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MAX-PLANCK-GESELLSCHAFT



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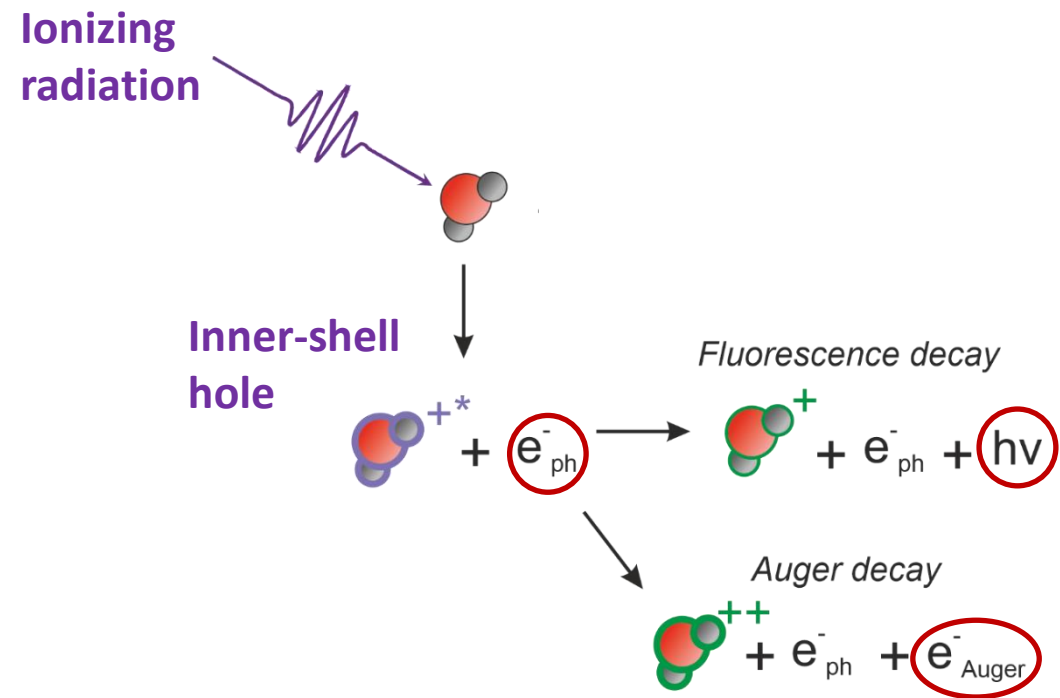
Processus de relaxation électronique non-locaux d'ions solvatés

Rémi Dupuy

CNRS, Sorbonne Université – Laboratoire de Chimie Physique, Matière et Rayonnement

T. Buttersack, F. Trinter, C. Richter, S. Gholami, O. Björneholm, U. Hergenahn, B. Winter and H. Bluhm

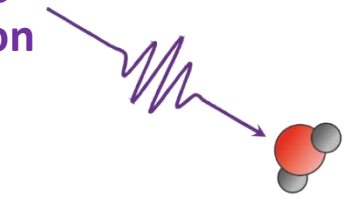
Non-local decay processes



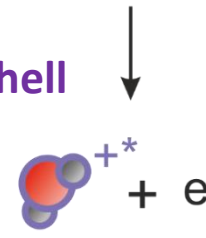
X-ray based spectroscopies

Non-local decay processes

Ionizing radiation



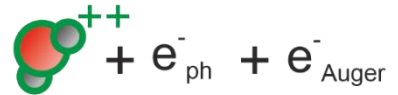
Inner-shell hole



Fluorescence decay



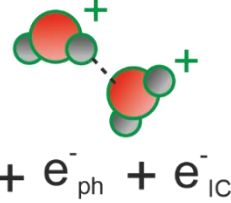
Auger decay



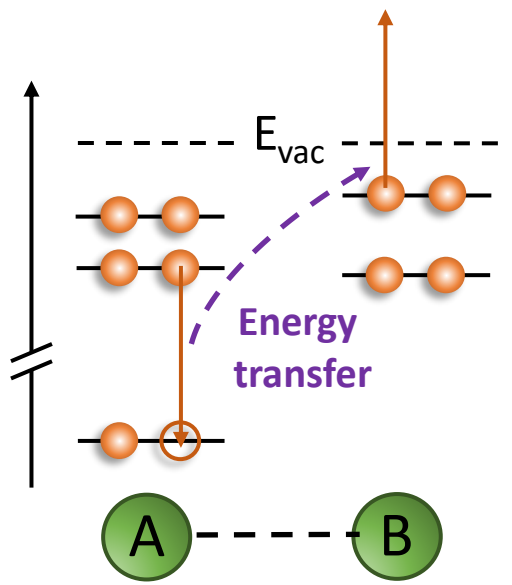
Electron Transfer Mediated Decay (ETMD)



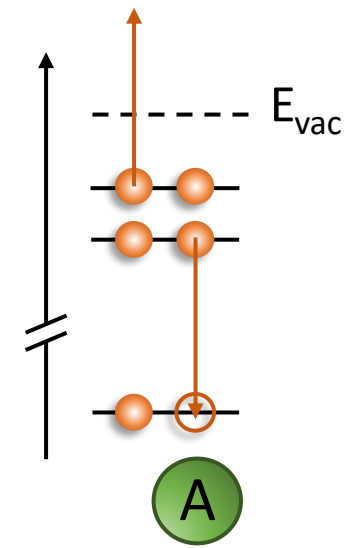
Intermolecular Coulombic Decay (ICD)



Non-local processes



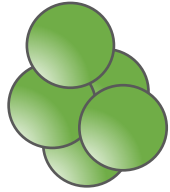
Intermolecular Coulombic Decay



Auger decay

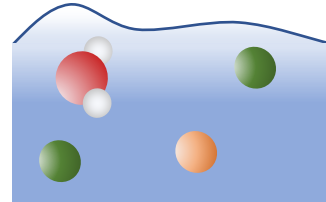
Non-local decay processes

Exhaustive review : Jahnke et al. 2020, *Chemical Reviews* 120 (20) 11295



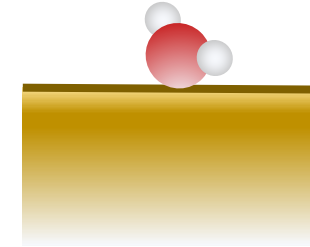
Clusters

- Model systems
- First evidence
- Large body of works covering many aspects



Liquids

- Highly relevant (e.g. radiolysis)
- Several works on pure solvents and dissolved simple ions



Solids, quantum dots...

