Ionic liquids at surfaces and interfaces

ENGINEERING OF ADVANCED MATERIALS

IONIC LIQUIDS
DFG – SPP 1191

F. Maier (florian.maier@fau.de)

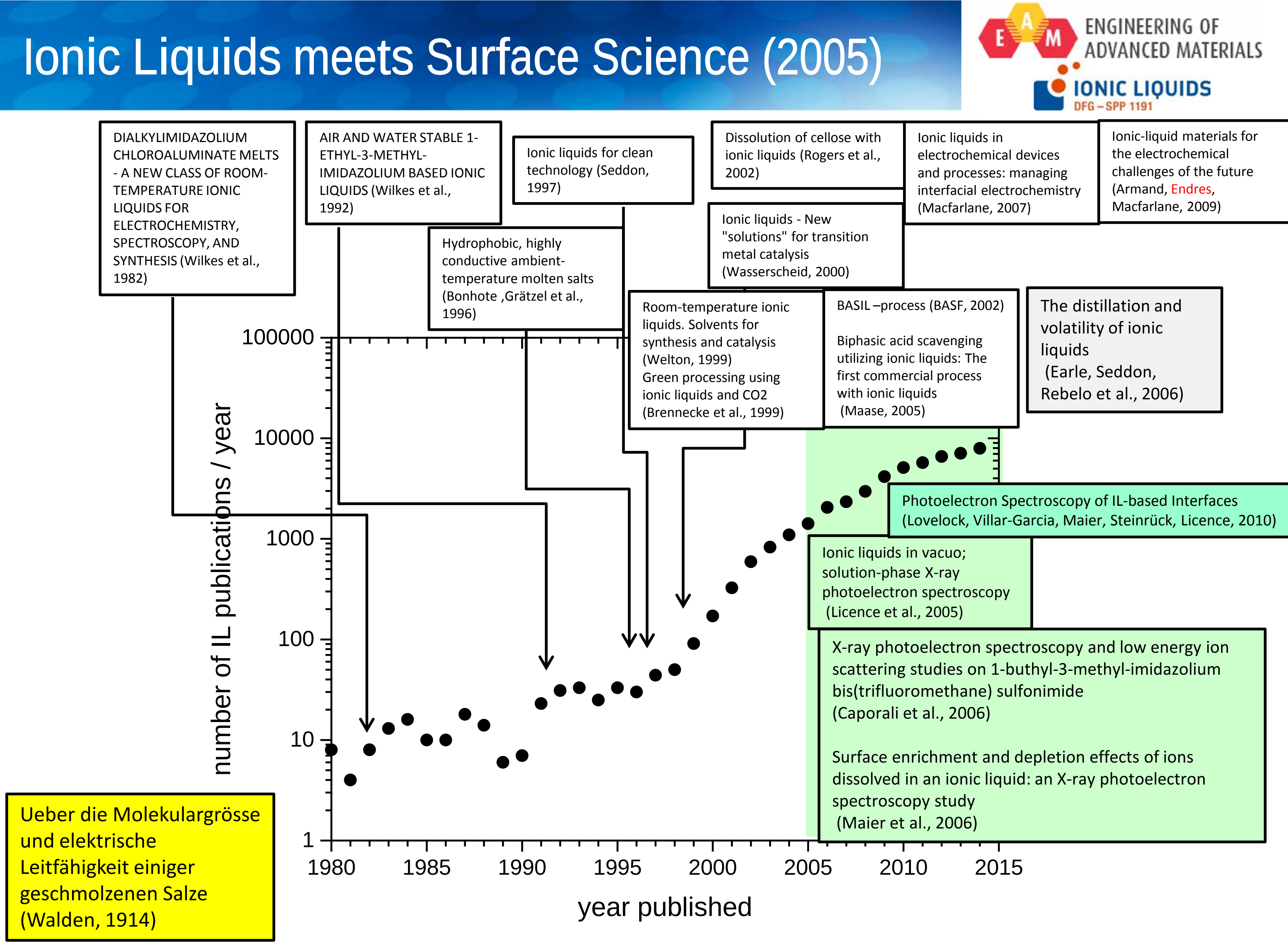
Lehrstuhl Physikalische Chemie II, Universität Erlangen-Nürnberg

(Symposium on Material Synthesis in Ionic liquids and Interfacial Processes. April 13-15th 2016, Goslar)

FRIEDRICH-ALEXANDER UNIVERSITÄT ERLANGEN-NÜRNBERG
NATURWISSENSCHAFTLICHE FAKULTÄT

PC-II

Ionic Liquids meets Surface Science (2005)



Maier, Web of Science, ionic_liquid* in Topic, 16.5.2015

Properties and applications of ionic liquids

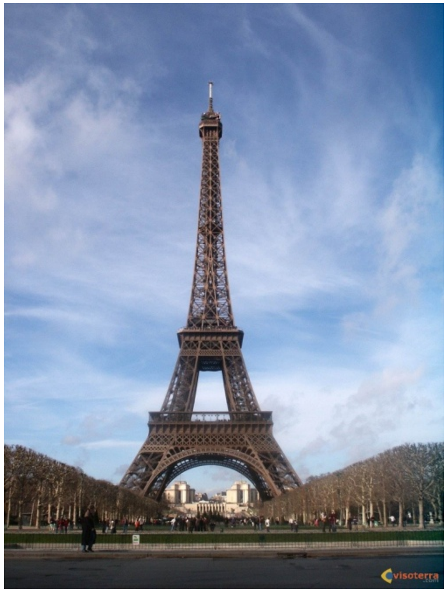
ENGINEERING OF ADVANCED MATERIALS
IONIC LIQUIDS
DFG – SPP 1191

➔ What is an ionic liquid?

- Consists entirely of ions ("molten salt")
- Liquid below 100°C
- Physico-chemical properties tunable by varying the molecular structure
- Extremely low vapor pressure (<10^{-9} mbar at 300 K)

"..The vapour pressure of e.g. [C_2C_1Im][$EtOSO_3$], is at room temperature in the same order of magnitude as the vapour pressure of a piece of iron…"

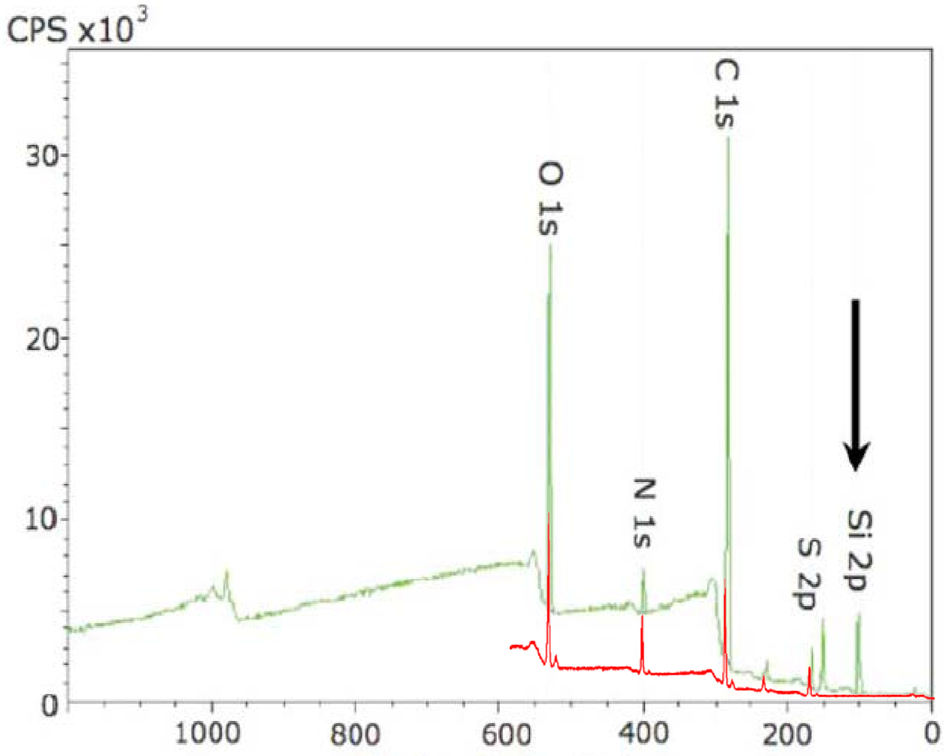
Prof. Andreas Heintz, University Rostock, private communication



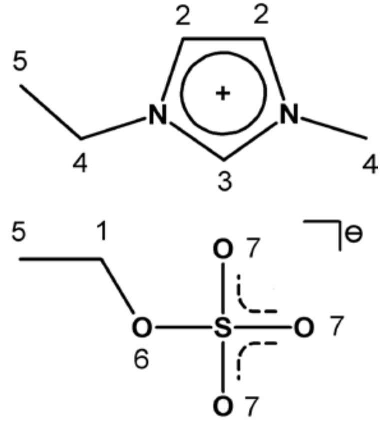
➔ Surface Science studies under UHV conditions are possible !!!!

➔ **What is an ionic liquid?**

- Consists entirely of ions ("molten salt")
- Liquid below 100°C
- Physico-chemical properties tunable by varying the molecular structure
- Extremely low vapor pressure (<10^{-9} mbar at 300 K)



[C_2C_1Im] [$EtOSO_3$] (commercially: ECOENG 212)



self-synthesized IL (surface clean)

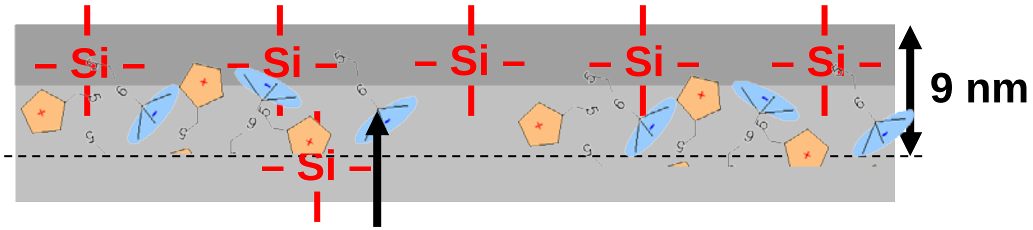
E. Smith, P. Licence *et al.* (Nottingham), Chem.Comm., **2005**, 5633.

J.M. Gottfried, F. Maier et al., Z. Phys. Chem., **2006**, 220, 1439.

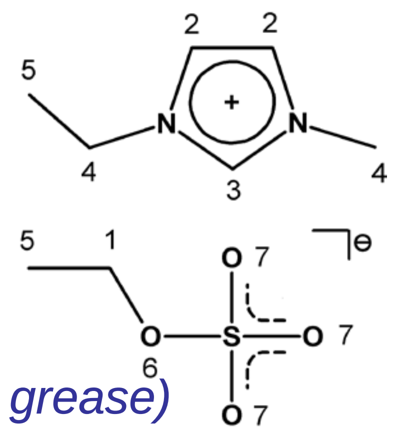
Properties and applications of ionic liquids

➔ What is an ionic liquid?

