Core level spectroscopy of liquids

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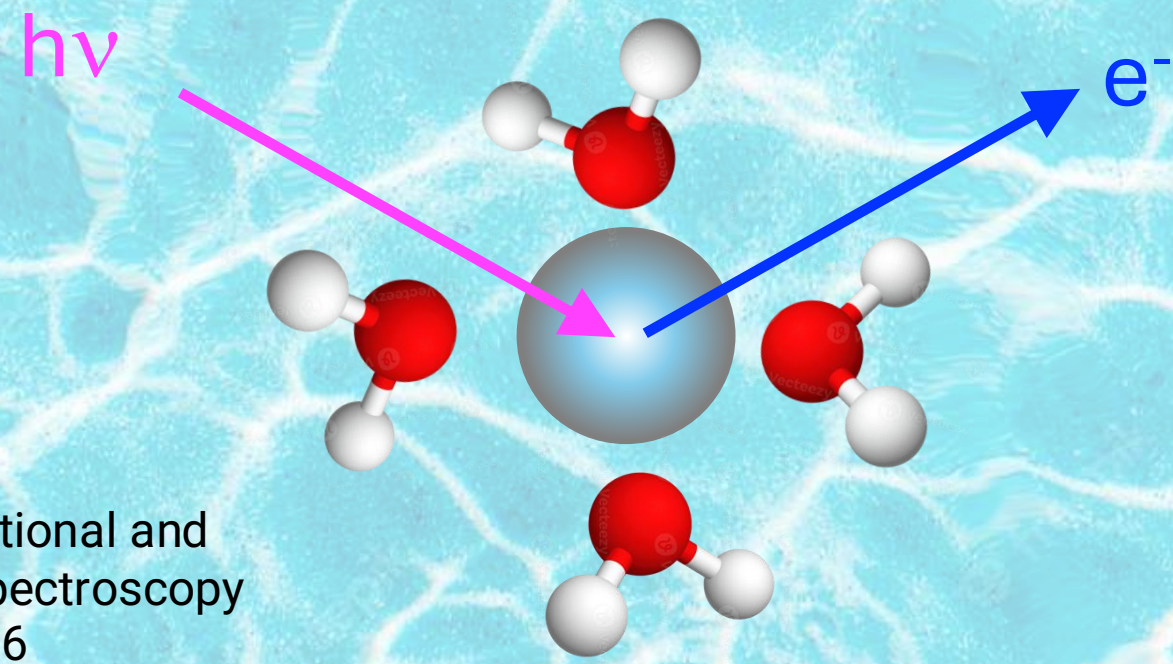

Summer School on Computational and
Experimental Photoelectron Spectroscopy
Tartu July 28-30, 2026

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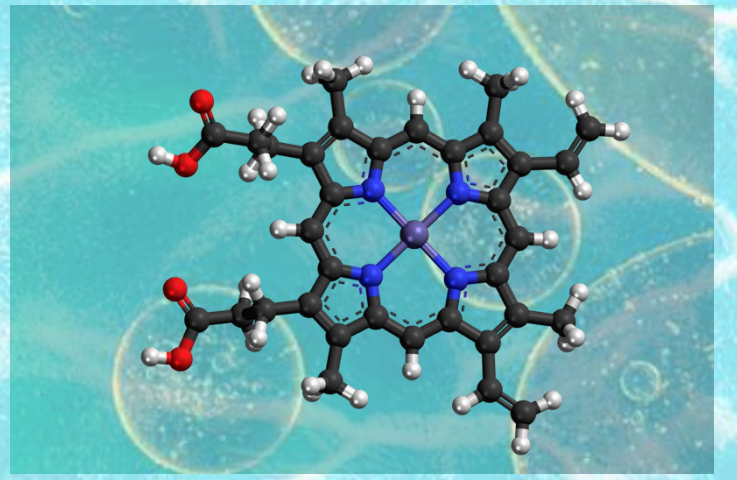
Why liquids?

Chemistry

Biology

Environmental science

…

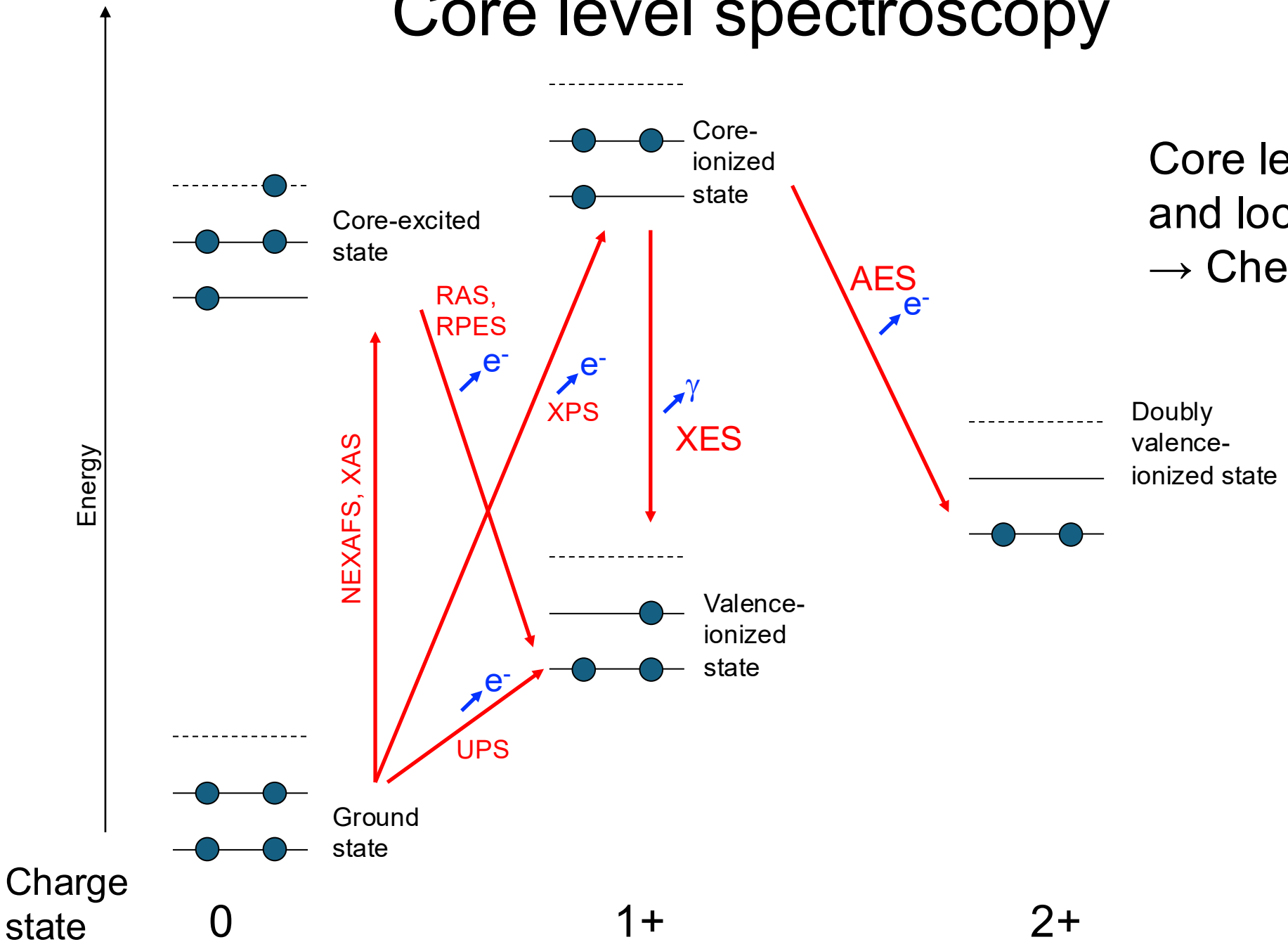


Core level spectroscopy

Specific aspects of studying liquids with core level spectroscopy

Selected examples of studying liquids with core level spectroscopy

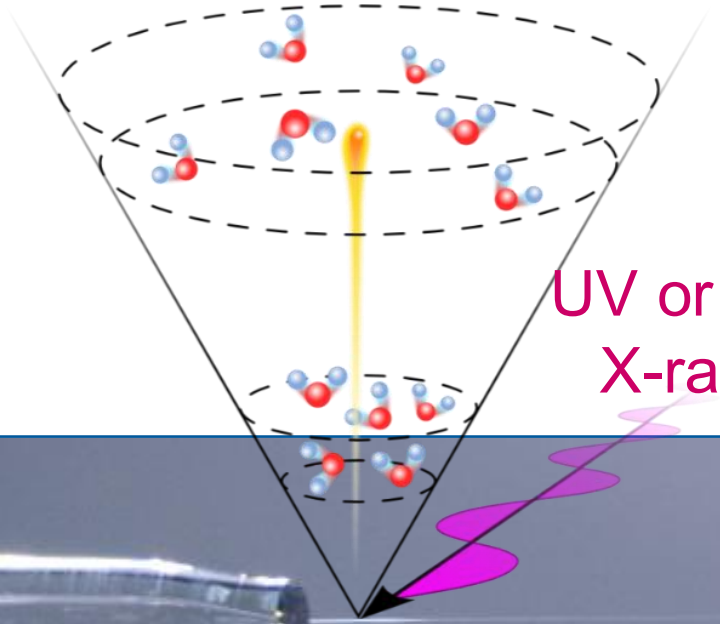
Core level spectroscopy



Core levels are atomic-like and localized
→ Chemical selectivity

Specific aspects of studying liquids with core level spectroscopy

Problem:
Electron spectroscopy requires vacuum
Liquids have high vapor pressures



Solution: The liquid microjet

jet diameter ≈ 15-25 μm
jet velocity ≈ 80 ms^{-1}

vacuum
~10^{-4} mbar

First steps

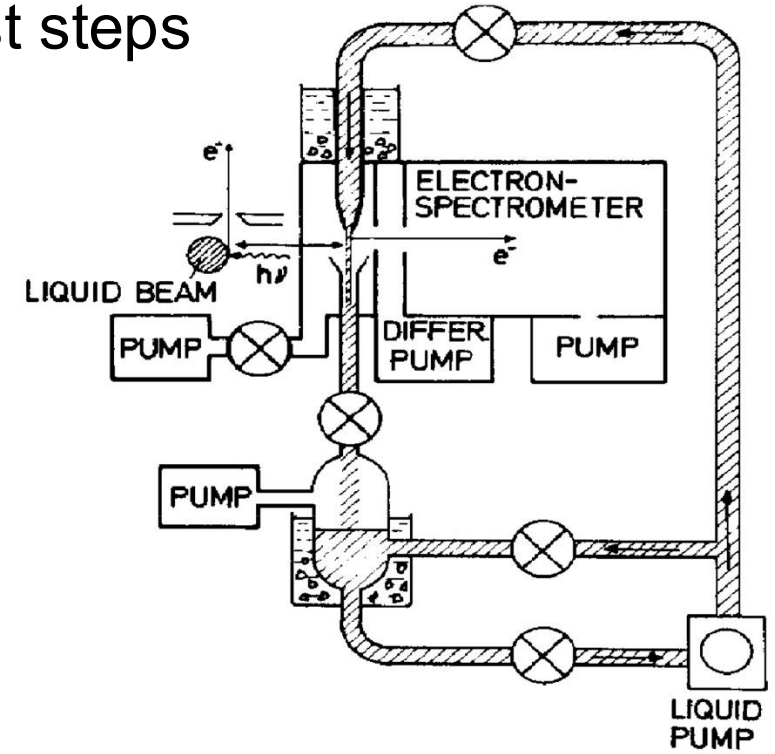
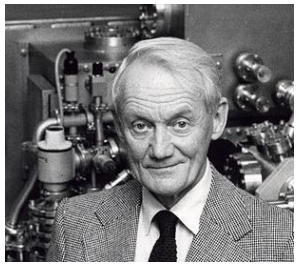


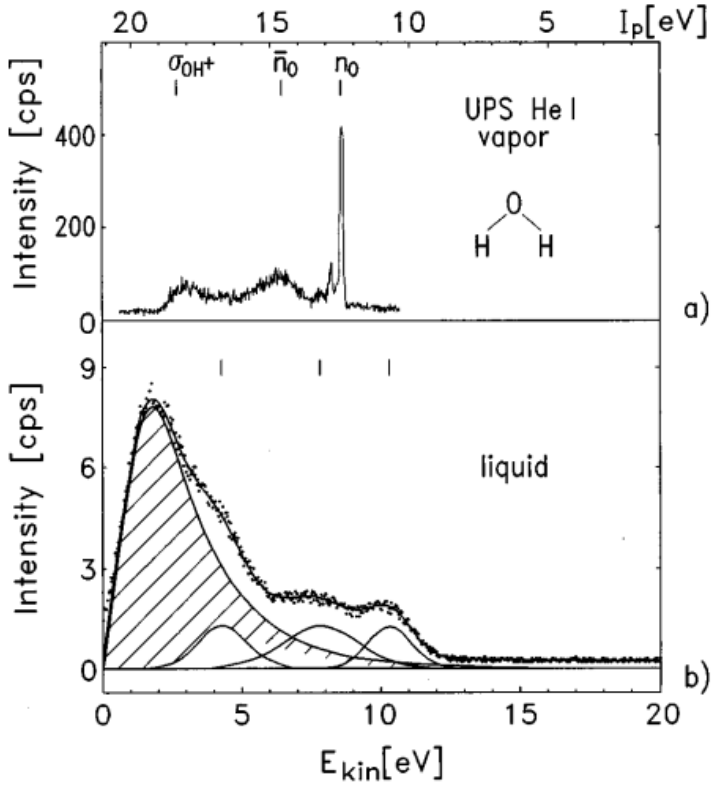
Figure 1. Principle of the liquid beam arrangement.



Hans Siegbahn and Kai Siegbahn
J. Electron Spectrosc. Relat. Phenom. 2, 319 (1973)
Limited to liquids with low vapour pressure (not water)

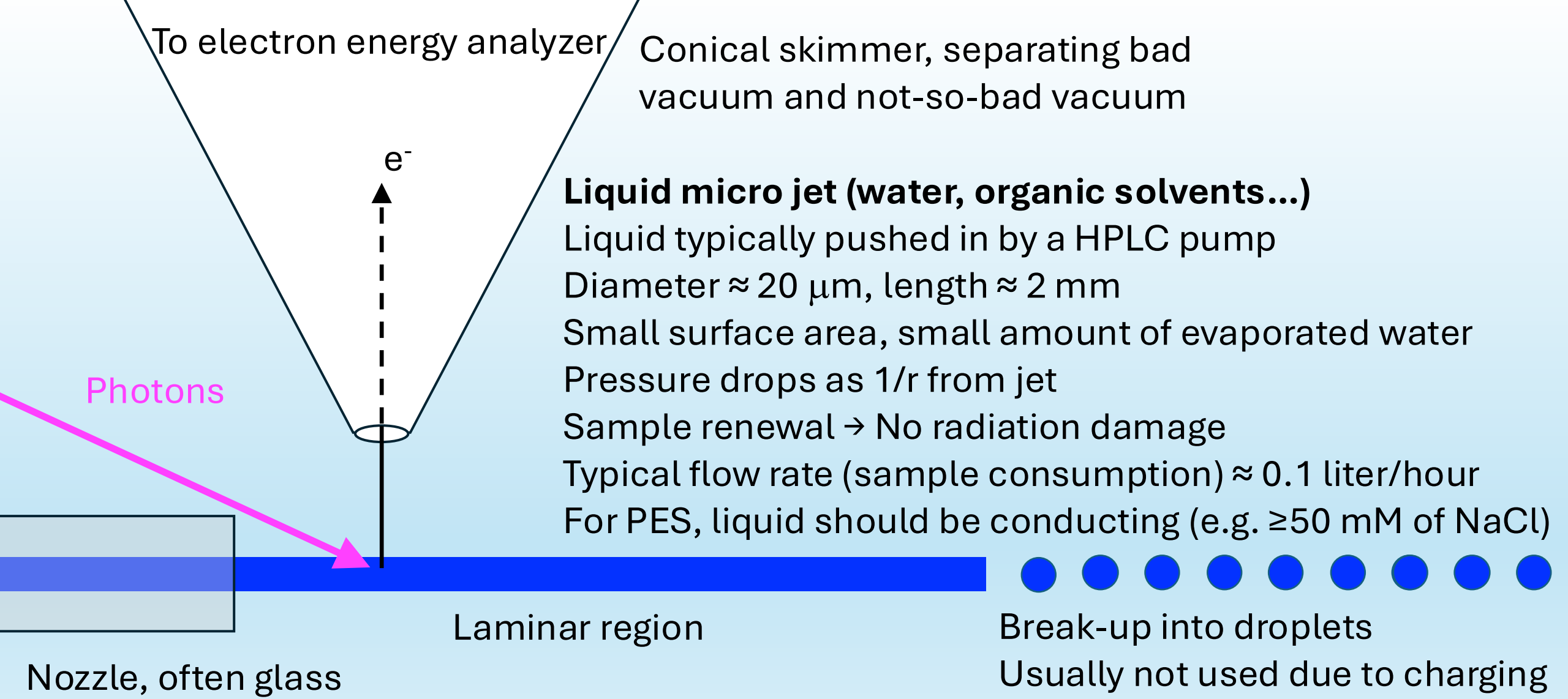
First reported liquid-water PES spectrum

Faubel et al., *JCP 106 (1997)*



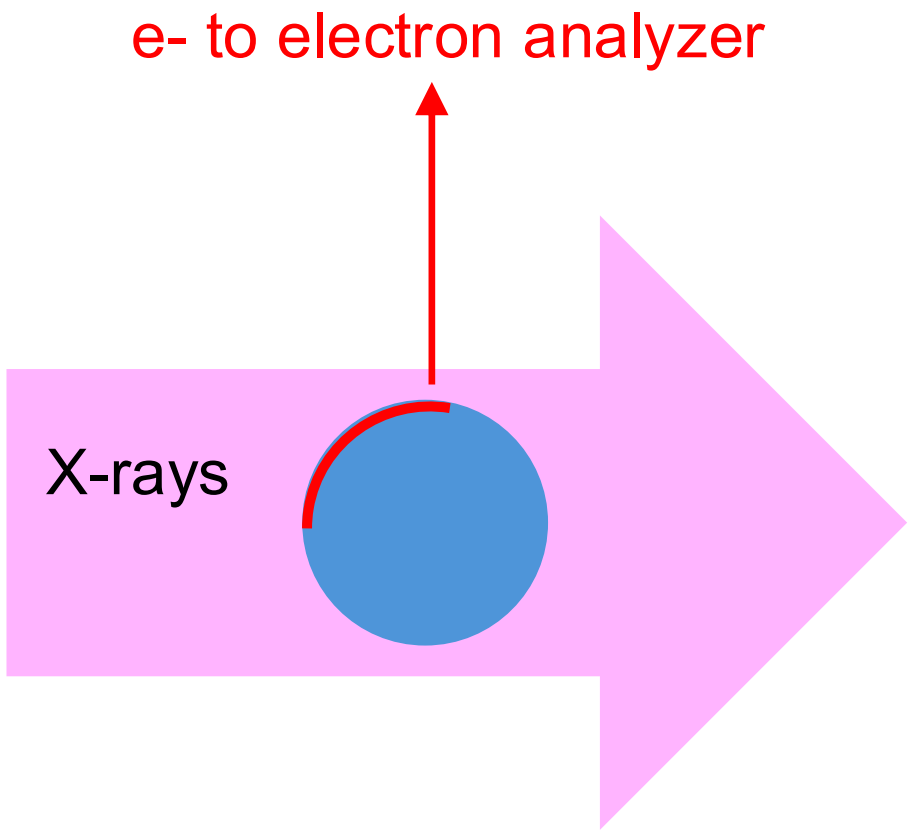
Manfred Faubel — Liquid jet PES

Bernd Winter — Liquid jet + SR


To electron energy analyzer
Conical skimmer, separating bad vacuum and not-so-bad vacuum
e-
Liquid micro jet (water, organic solvents…)
Liquid typically pushed in by a HPLC pump
Diameter ≈ 20 μm, length ≈ 2 mm
Small surface area, small amount of evaporated water
Pressure drops as 1/r from jet
Sample renewal → No radiation damage
Typical flow rate (sample consumption) ≈ 0.1 liter/hour
For PES, liquid should be conducting (e.g. ≥50 mM of NaCl)
Photons
Laminar region
Break-up into droplets
Usually not used due to charging
Nozzle, often glass

Different jet geometries

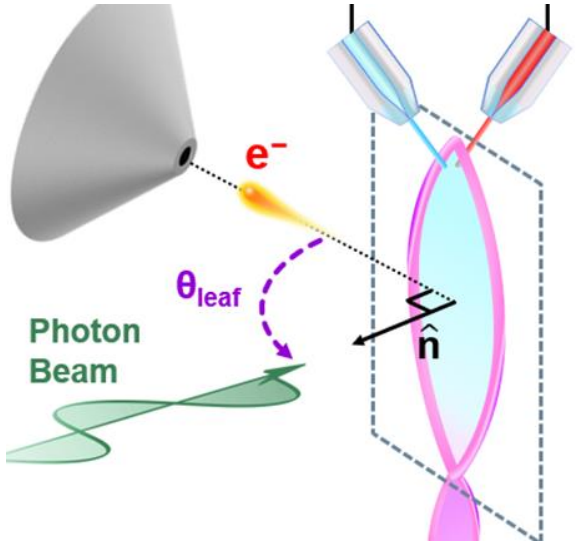
Cylindrical liquid jet



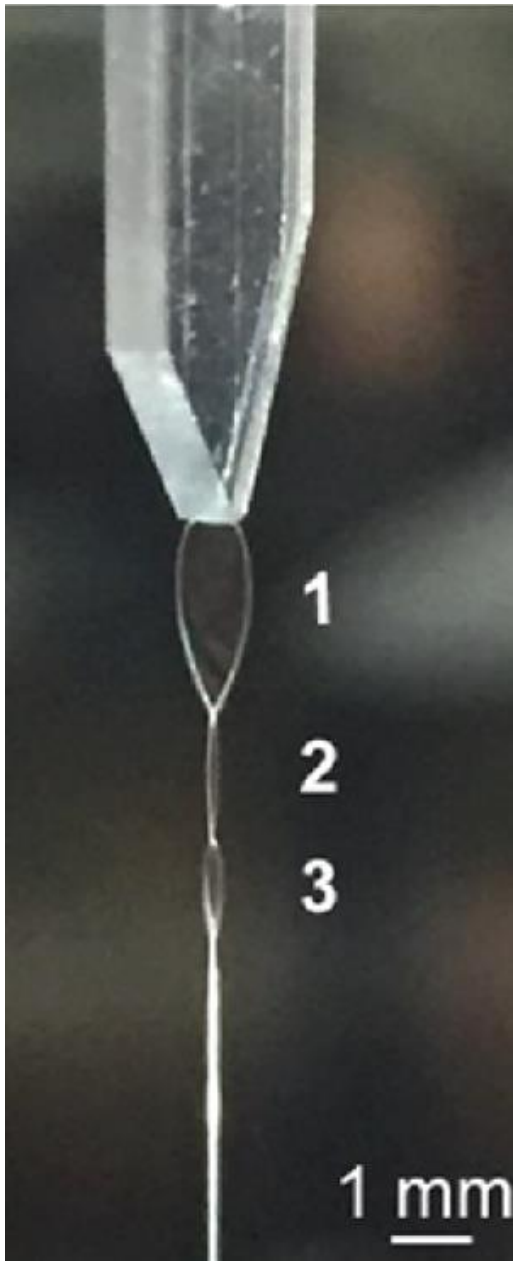
Averaging over many surface orientations

Flat liquid jet

Formed by two colliding jets

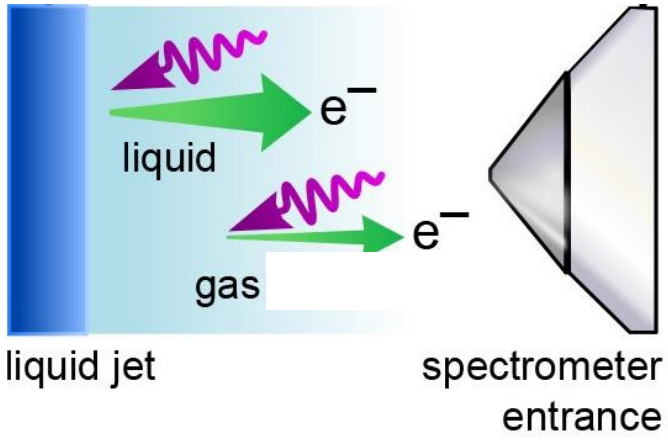


More controlled surface orientation
Mixing of two liquids possible

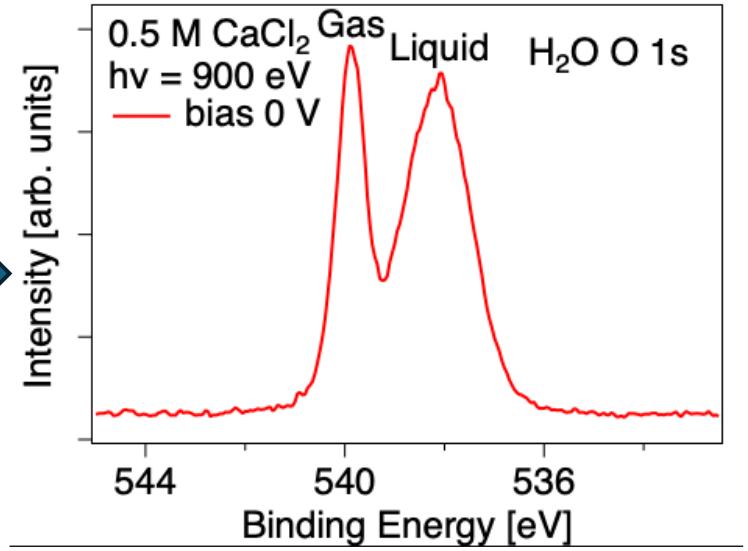


C. Lee et al., JPC. A 126, 3373 (2022)

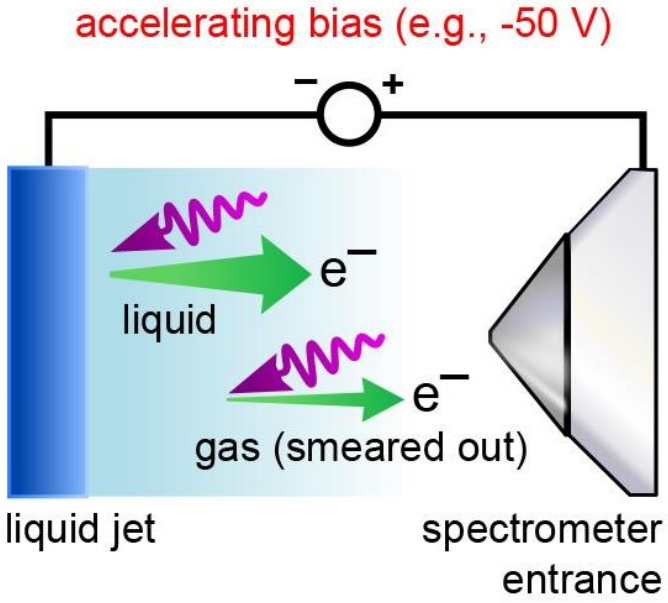
Problem: Gas-phase of volatile liquids



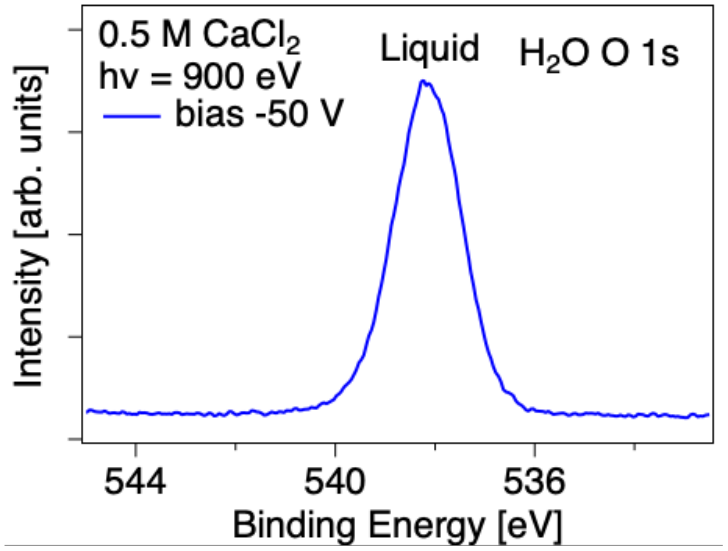
XPS spectra with liquid and gas contributions



Soultion: Applying a voltage to the jet



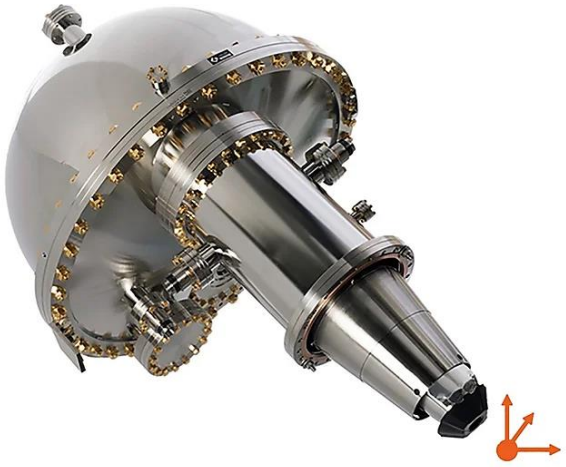
XPS spectra with only liquid contribution

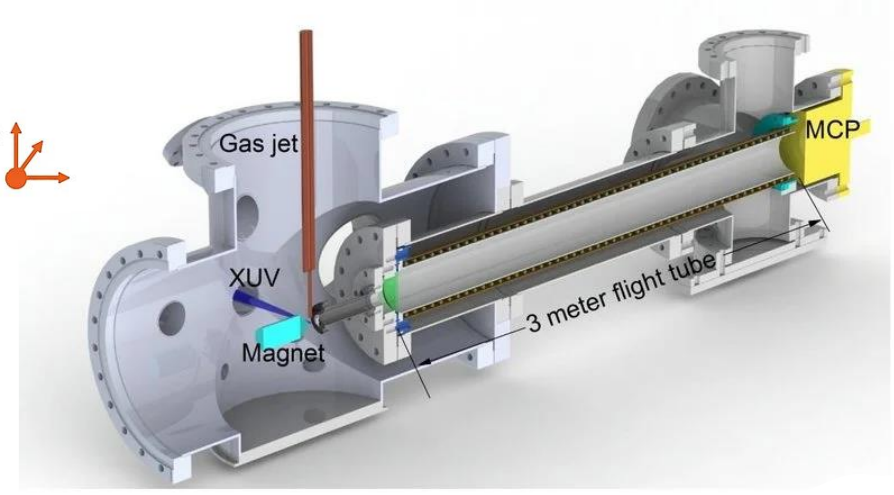


An electric bias can be used to remove the gas phase signal.

