V	Cr (D)	Mn	Fe D	Co	Ni	Cu	3d
Y	Zr	Nb	Mo (D)	Tc	Ru	Rh	Pd	Ag	4d
La	Hf	Ta (D)	W D	Re	Os	Ir	Pt	Au	5d

NO

Sc	Ti	V	Cr	Mn	Fe	Co	Ni D+M	Cu	3d
Y	Zr	Nb	Mo	Tc	Ru M	Rh	Pd M	Ag	4d
La	Hf	Ta	W	Re	Os	Ir D+M	Pt M	Au	5d

Dissociate in a way that it doesn't want to stay on the surface after dissociation

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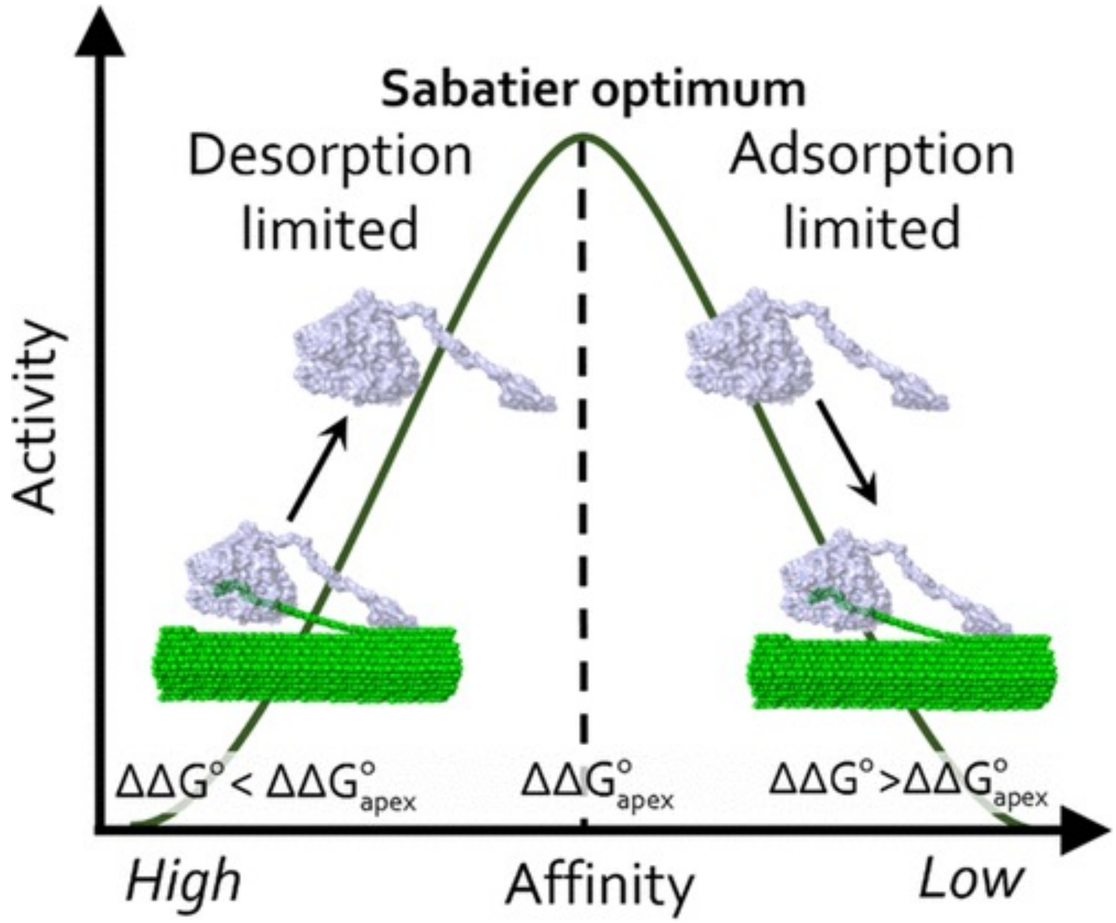
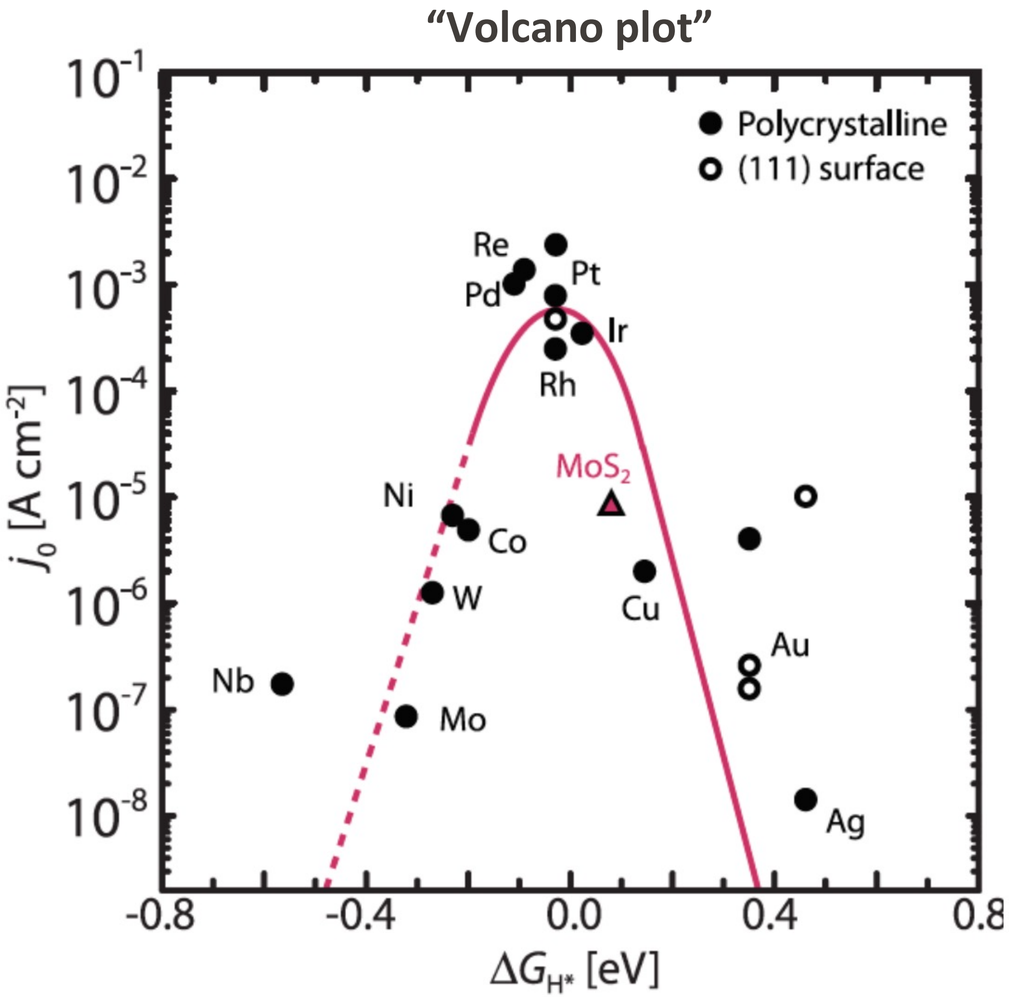
Balance Between Adsorbing Strongly But not too Strongly