- Consists entirely of ions ("molten salt")
- Liquid below 100°C
- Physico-chemical properties tunable by varying the molecular structure
- Extremely low vapor pressure ($<10^{-9}$ mbar at 300 K)



$[C_2C_1Im]$
$[EtOSO_3]$
(commercially:
ECOENG 212)



→ SiO_xR_y-impurities of unknown origin (polysiloxane from glassware grease) contaminate the near-surface region (in-situ cleaning via sputtering possible)

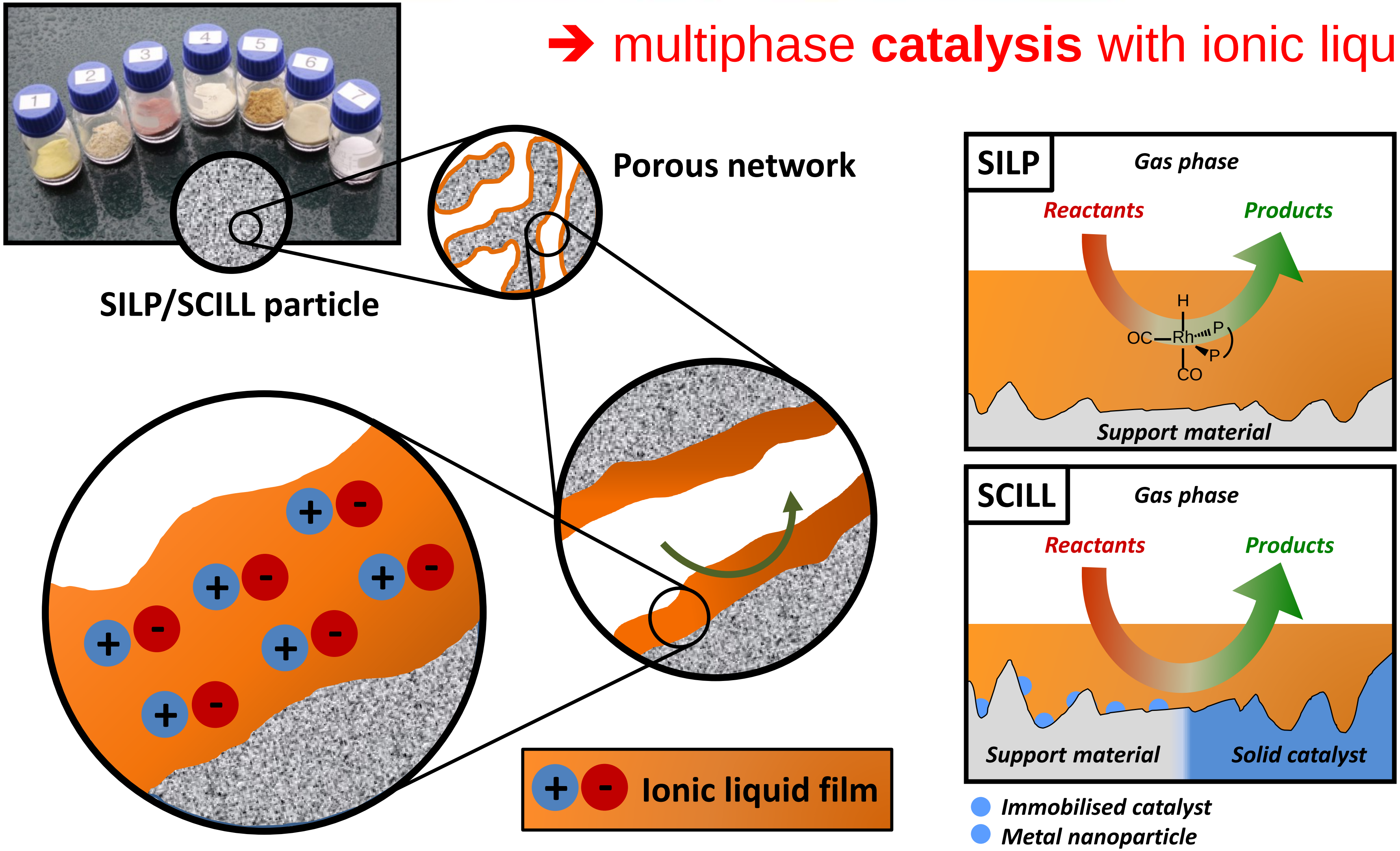
Surface active species may strongly modify surface properties (surface tension, surface activity, …)

J.M. Gottfried, F. Maier et al., Z. Phys. Chem., **2006**, 220, 1439.

Why studying *interfaces* of ionic liquids?

ENGINEERING OF ADVANCED MATERIALS
IONIC LIQUIDS DFG – SPP 1191

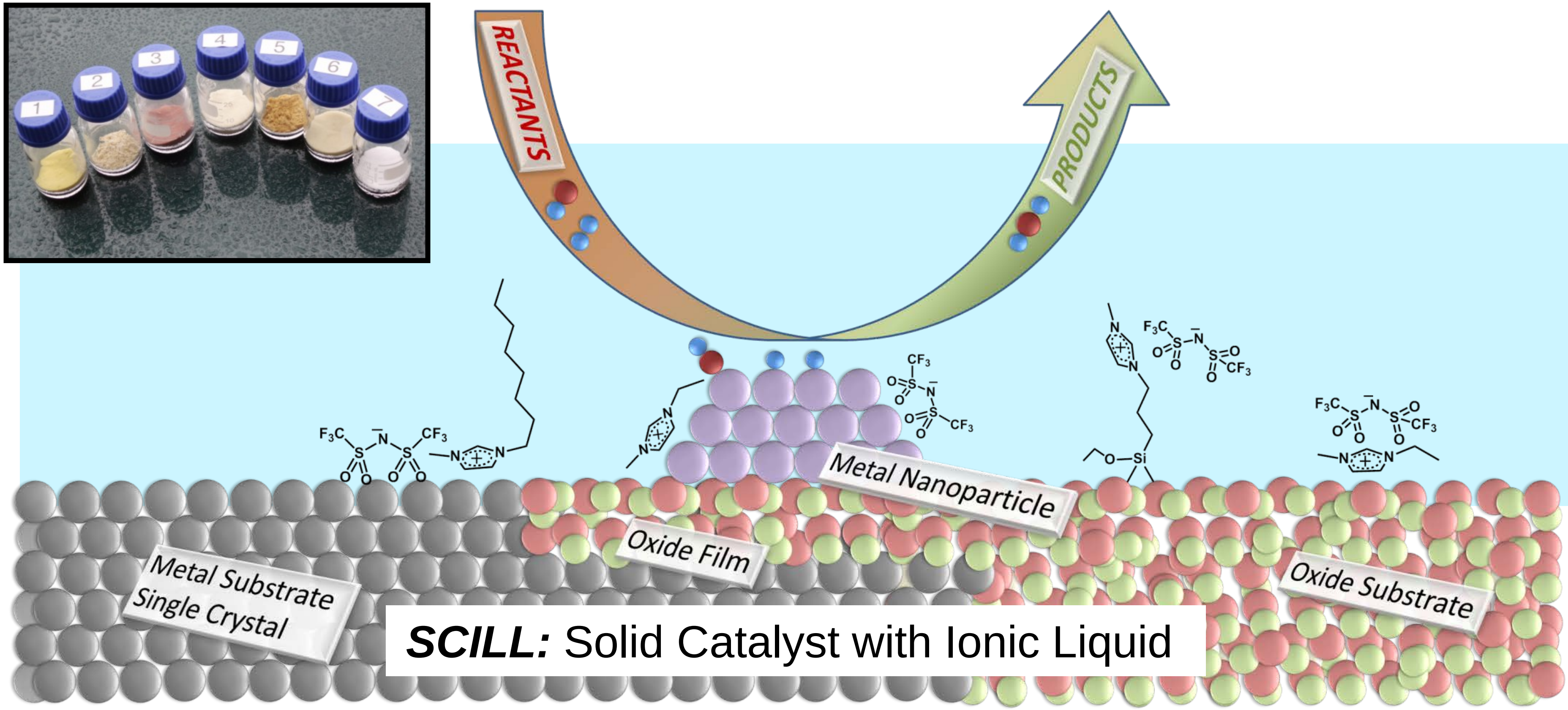
➔ multiphase **catalysis** with ionic liquids



SILP: Supported Ionic Liquid Phase - Riisager et al., *Ind. Eng. Chem. Res. 44 (2005) 9853*

SCILL: Solid Catalyst with Ionic Liquid Layer - Kernchen et al. , *Chem. Eng. Technol. 8* (2007) 985

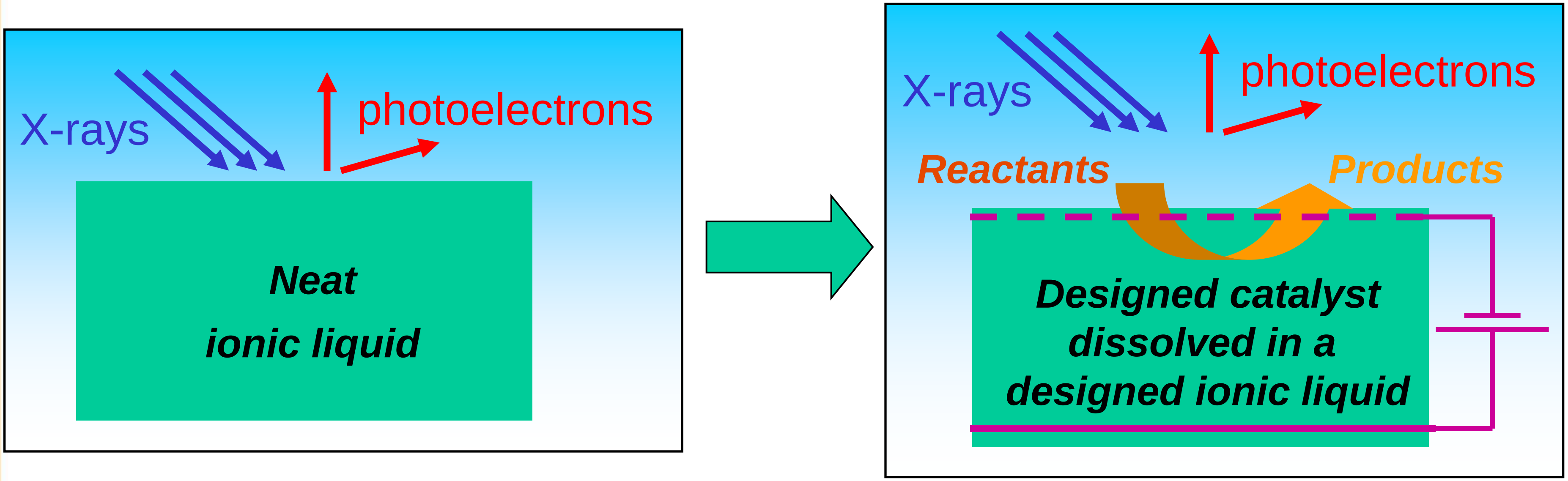
Why studying *interfaces* of ionic liquids?