Electron energy analysers:

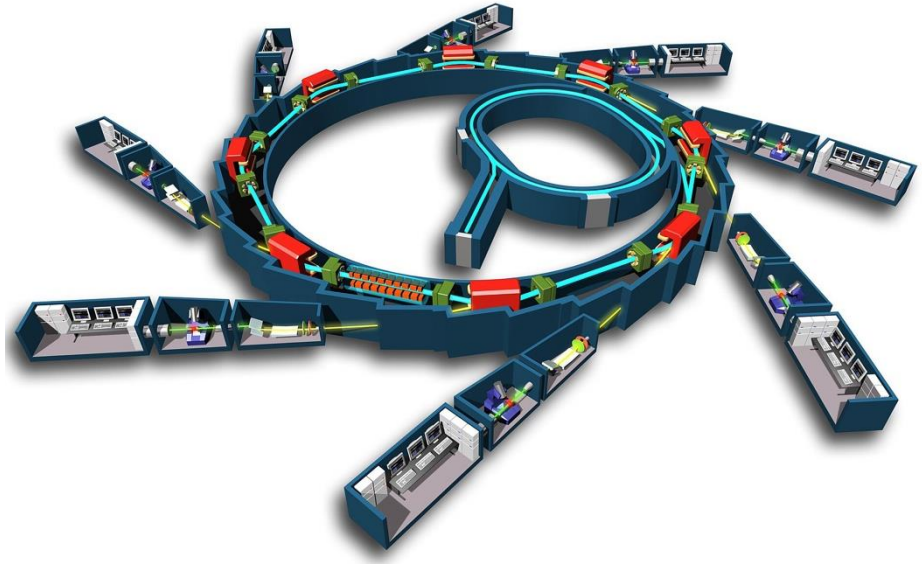
- Hemispherical
- Magnetic bottle
- Velocity map imaging



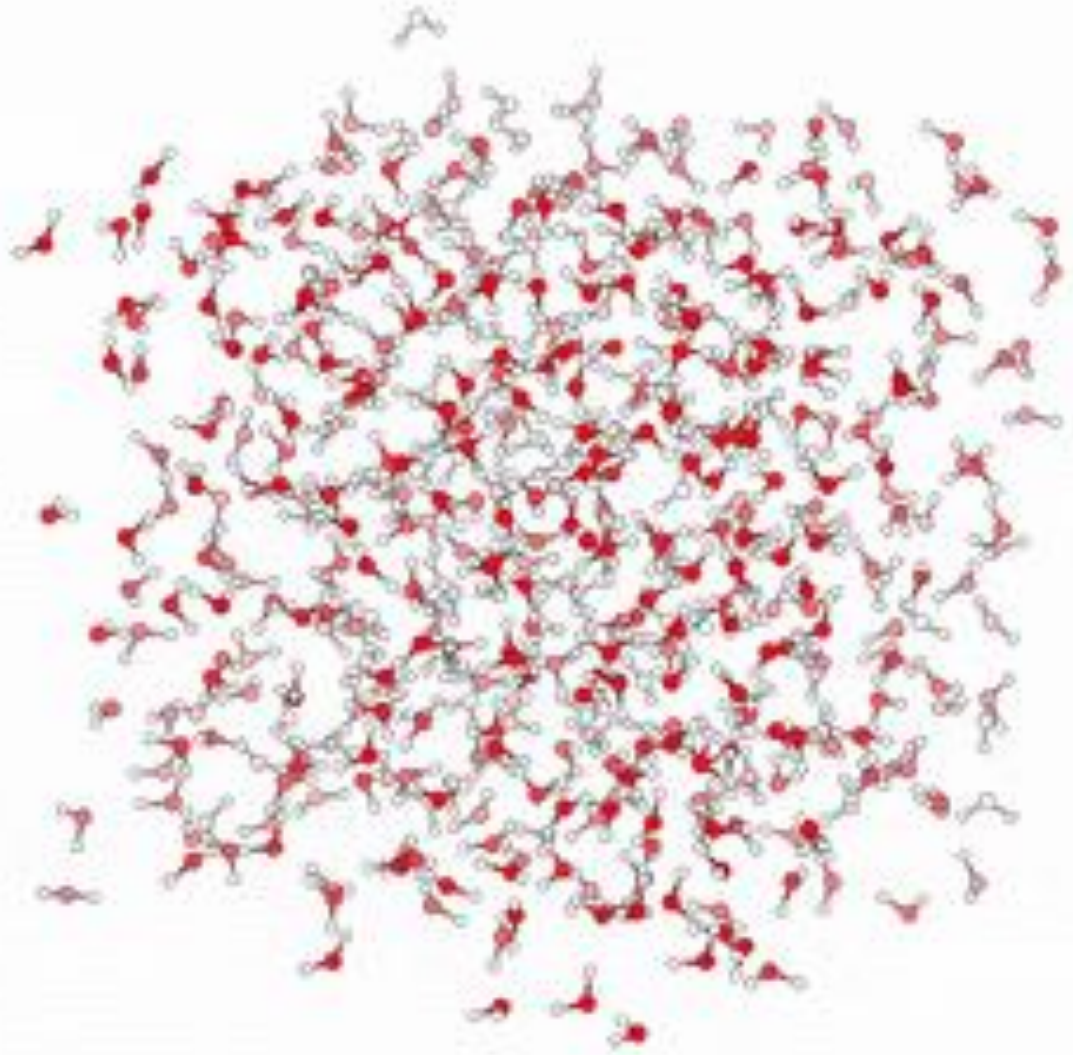


Light sources:

- Synchrotron radiation
- He lamps
- Time-resolved studies:
- High harmonic generation lasers
- Free electron lasers



Simulating XPS spectra for liquids

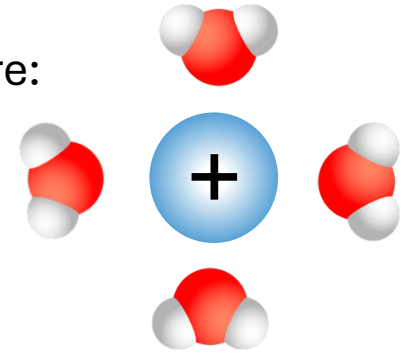


What do you need to know to simulate XPS spectra?

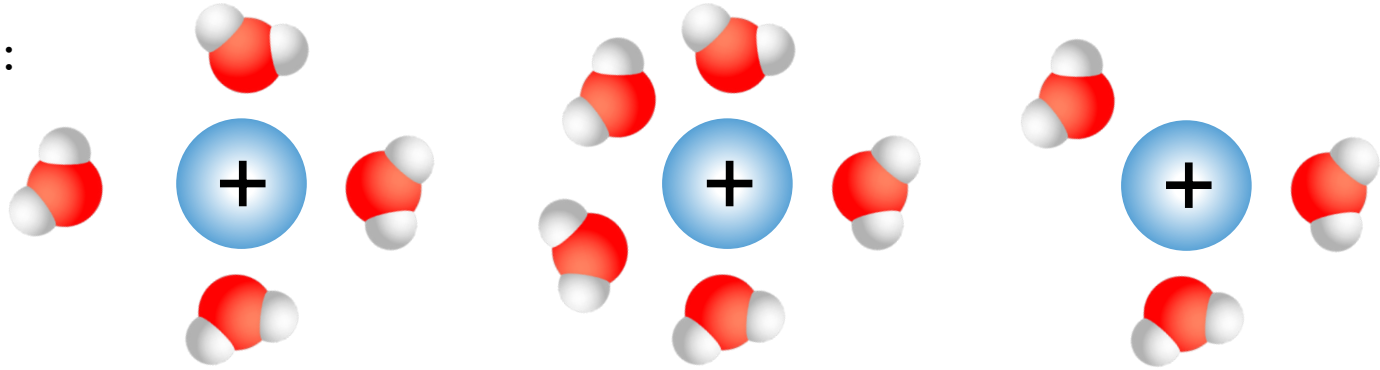
Simulating XPS spectra for liquids

Liquids are dynamic and disordered → there is not a single, static molecular configuration

Cation in water
Idealized structure:



Real
structures:



Solution:

Generate a representative liquid structure using molecular dynamics

Extract a statistically significant number of snapshots

For each extracted liquid snapshot, calculate the relevant binding energies

Often 1-2 solvation shells are treated explicitly with QM, further shells are replaced by a continuum

Average the calculated binding energies over all liquid snapshots

What is an aqueous solution?

Dynamically disordered condensed matter?

Delocalized electronic structure

Fermi level

Work function

…

Many weakly interacting molecules together?

Localized orbitals

Intermolecular bonding not covalent,

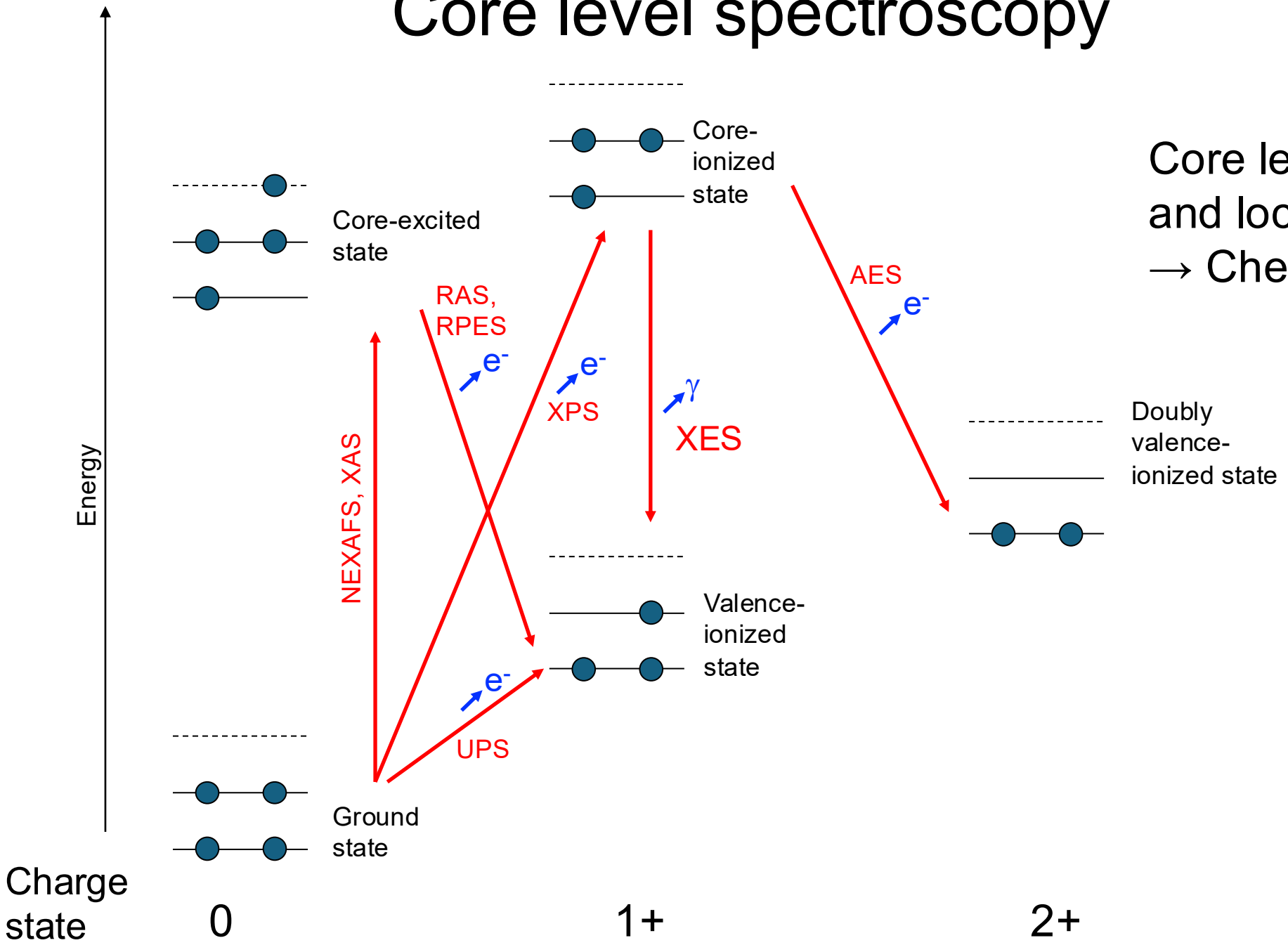
but ion-dipole, hydrogen bonding, dipole-dipole etc

Local vs non-local processes

…

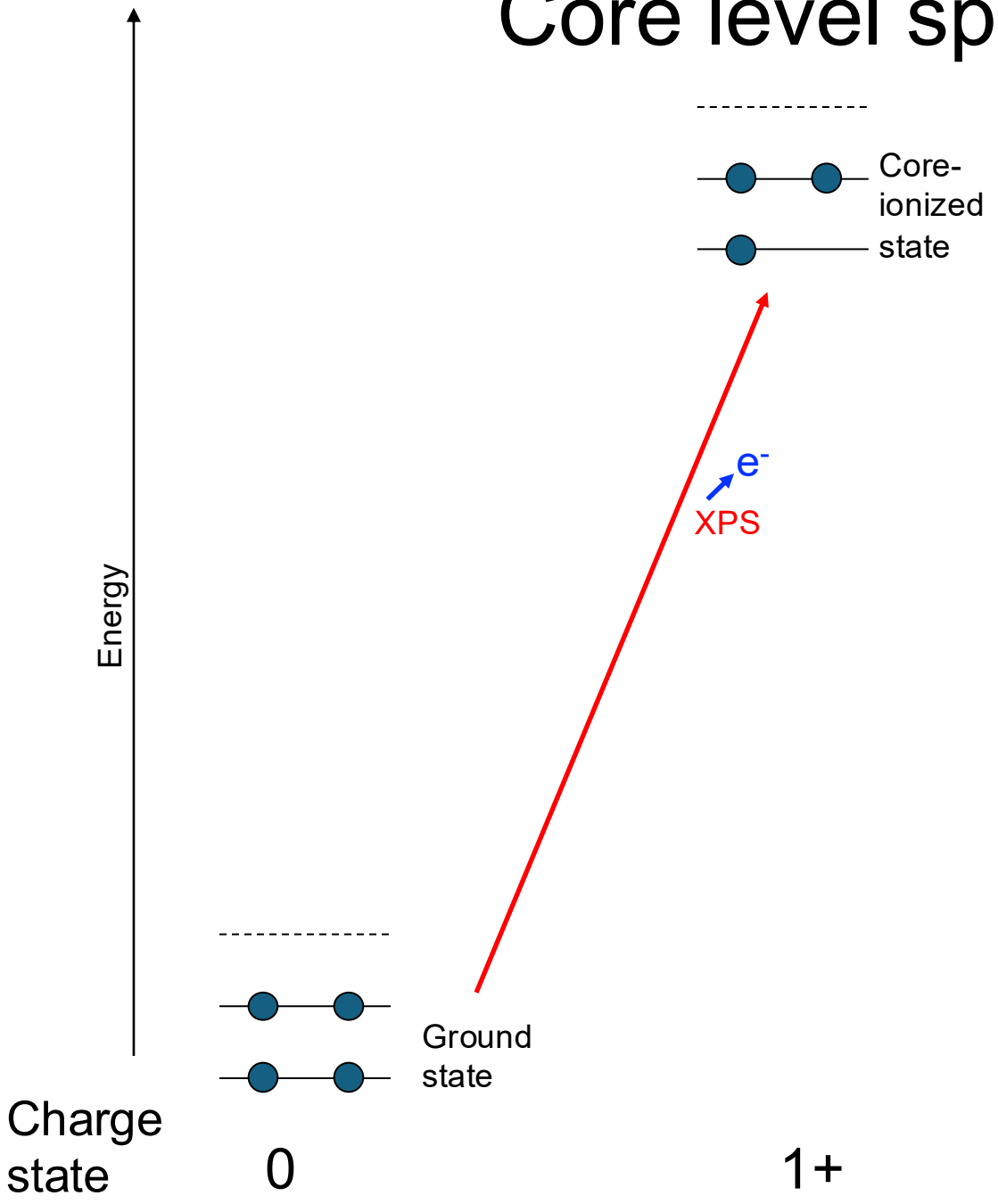
Selected examples of studying liquids with core level spectroscopy

Core level spectroscopy



Core levels are atomic-like and localized
→ Chemical selectivity

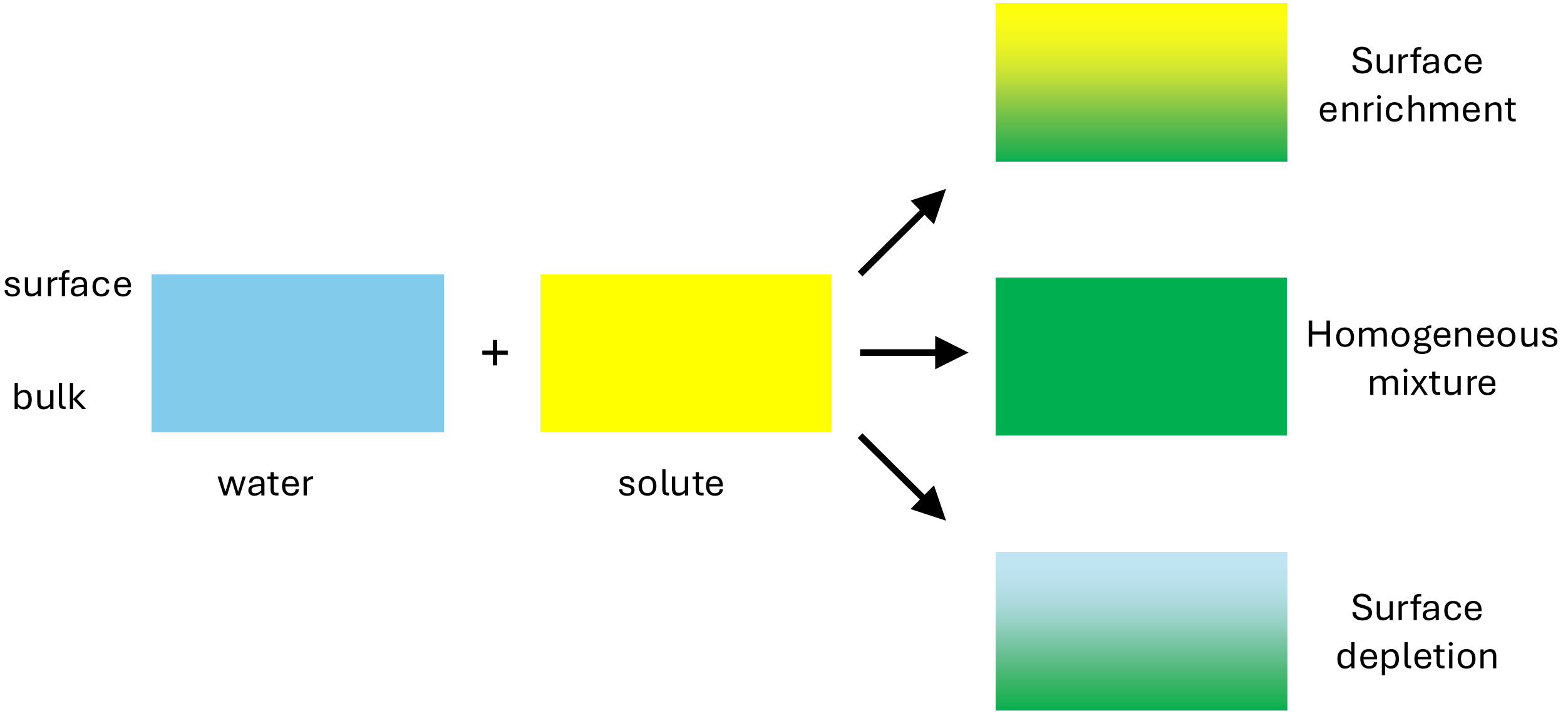
Core level spectroscopy



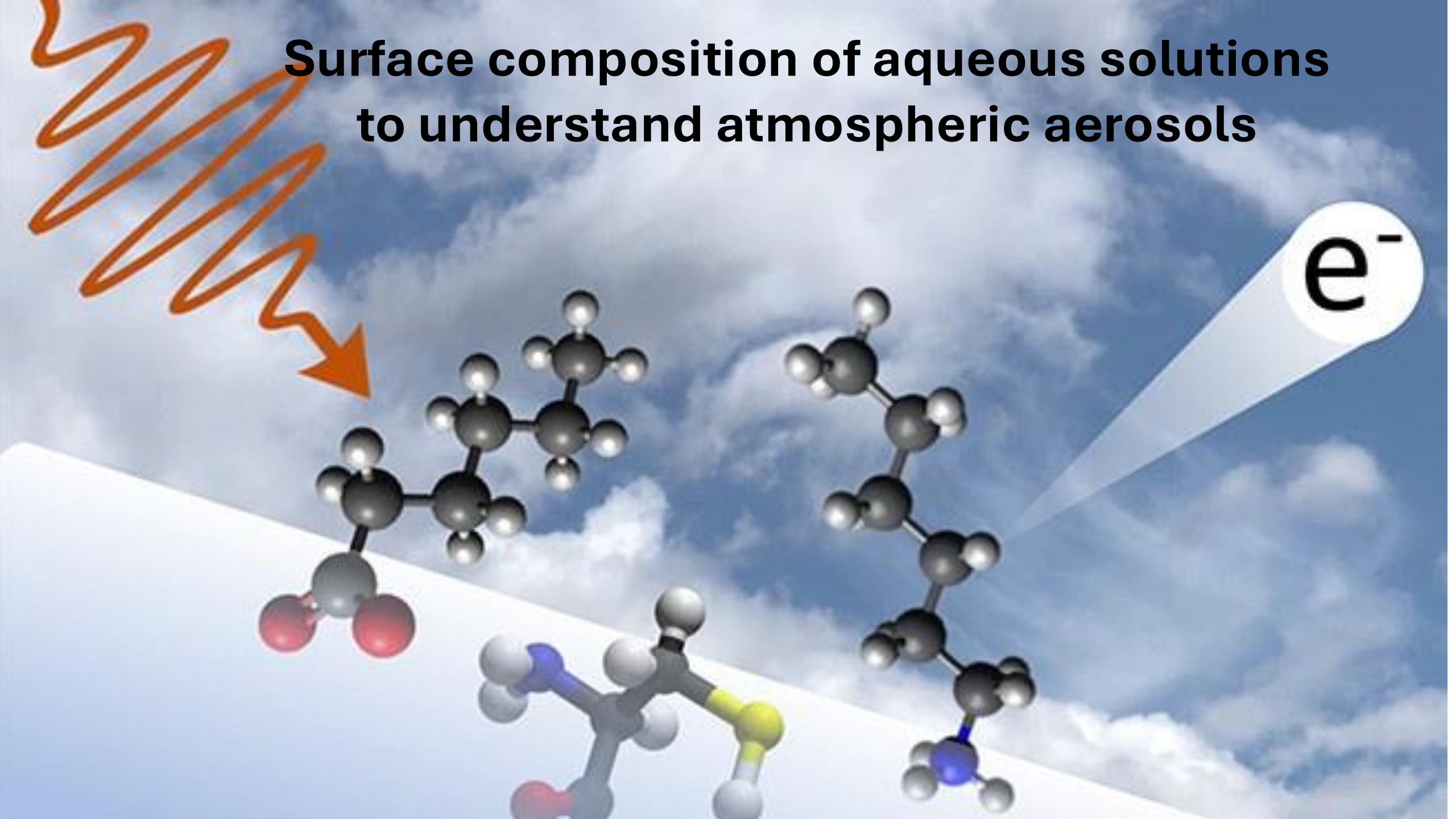
Core levels are atomic-like and localized
→ Chemical selectivity