- Few works, often indirect evidence

Liquid microjet photoemission spectroscopy

Instrument EASI of the
group of Bernd Winter

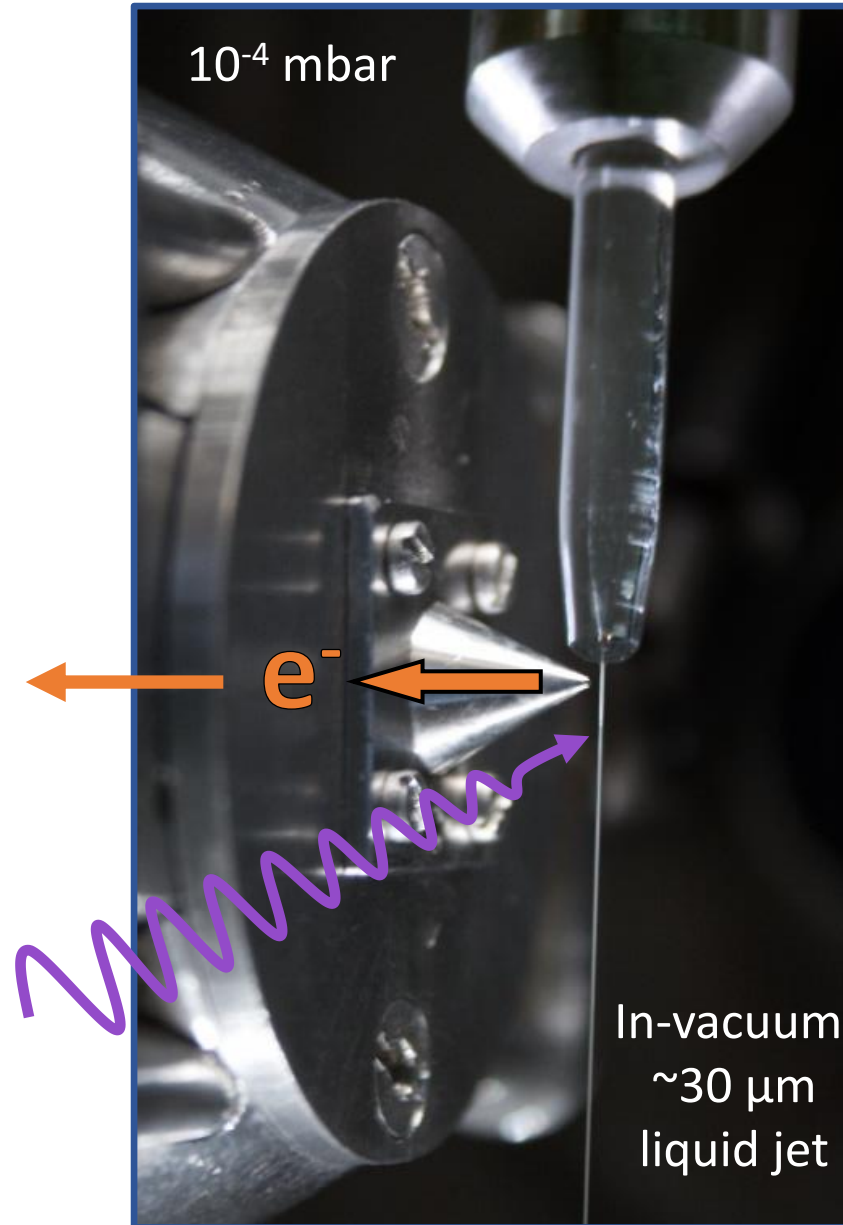
Hemispherical
electron analyzer

Synchrotron beam



PETRA III

P04
beamline



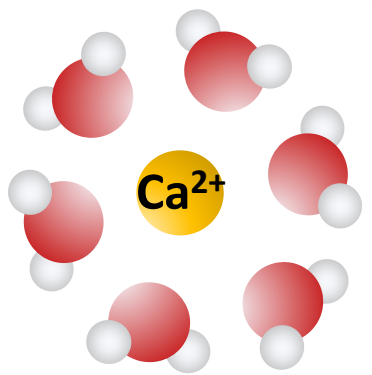
Winter & Faubel 2006
Chem. Rev. 106 (4) 1176

Seidel et al. 2011
J. Phys. Chem. Lett. 2 (6) 633

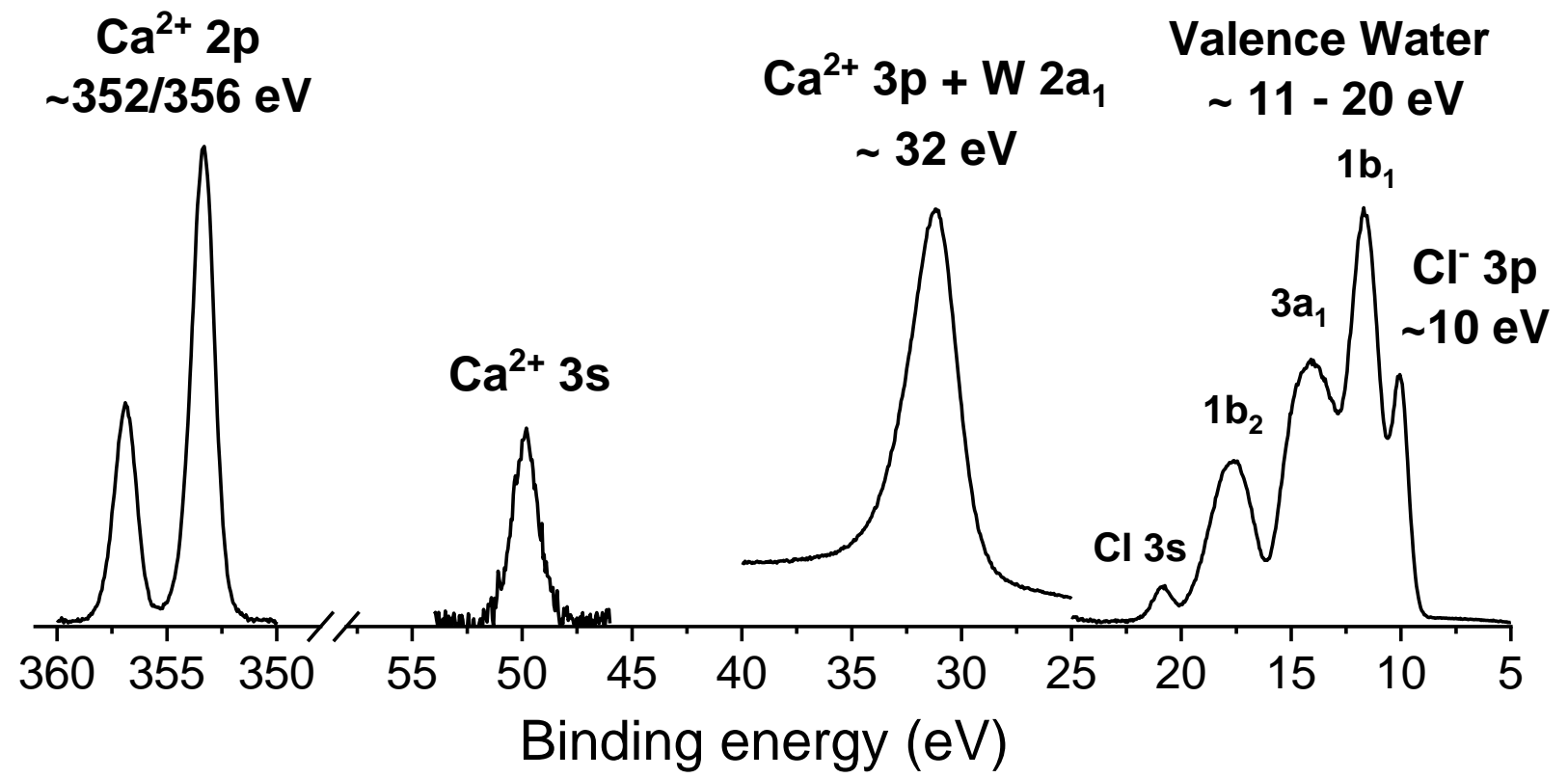
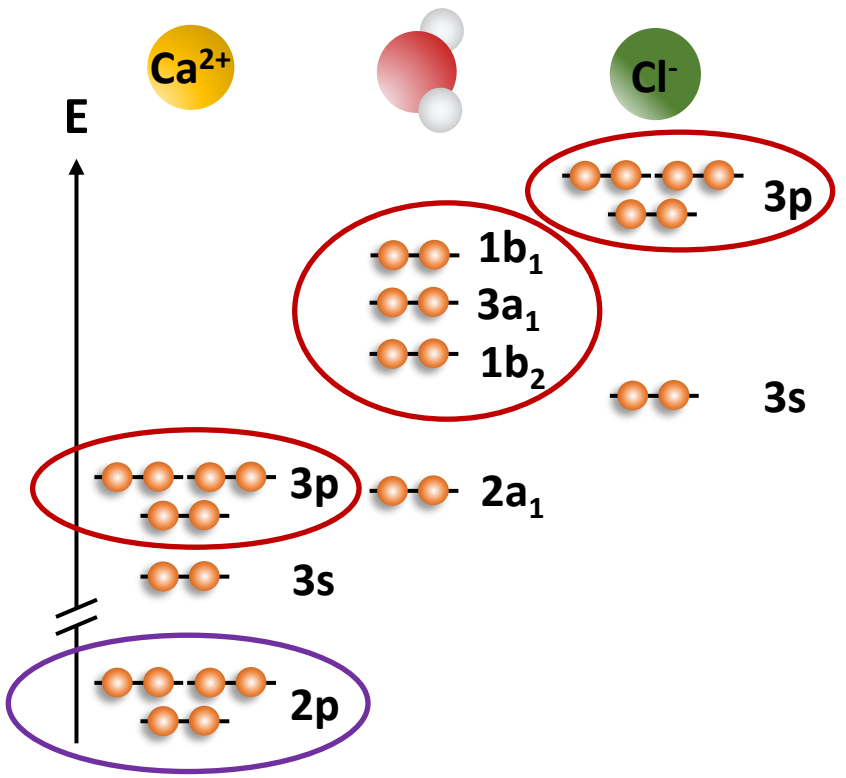
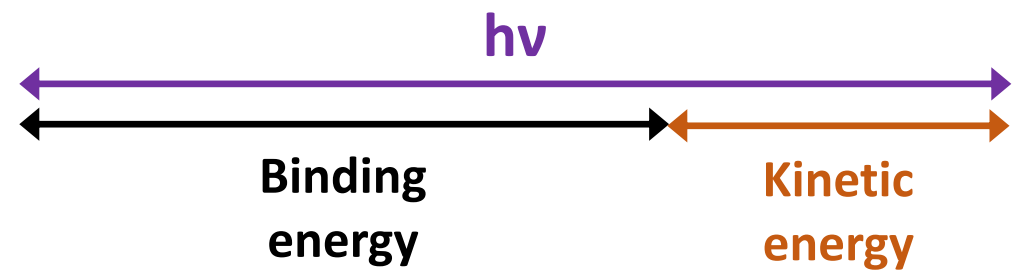
Ammann et al. 2018