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

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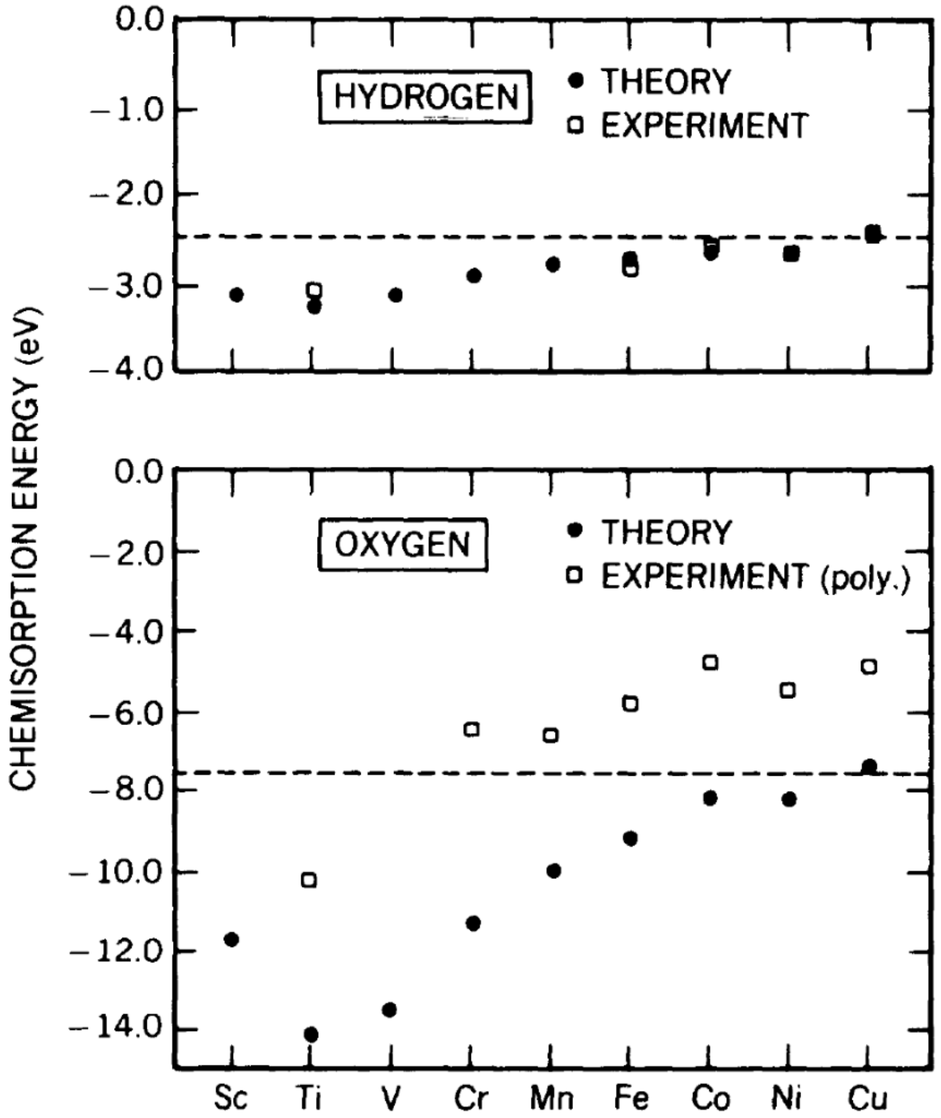
Different Adsorption Energy from Gas to Gas/Metal to Metal