Surface sensitivity

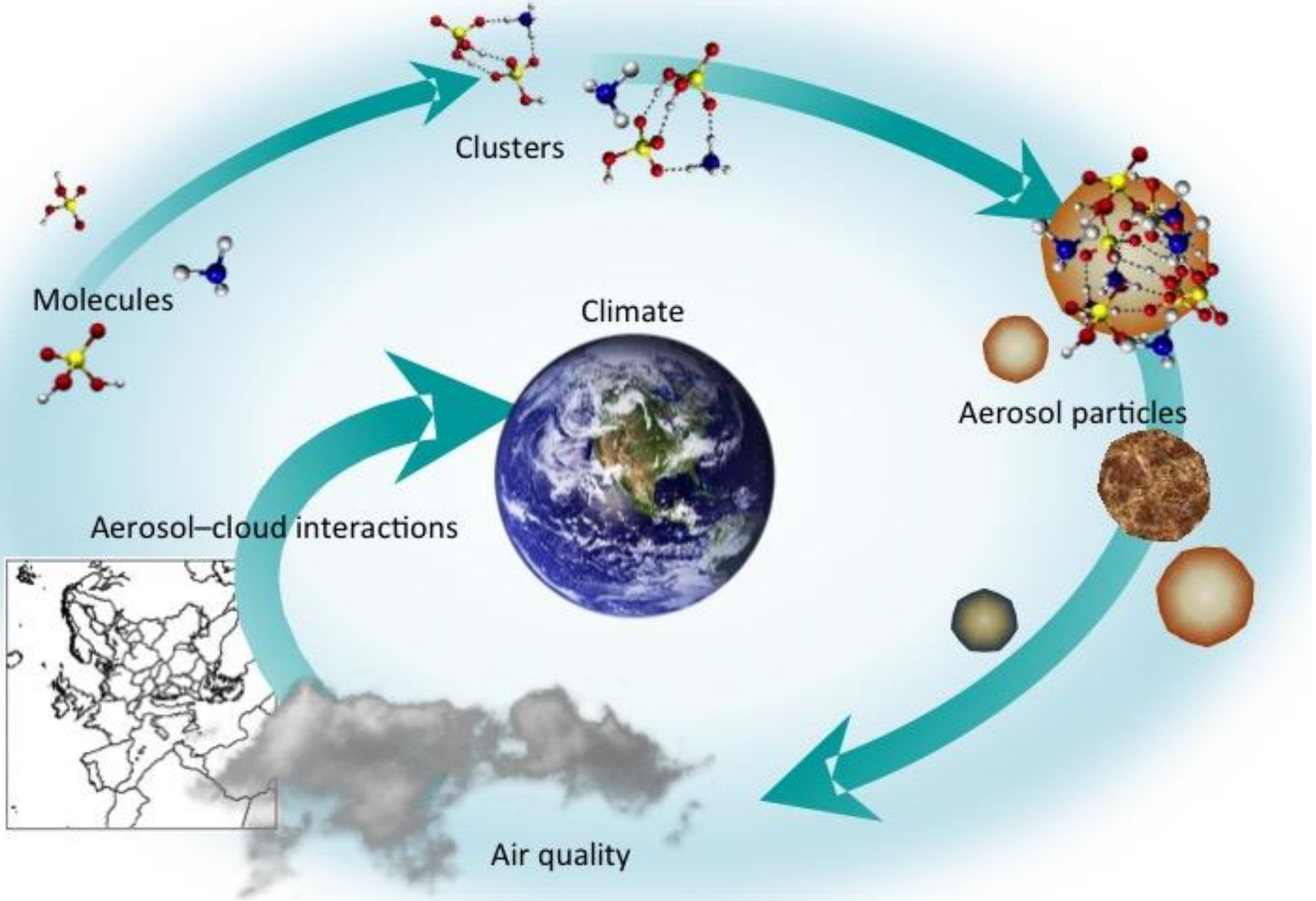
Surface composition of aqueous solutions



Surface composition of aqueous solutions to understand atmospheric aerosols



Atmospheric aerosols



Reflect sunlight

+

Promote cloud formation

↓

Cool the Earth

IPCC: Large uncertainty in climate models

Complex composition

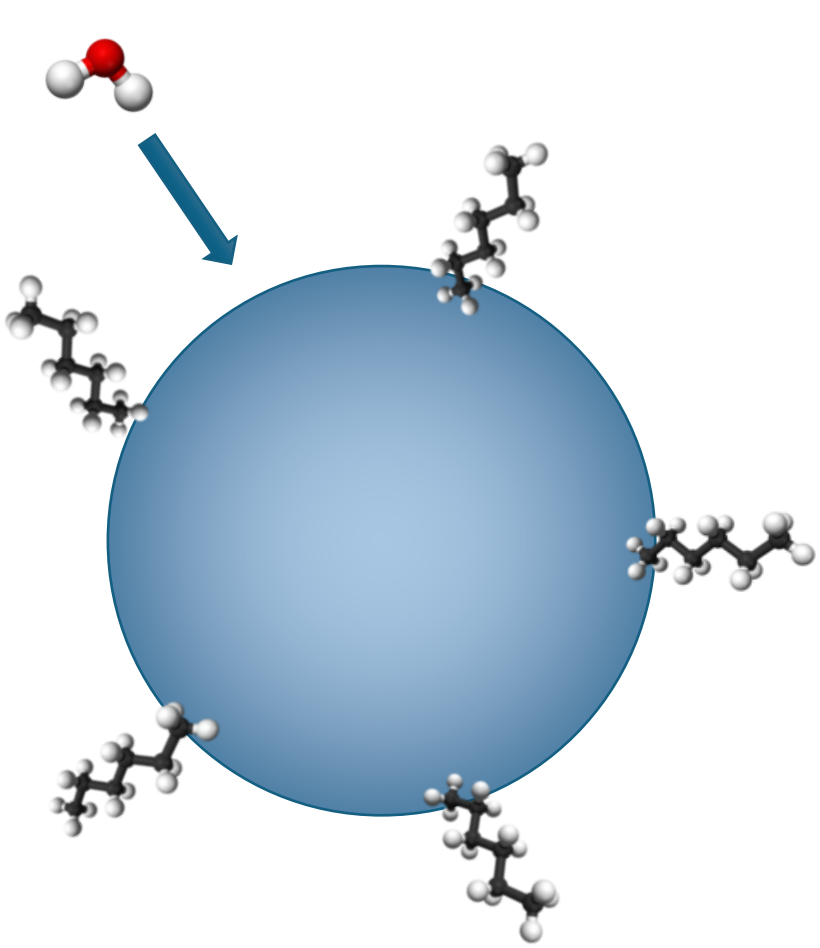
Small size

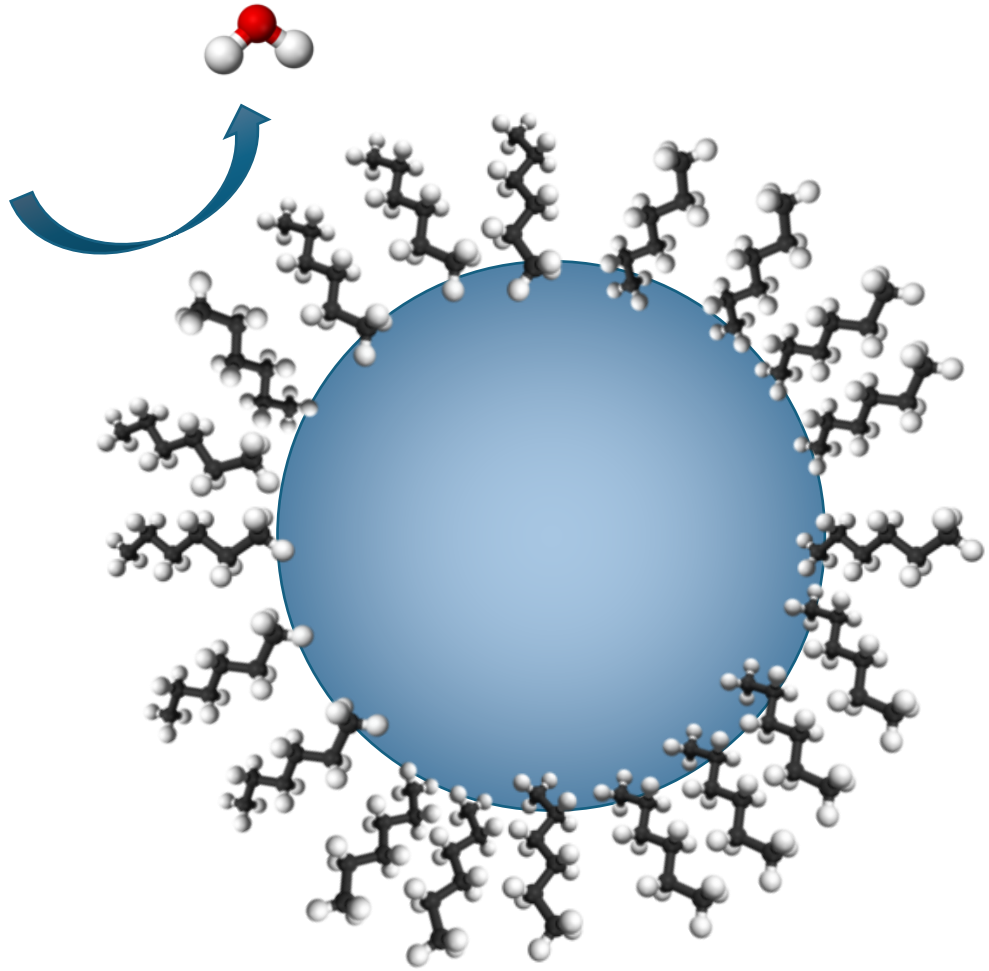
↓

Surface important

Water accommodation

Nanoparticles → Cloud droplets → Raindrops



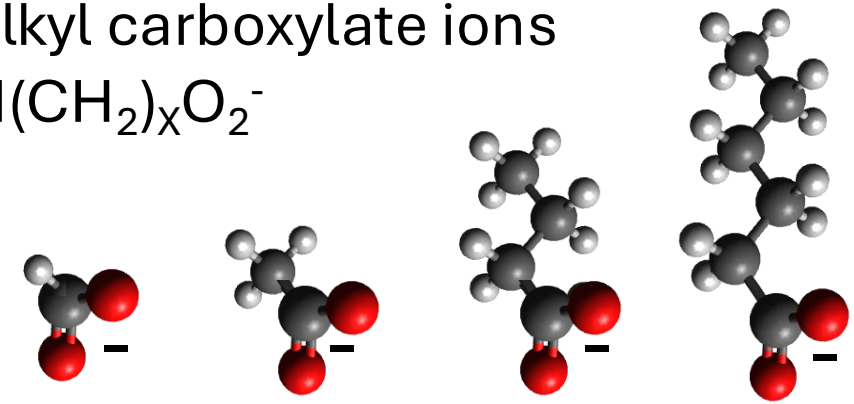


Affected by organic surfactants

How do organic ions behave at aerosol surfaces?

Alkyl carboxylate ions

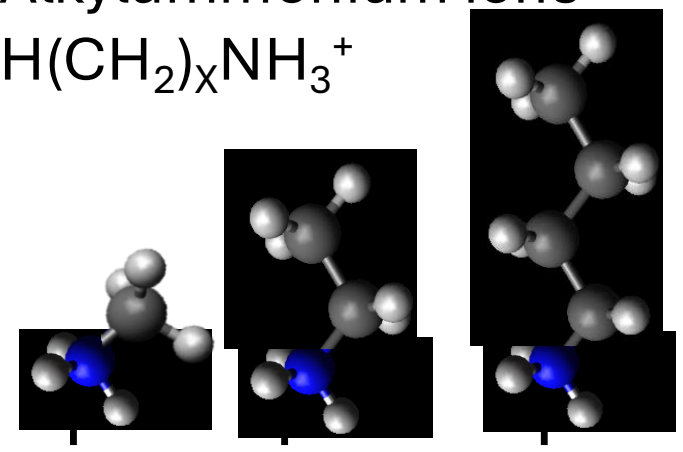
$H(CH_2)_XO_2^-$

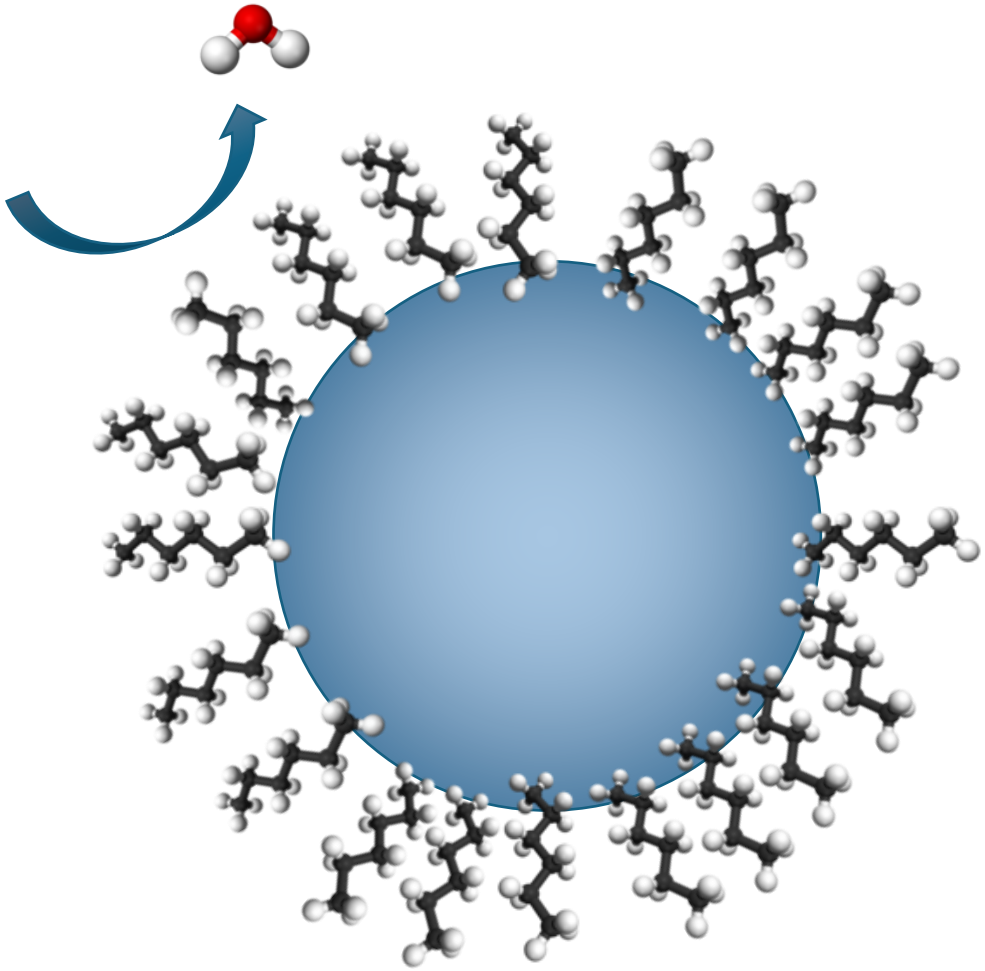


X=1,2,4,6

Alkylammonium ions

$H(CH_2)_XNH_3^+$





How do organic ions behave at aqueous surfaces?

Alkyl carboxylate ions

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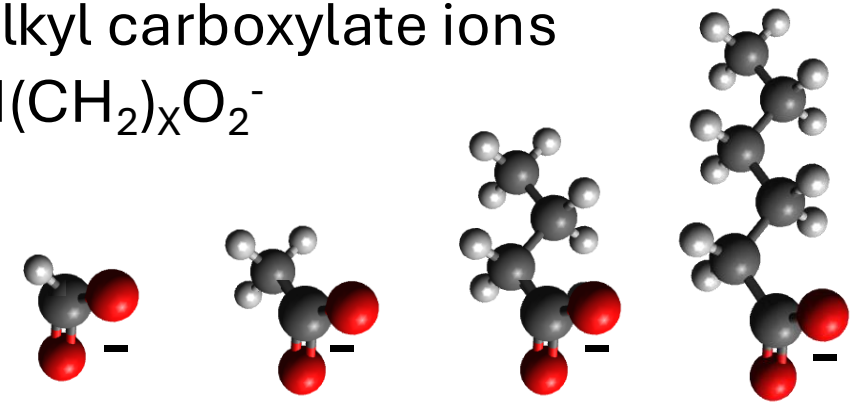

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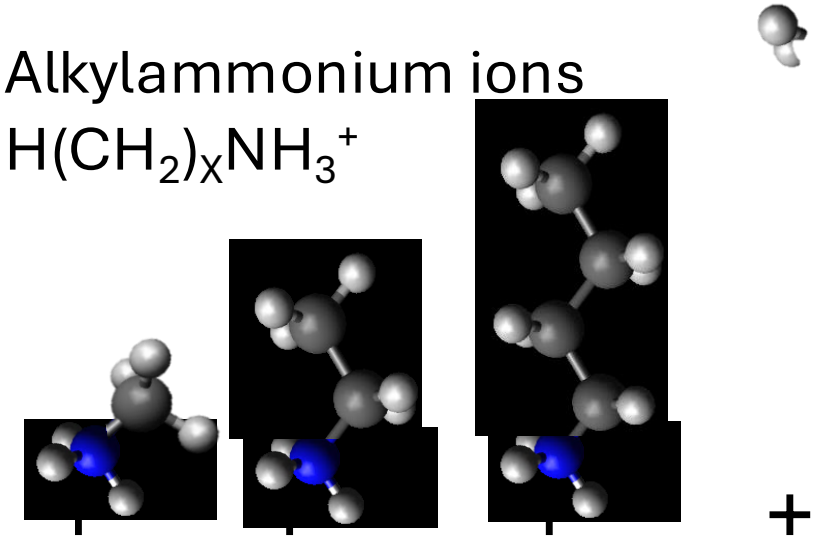

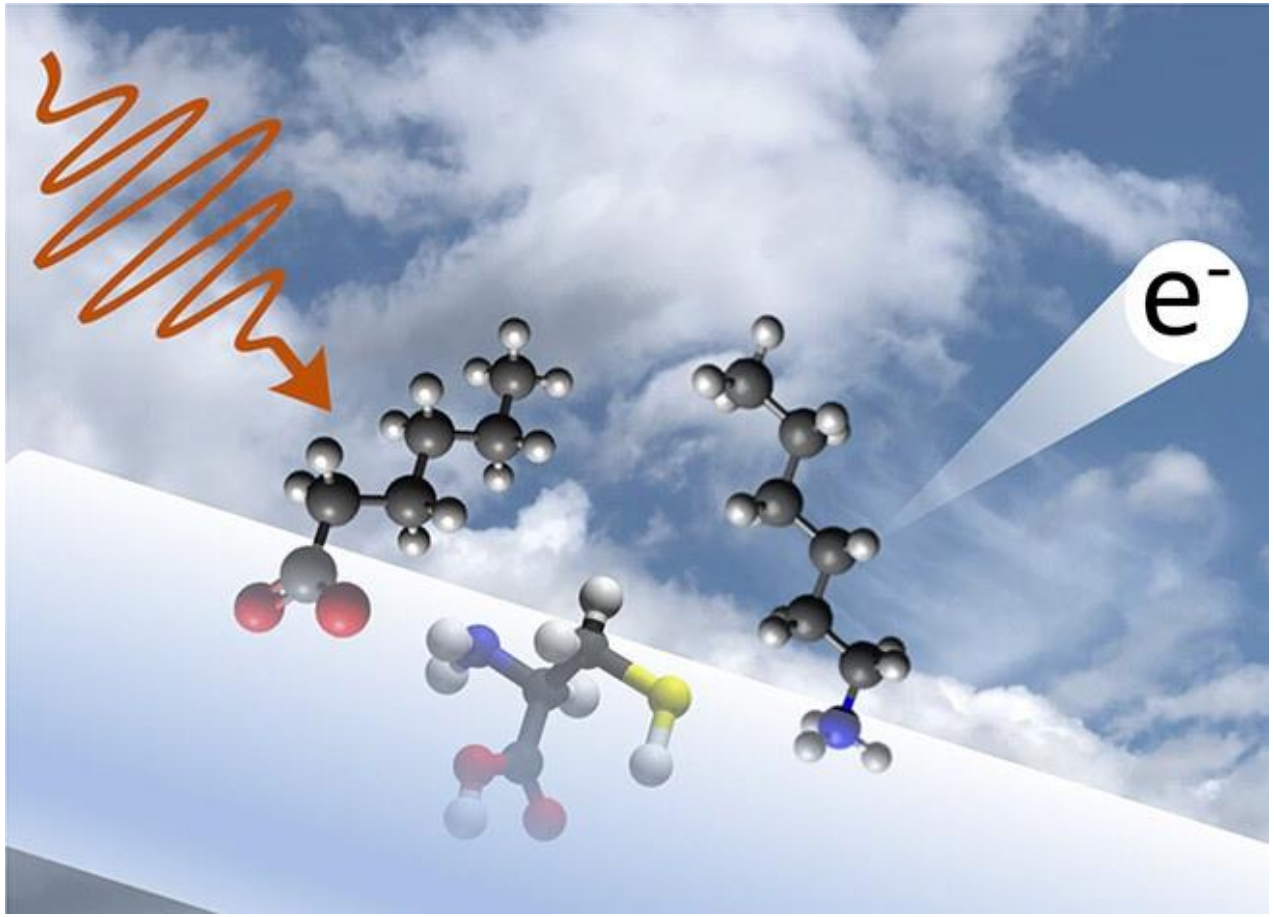

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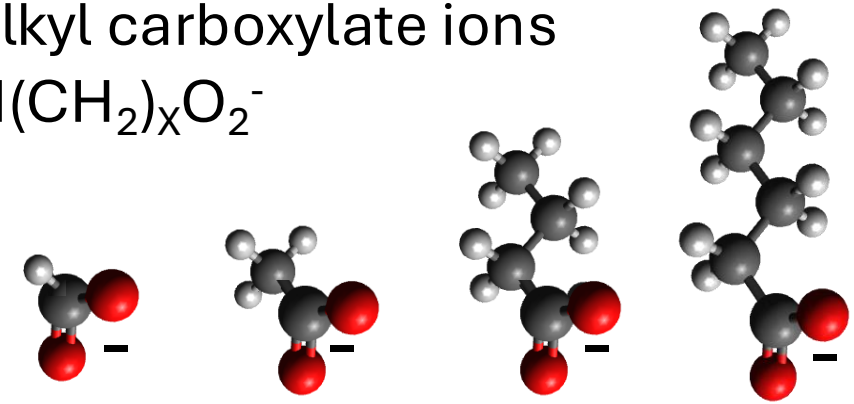

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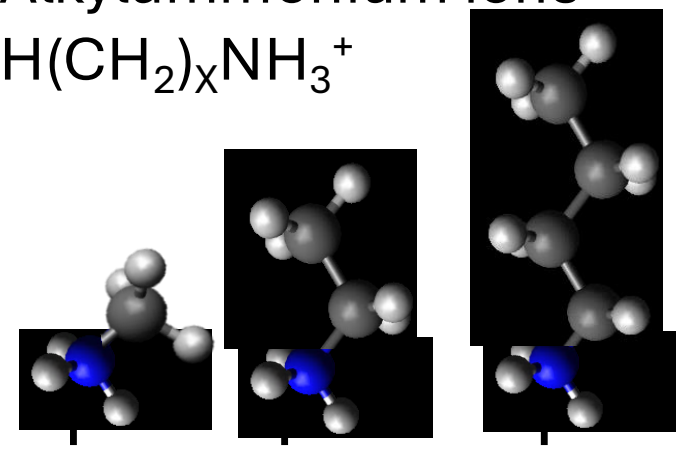
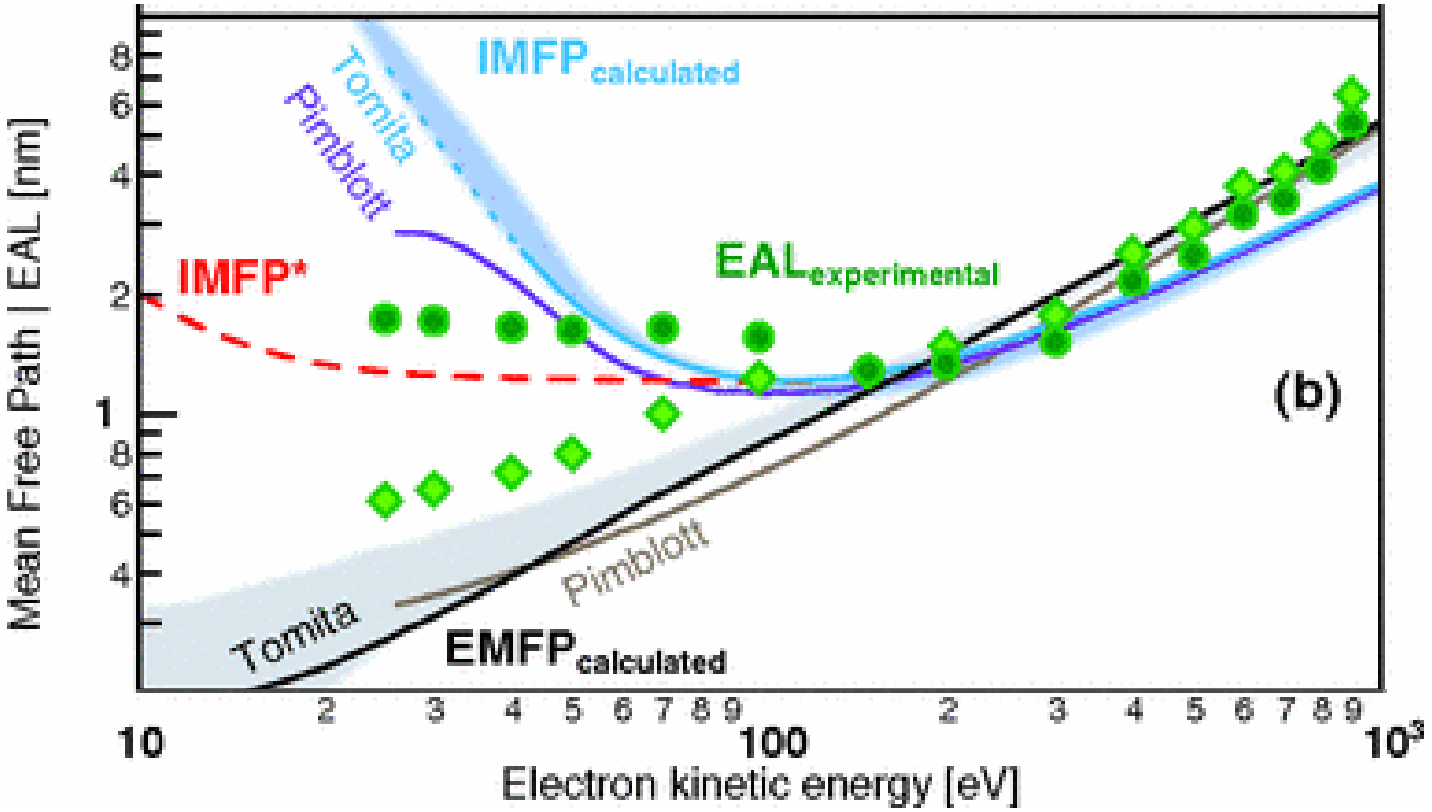