Dupuy et al. 2021
J. Chem. Phys. 154 (6) 060901

Electronic structure of the CaCl₂ solution



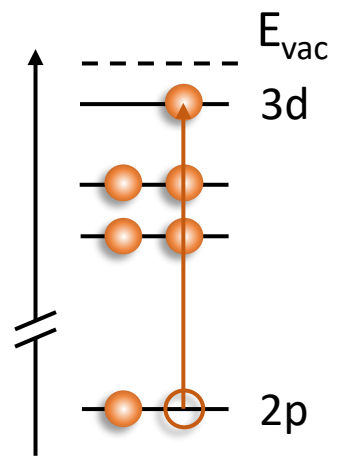
Energy levels measured by photoelectron spectroscopy (XPS) :



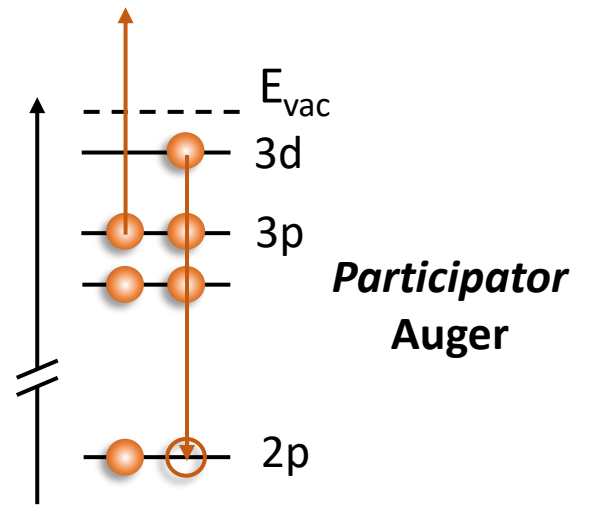
What about resonant ICD?

2

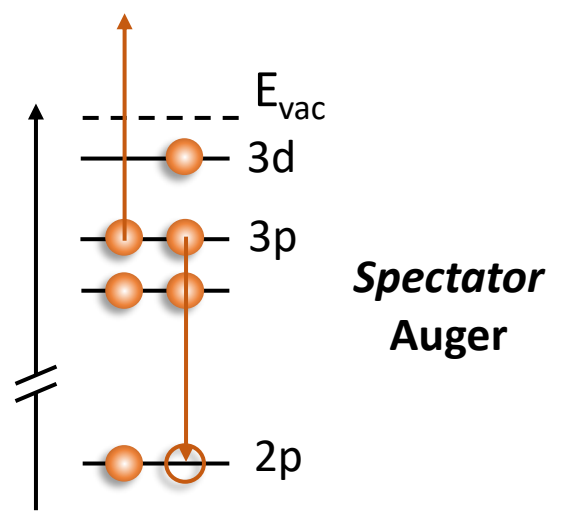
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Initial step:
**Resonant
excitation**