Hydrogen adsorption does not cause major surface reconstructions

Oxygen adsorption often induces reconstruction of metal surface (*e.g.* formation of oxide layers)

Hard to account for theoretically



Hydrogen primarily interacts with metal surfaces through 1s orbital

Simply bonding interaction with metal's conduction (s or d) bands

Oxygen interacts with metal surfaces through 2p orbitals

Overlap with metal d-bands (strong covalent bonding)

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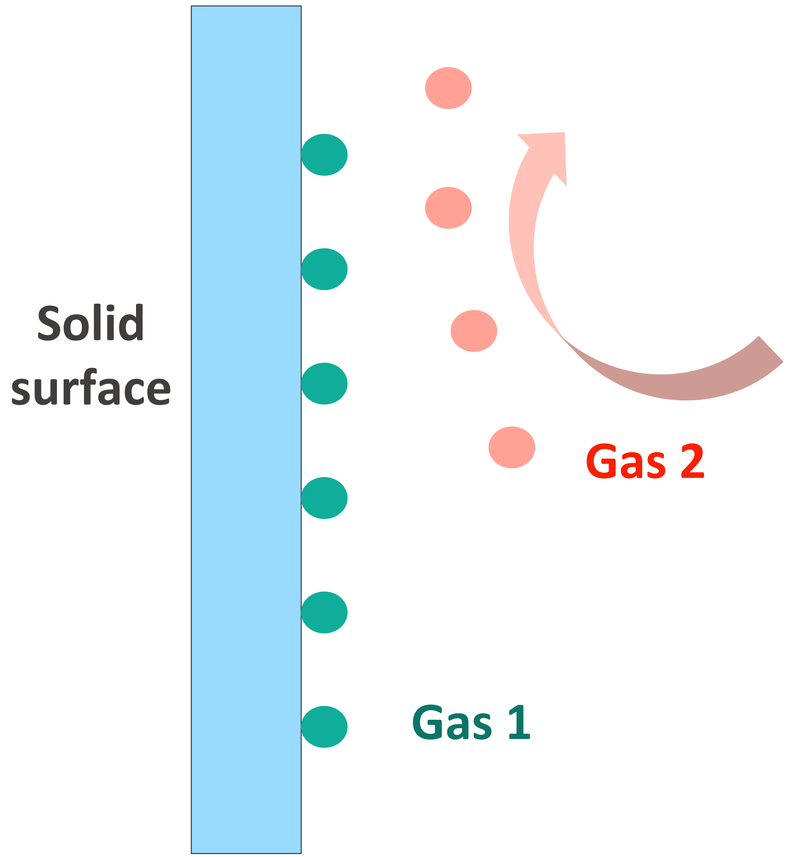
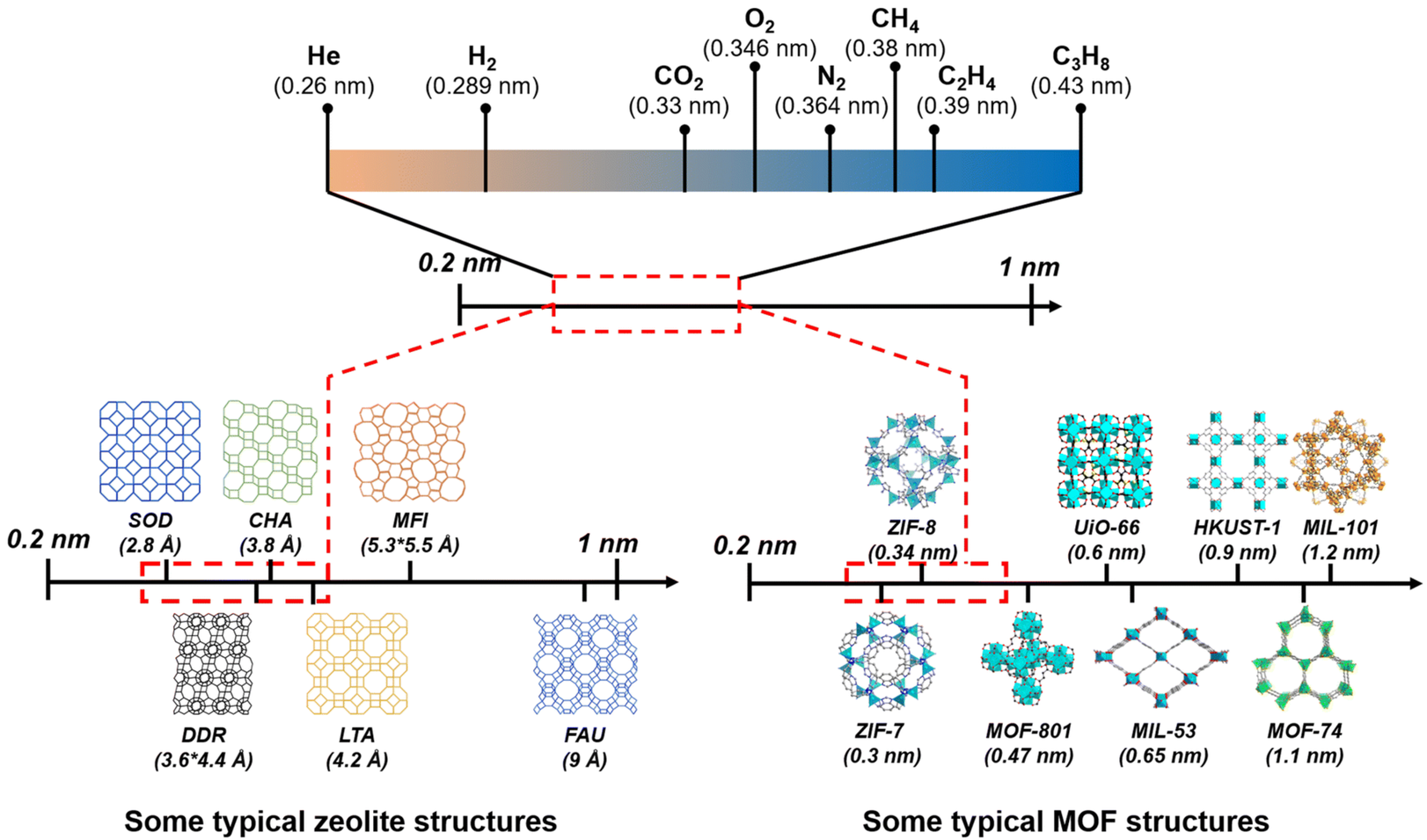
Important Application: Gas Separation for Sustainability

Different molecules absorbing differently on different surfaces based on:

- Formation of specific bonds
- d-band of the material

Need materials with high surface area:volume ratio (Porous structures)





Chen *et al., Chem. Soc. Rev., 52,* **2023**

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Catalysis Performance Metrics: Activity and Turnover Frequency

Specific activity: When the reaction rate is normalized to the surface area of the active component in the catalyst

Turnover frequency (TOF): Number of times a single active site on catalyst converts a reactant into a product per second

Provides measure of catalyst's efficiency ➔ higher TOF means more active catalyst

$$\underset{(s^{-1})}{\mathrm{TOF}} = \frac{r}{N_{\mathrm{active}}}$$

Reaction rate (mol s^{-1})

Number of active sites on catalyst (mol)