+

Electron inelastic scattering in liquid water



→ High surface sensitivity

Thürmer et al., Phys. Rev. Lett. **111**, 173005 (**2013**)

Alkyl carboxylate ions

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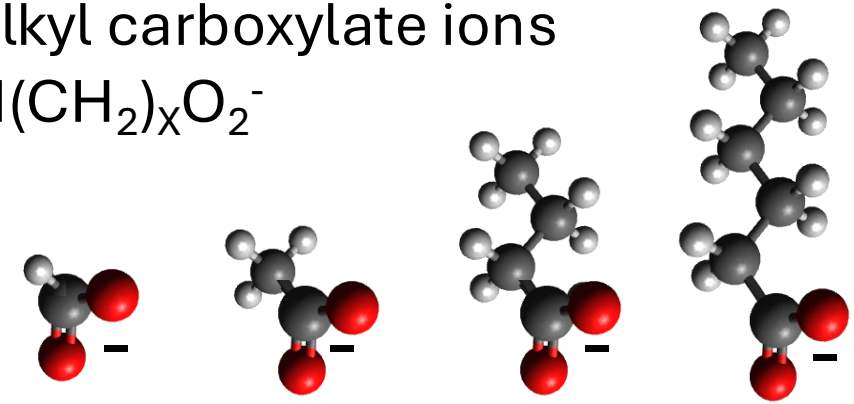

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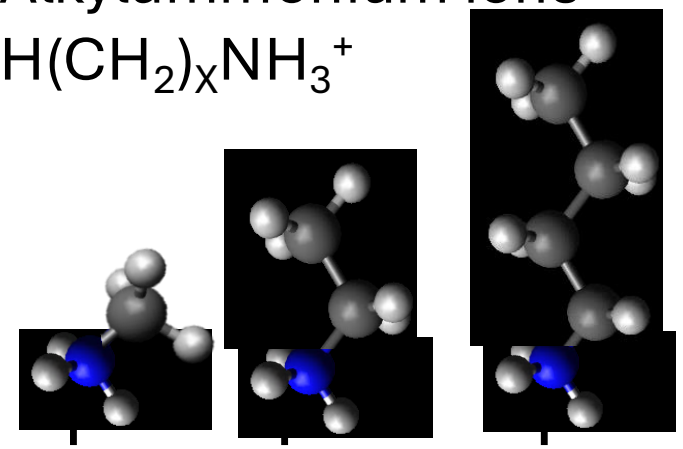
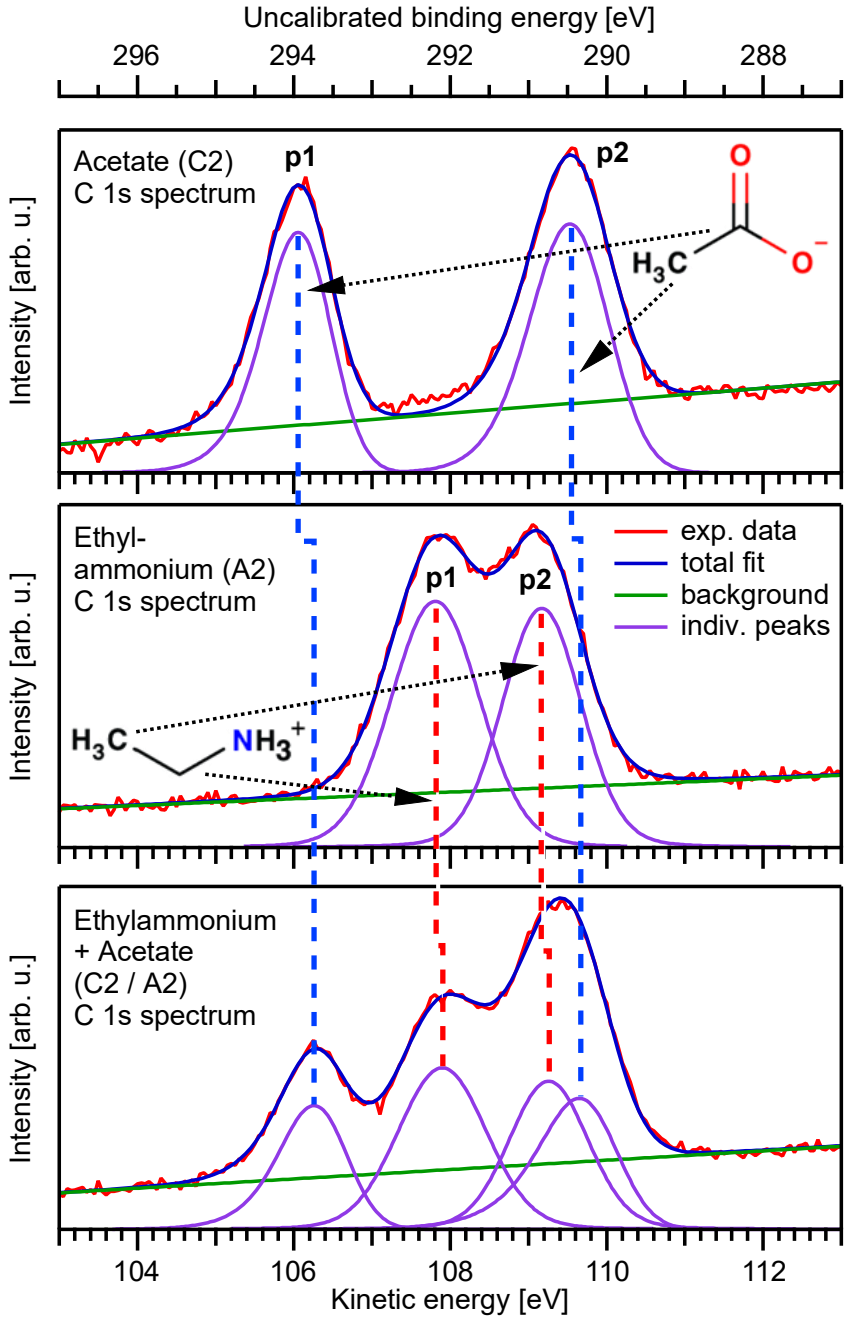


Surface-sensitive C 1s XPS



Alkyl carboxylate ions

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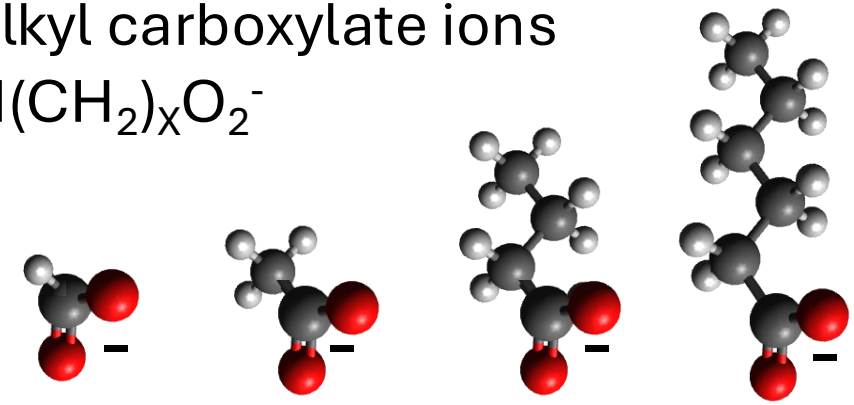

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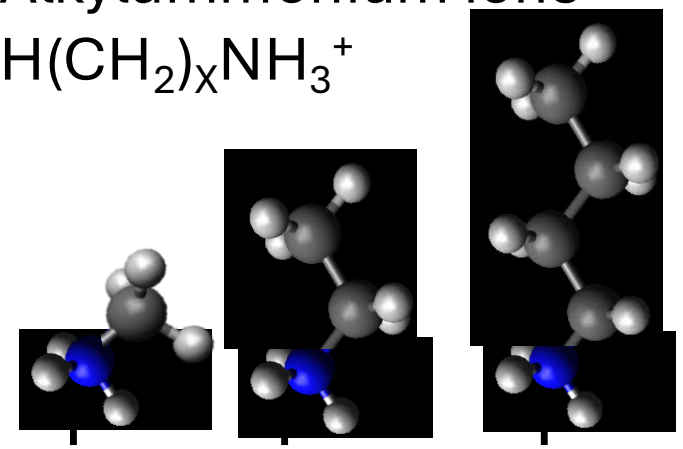
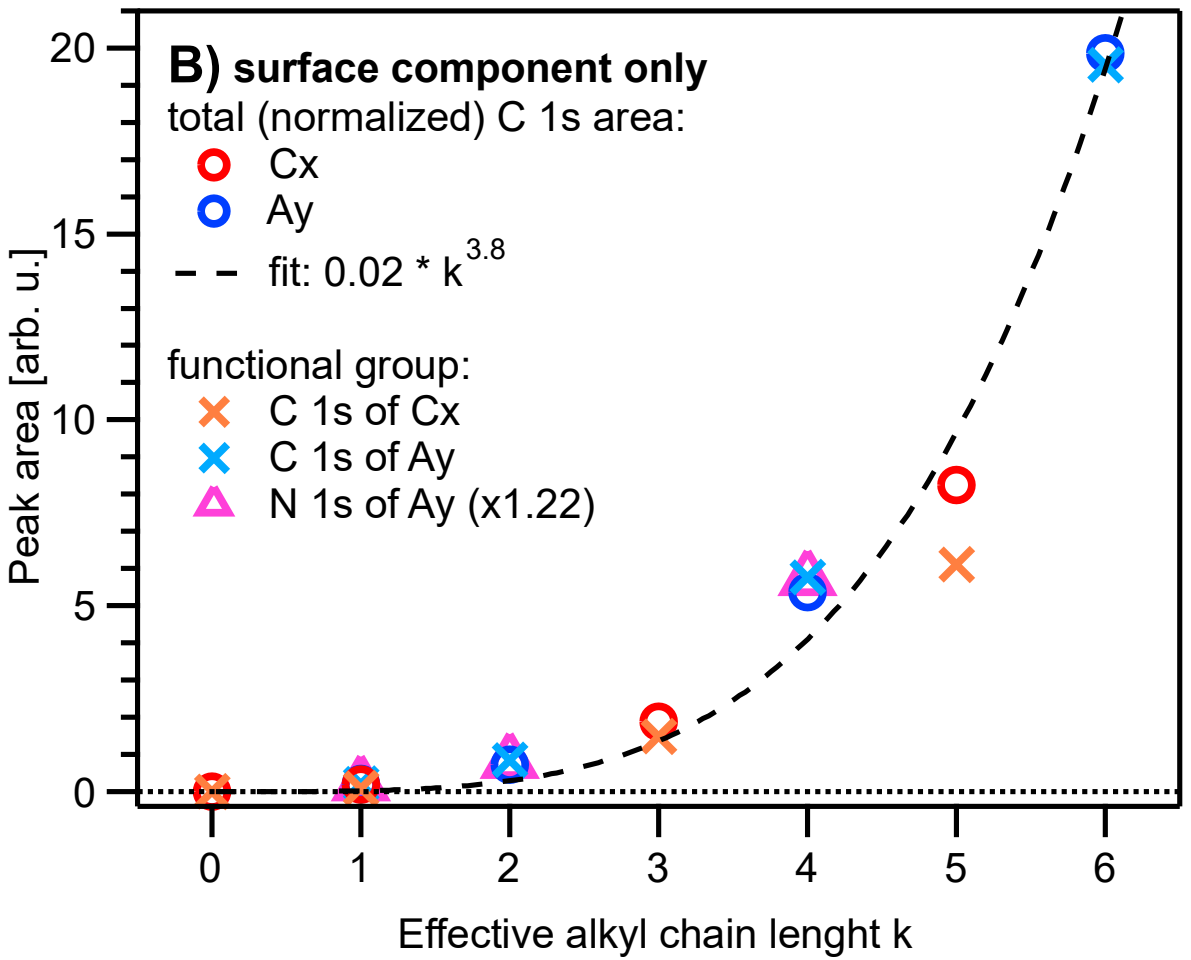


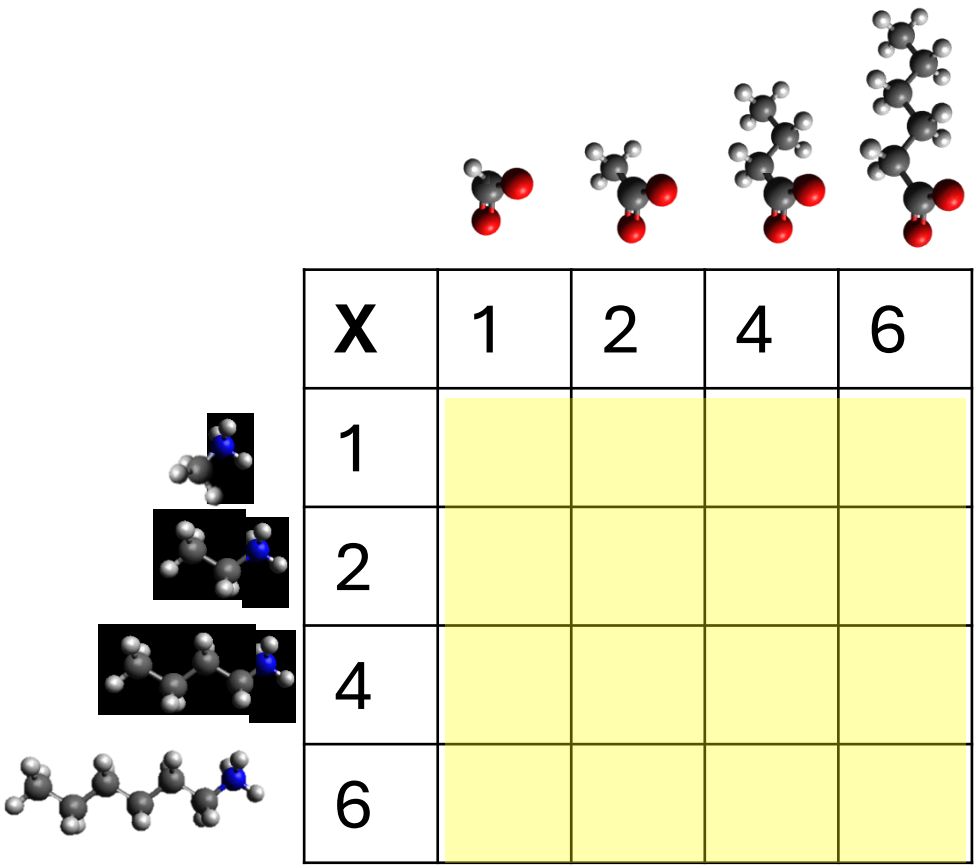
+

Surface-contribution of C 1s XPS intenisty / X



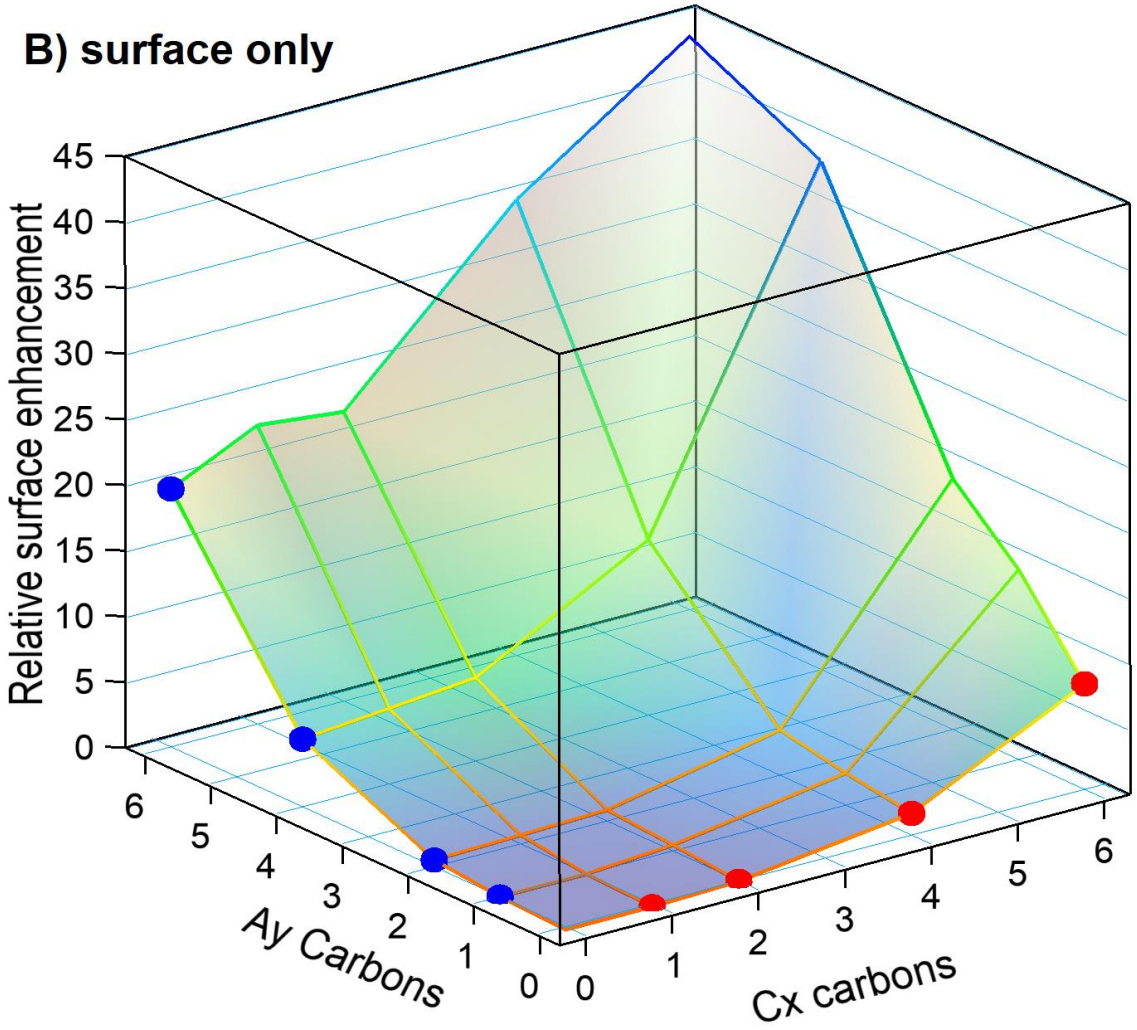
Surface propensity increases with alkyl chain length

How do they behave together?



X	1	2	4	6
1				
2				
4				
6				

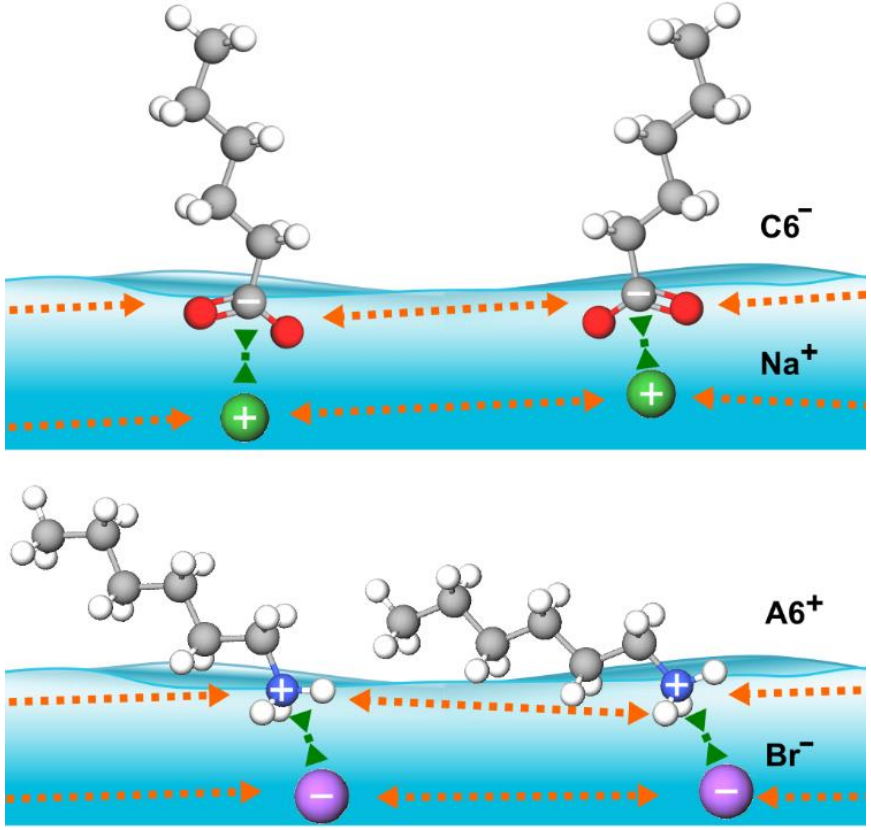
Surface-contribution of C 1s XPS intenisty / X



→ Strong co-operative surface propensity

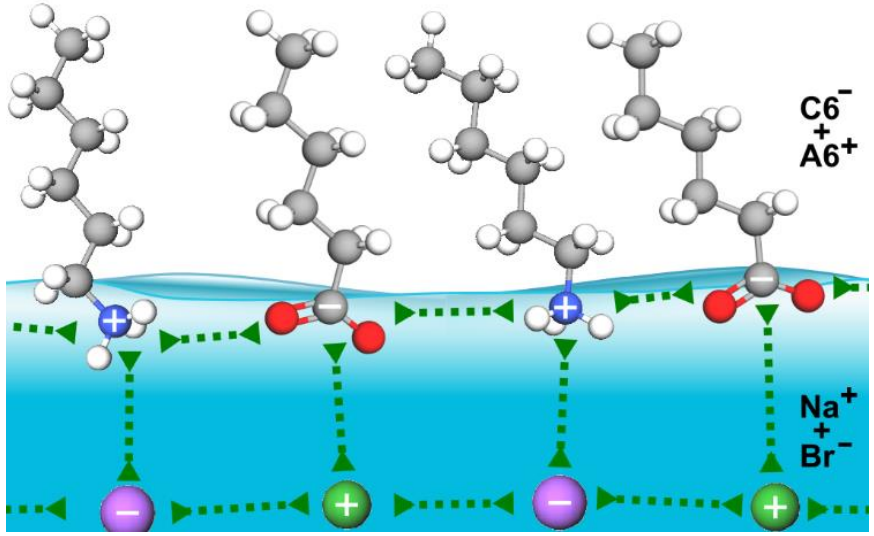
Mechanism of co-operative surface propensity

Organic ions + inorganic counter ions



Repulsion between surfactants
Low surface propensity

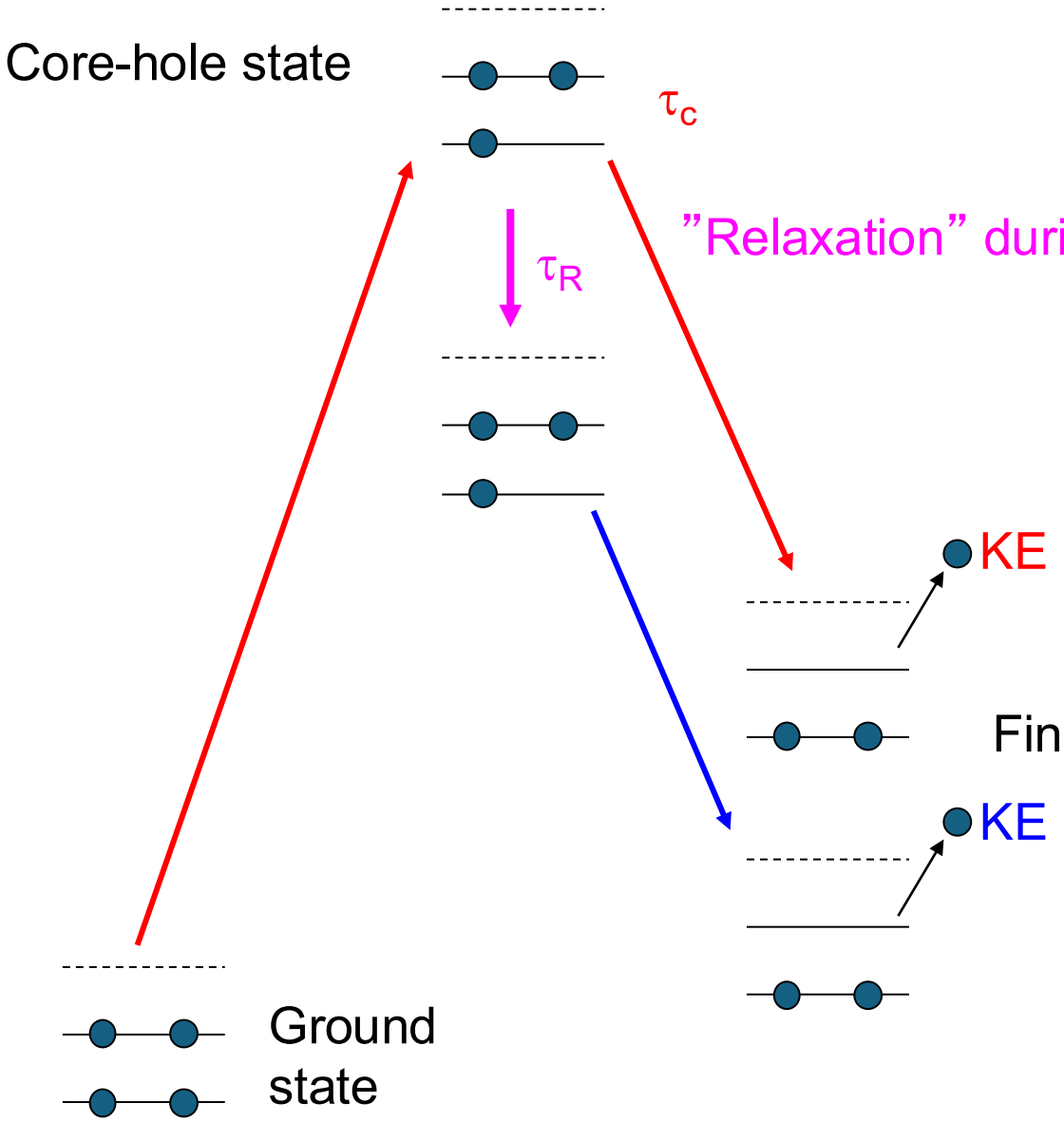
Organic cations + organic anions



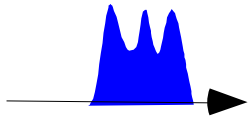
Attraction between surfactants
High surface propensity