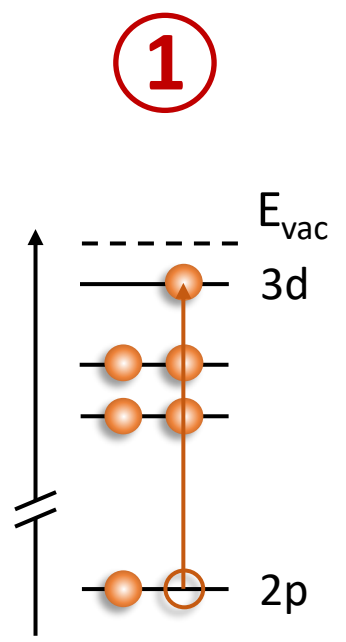


*Participator
Auger*

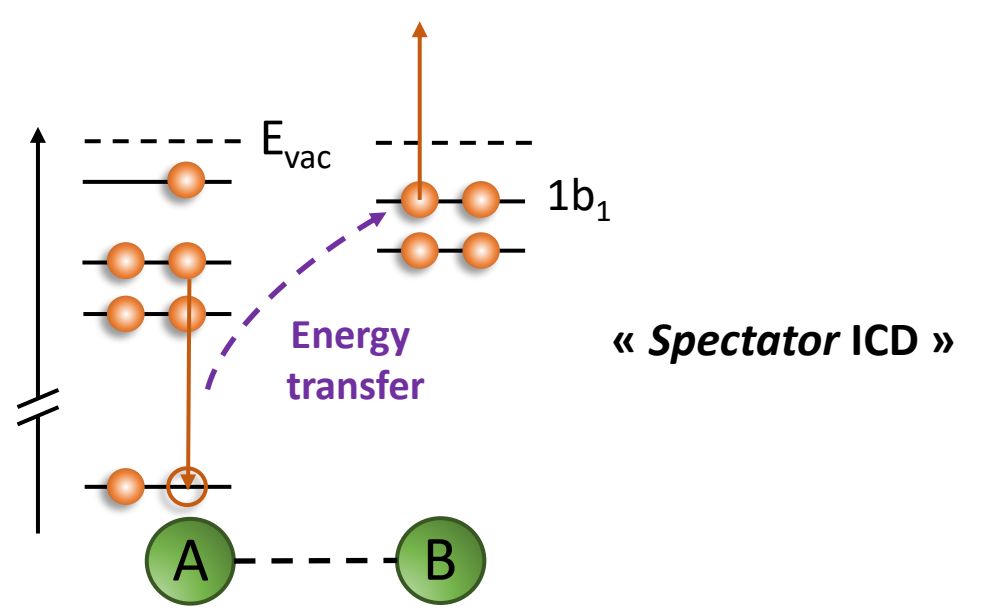
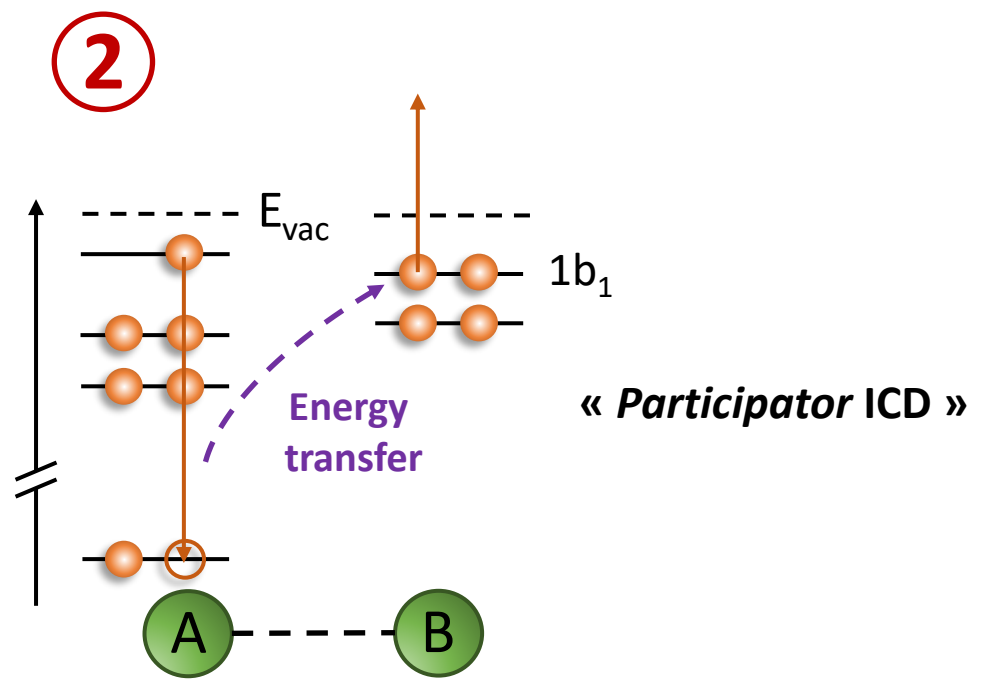
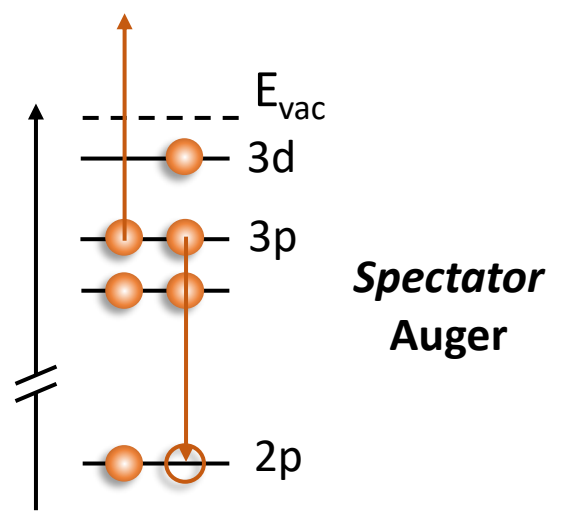
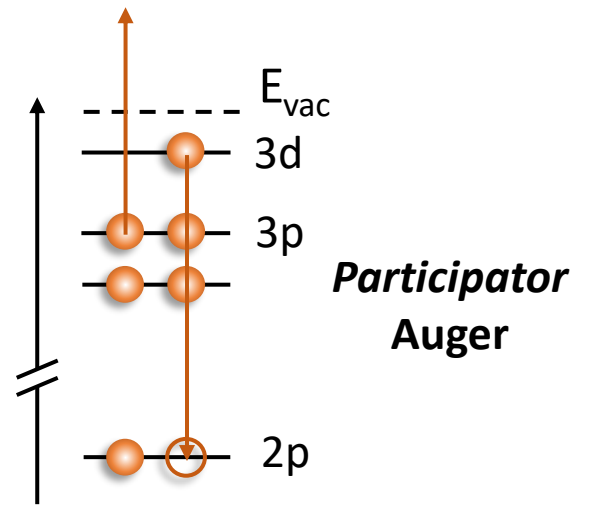


*Spectator
Auger*

What about resonant ICD?