SCILL: Solid Catalyst with Ionic Liquid

Why studying *interfaces* of ionic liquids?

Concept: From simple to complex systems



Ionic Liquid Surface and Interface Science

ENGINEERING OF ADVANCED MATERIALS
IONIC LIQUIDS DFG – SPP 1191

Physical Chemistry II

PC-II

group Prof. Dr. Hans-Peter Steinrück

SURFACE SCIENCE

- Photoelectron spectroscopy (ARXPS)
- Surface properties
- *In-situ* gas-phase reactions

Chemical Reaction Engineering

crt Lehrstuhl für Chemische Reaktionstechnik

group Prof. Dr. Peter Wasserscheid

IONIC LIQUID CHEMISTRY

- New IL structures, quality assessment
- Physico-chemical properties
- Metal complexes in ILs, IL catalysis

ILSS-project (2006-2012)

IL-solid interfaces (2008-2017)

IONIC LIQUIDS
DFG – SPP 1191

ENGINEERING OF ADVANCED MATERIALS

Acknowledgements

ENGINEERING OF ADVANCED MATERIALS

IONIC LIQUIDS DFG – SPP 1191

Prof. Dr. Peter Wasserscheid







crt Lehrstuhl für Chemische Reaktionstechnik

P. Schulz | N. Taccardi | N. Paape | W. Wei | M. Bahlmann | J. Schwegler

Prof. Dr. Hans-Peter Steinrück







C. Kolbeck | I. Niedermaier | B. May | K. Lovelock | A. Deyko | T. Matsuda

PC-II





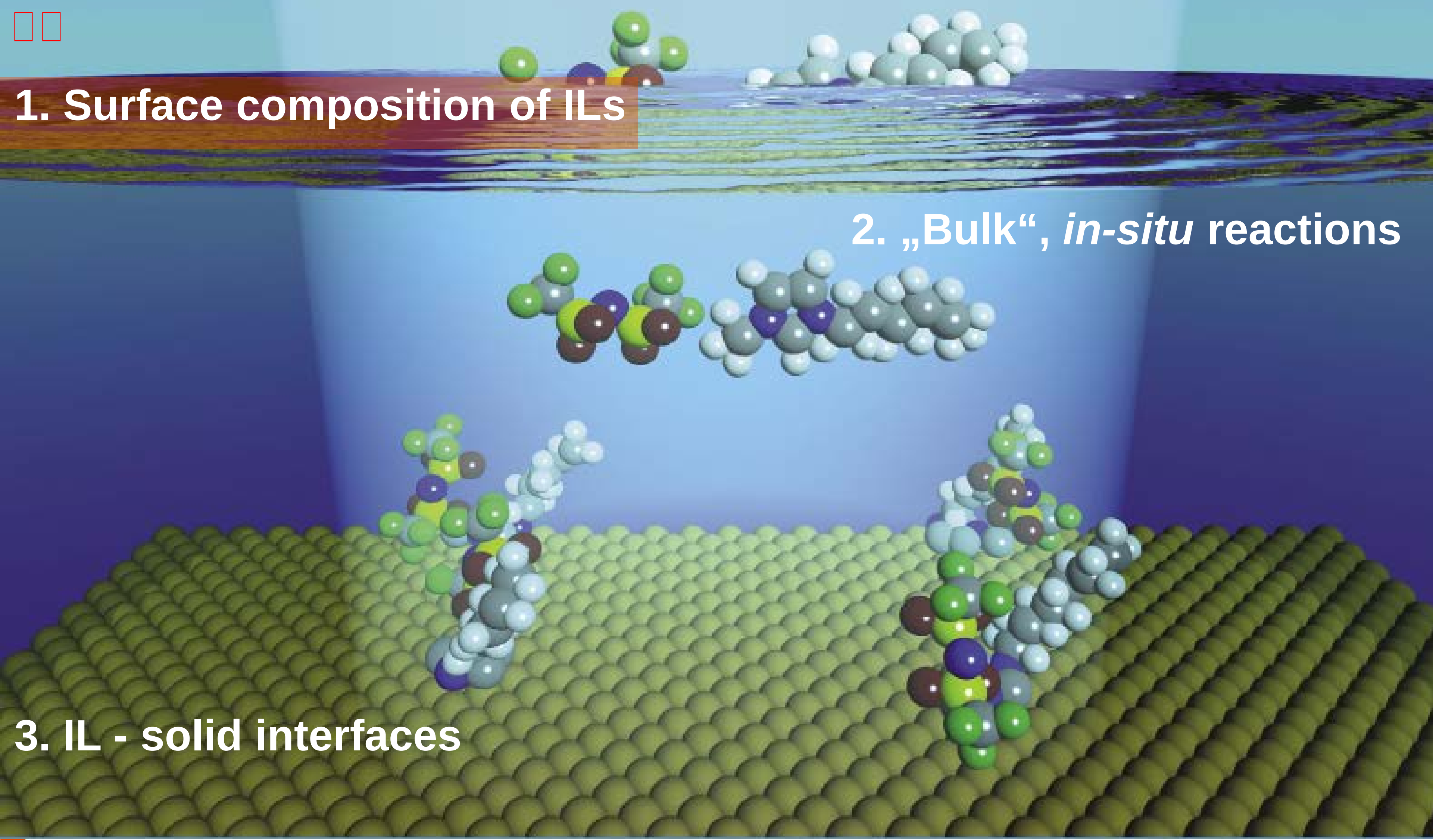
T. Cremer | F. Rietzler | P. Schreiber | B. Heller

Collaborations:

P. Licence, R. Jones, B. Kirchner, A. Fröba, J. Libuda, S. Baldelli, J. Behm, J. Schatz, J. Lopes ...

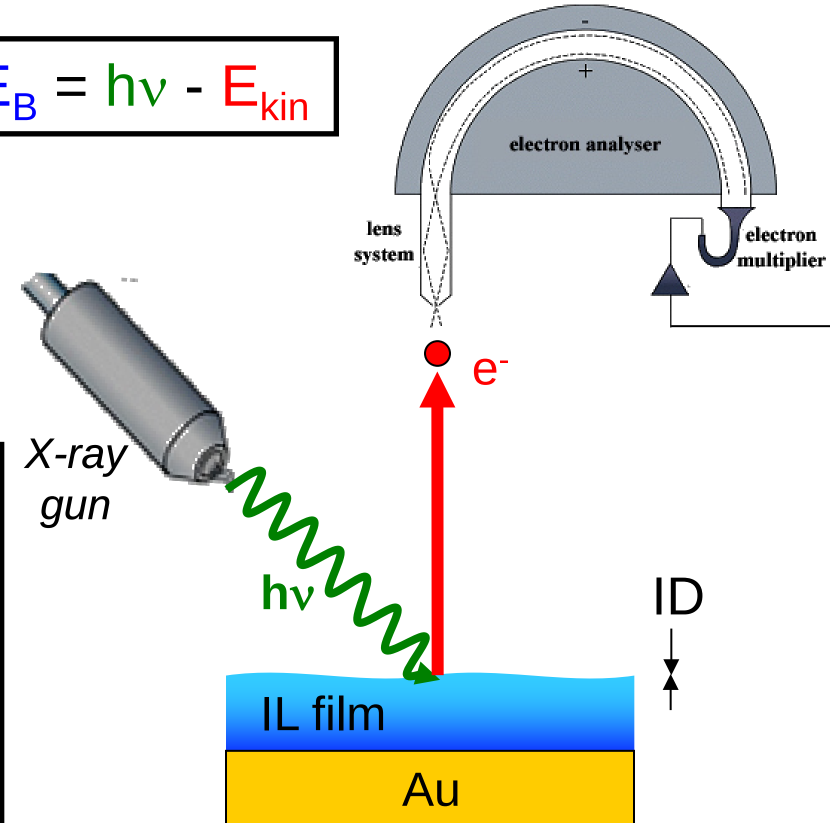
Supported by: DFG (SPP 1191, CoE-EAM, STE 620/9-1), A.v.Humboldt- and Max-Buchner-Stiftung, Industry

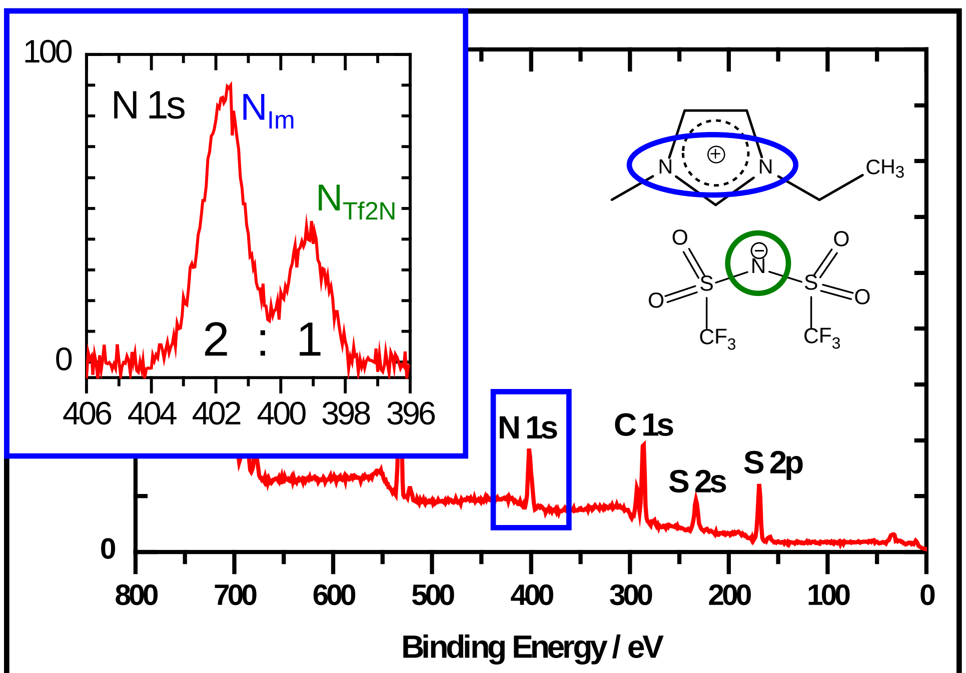
Surface and Interface Science of Ionic Liquids