ACS Catalysis

Viewpoint

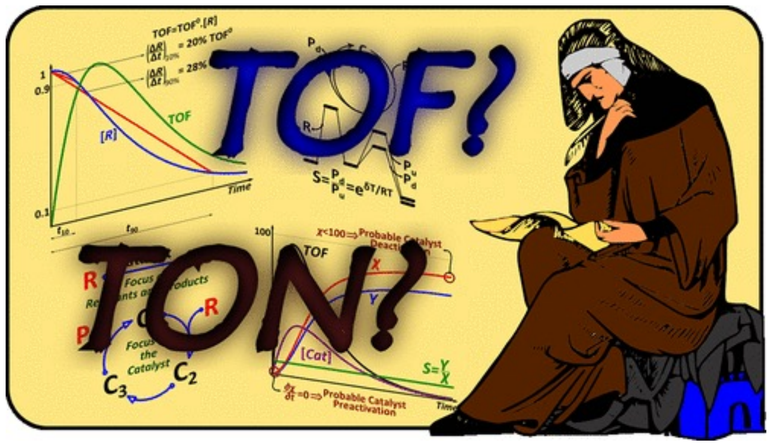
pubs.acs.org/acscatalysis

"Turning Over" Definitions in Catalytic Cycles

Sebastian Kozuch*,† and Jan M. L. Martin†,‡

†Department of Organic Chemistry, Weizmann Institute of Science, IL-76100 Rechovot, Israel

‡Center for Advanced Scientific Computing and Modeling (CASCAM), Department of Chemistry, University of North Texas, Denton, Texas 76203, United States



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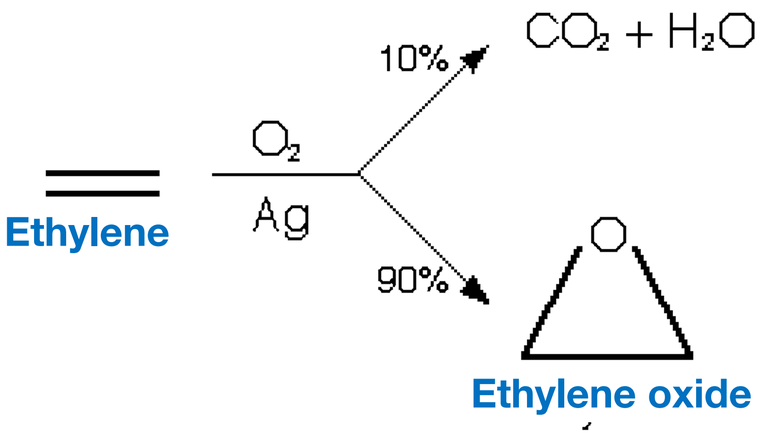
Catalysis Performance Metrics: Selectivity

Selectivity completely depends on the catalyst surface chemistry

By changing a catalyst, completely different products can be obtained

$$\text{Selectivity} = \frac{\text{Formation rate of a particular product}}{\text{Formation rate of all products}}$$

Two oxidation paths for ethylene:



90% of the ethylene molecules are converted into ethylene oxide

Commercial ethylene oxide procedure runs with 90% selectivity

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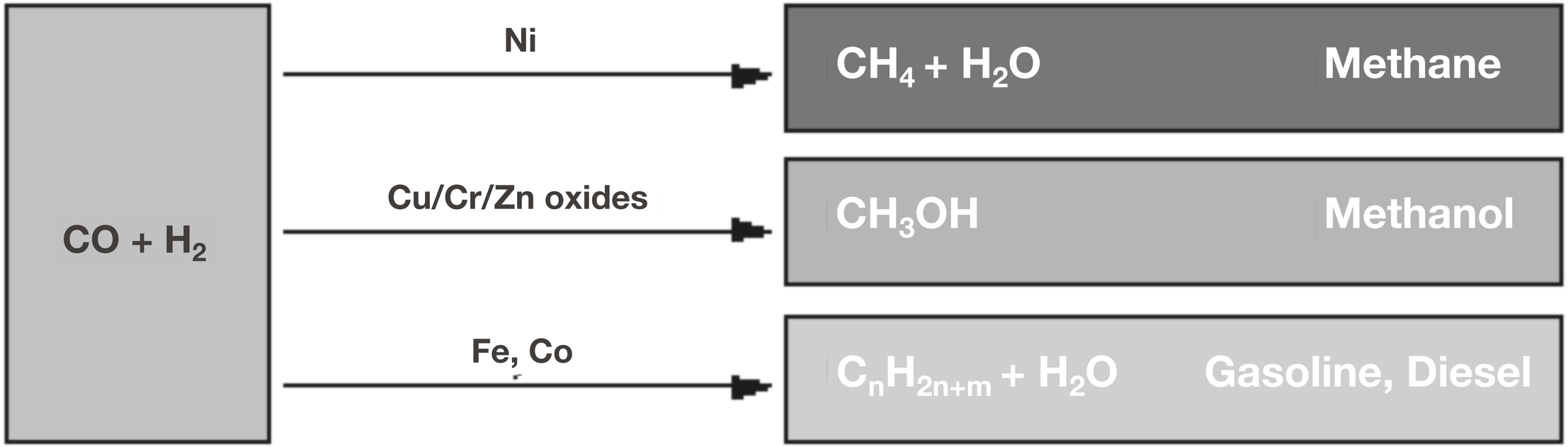