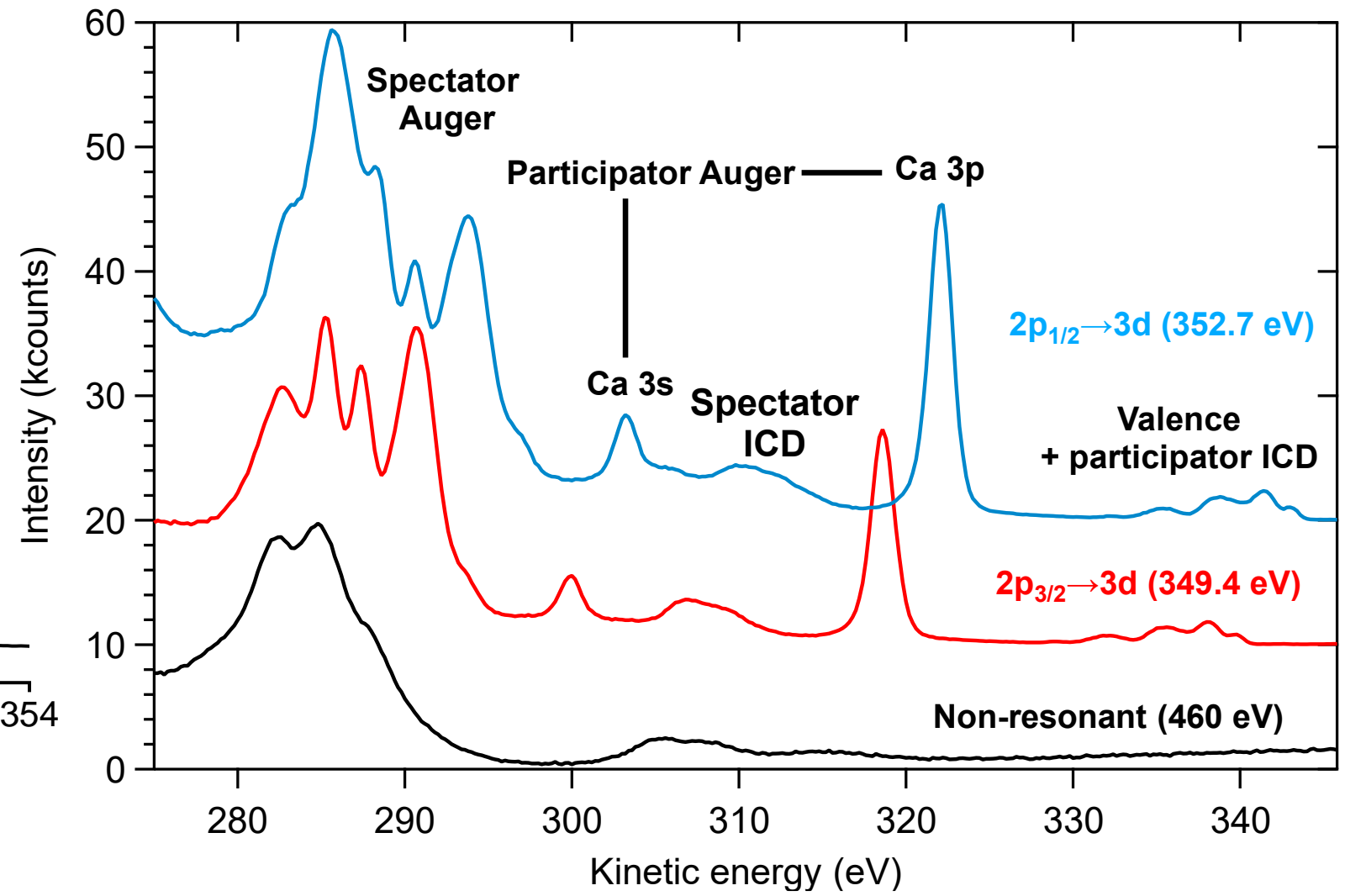
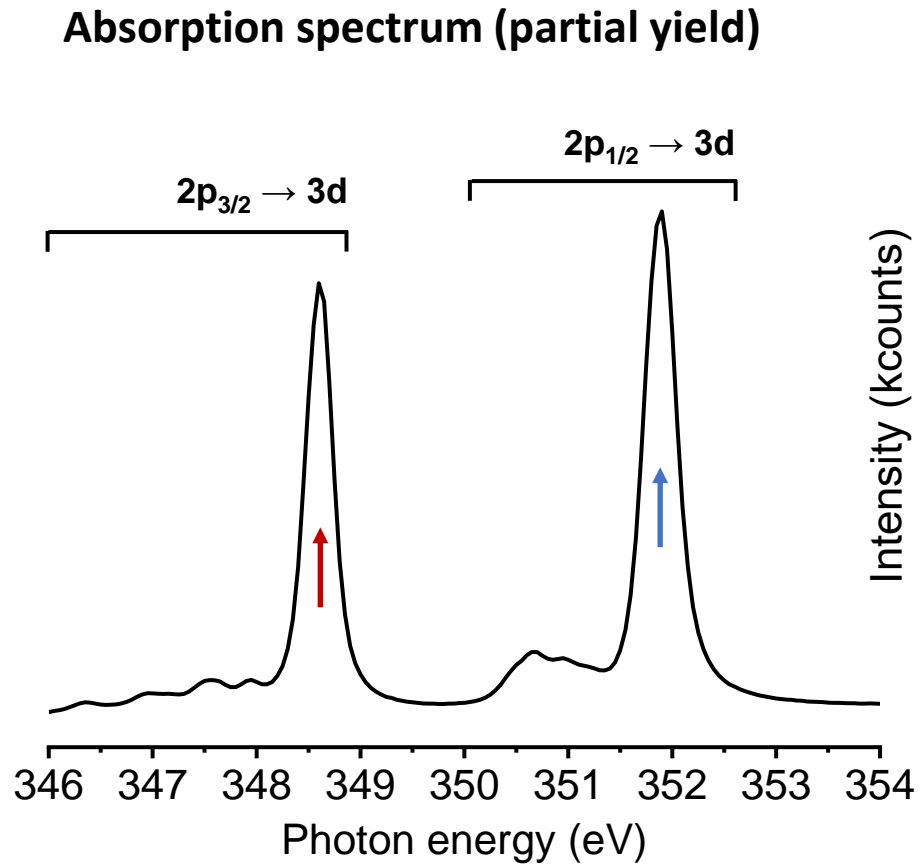
Initial step:
Resonant excitation



Ca 2p absorption edge and resonant spectra

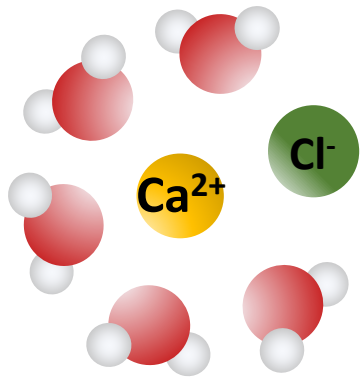
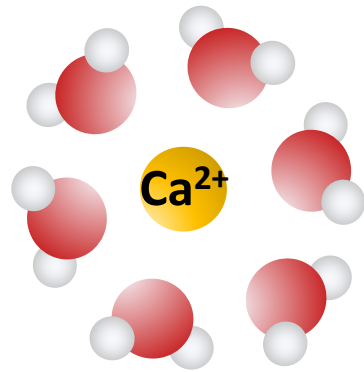
2