X-ray photoelectron spectroscopy (XPS)

$$E_B = h\nu - E_{kin}$$

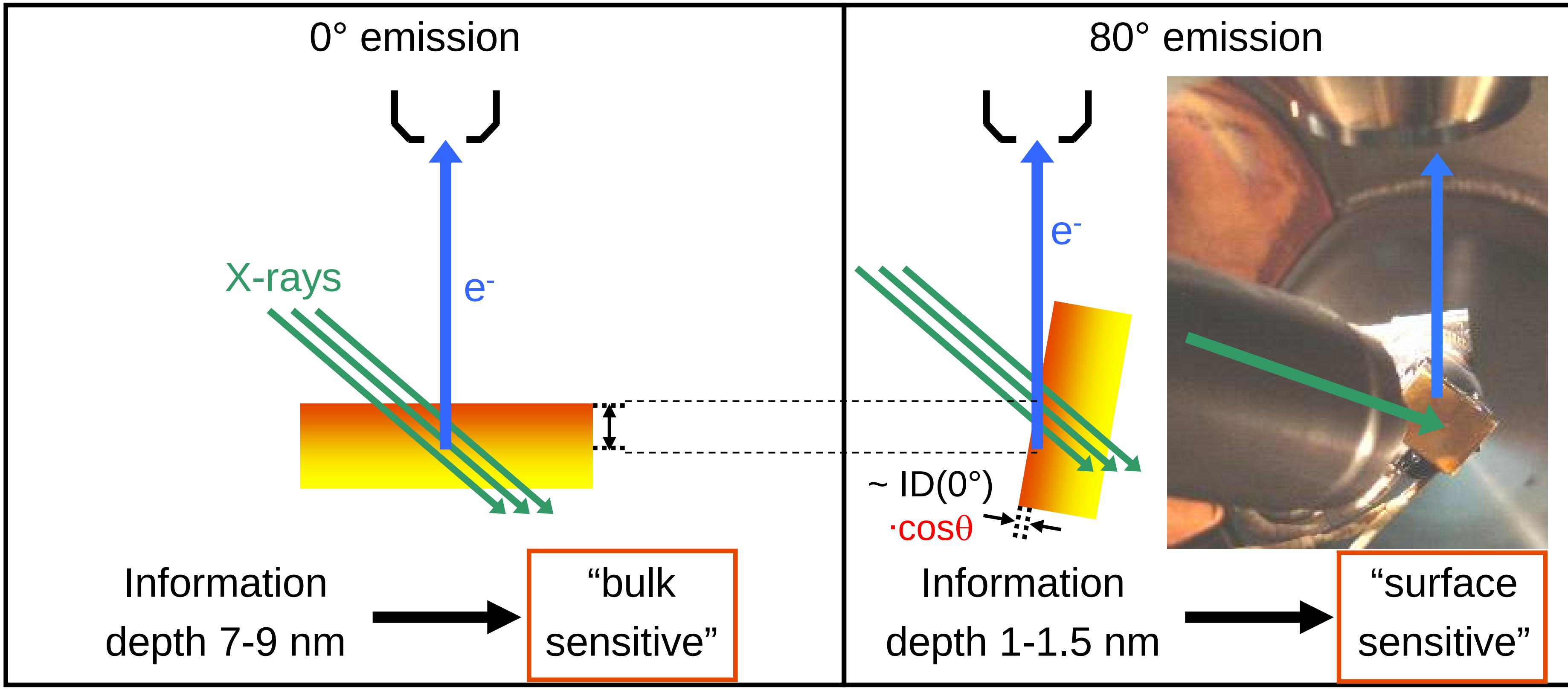




- → Element specific
- → Chemical shift
- → Quantitative analysis
- → Surface sensitive (ID_{max} ≈ 9nm)

Angle-resolved XPS (ARXPS)

variation of surface sensitivity by varying electron detection angle



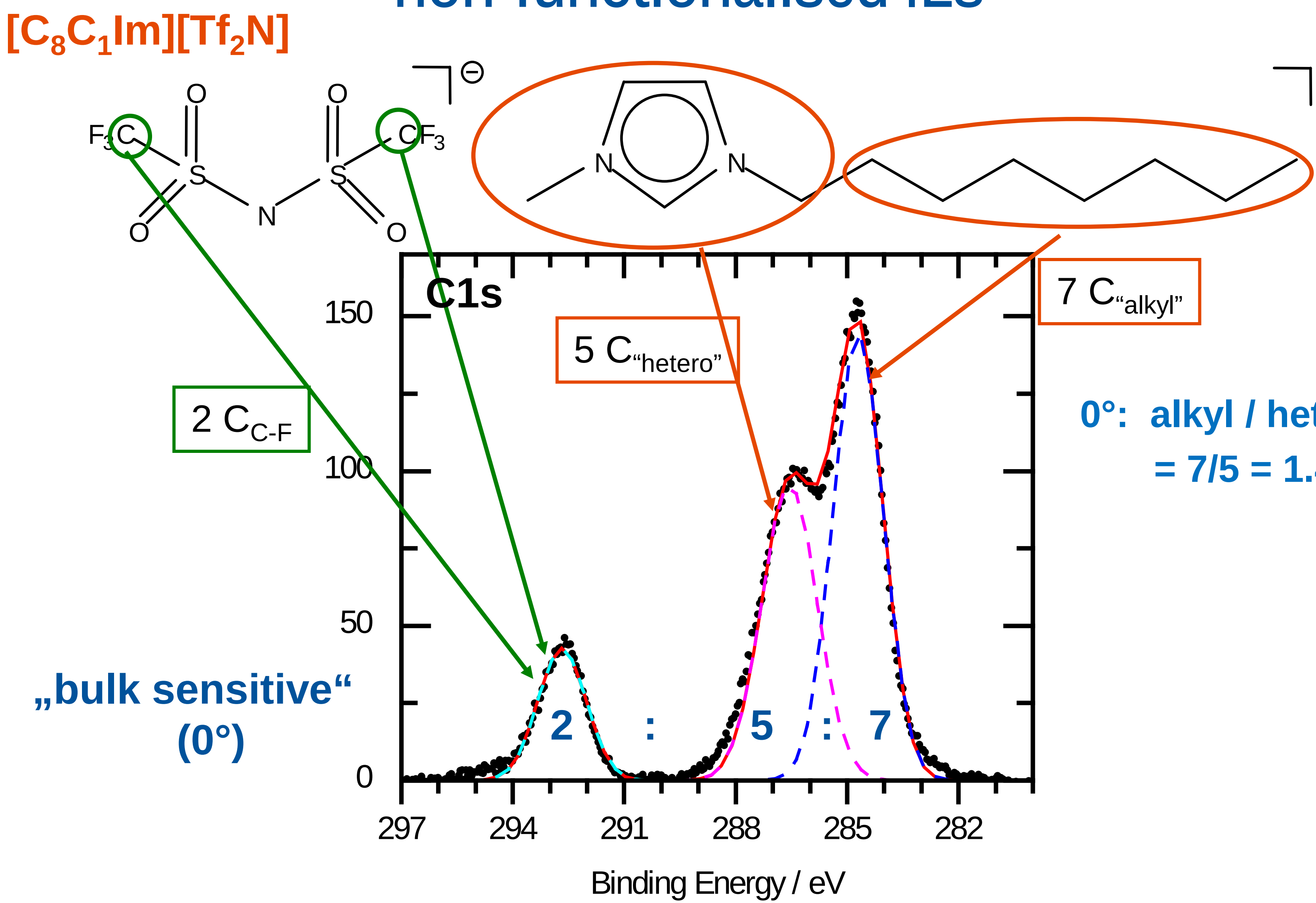
Key message

0° ⇒ 80°: Intensity of one species increases

→ enhancement of that species at surface region

Influence of chain length $[C_nC_1Im]^+$

non-functionalised ILs

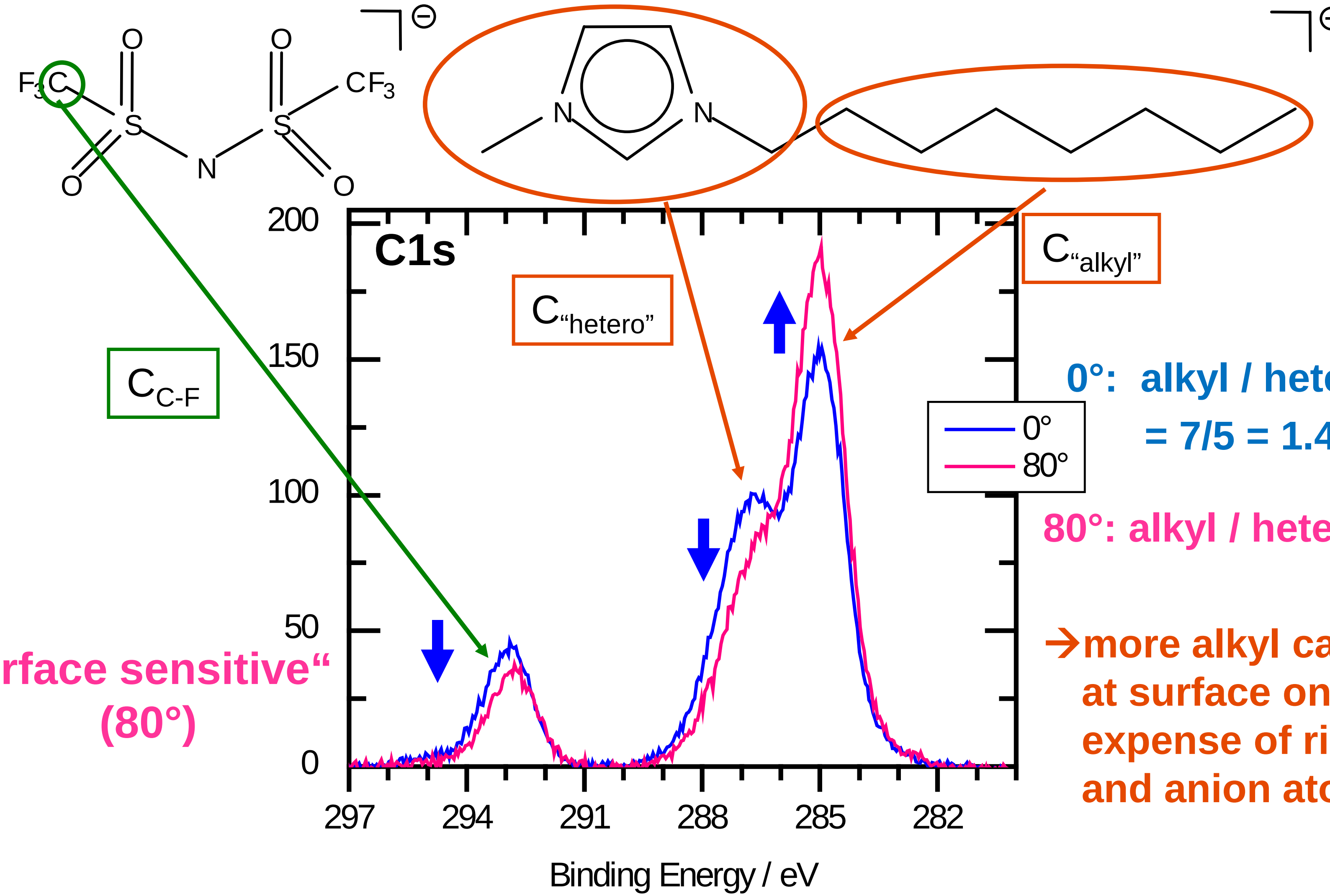


0°: alkyl / hetero =
= 7/5 = 1.4

„bulk sensitive“ (0°)