H Kaur et al, ACP 25, 3503 (2025)
EASI@PO4 at PETRA III

Auger-Meitner decay



Resulting AM spectra



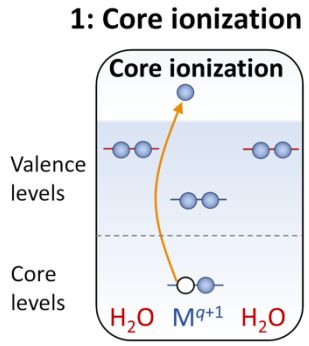
Core hole life time τ_c ≈ a few fs

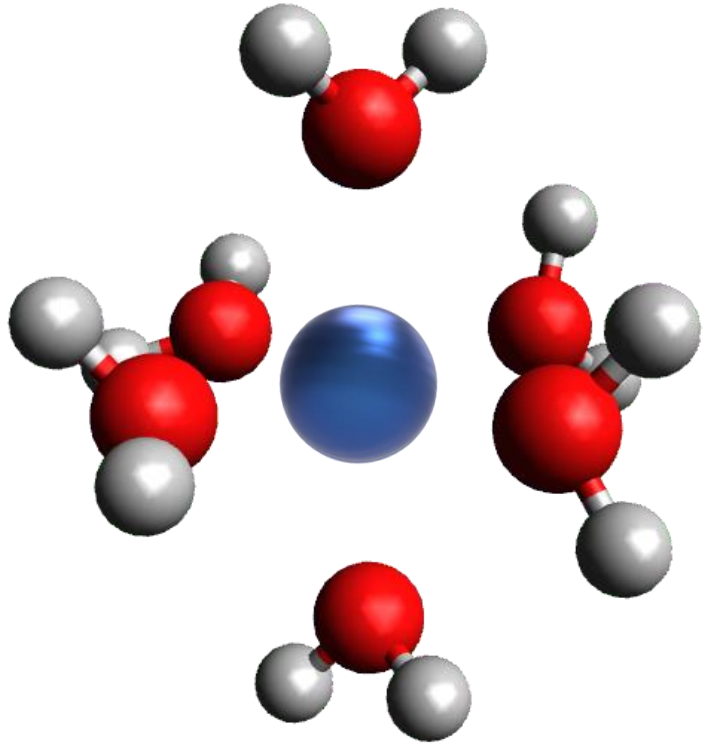
AM spectrum may reflect ultrafast dynamics

→ "Core-hole clock"

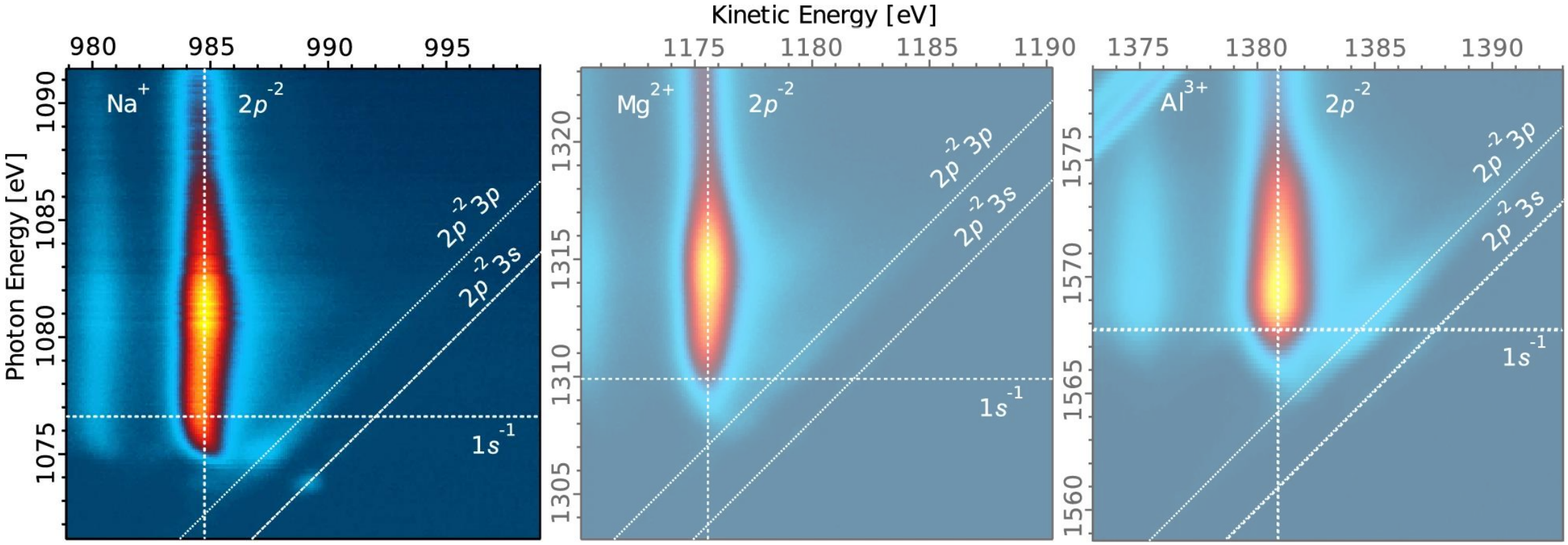
How do core-ionized ions decay in water?

Core excitation/ionization





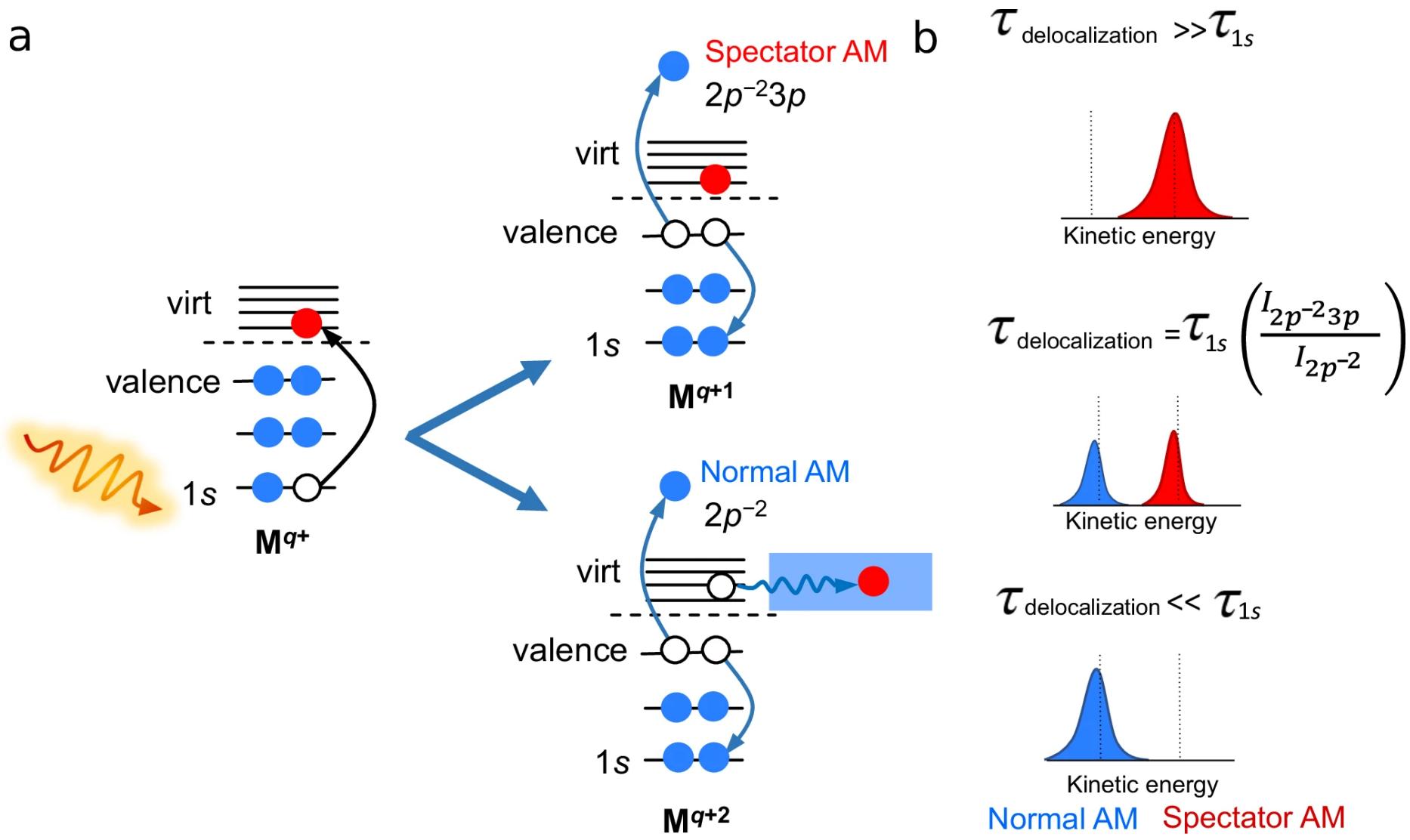
KLL Auger maps for Na^{+}, Mg^{2+}, and Al^{3+} ions in water



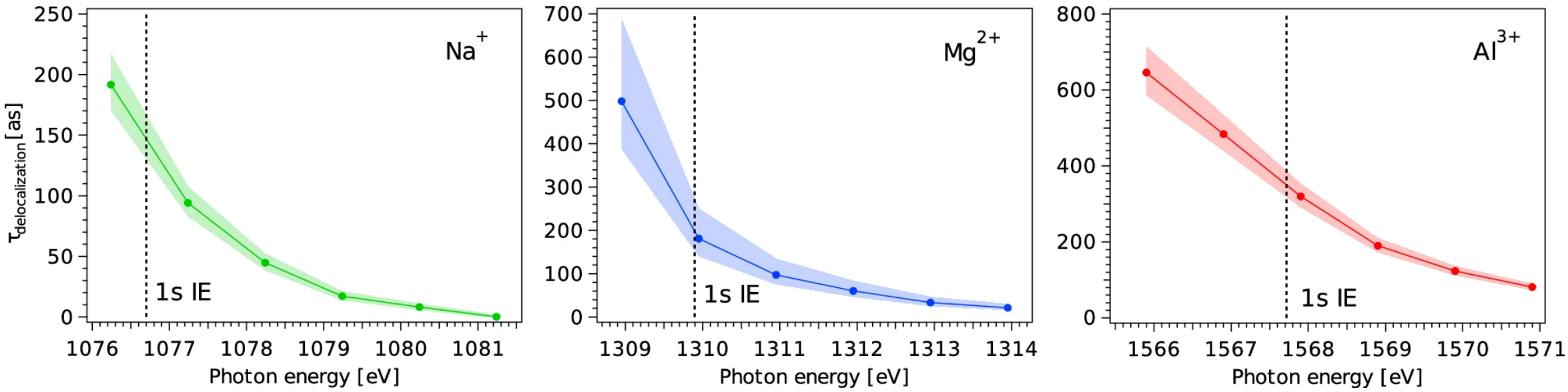
$2p^{-2}$ observed for hν well below 1s binding energy

$2p^{-2}3p$ observed for hν well above 1s binding energy

Dynamics of the excited electron from the core-hole-clock

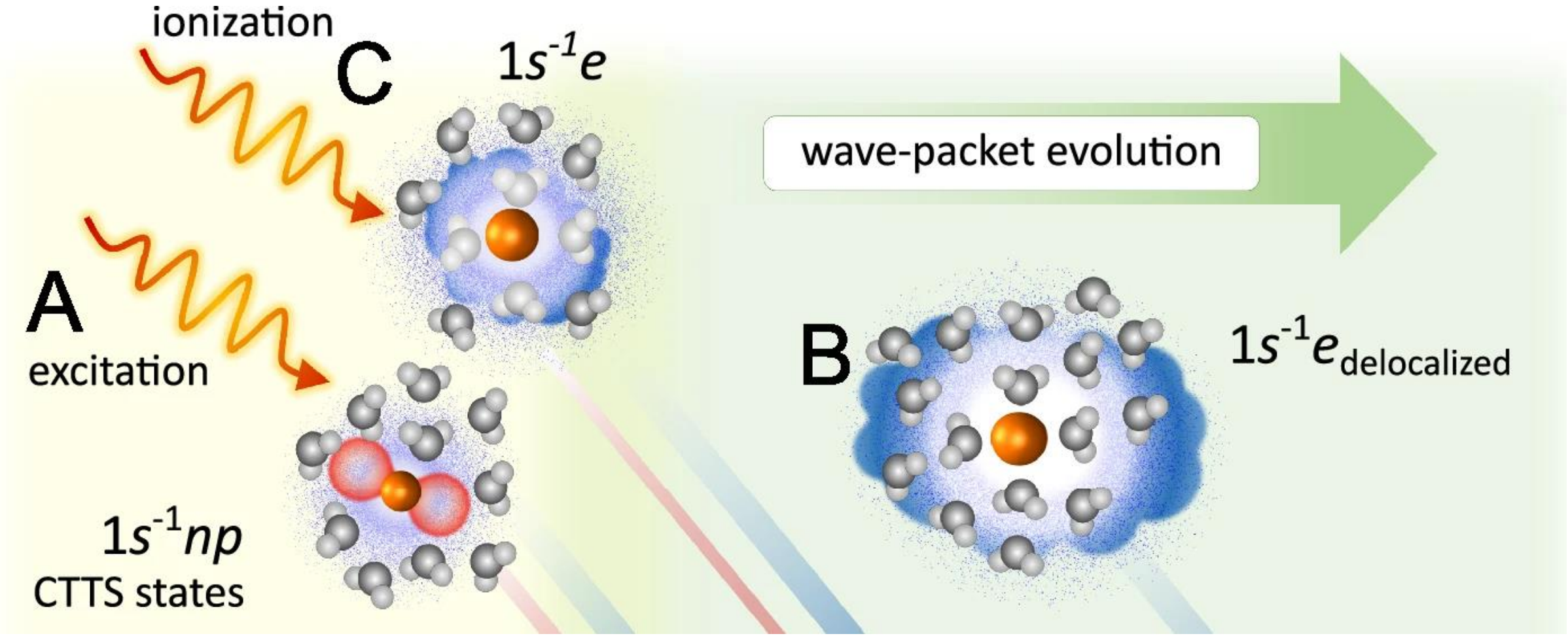


Core-hole clock → $\tau_{delcolaiztion}$



E. Muchová *et al.*,
Nat Commun **15**, 8903 (2024)
EASI@P04, PETRA III

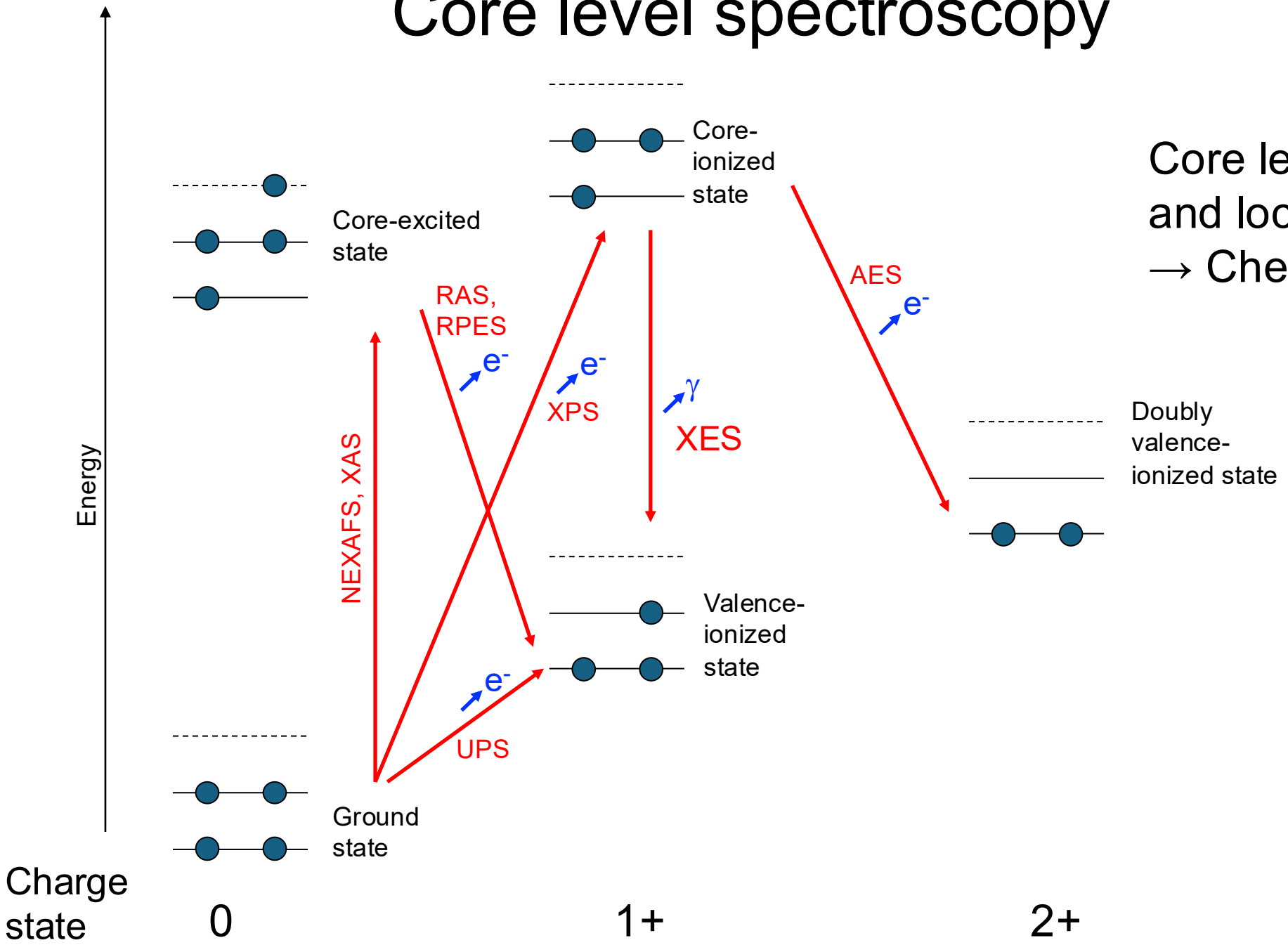
Core-hole clock → $\tau_{delcolaiztion}$



Wave-packet-evolution on the attosecond timescale
First steps in the formation of a solvated electron

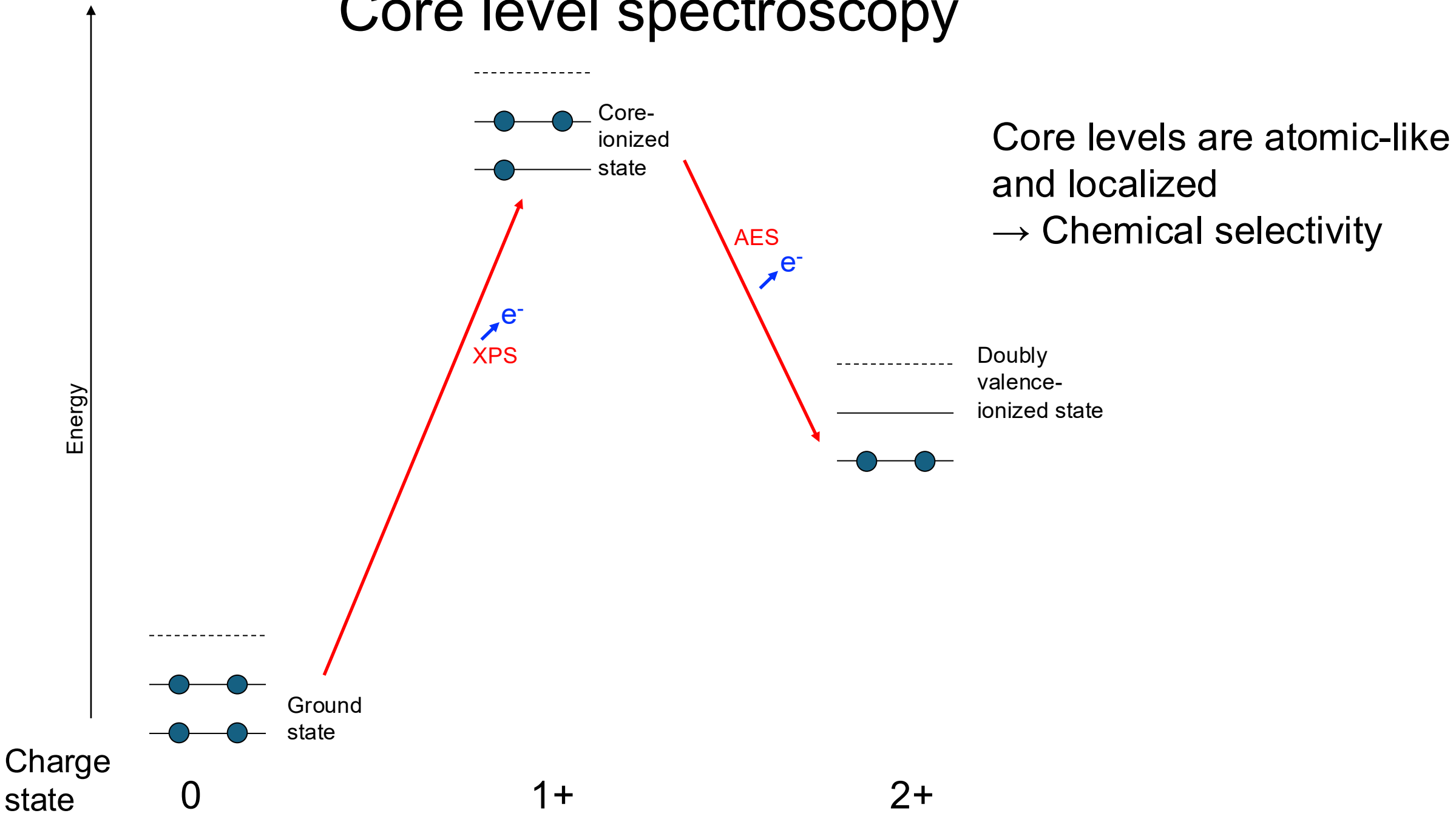
E. Muchová *et al.*,
Nat Commun **15**, 8903 (2024)
EASI@P04, PETRA III

Core level spectroscopy



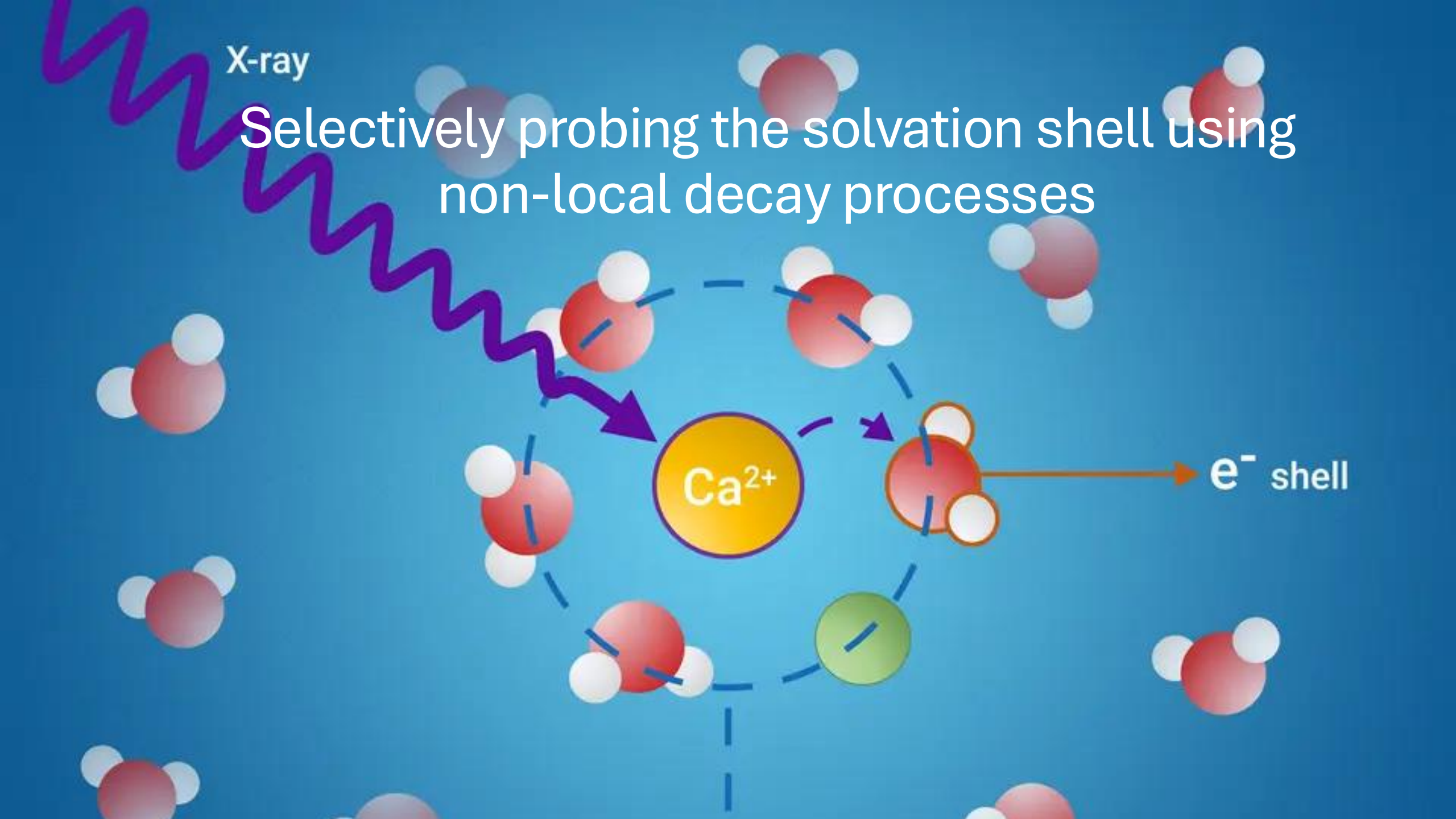
Core levels are atomic-like and localized
→ Chemical selectivity