1



Conclusion 1 : we detect ICD

Spectator ICD to probe ion pairing



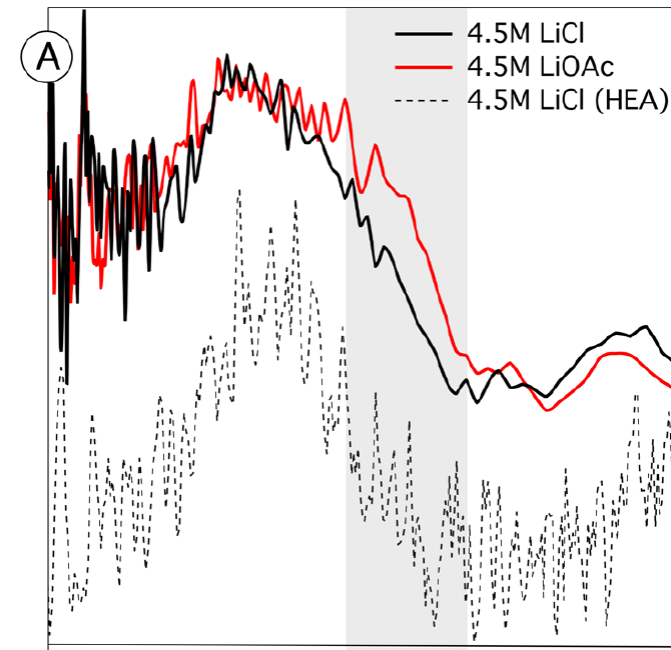
Contact ion pair

ICD-like processes depend on neighbours and inter-molecular distance
=> potential structural probe

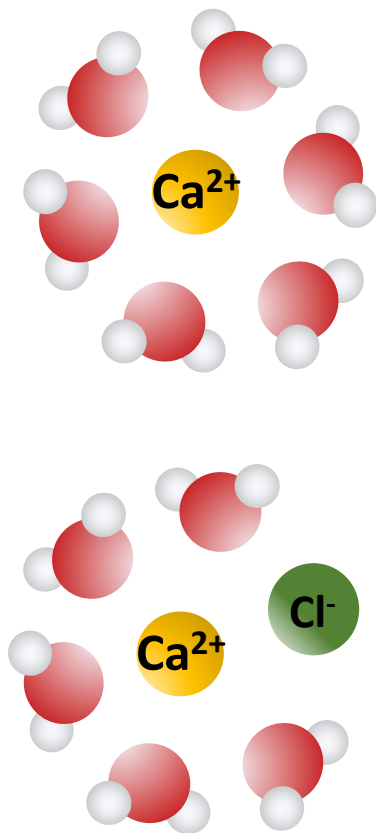
E.g. Pokapanich et al. 2014, *ScienceAsia* 40 (4) 290
on K Halides solutions : no signature found

Pohl et al. 2017, *J. Phys. Chem. B* 121 (32) 7709 :

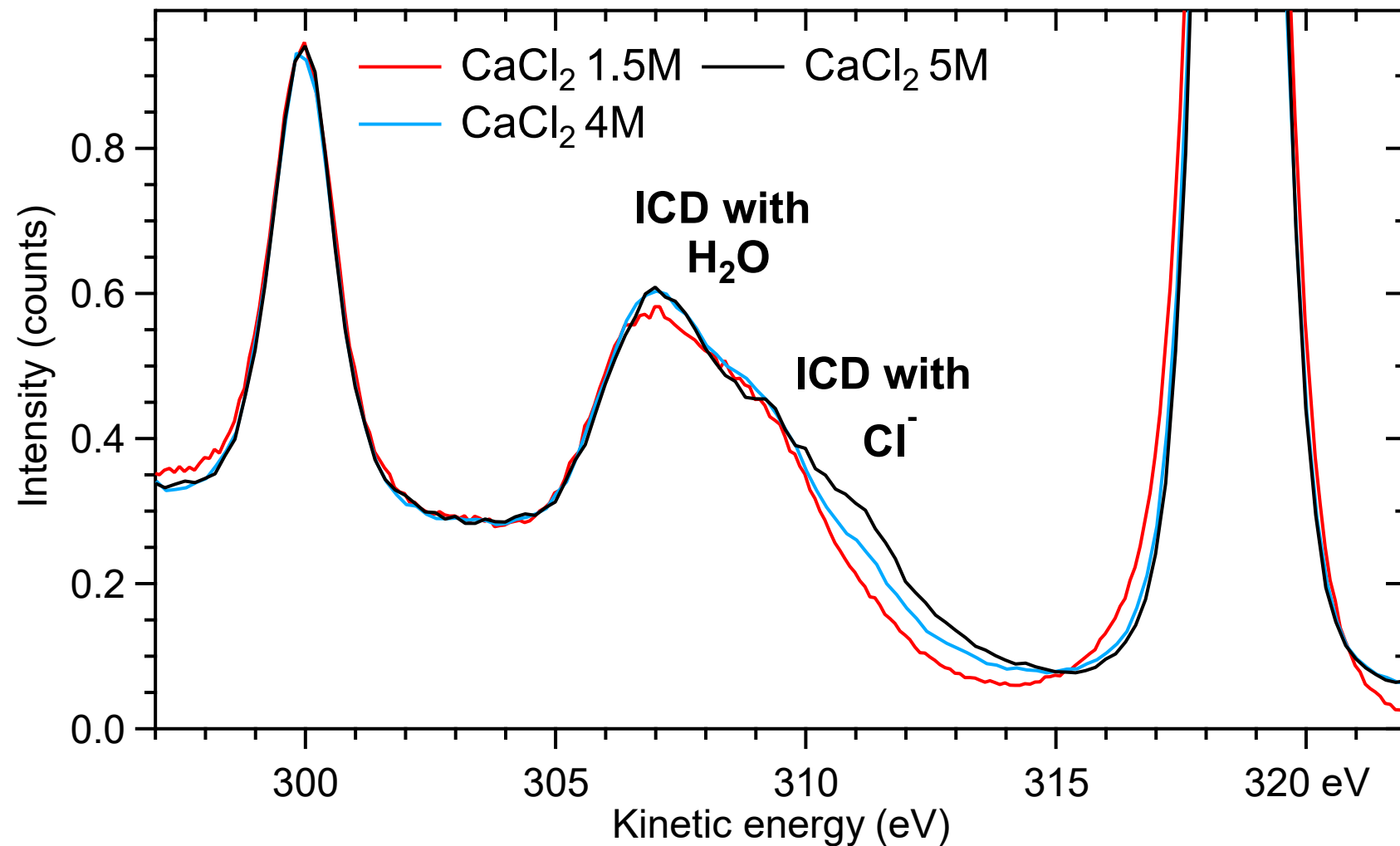
Lithium acetate forms ion pairs:
Signature observed in ETMD spectrum