Influence of chain length $[C_nC_1Im]^+$

$[C_8C_1Im][Tf_2N]$



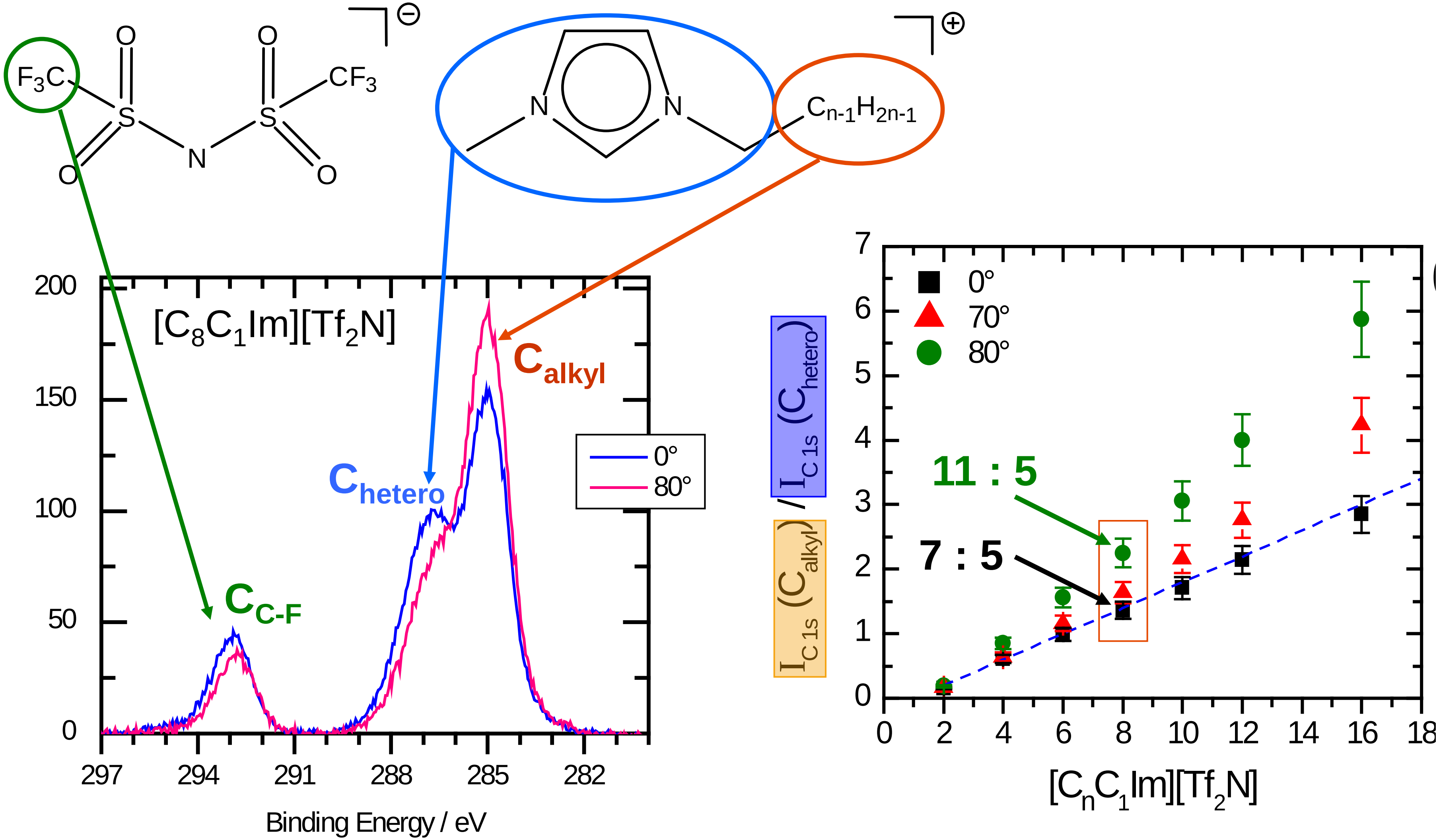
„surface sensitive“ (80°)

0°: alkyl / hetero = = 7/5 = 1.4

80°: alkyl / hetero = 2.2

→more alkyl carbon at surface on expense of ring and anion atoms

Influence of chain length $[C_nC_1Im]^+$



→ longer chains, more alkyl carbon at surface

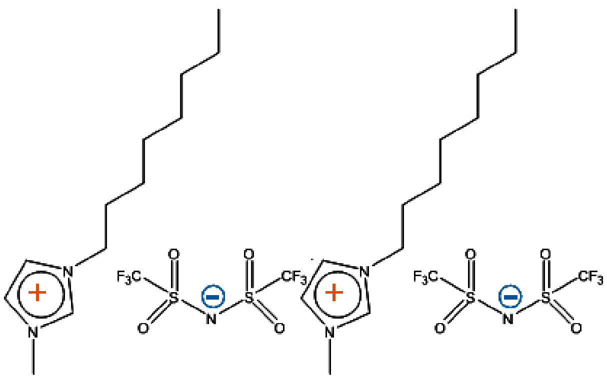
Lovelock *et al. J Phys. Chem B*, **2009**, 113, 2854-2864.

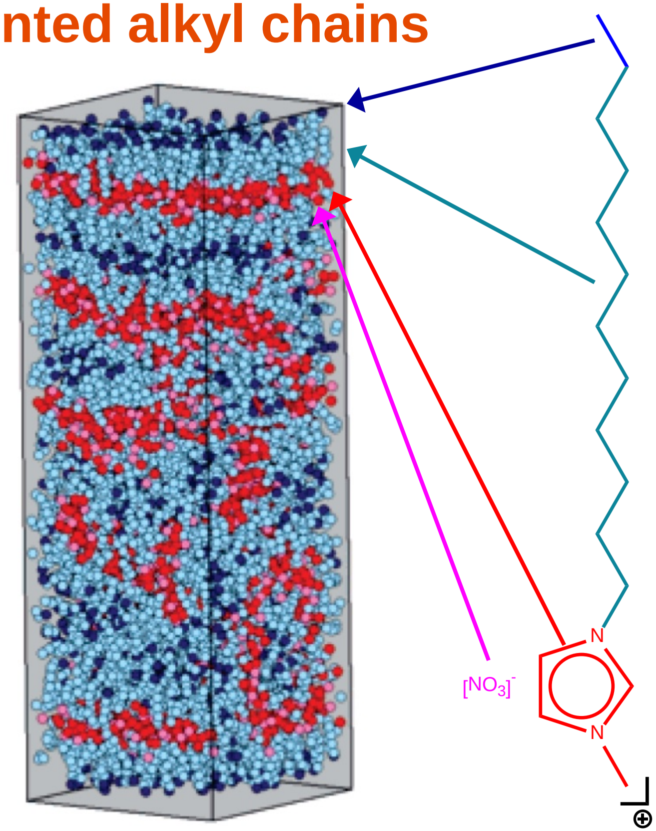
Maier *et al.*, *PCCP*, **2010**, 12, 1905-1915.

Influence of chain length $[C_nC_1Im]^+$

- **surface composed primarily of highly oriented alkyl chains**

model for surface layer





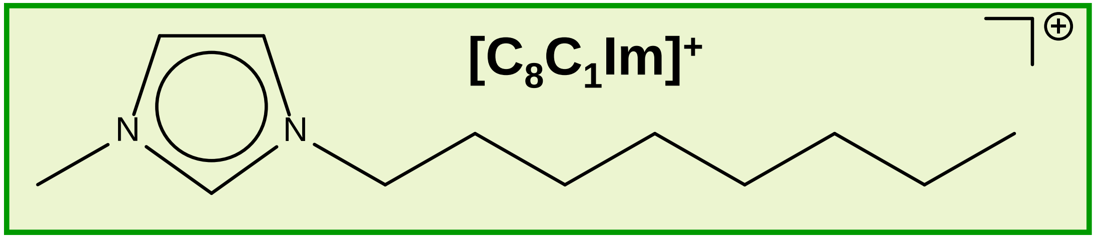
Jiang *et al. J. Phys. Chem. C* **2008**, 112, 1132-1139.

- **correlation with surface tension**

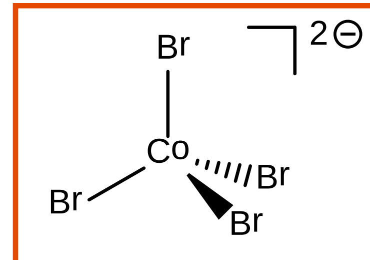
Cation	Anion	V_m / nm^3	σ / mN m^{-1}
$[C_1C_1Im]^+$	$[Tf_2N]^-$	0.400	36.3
$[C_4C_1Im]^+$	$[Tf_2N]^-$	0.485	30.7
$[C_8C_1Im]^+$	$[Tf_2N]^-$	0.603	29.5

Kolbeck, Lehmann, Paape et *al.*, *J. Phys. Chem. B,* **2010**, 114, 17025 *(Fröba, Wasserscheid, Steinrück)*