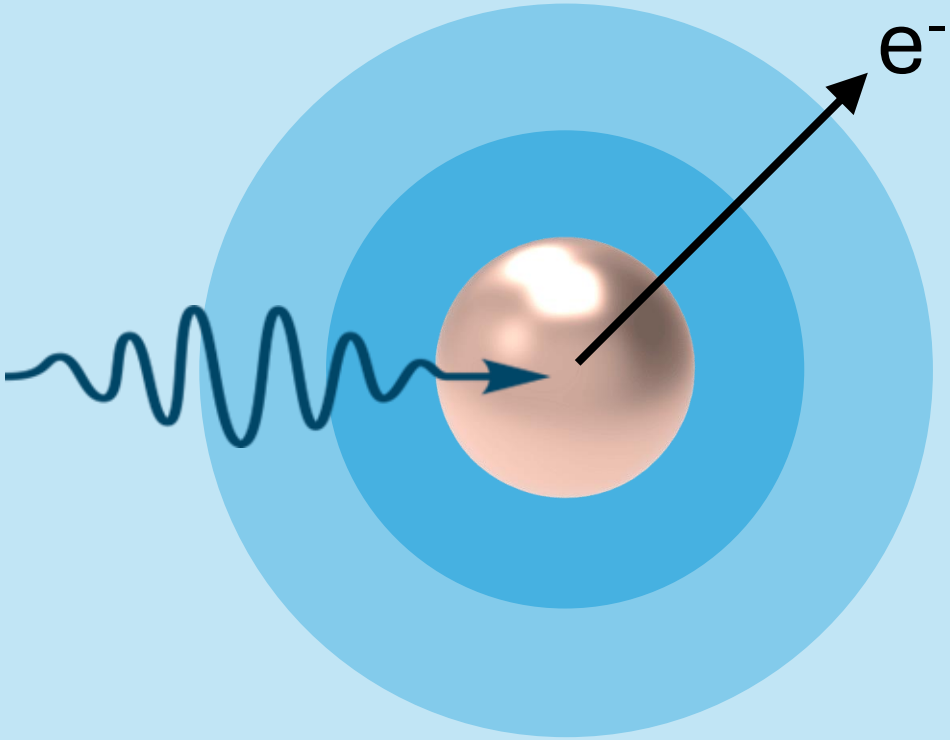
Core level spectroscopy

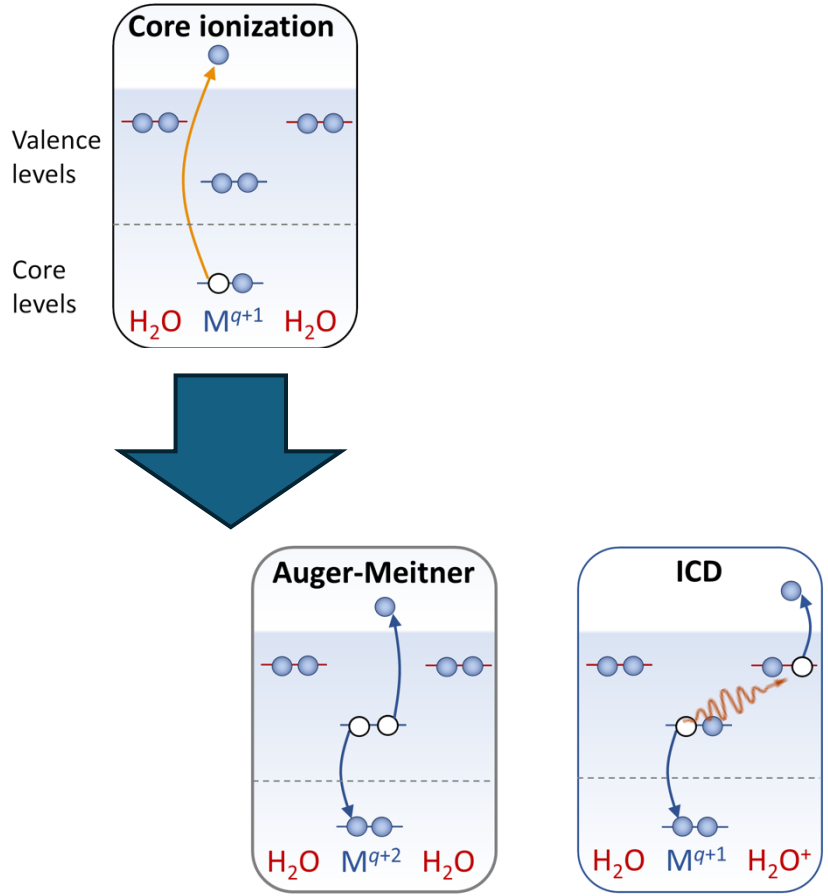


Core levels are atomic-like
and localized
→ Chemical selectivity

Selectively probing the solvation shell using non-local decay processes

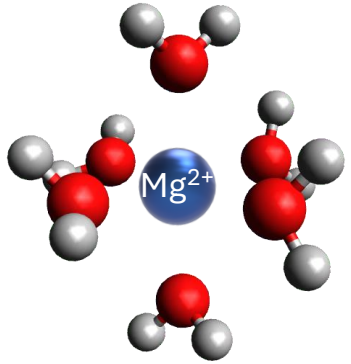



e-


Core ionization
Valence levels
Core levels
H2O
Mq+1
H2O
Auger-Meitner
H2O
Mq+2
H2O
ICD
H2O
Mq+1
H2O+

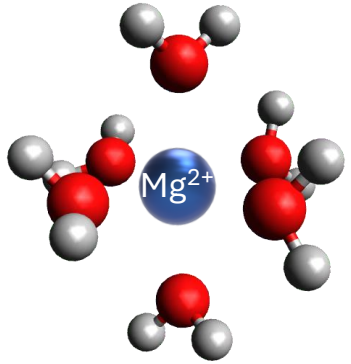
Mg^{2+} in water

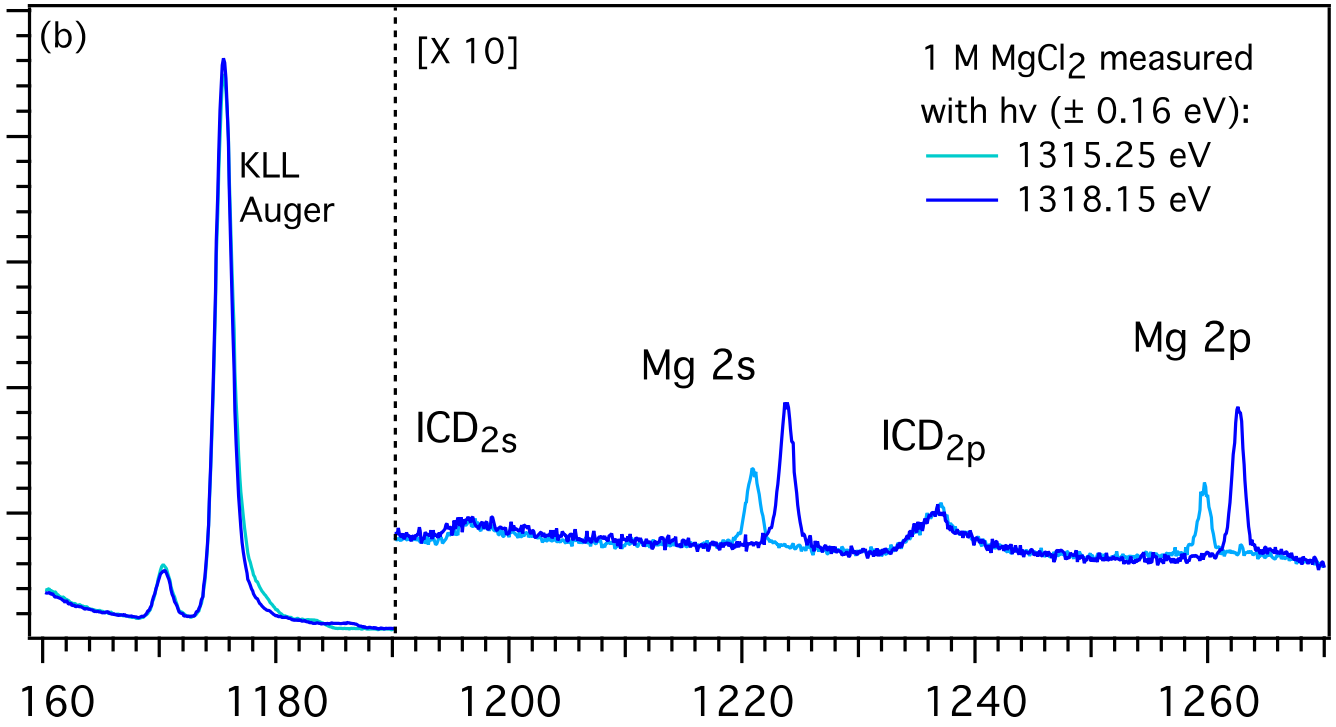
Mg $1s^{-1}$ core-hole decay



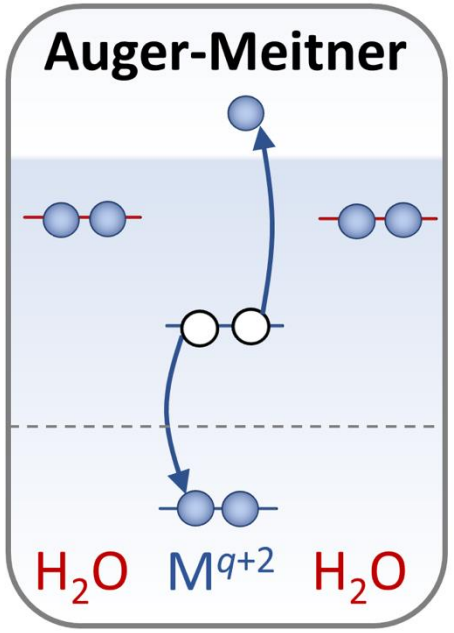
G Gopakumar et al, PCCP **24**, 8661 (2022)
EASI@P04, PETRA III

Mg^{2+} in water
Mg $1s^{-1}$ core-hole decay

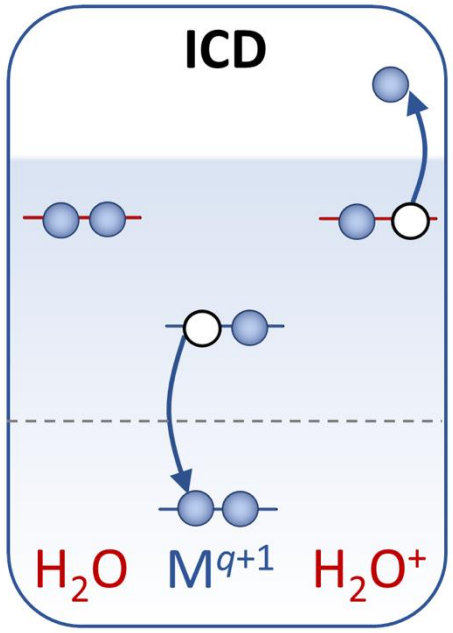




KLL Auger decay
$1s^{-1} \rightarrow 2p^{-2} + e^-$

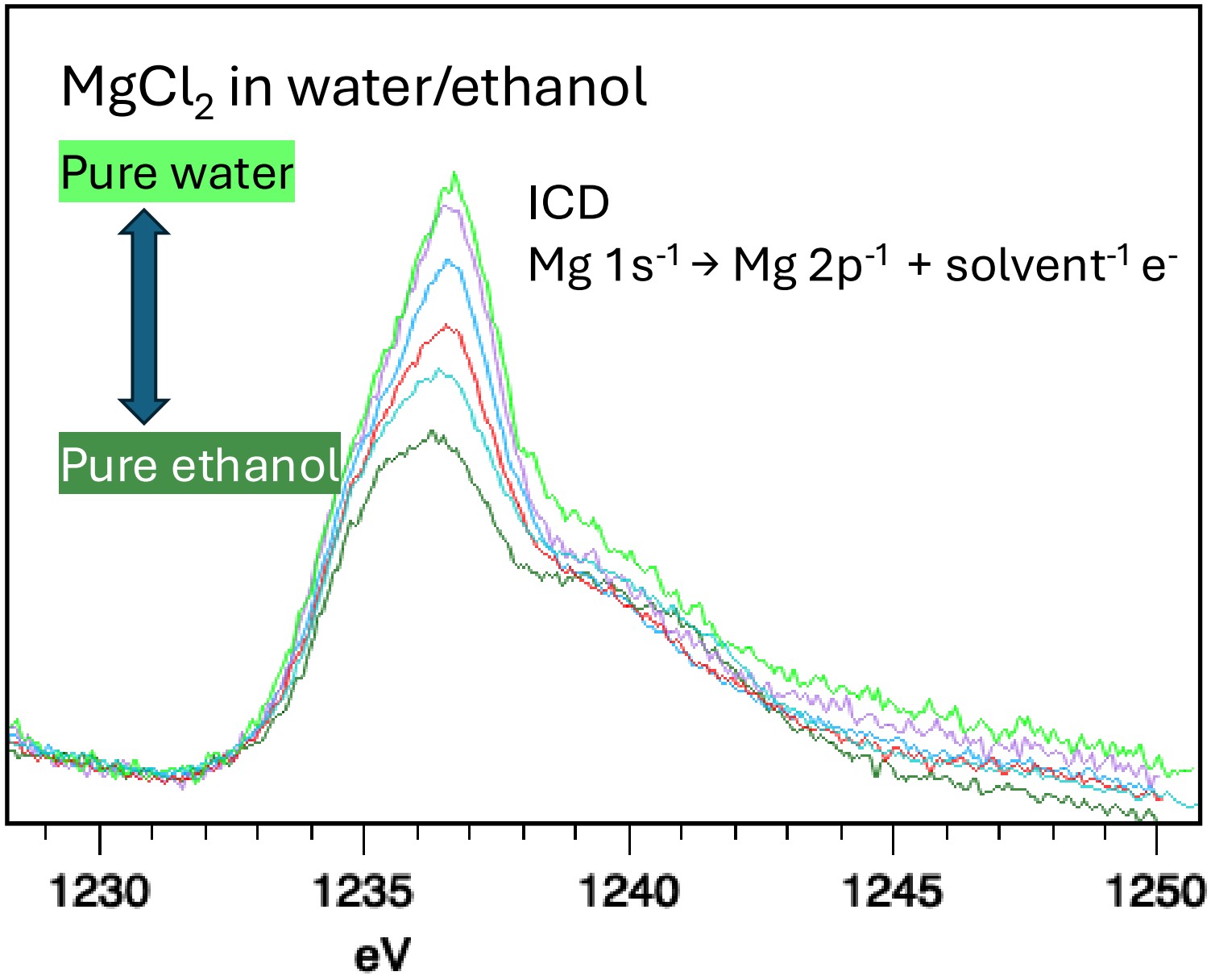


ICD decay involving water
$1s^{-1} \rightarrow 2p^{-1} + W^{-1} + e^-$



G Gopakumar et al, PCCP **24**, 8661 (2022)
EASI@P04, PETRA III

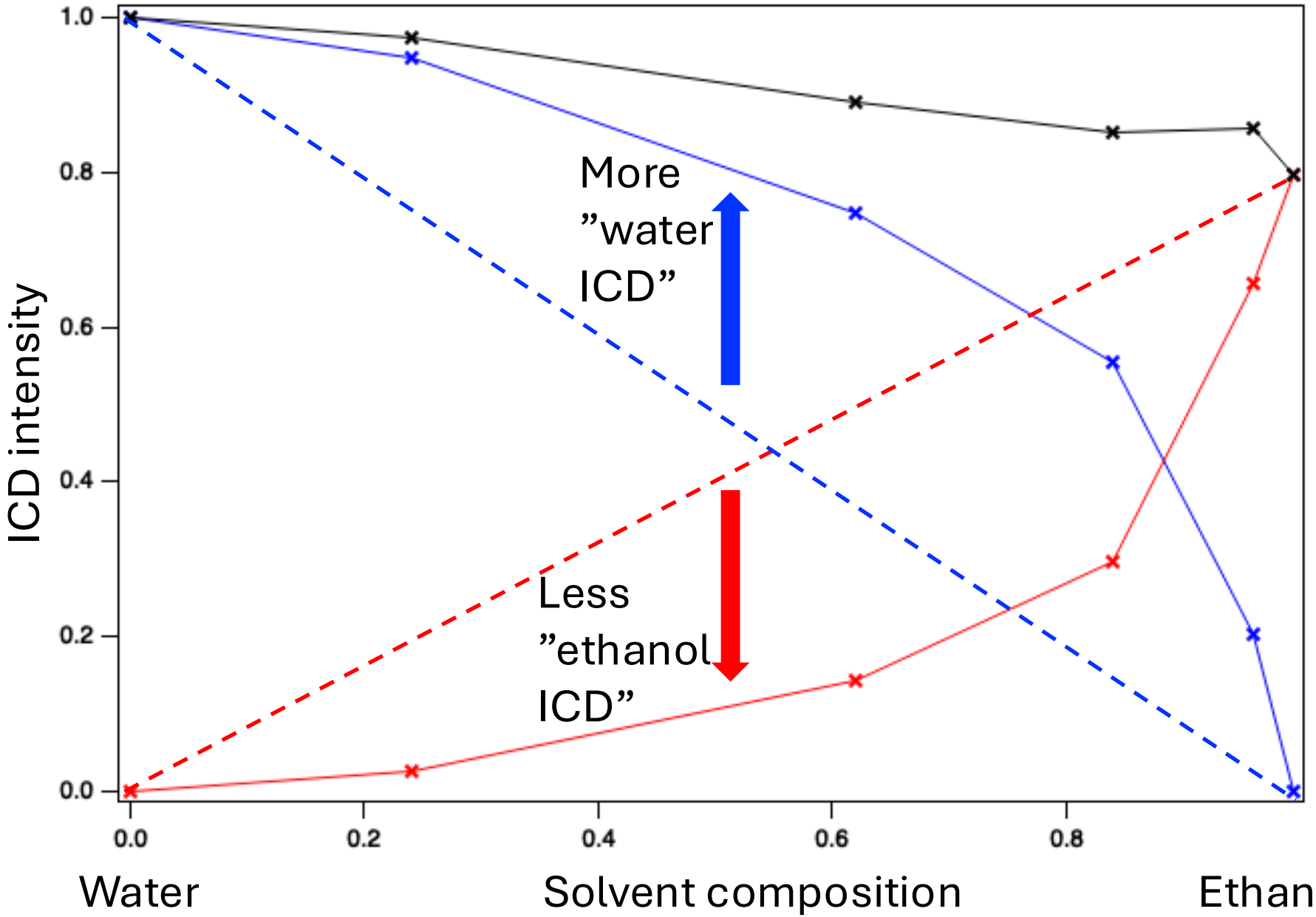
What happens in a mixed liquid?



Normalized to Mg KLL

ICD peak changes shape from water to ethanol

Model:
Decompose into ”water” and ”ethanol” contributions



Total ICD intensity

Ethanol ICD

Different probabilities for water and ethanol molecules to be in the Mg solvation shell

→ $P_w/P_{etoh} \approx 7.4$

Qualitative aggreement with MD

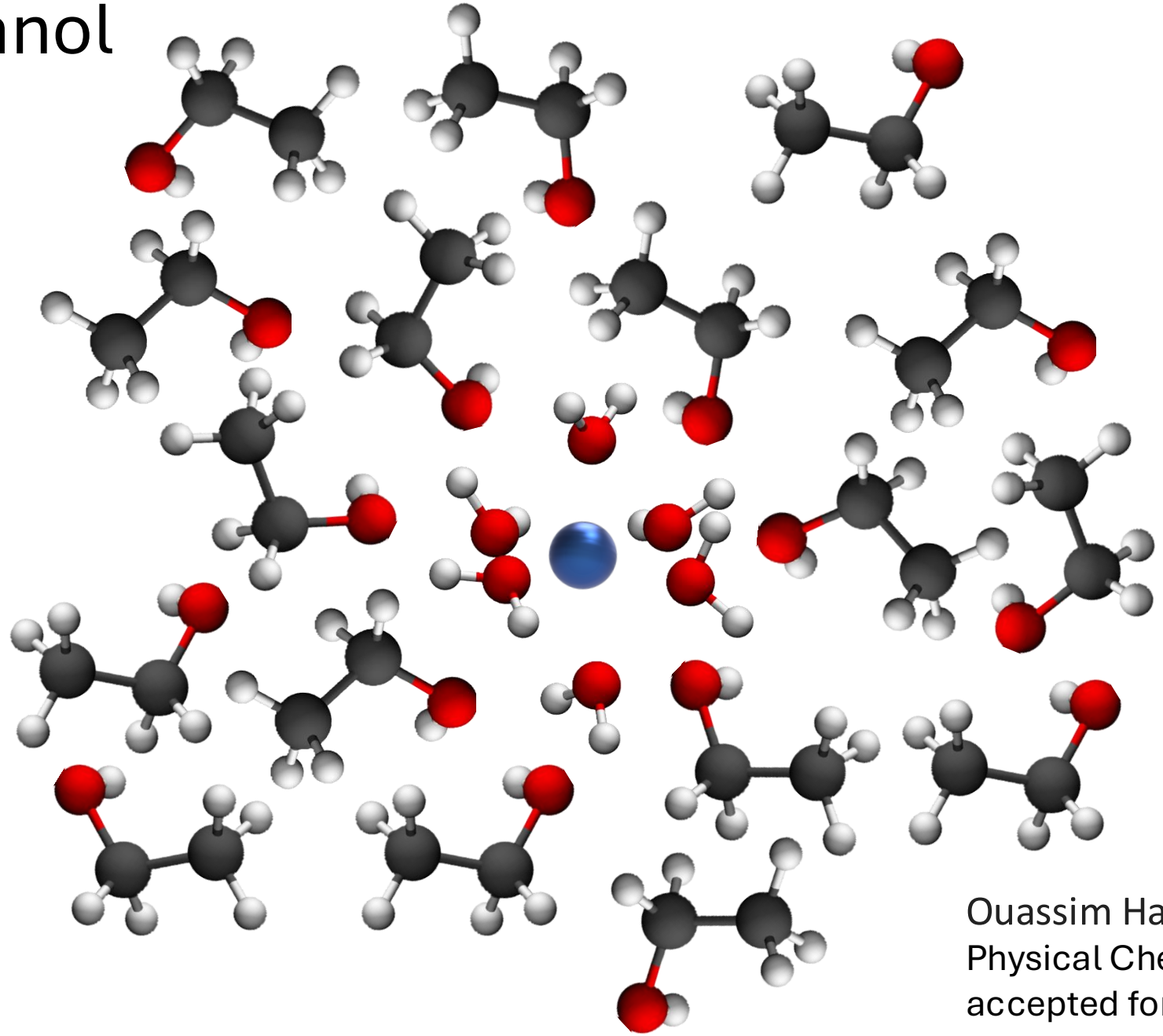
Water ICD

Mg^{2+} in water/ethanol

Water enriched in first solvation shell

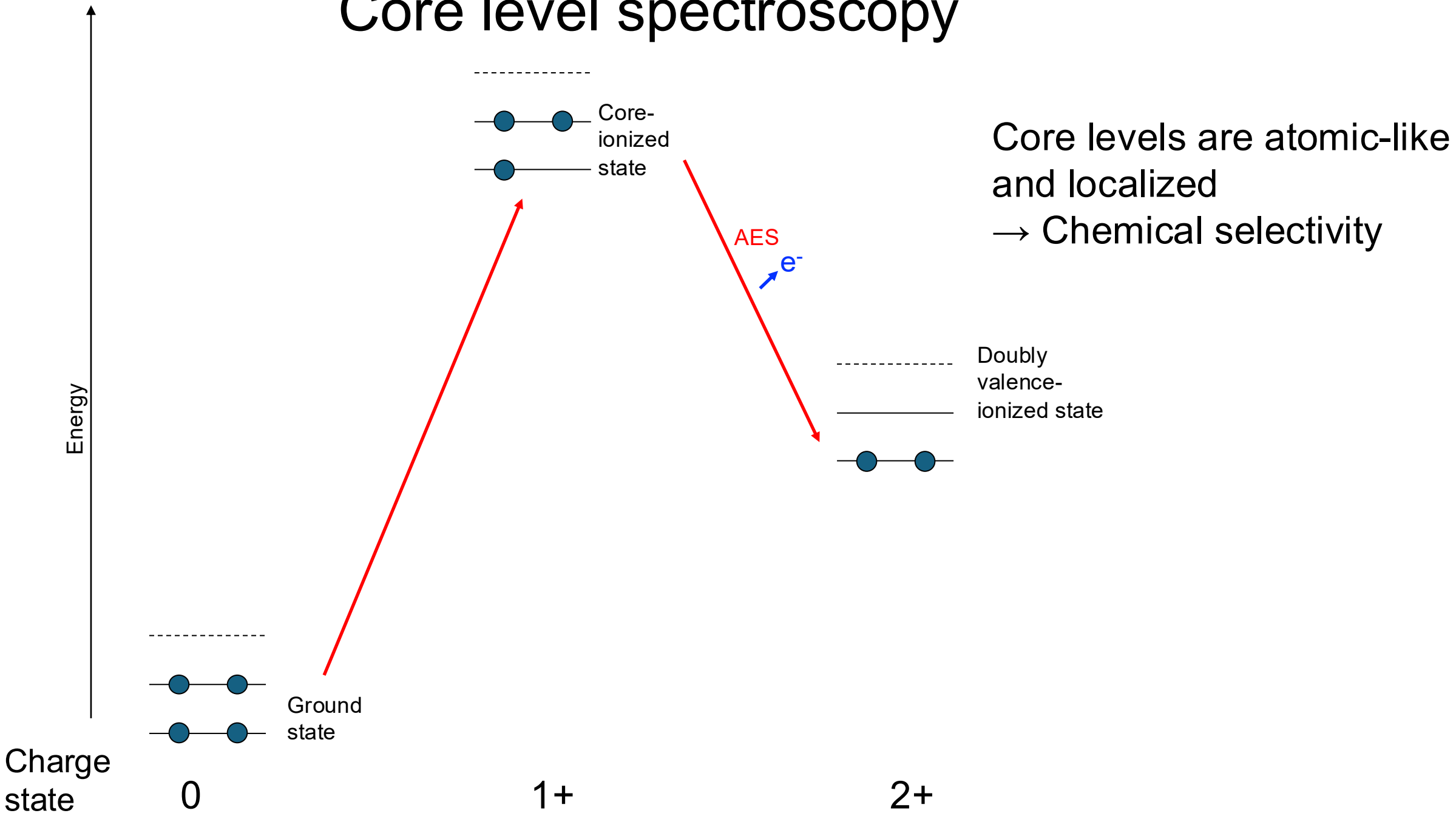
Preferential solvation

Quantitative information on coordination numbers



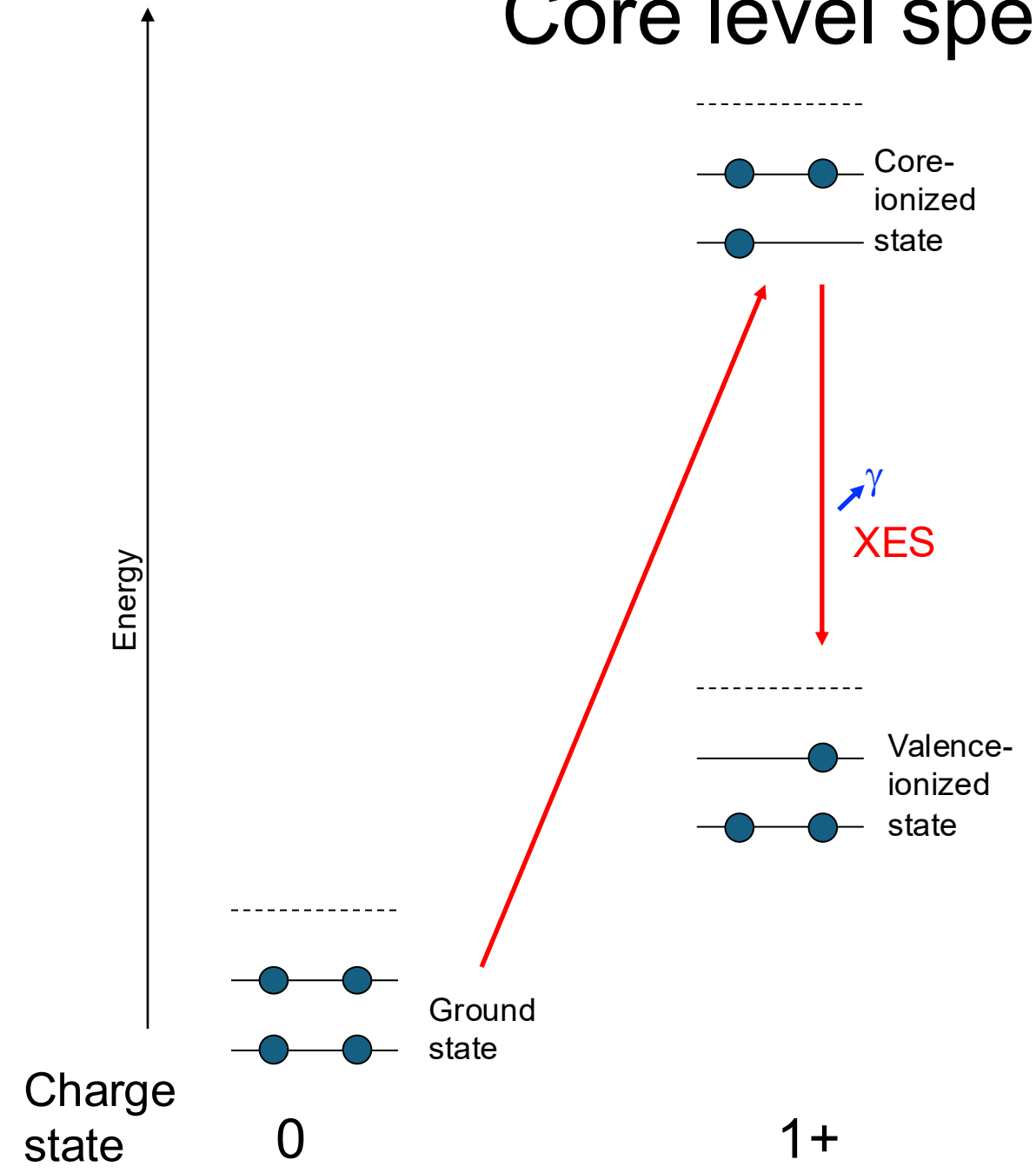
Ouassim Hafiani et al
Physical Chemistry Au, accepted for publication
EASI@P04, PETRA III