Spectator ICD to probe ion pairing

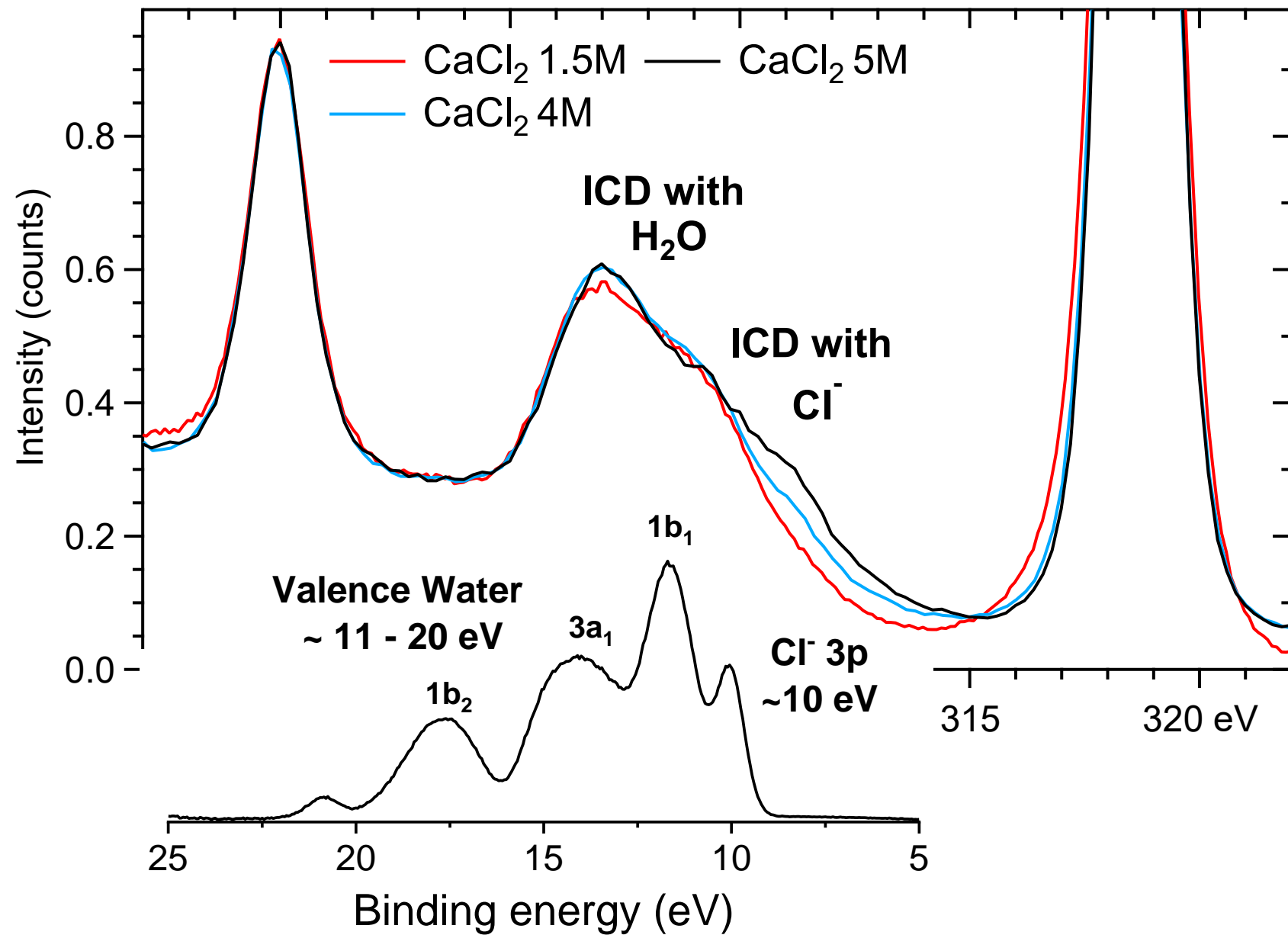
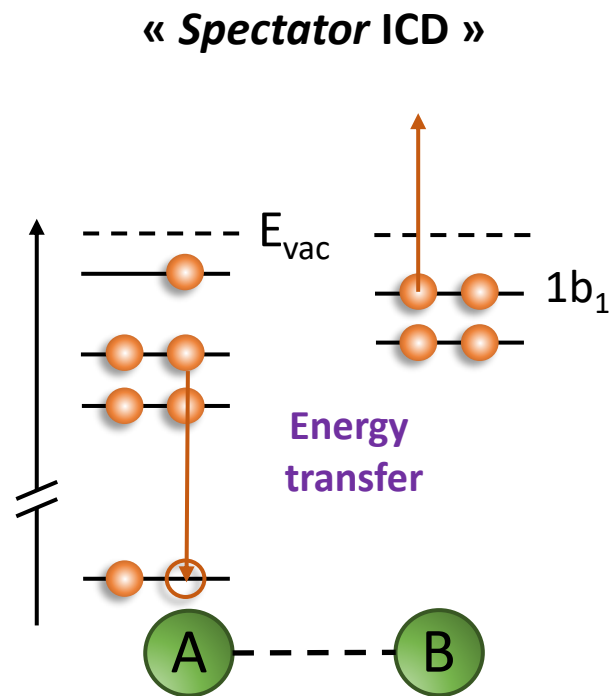