Influence of the anion

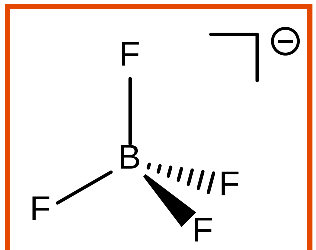


$[C_8C_1Im]^+$

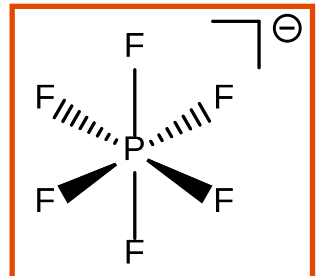


$[CoBr_4]^{2-}$

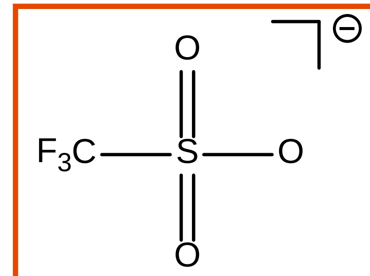
Cl^- Br^- I^-



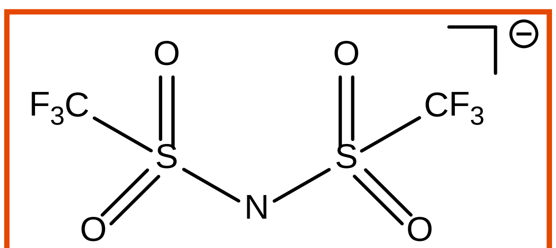
$[BF_4]^-$



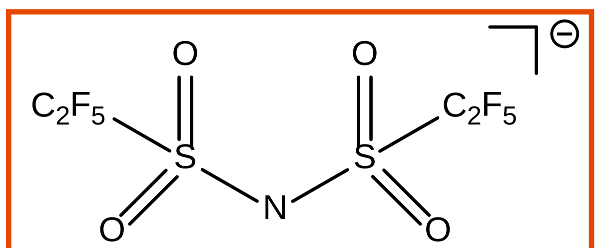
$[PF_6]^-$



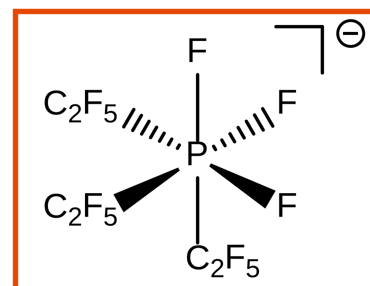
$[TfO]^-$



$[Tf_2N]^-$



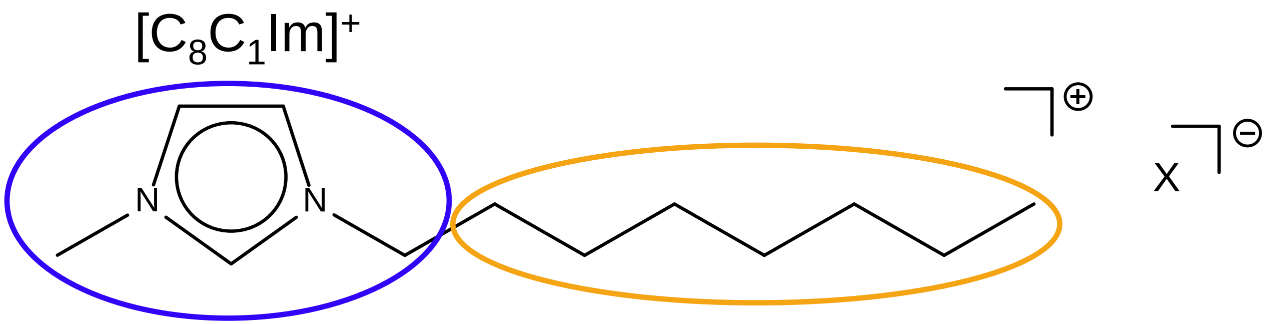
$[Pf_2N]^-$

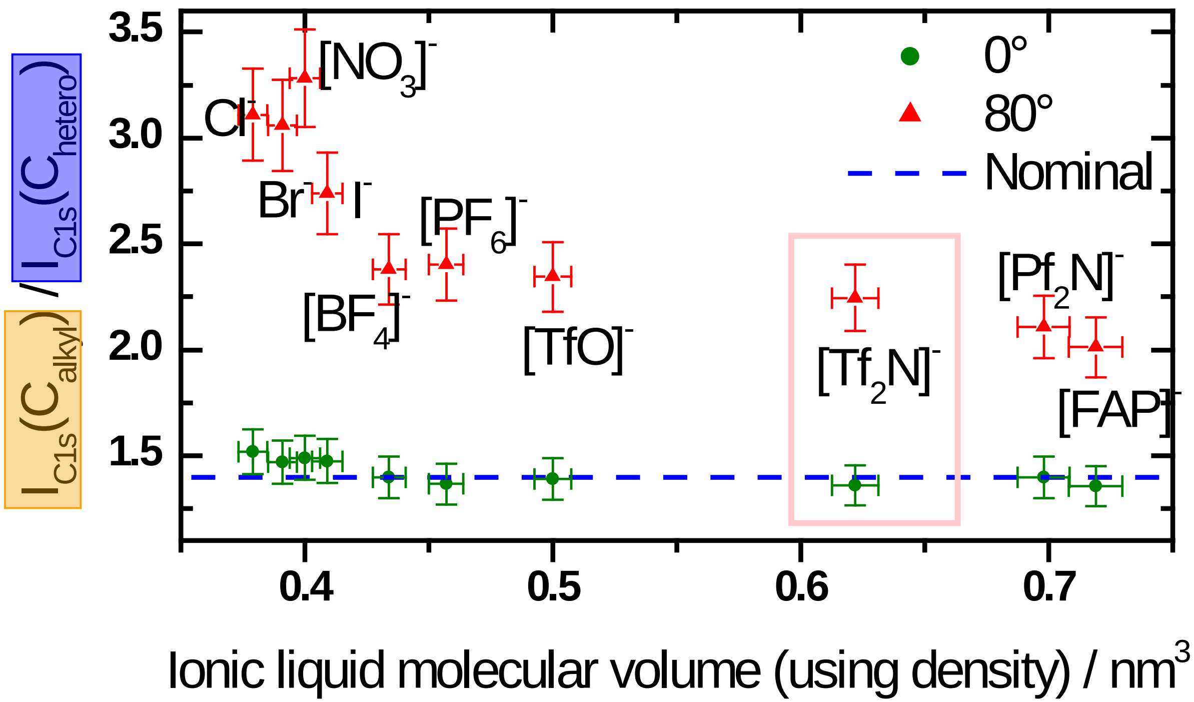


$[FAP]^-$

➔ **from small (strongly coordinating) to large (weakly coordinating)**

Influence of the anion ...
... on surface composition



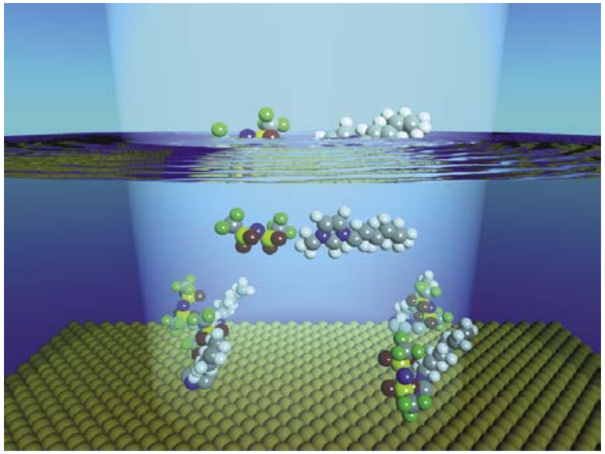


- more surface alkyl carbon for smaller anions
- increased packing density of chains for smaller anions

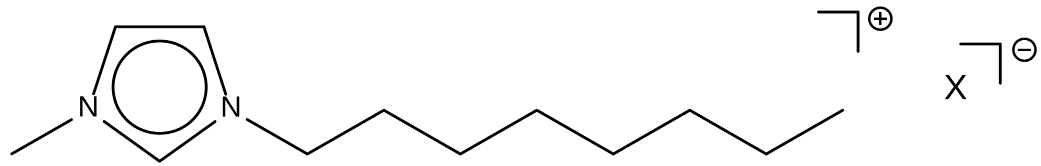
Kolbeck *et al.,* J. Phys. Chem. B, **2009**, 113, 8682-8688.
Maier *et al.*, PCCP, **2010**, 12, 1905-1915. Lovelock *et al.*, Chem. Soc. Rev., **2010**, 110, 5158–5190.

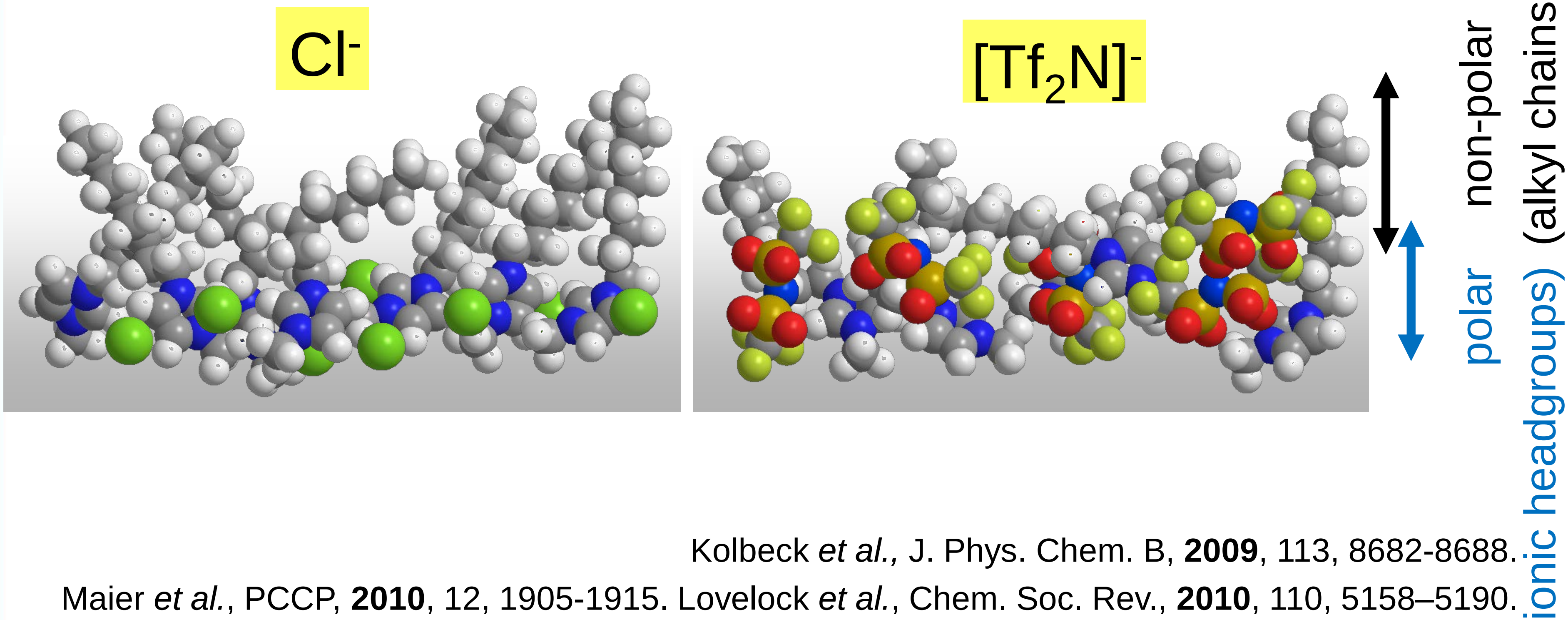
Surface composition of non-functionalized ILs

ENGINEERING OF ADVANCED MATERIALS
IONIC LIQUIDS
DFG – SPP 1191



Model for outer surface layer (interface vacuum / IL bulk)