Core level spectroscopy



Core levels are atomic-like
and localized
→ Chemical selectivity

Core level spectroscopy



Core levels are atomic-like
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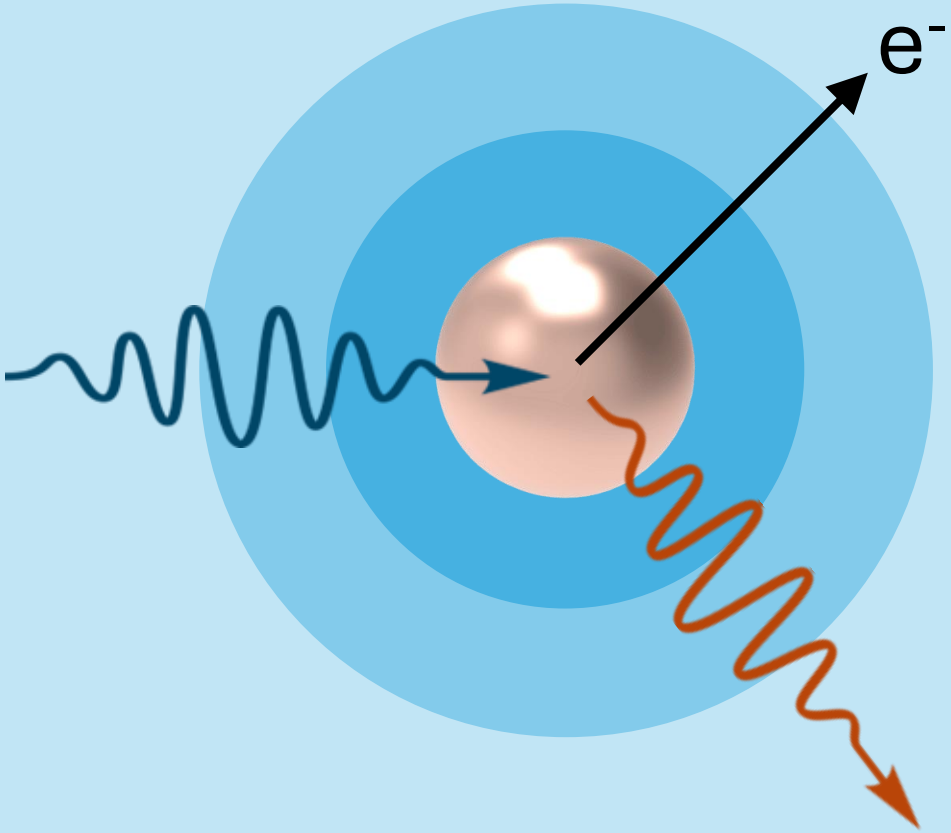
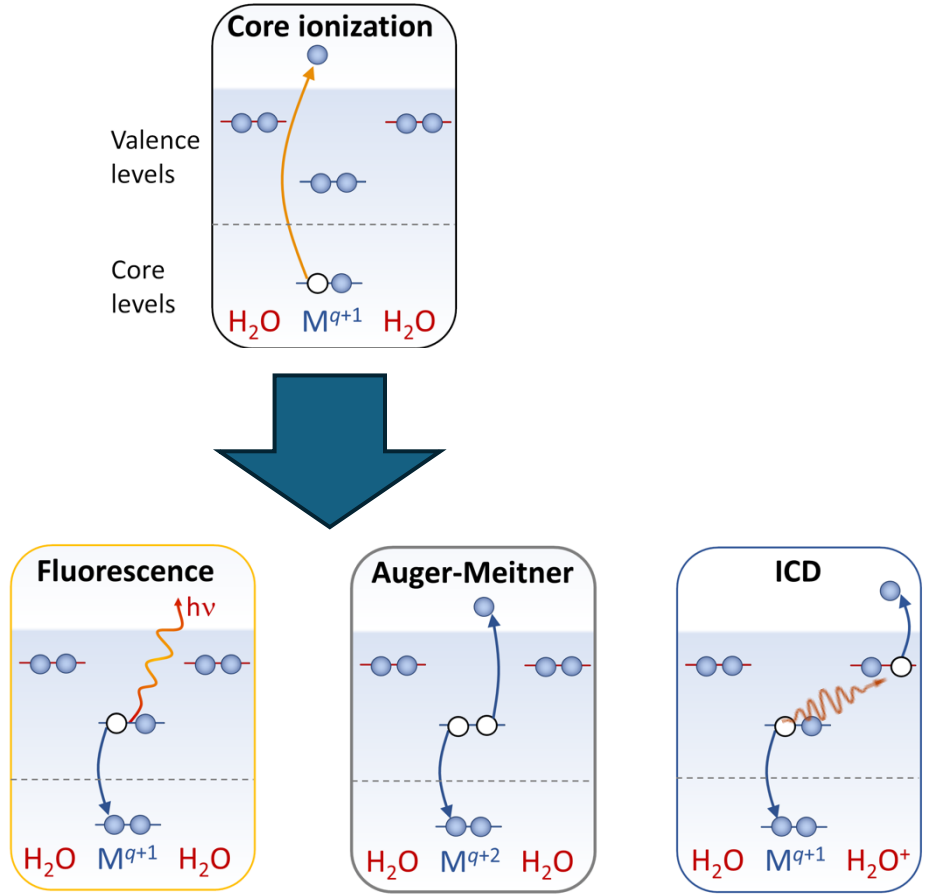


?



Non-local ICD decay
Preferential solvation

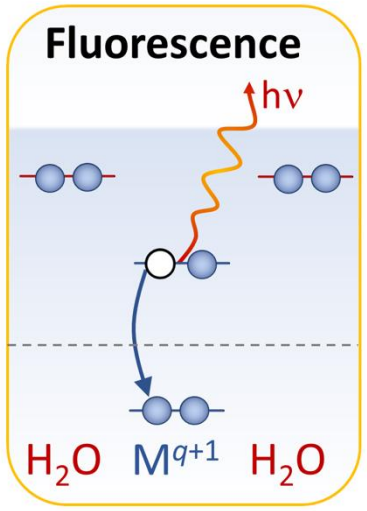
X-ray emission after 1s ionization of Na^+ and Mg^{2+} in water

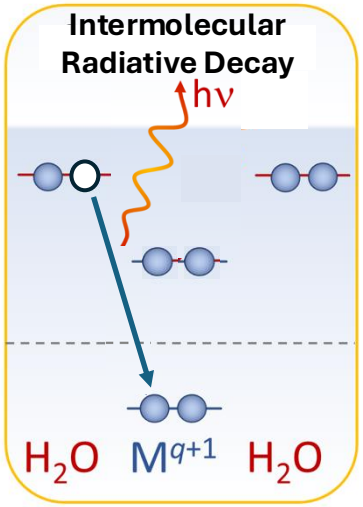
Local K_α decay

$M^q + h\nu \rightarrow$

$M^{q+1}\ 1s^{-1} + e^- \rightarrow$

$M^{q+1} + h\nu_{K\alpha}$



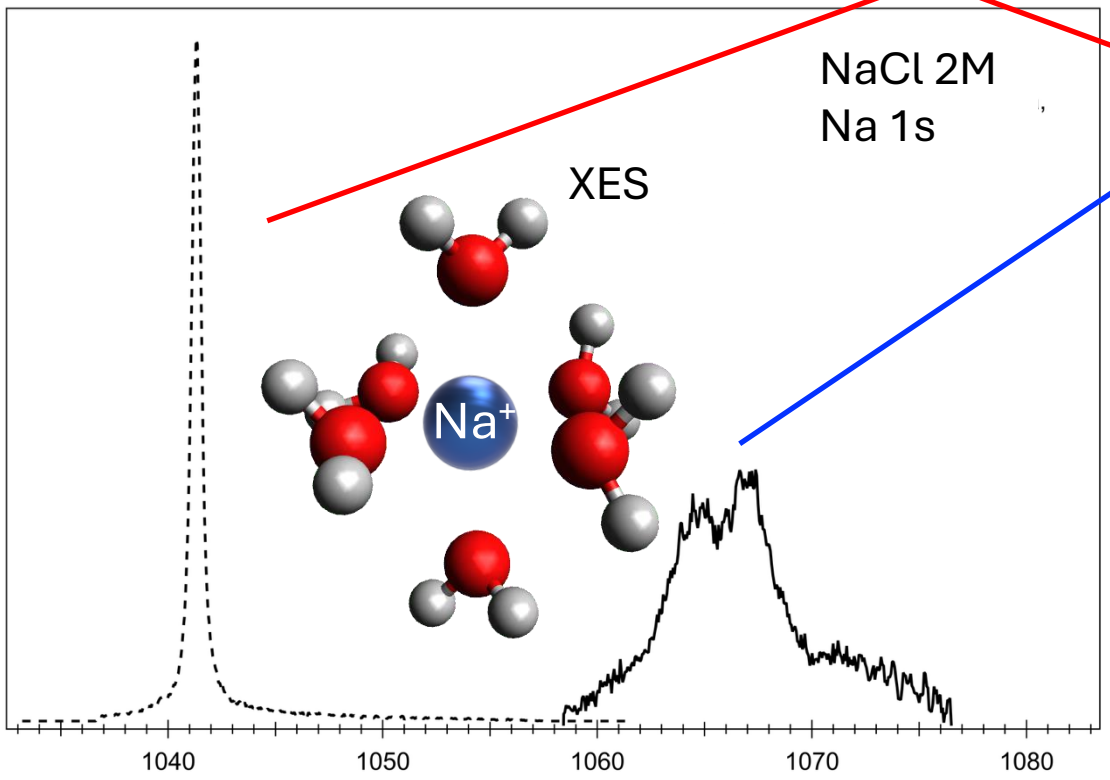


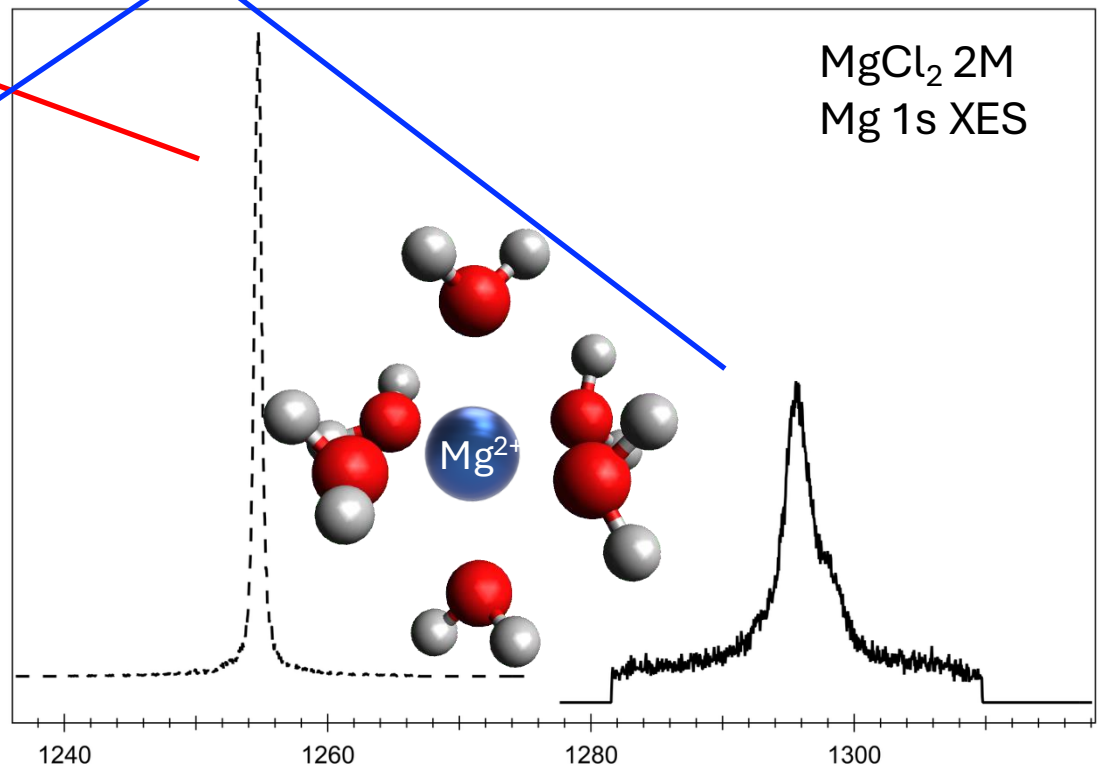
Non-local Intermolecular Radiative Decay

$M^q + H_2O + h\nu \rightarrow$

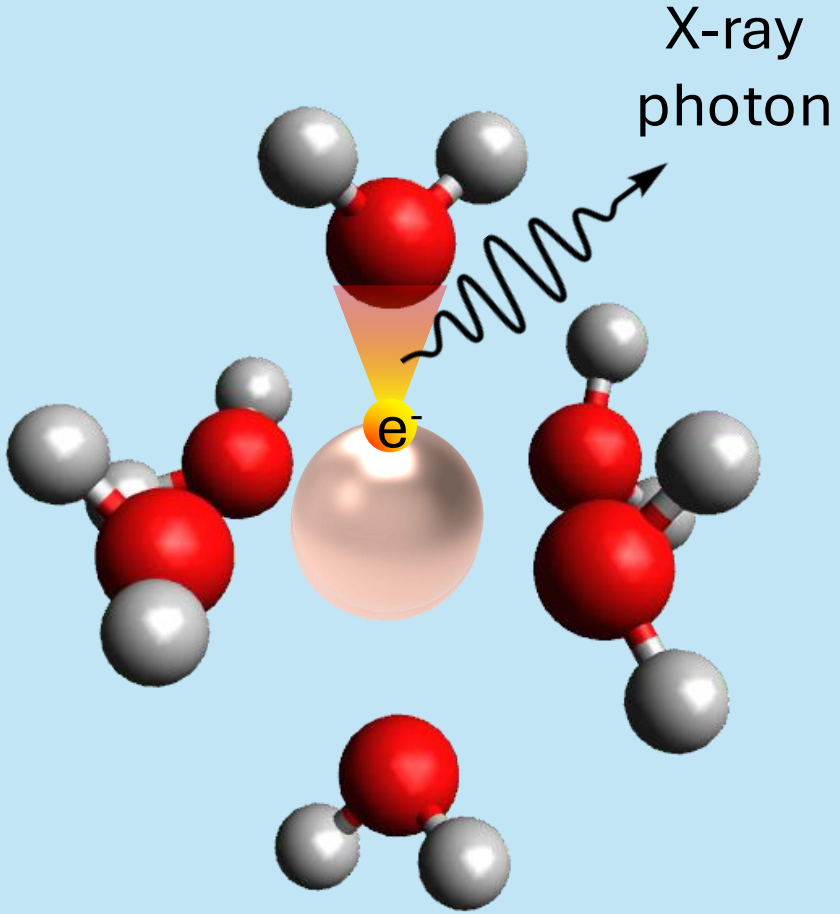
$M^{q+1}\ 1s^{-1} + H_2O + e^- \rightarrow$

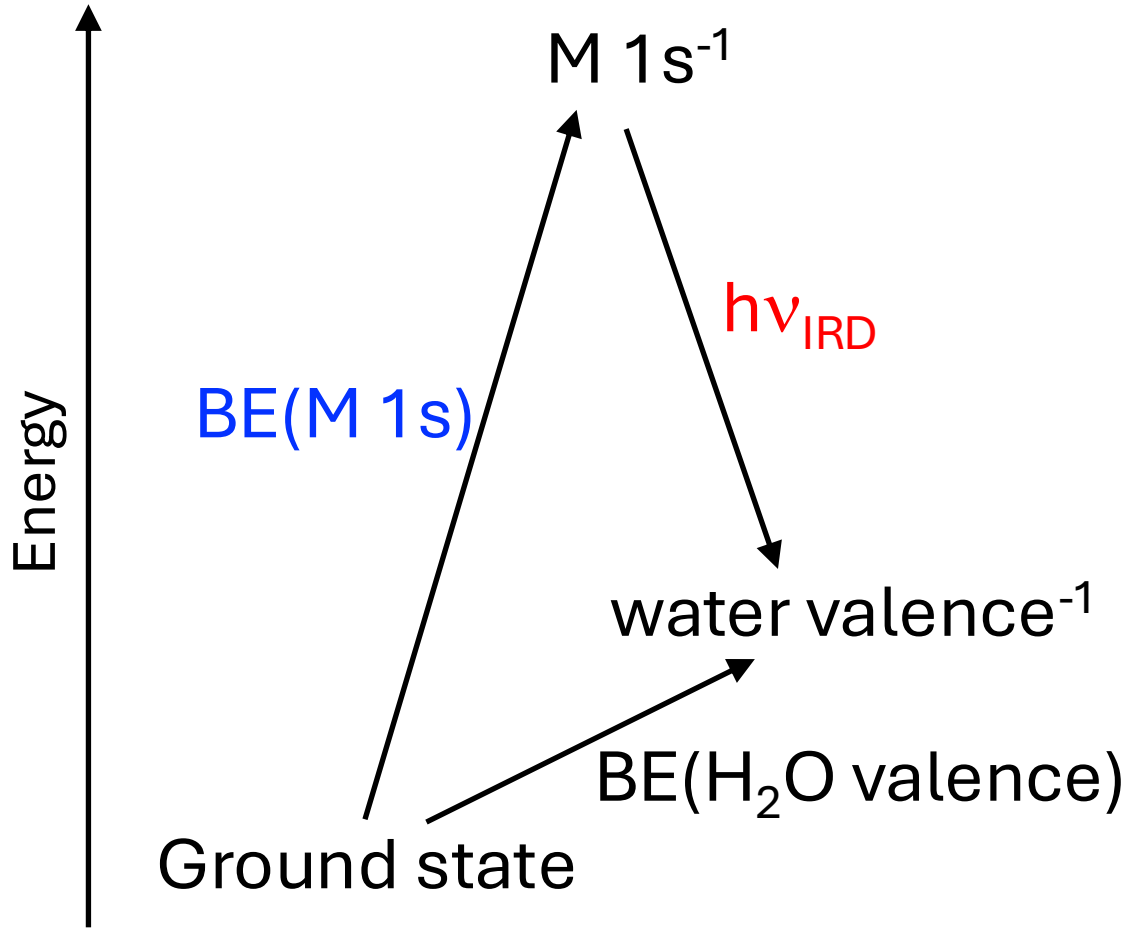
$M^q + H_2O^+\ val^{-1} + h\nu_{IRD}$





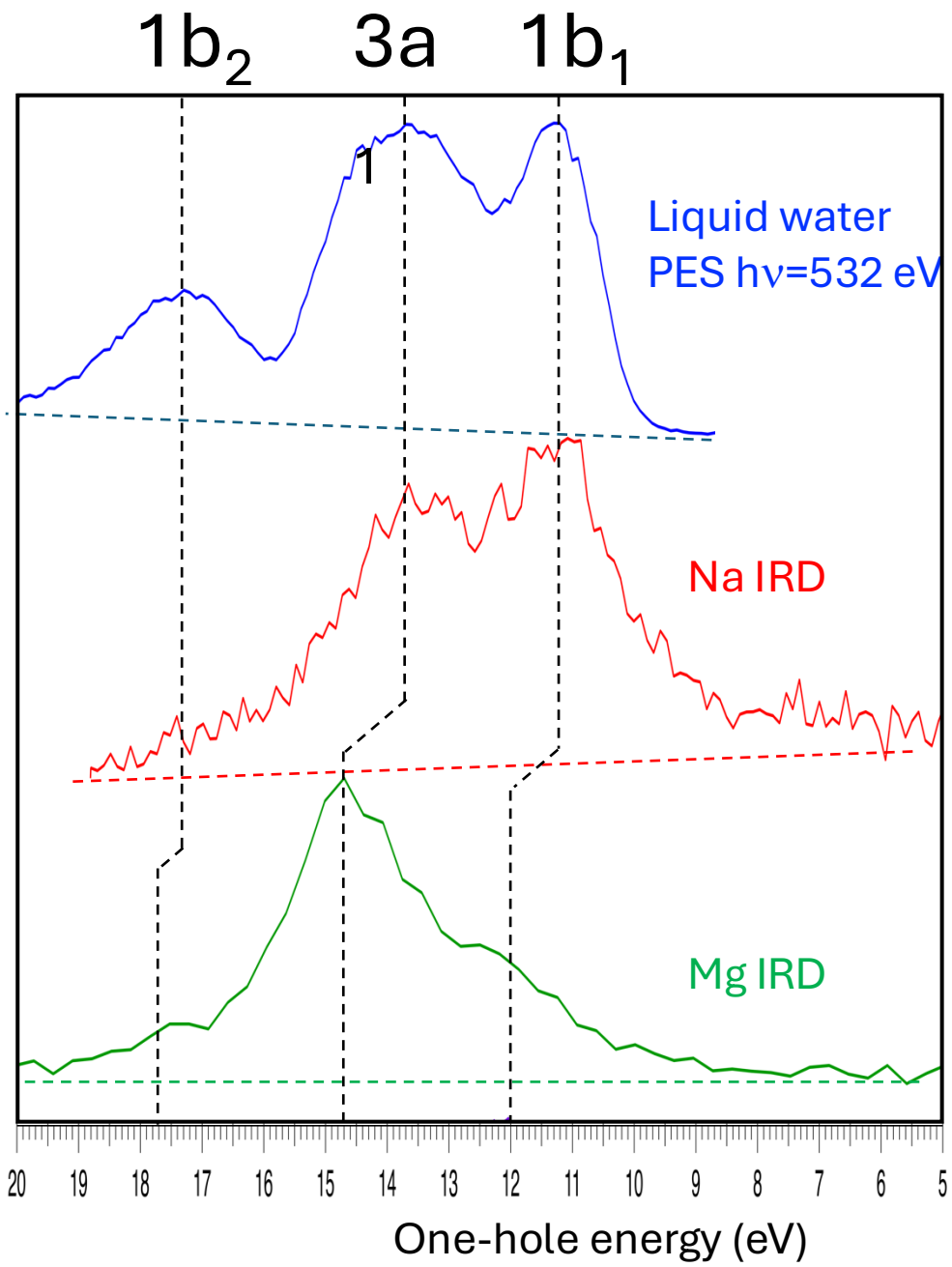
What can we learn from the IRD energies?





IRD → BE(M 1s) - $h\nu_{IRD}$ = E(solvation shell H_2O valence^{-1})

PES → E(bulk H_2O valence^{-1})



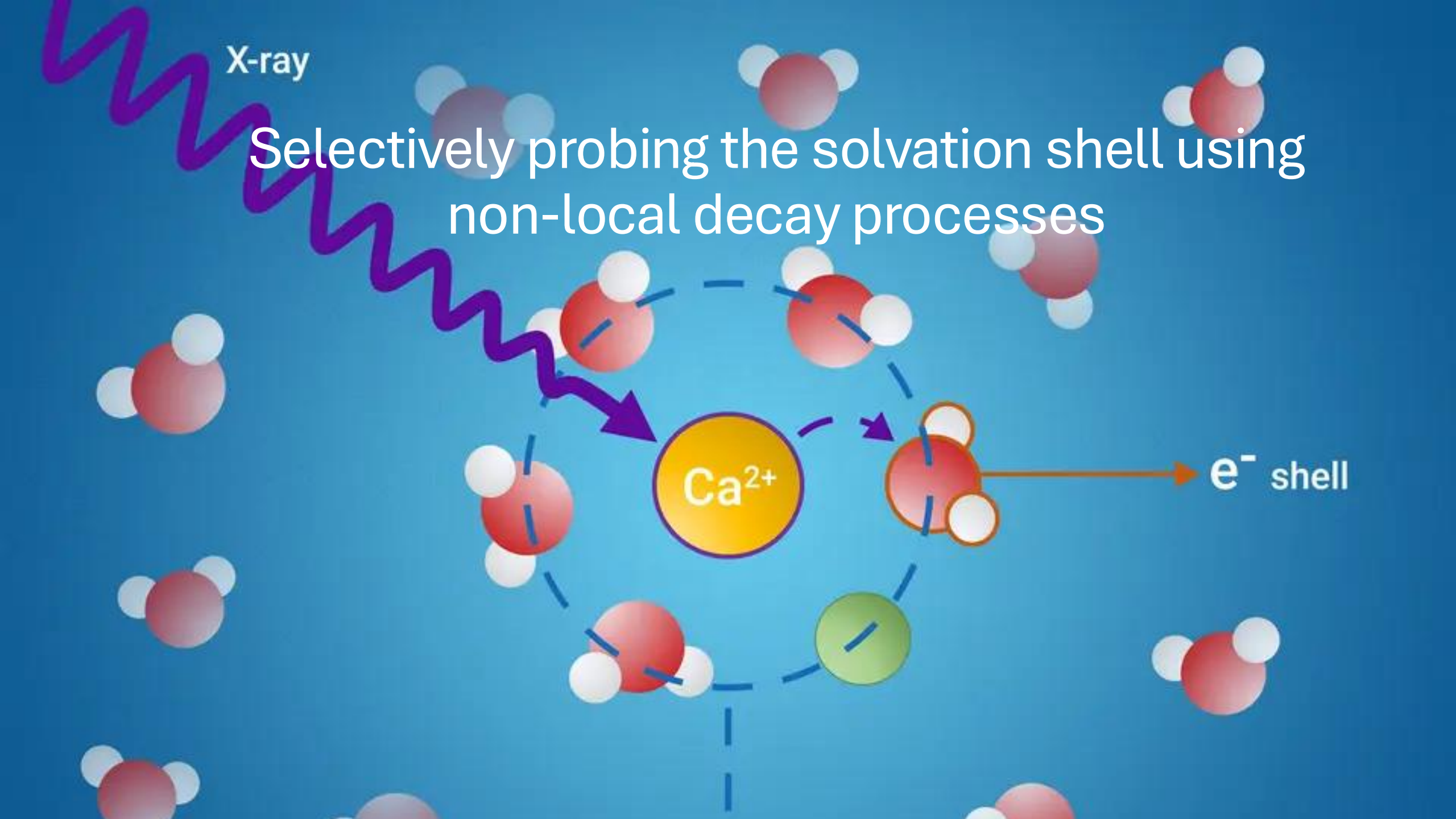
PES → Valence orbitals of bulk water

IRD → Valence orbitals in first solvation shell water

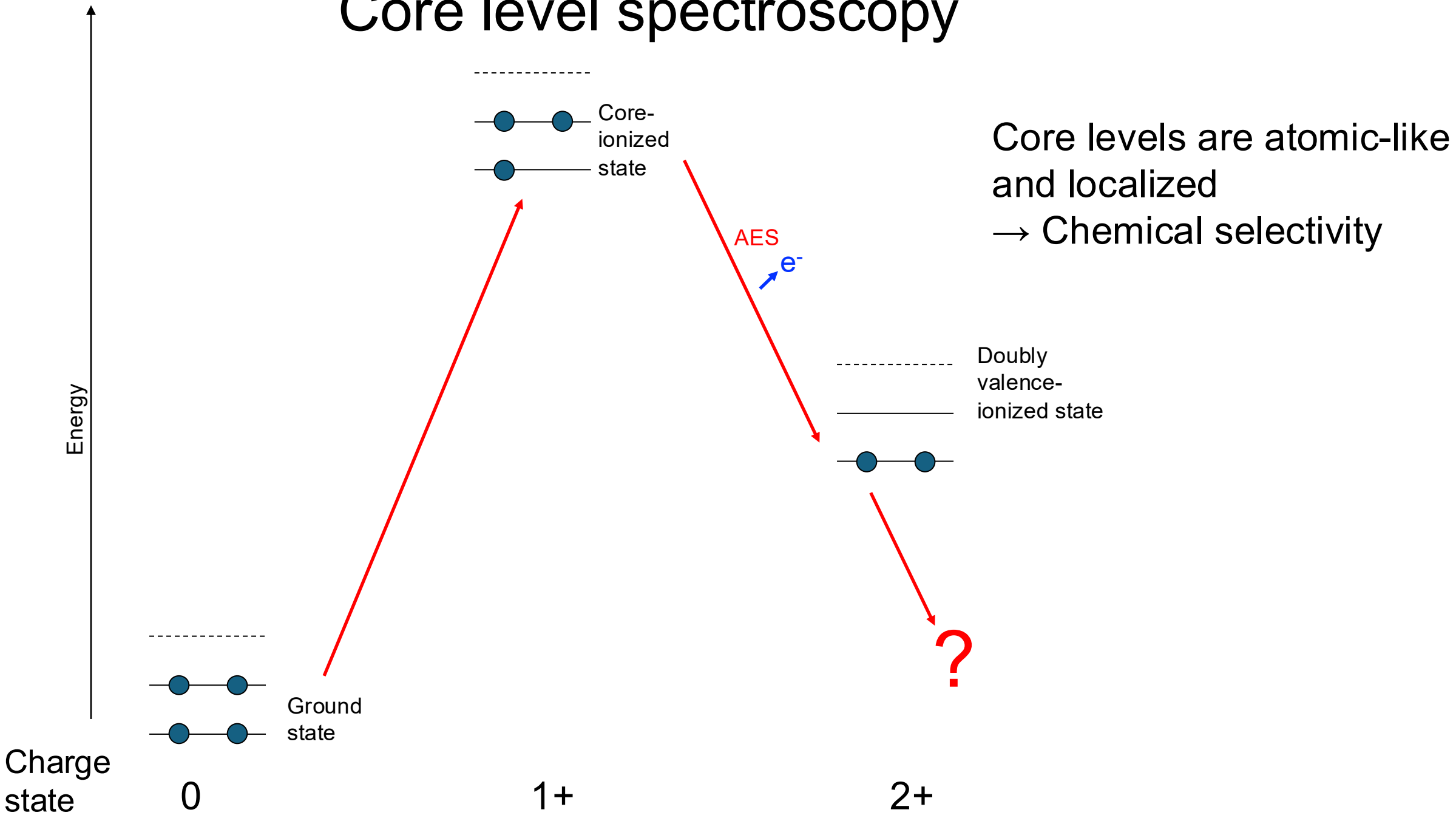
Na: Solvation shell 1-hole energies ≈ Bulk water one-hole energies