Contact ion pair

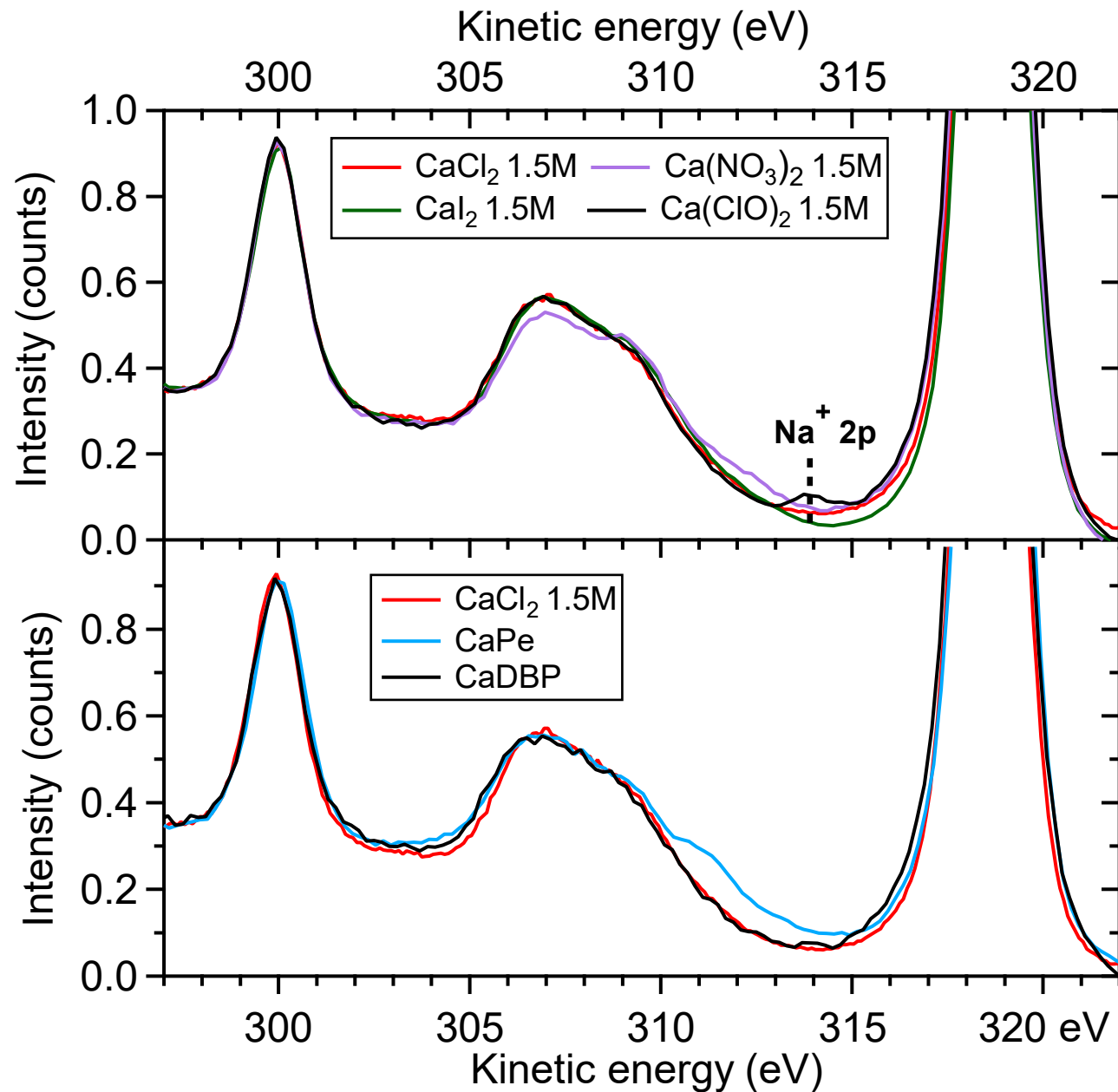


CaCl₂ in solution starts forming ion pairs around 4M (X-ray diffraction) : *Badyal et al. 2004 J. Phys. Chem. A 108 11819*
CaCl₂ forms no ion pairs even at 6.4 M (saturation) (Neutron diffraction) : *Megyés et al. 2004 J. Phys. Chem. A 108 7261*

Spectator ICD to probe ion pairing



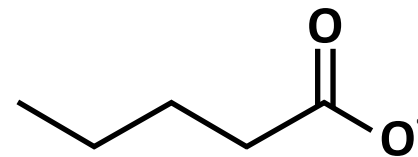
Spectator ICD to probe ion pairing



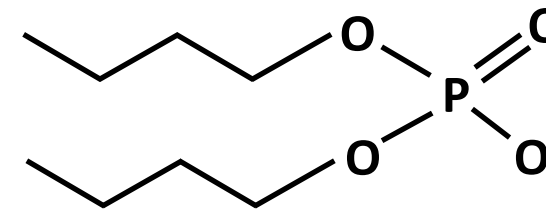
Conclusion 2 :

ICD can indeed be used as a new spectroscopic tool

Pe (pentanoate):



DBP (dibutyl phosphate):





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Thank you!

From the Fritz-Haber-Institut:

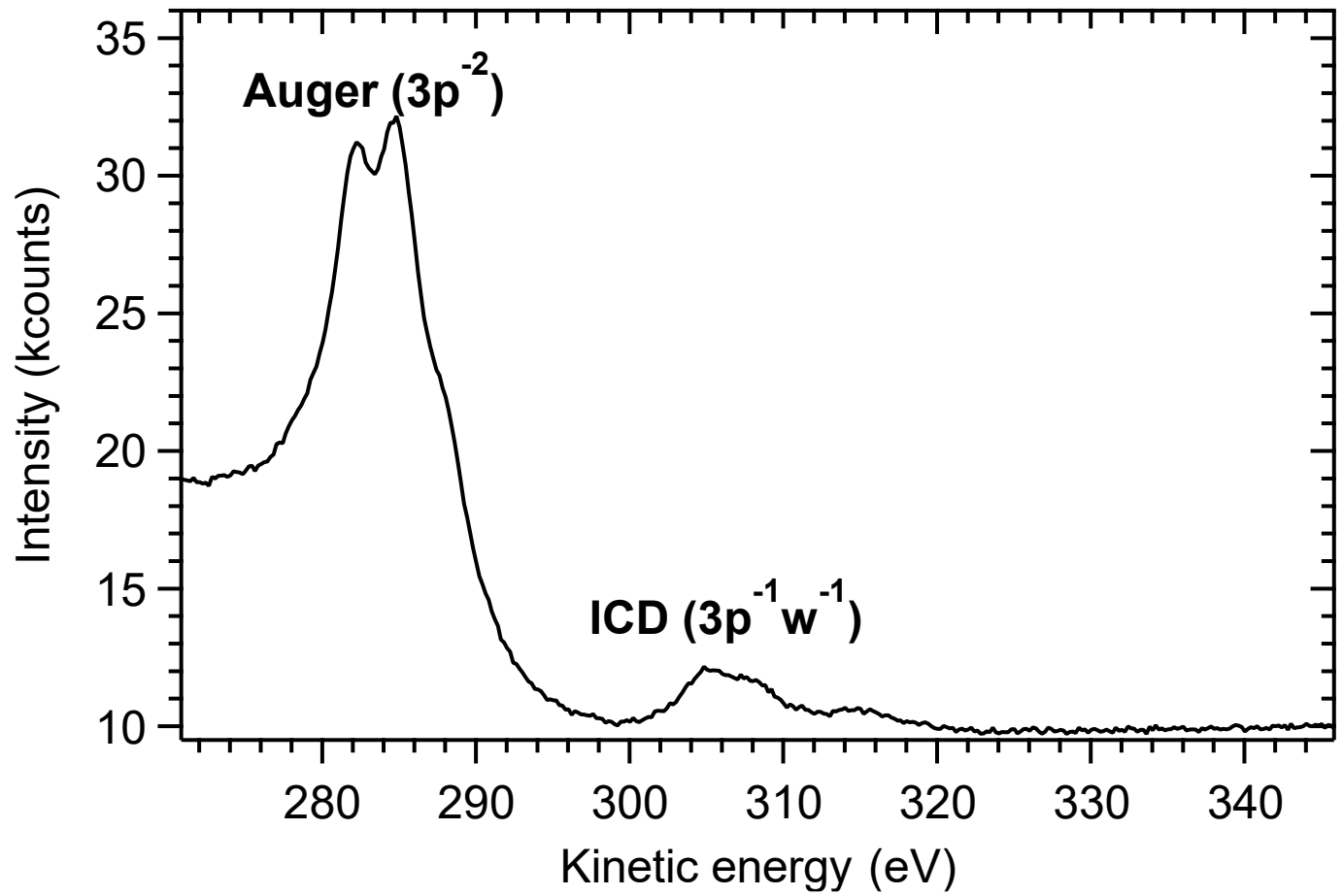
Tillmann Buttersack
Clemens Richter
Shirin Gholami
Florian Trinter

Uwe Hergenahn
Bernd Winter
Hendrik Bluhm

Collaborators:

Olle Björneholm (Uppsala uni)

Non-resonant Auger and ICD decay

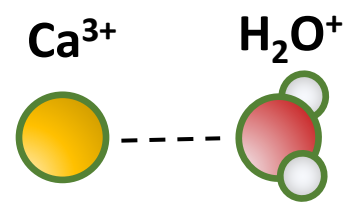


« Final state energy »

$$\begin{aligned}
 FSE &= h\nu - E_{K,ph} - E_{K,Auger} \\
 &= E_B(Ca^{2+} 2p) - E_{K,Auger}
 \end{aligned}$$

ICD Final state:

$$E_B(Ca^{2+} 3p) + E_B(partner) + \Delta E_C > 0$$



$$\begin{aligned}
 \text{Auger } 3p^{-2} &\sim 60 \text{ eV} + \Delta E_C \\
 \text{ICD } 3p^{-2} w^{-1} &\sim 40 \text{ eV} + \Delta E_C'
 \end{aligned}$$

Already observed in Pokapanich et al. 2011,
J. Am. Chem. Soc. 133 (34) 13430

Electronic structure of the CaCl₂ solution