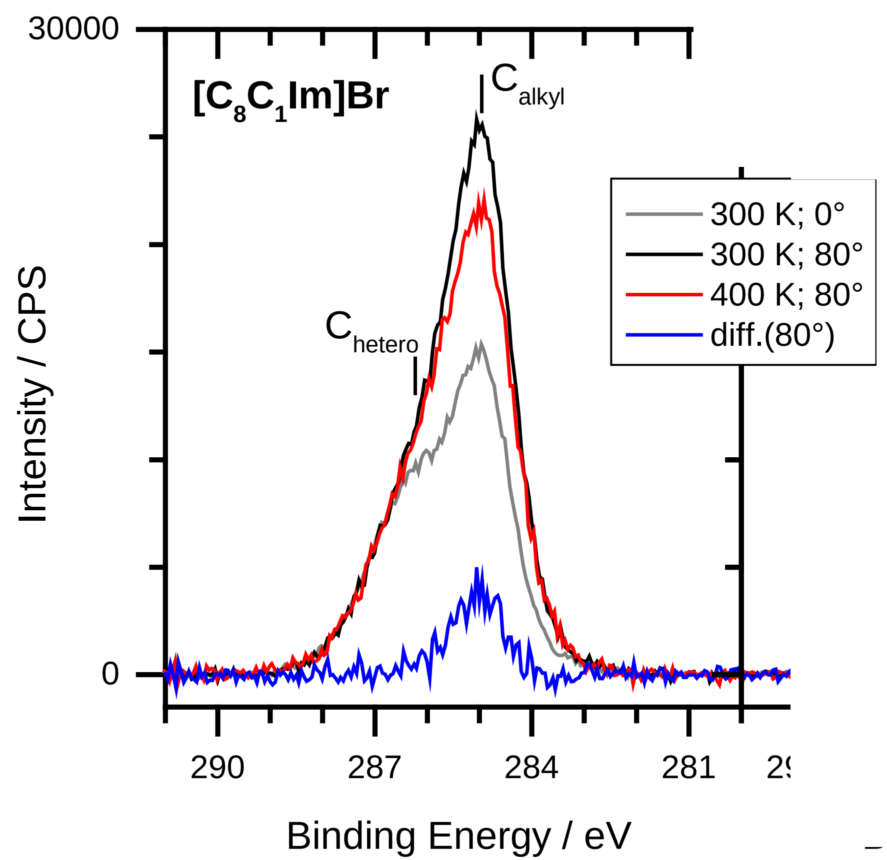




Kolbeck *et al.,* J. Phys. Chem. B, **2009**, 113, 8682-8688.
Maier *et al.*, PCCP, **2010**, 12, 1905-1915. Lovelock *et al.*, Chem. Soc. Rev., **2010**, 110, 5158–5190.

Surface composition of non-functionalized ILs

TEMPERATURE - Dependence



➔ **Surface enrichment less pronounced at higher temperature**

➔ **Due to entropic effects**

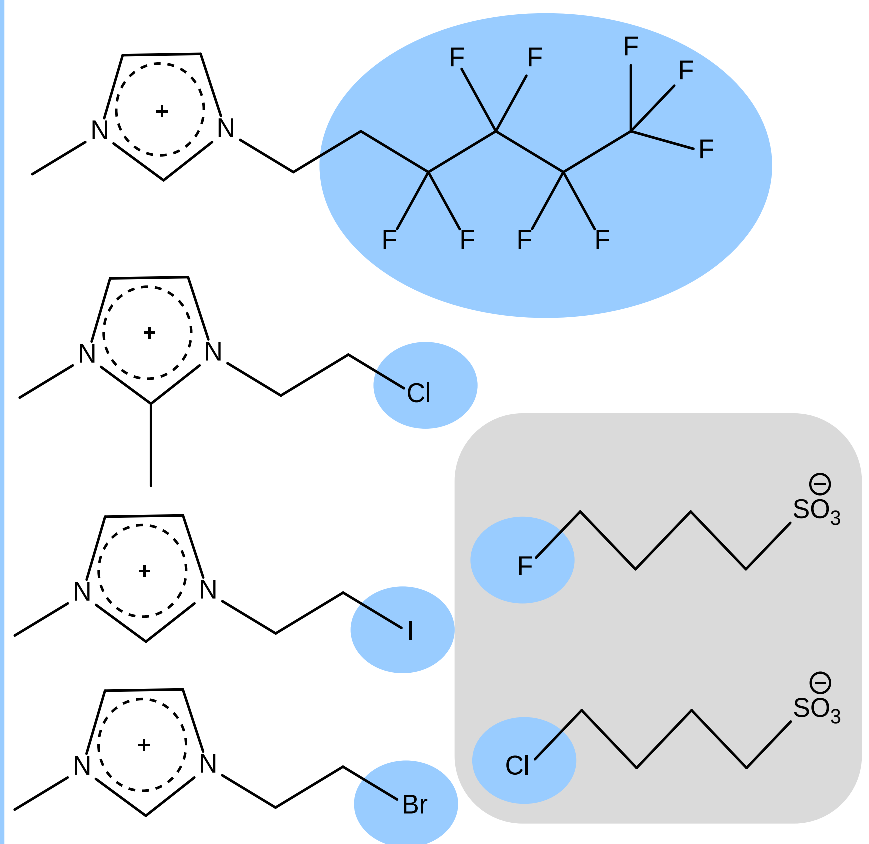
Kolbeck et al., ChemPhysChem 14 (2013) 3726

Surface composition of functionalized ILs

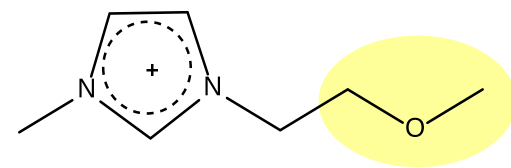
ENGINEERING OF ADVANCED MATERIALS
IONIC LIQUIDS
DFG – SPP 1191

Functionalisation of side chains

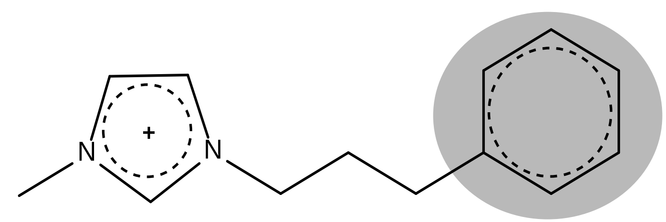
Halogen



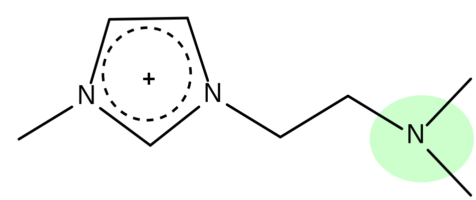
Ether & Thioether



Phenyl



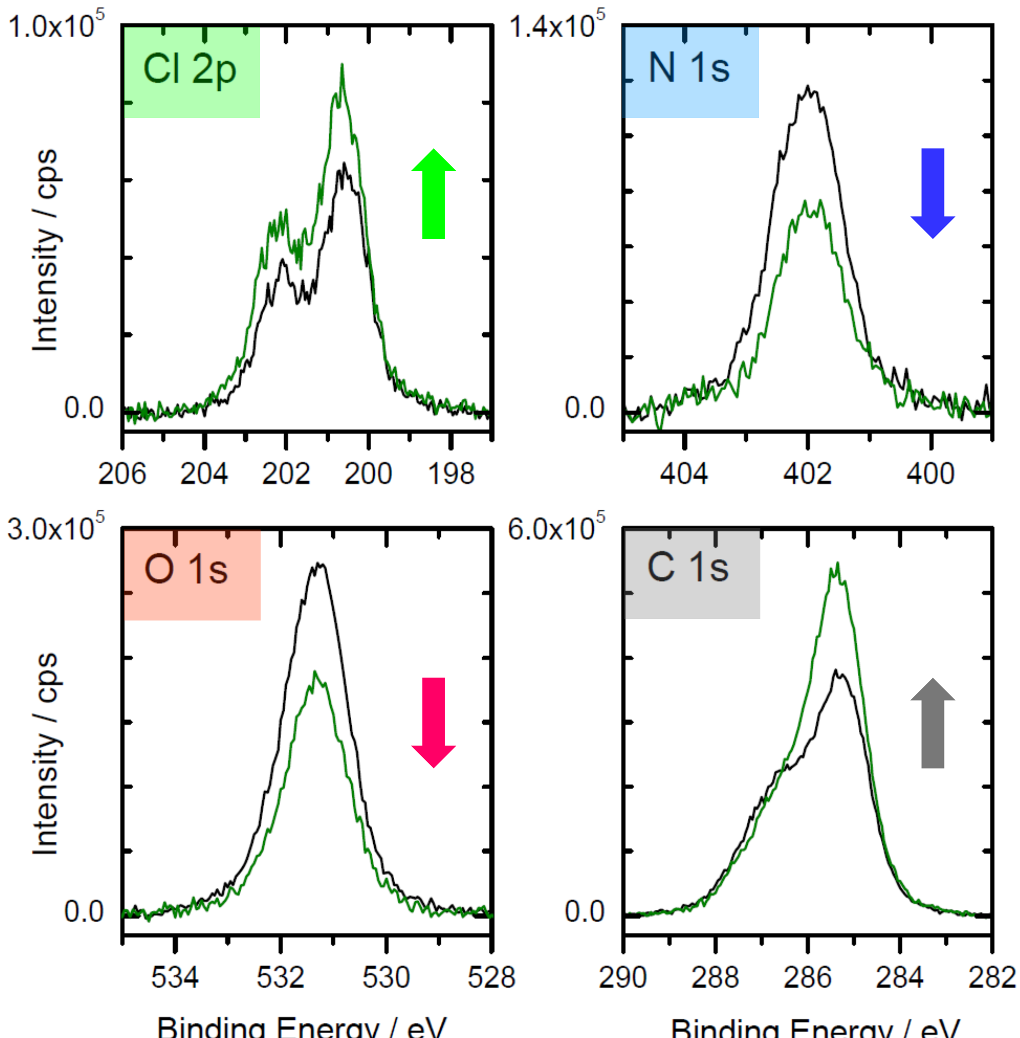
Amine

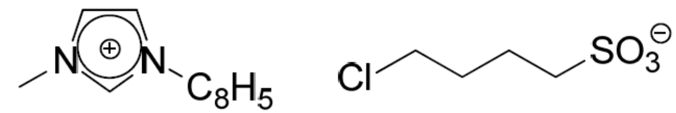


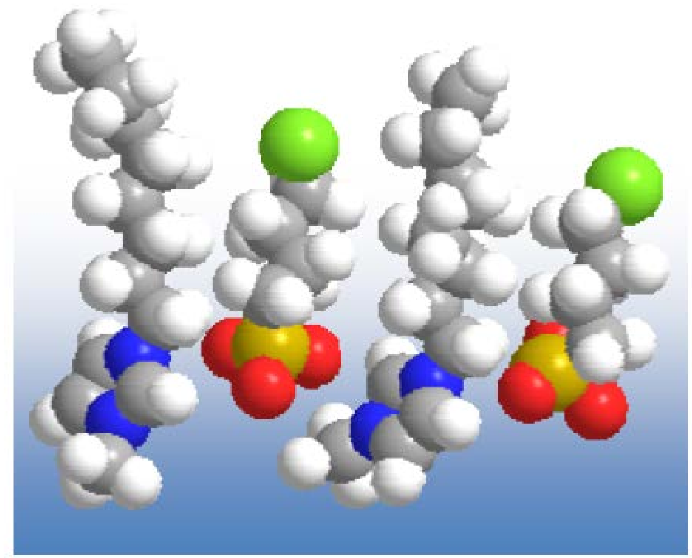
C. Kolbeck et al., *Chem. Eur. J.* *20* **(2014)** 3954