Mg: Solvation shell 1-hole energies > Bulk water one-hole energies

Selectively probing the solvation shell using non-local decay processes

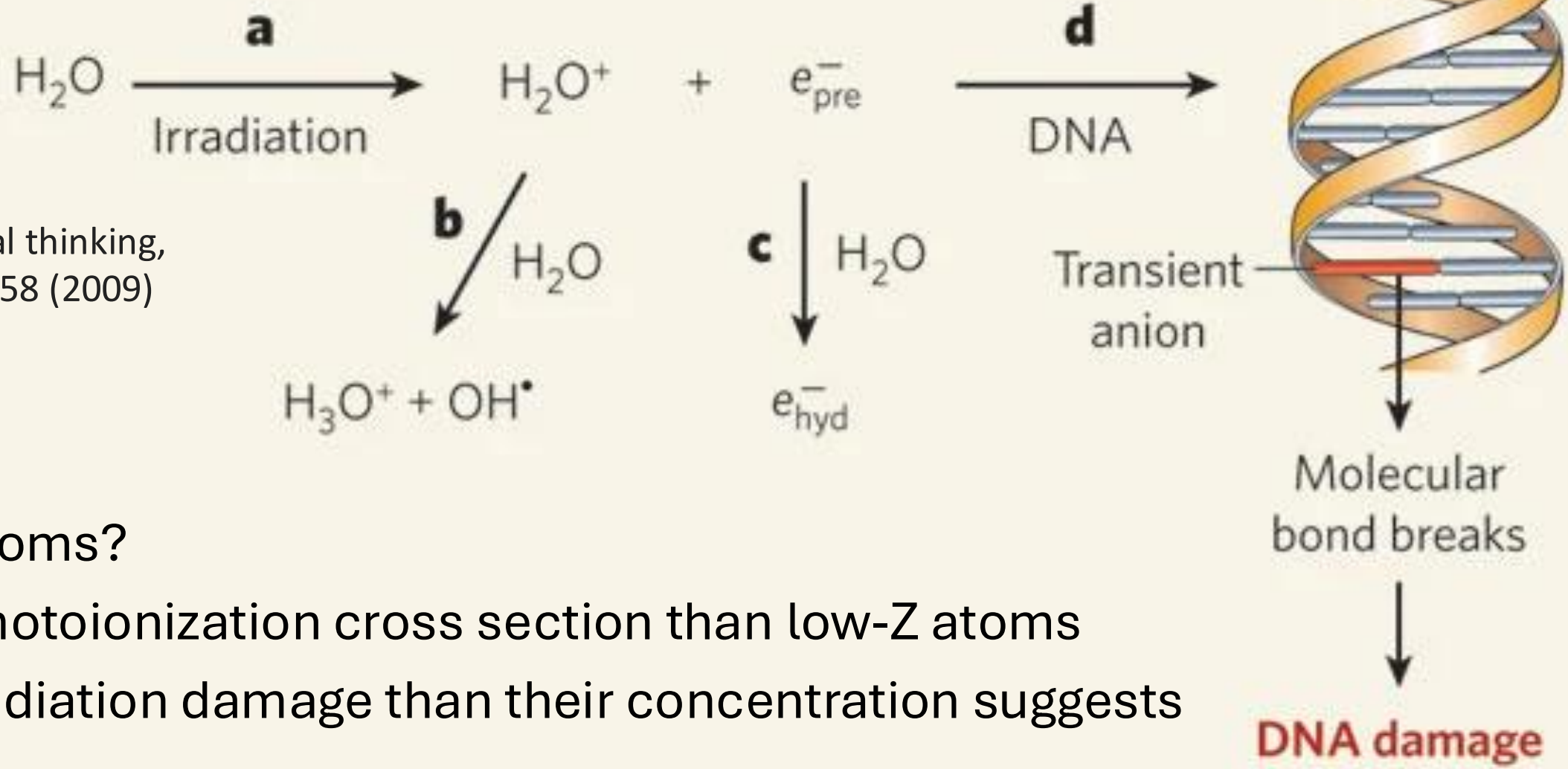


Core level spectroscopy



Core levels are atomic-like
and localized
→ Chemical selectivity

Radiation damage in DNA



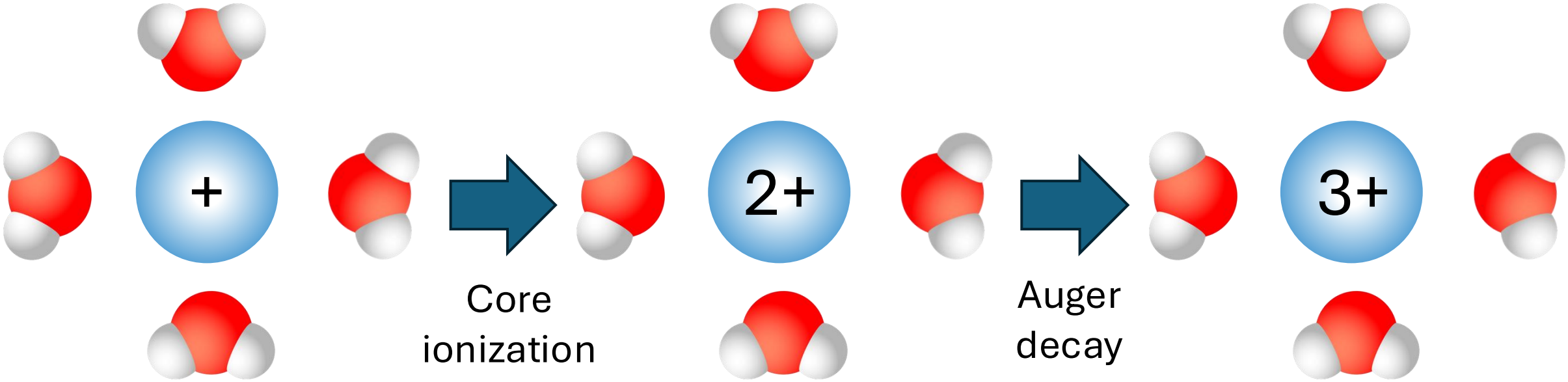
L. Sanche,
Beyond radical thinking,
Nature **461**, 358 (2009)

High-Z atoms?

Higher photoionization cross section than low-Z atoms

→ More radiation damage than their concentration suggests

High-Z atoms:
What happens after local Auger decay?

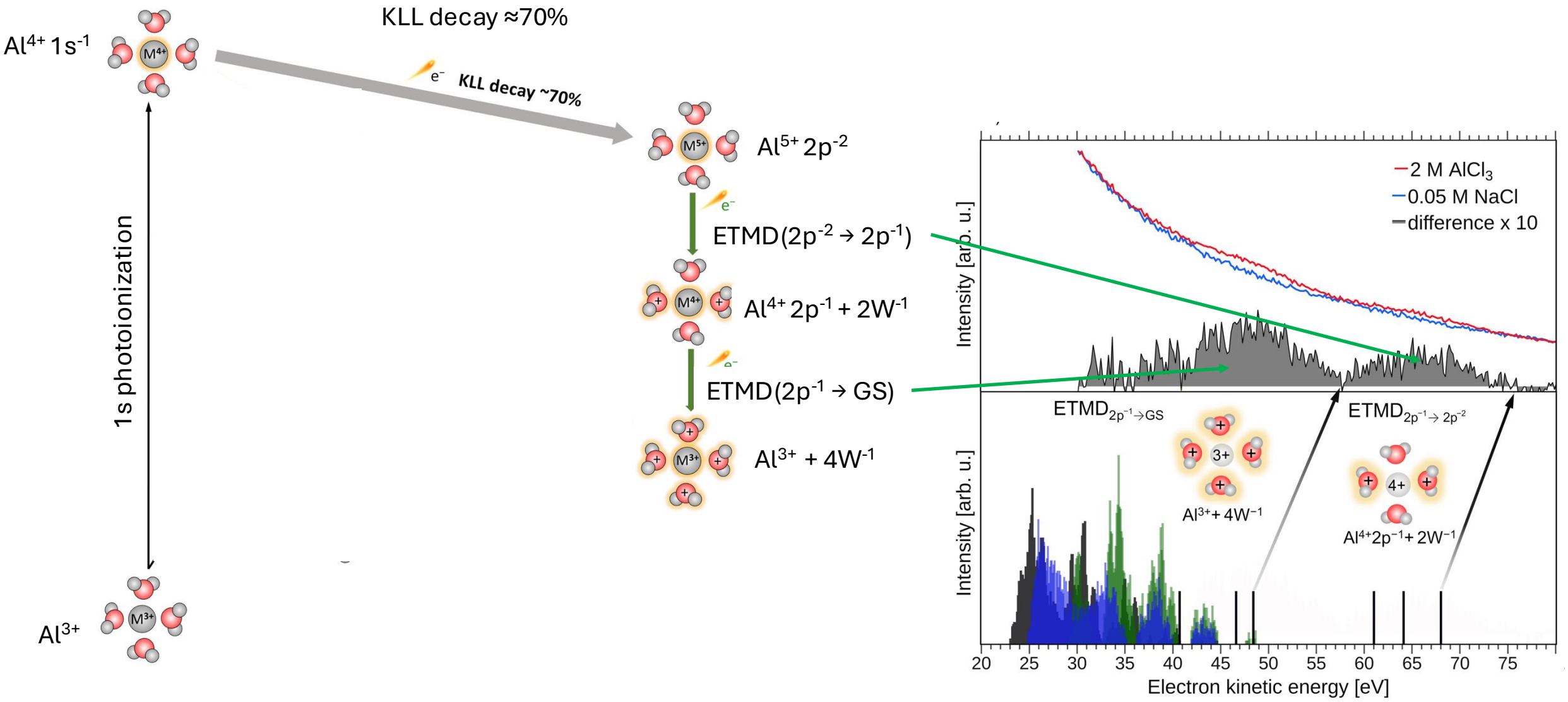


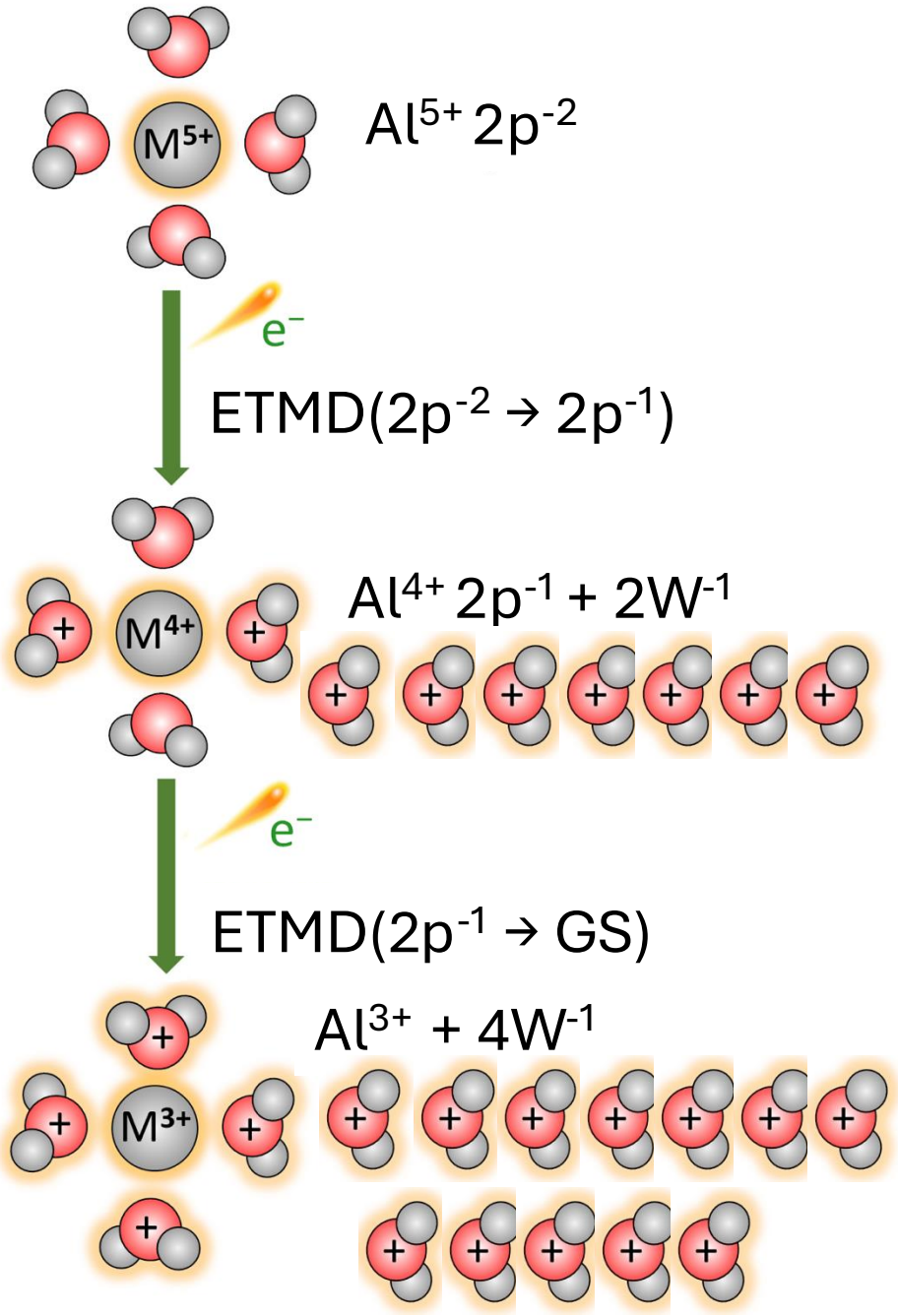
Ground state

Core ionized state

Post-Auger state

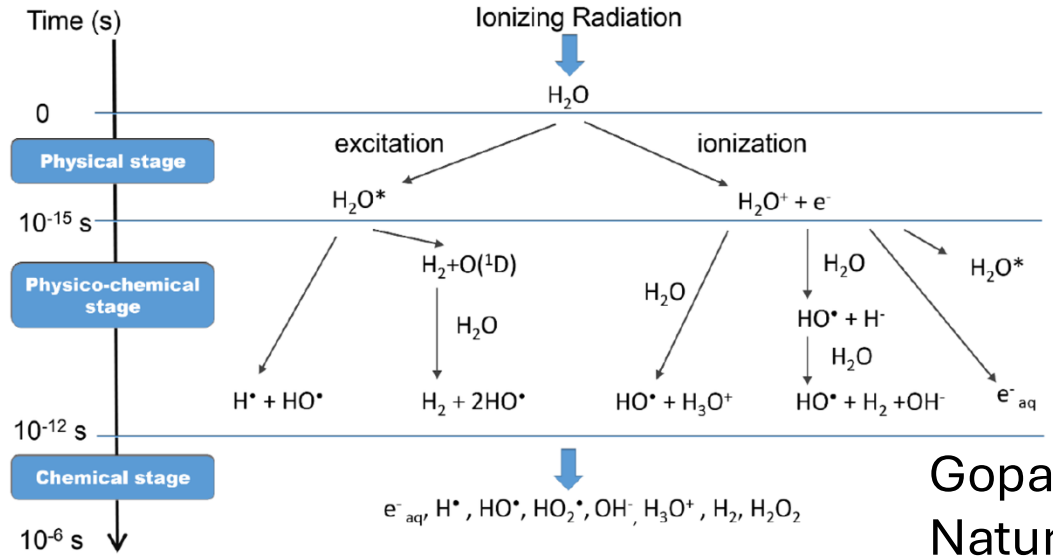
Al^{3+} in water: Electron Transfer Mediated Decay (ETMD)





Summing up post-Auger-Meitner processes:

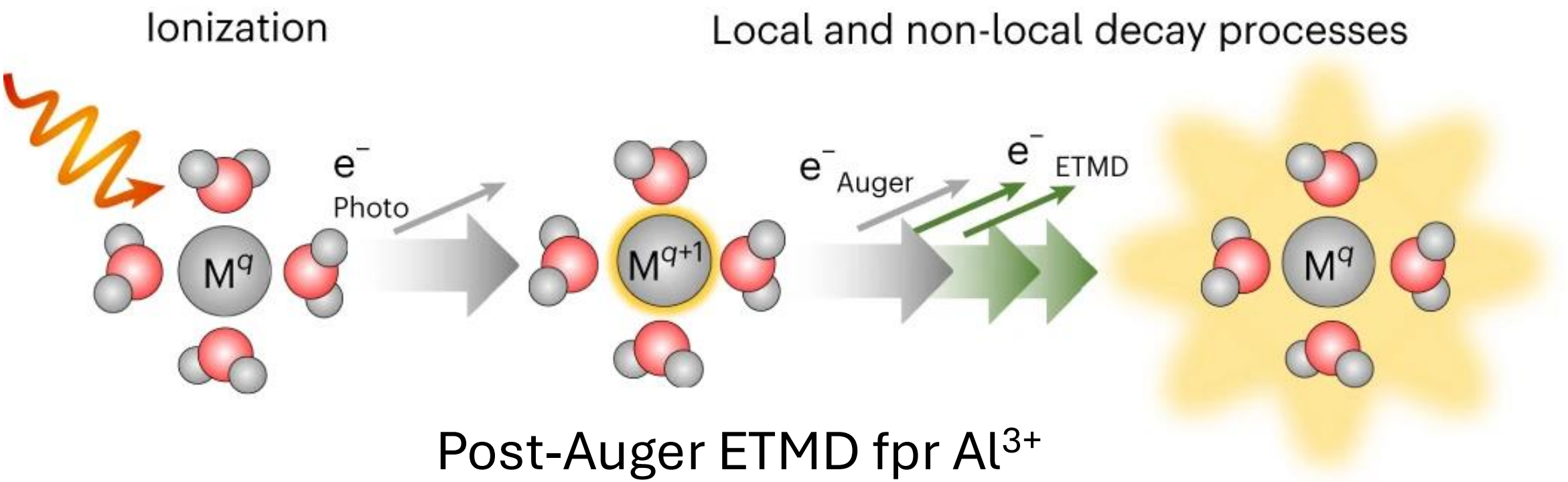
- First ETMD step → 2 W^{-1} + 70 eV KE e^-
- Second ETMD step → 2 W^{-1} + 50 eV e^-
- Low KE e^- → short inelastic mean free path → local formation of W^{-1}
- 70 eV KE e^- → ≈ 7 more W^{-1}
- 50 eV KE e^- → ≈ 5 more W^{-1}
- Total ≈ 16 W^{-1} formed locally by the ETMD decay of Al^{5+}
- W^{-1} → Radical formation



Macdonald, D.D. et al, *Corros. Mater. Degrad.* 3, 470 (2022)

Gopakumar et al, Nature Chemistry **15,** 1408 (2023)

EASI@P04 at PETRA III



Post-Auger ETMD fpr Al^{3+}

Also seen for Mg^{2+} (D Bloß et al., *Nat Commun* **15**, 4594 (2024))

→ ≈ 16 W^{-1} formed locally

→ Radical formation

→ Hot-spot for radiation damage

Gopakumar et al,
Nature Chemistry **15,**
1408 (2023)
EASI@P04 at PETRA III

Core level spectroscopy of liquids

Specfic experimental aspects

Examples:

Surface of aqueous solutions using XPS

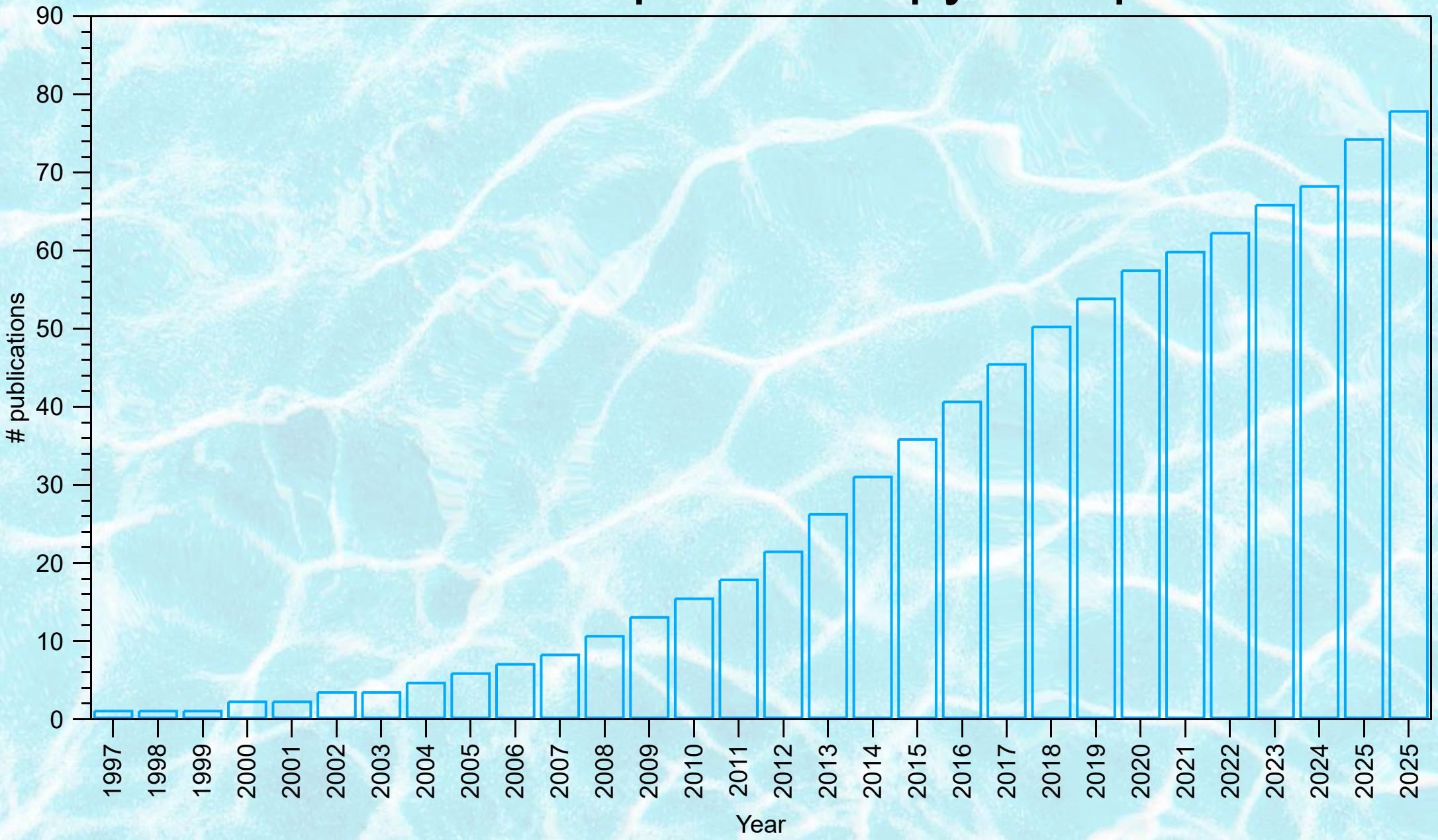
Ultrafast processes using the core-hole clock

Local environment using non-local decay processes

Radiation damage

→ Chemistry, biology, environmental science

Core level spectroscopy of liquids



Acknowledgements

Uppsala: G Gopakumar, I Unger, C Caleman, H Ågren, L Cornetta, D Vasconcelos, J Söderström, JE Rubensson, M Agåker, O Hafiani

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MAX IV: G Öhrwall, V Ekholm

SOLEIL: D Ceolin

Brasilia: R Marinho, A Mocellin

Kassel: D Bloß, A Hans

Pisa: V Caravetta

Kyoto: S Thürmer

Tartu: M Berholts

Campinas: A de Brito

Tohuku: Z Yin

Rio de Janeiro: L Costa, A Pereira

Prague: E Muchová, P Slavícek, L Tomanik