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Catalysis Optimization – Trade-Offs of Adsorption Energy

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

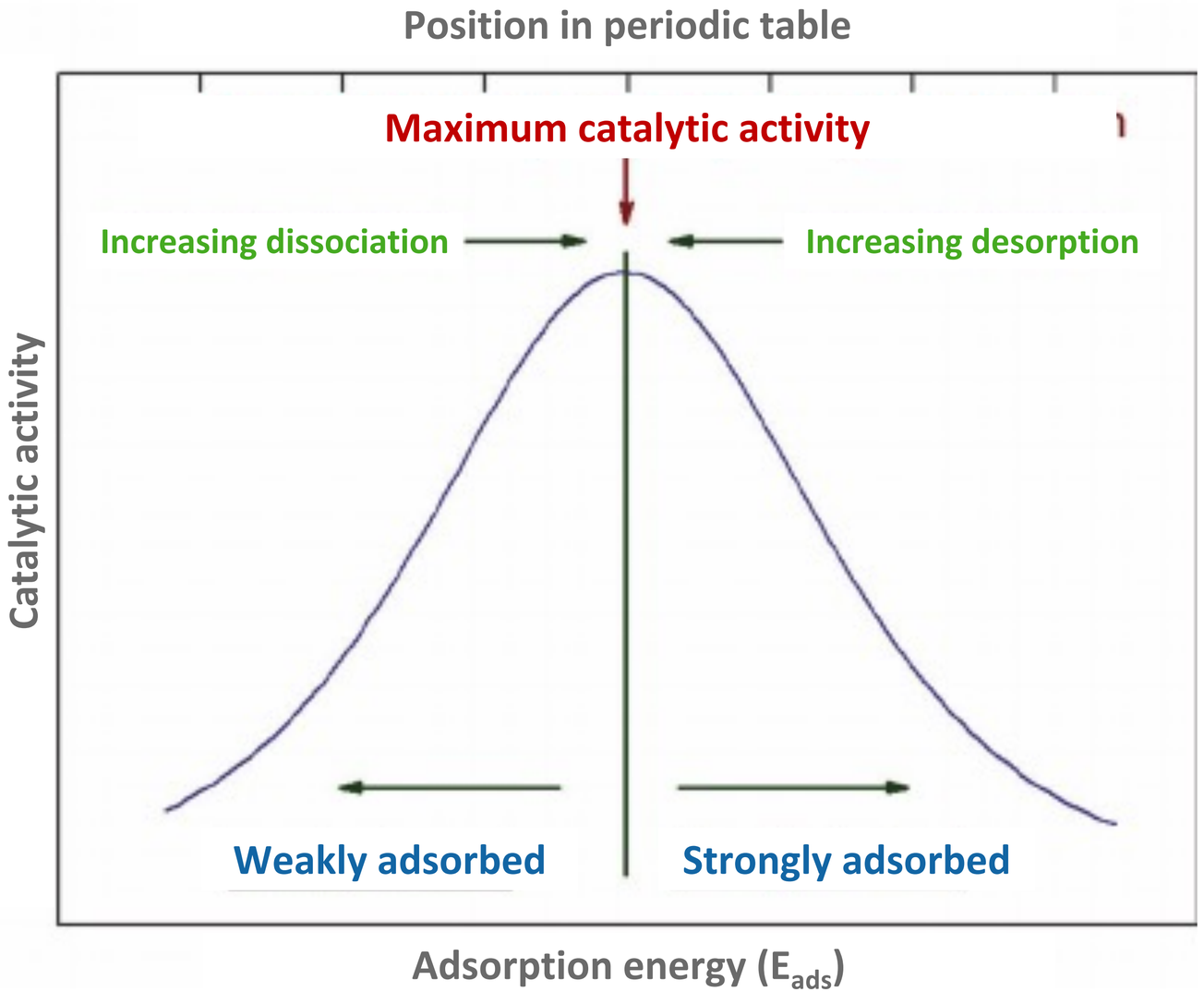
Low E_{ads}

↓

Reactants do not adsorb

↓

Low activity



High E_{ads}

↓

Products cannot desorb

↓

Surface sites are blocked

↓

Low activity

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Nanostructuring for Increased Active Sites at the Nanoscale

Increased surface:volume ratio

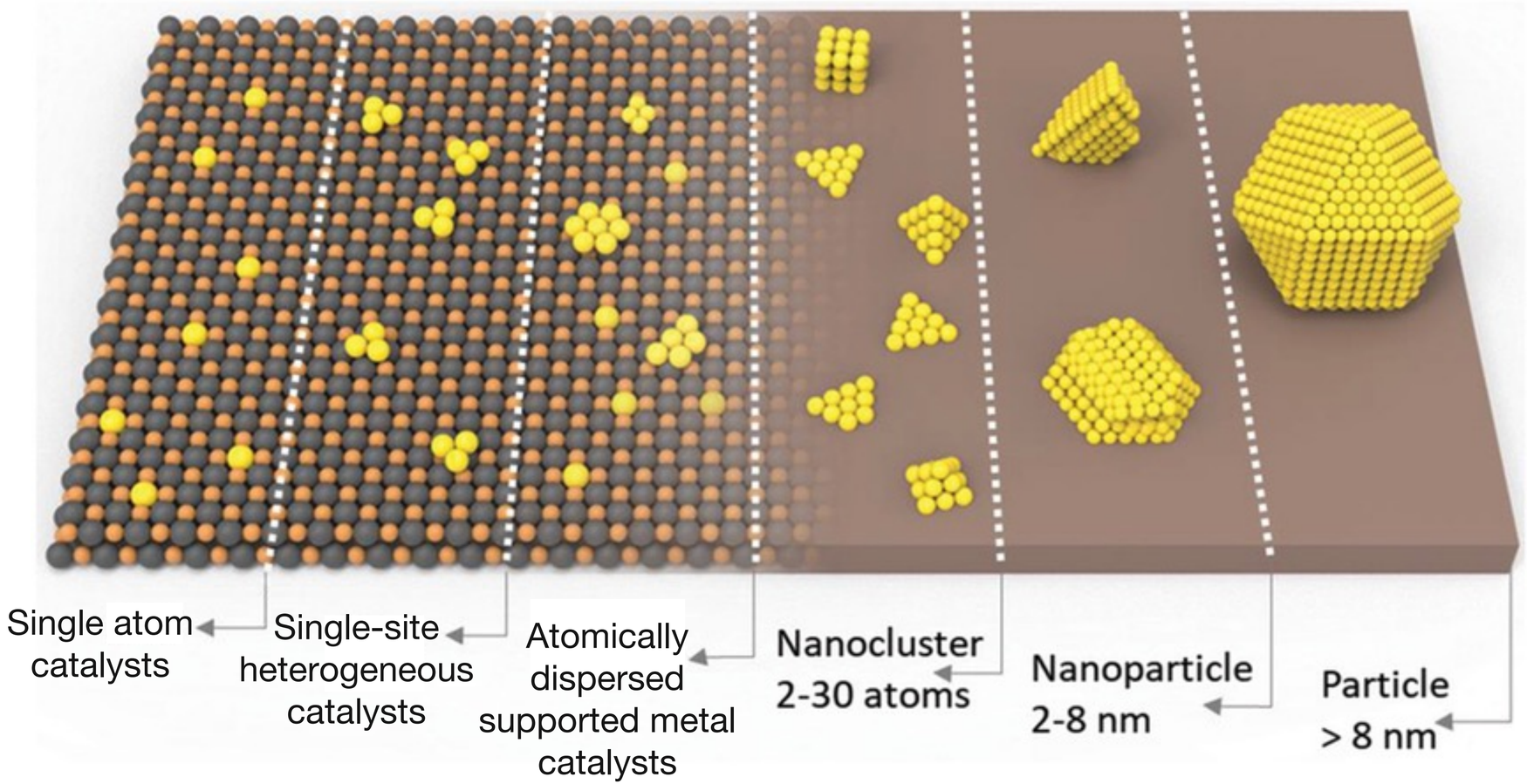
Higher density of defects, edges, corners, or steps ➔ active sites

More active sites exposed ➔ more interactions

At the nanoscale, electronic structure of materials can be tuned to optimize E_{ads}

Specific shapes can lead to greater selectivity

Metallic structures with plasmonic properties can undergo photocatalysis (light-driven chemical reactions)



Yu *et al.*, *Adv. Energ. Sustain. Res.*, *5*, **2024**

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Alloying Catalysts to Fine-Tune Adsorption

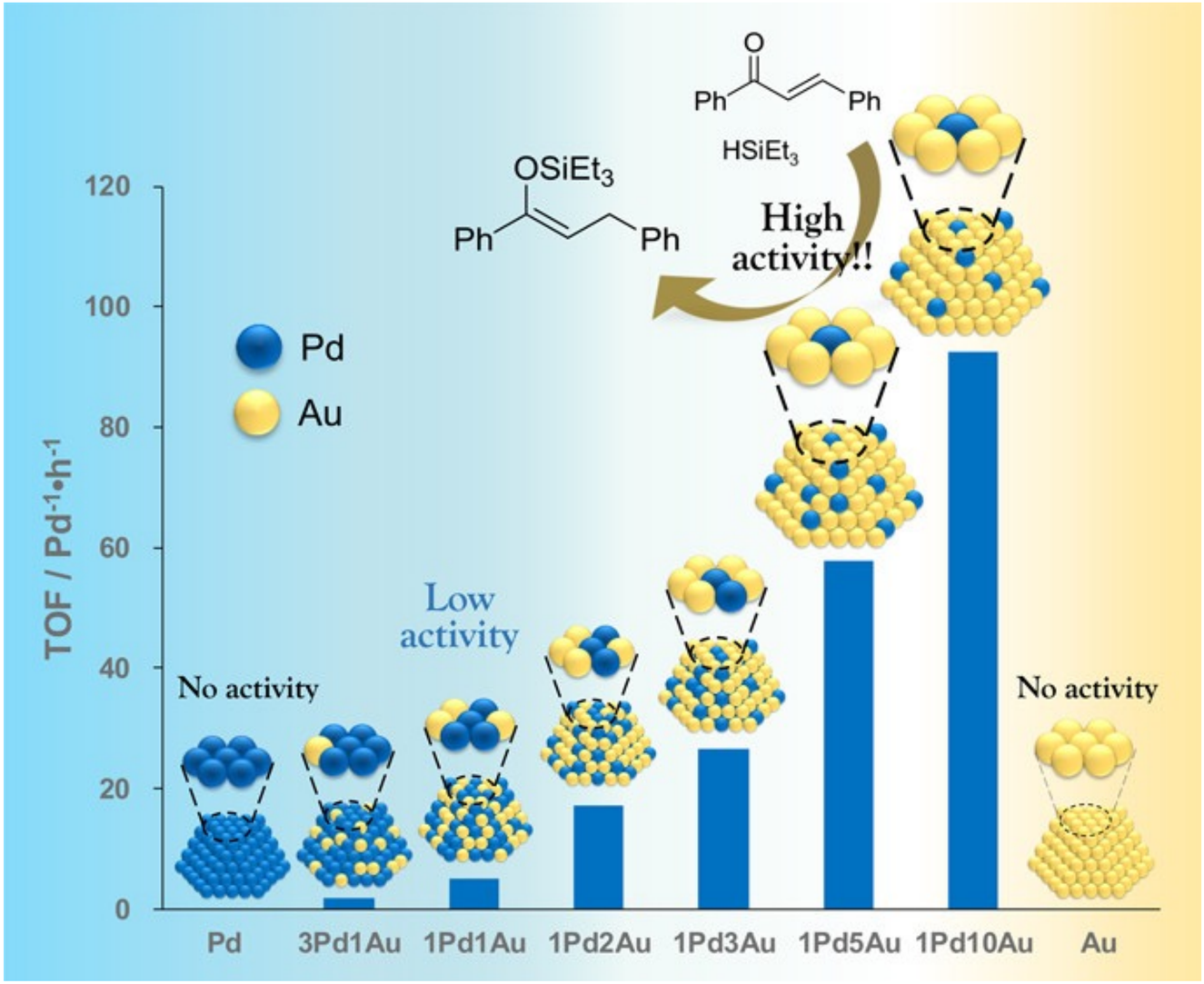
Alloying: combining metals to modify the surface's electronic structure

Introducing Au changes the electronic structure of Pd

Pd has a high d-band center (closer to E_F) (high E_{ads} ➔ low TOF)

When alloyed with Au, d-band center of Pd shifts downwards ➔ lowers E_{ads}

Incorporation of Au into Pd lattice introduces strain ➔ fine-tune surface reactivity



Miura *et al.*, *ACS Catalysis*, *7*, **2017**

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Summary of Today's Class

- Glucose Biosensor –Raman spectroscopy for non-invasive monitoring
- Recap on Challenges of Biosensors – remaining technological gaps
- Strategies to Overcome Challenges – aptamer biosensors and Debye lengths
- Catalysis – how surfaces serve as catalysts/review of molecular orbital theory
- Optimization of Catalysts – balancing act of performance metrics

Exercise Session: Surface catalysis – how surface modifications affect adsorption energy and reaction rates

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