Surface composition of functionalized ILs

0° / 80°







- Surface enrichment of Cl and C_{alkyl}
- Surface depletion of O, S and N

Niedermaier *et al. ChemPhysChem.* 13 **(2012)** 1725
C. Kolbeck et al., *Chem. Eur. J. 20* (**2014**) 3954

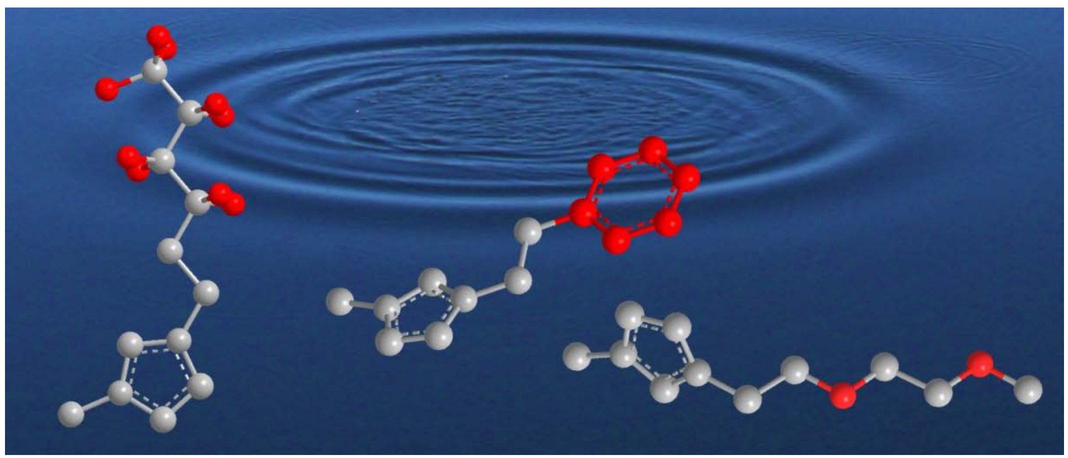
Surface composition of functionalized ILs

➔ **Surface orientation depends on interplay between**

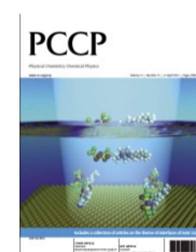
→ ionic head group interaction

→ functional groups/alkyl chain interaction and

→ interaction between ionic head groups and functional groups

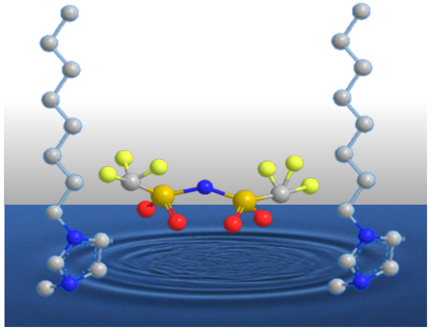


➔ **general conclusions**



C. Kolbeck et al., *Chem. Eur. J.* *20* (**2014**) 3954
H.-P. Steinrück, *Phys. Chem. Chem. Phys*. *14* (**2012**) 5010

Surface composition of functionalized ILs

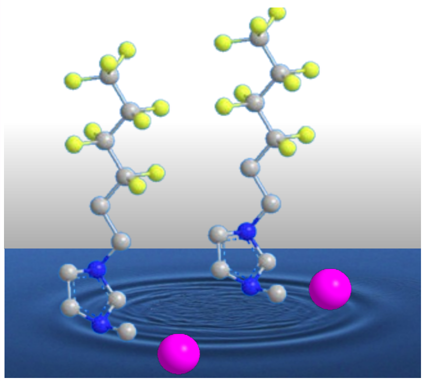


1) **weak interactions** between functional units and head groups:

➔ **surface enrichment for long chains** (n>4)

→ *non-, halogen-, alkoxysilane-, amine- ,thioether-functionalized ILs*

➔ for functionalization of cation or anion.

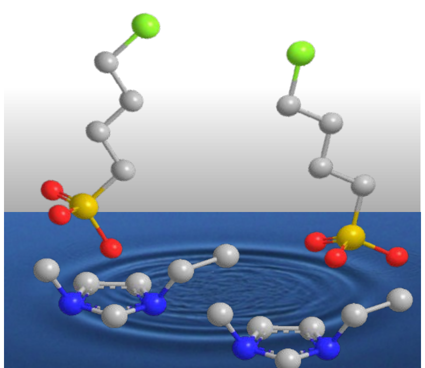


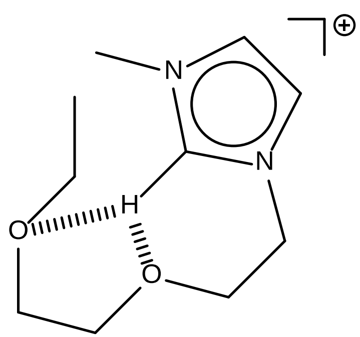
2) **significant interactions** of functional group with head groups:

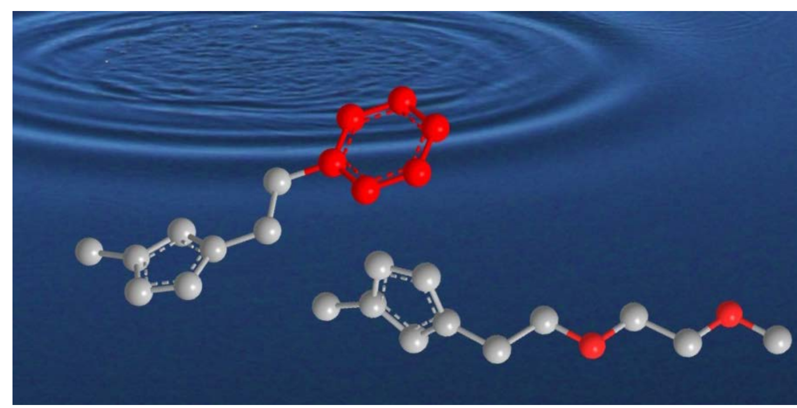
→ inter-/intramolecular *hydrogen bonding for ether groups*

→ *quadrupole interactions for phenyl groups*

➔ surface enrichment **reduced** or even **suppressed**

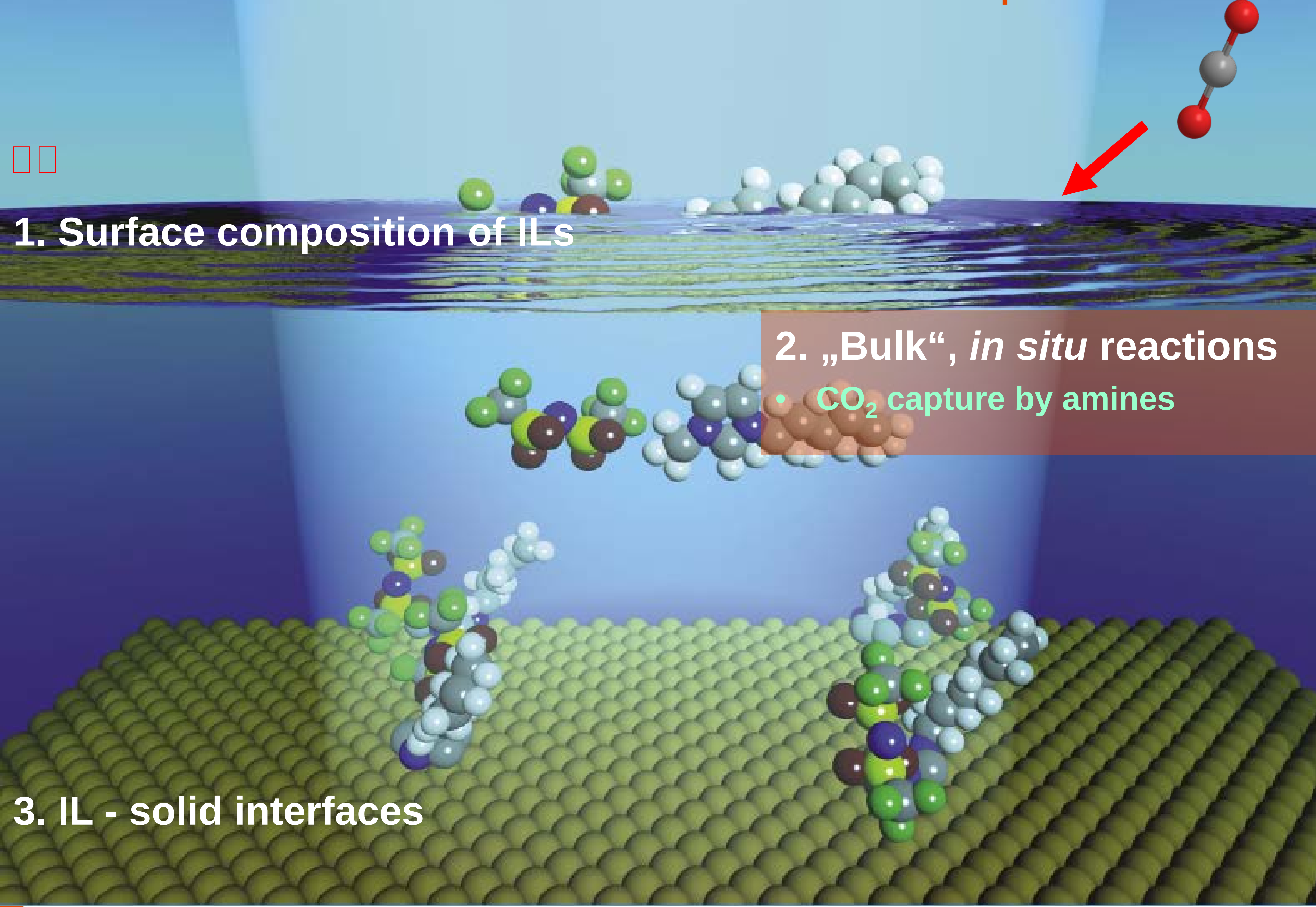






C. Kolbeck et al., *Chem. Eur. J.* *20* (**2014**) 3954

Surface and Interface Science of Ionic Liquids



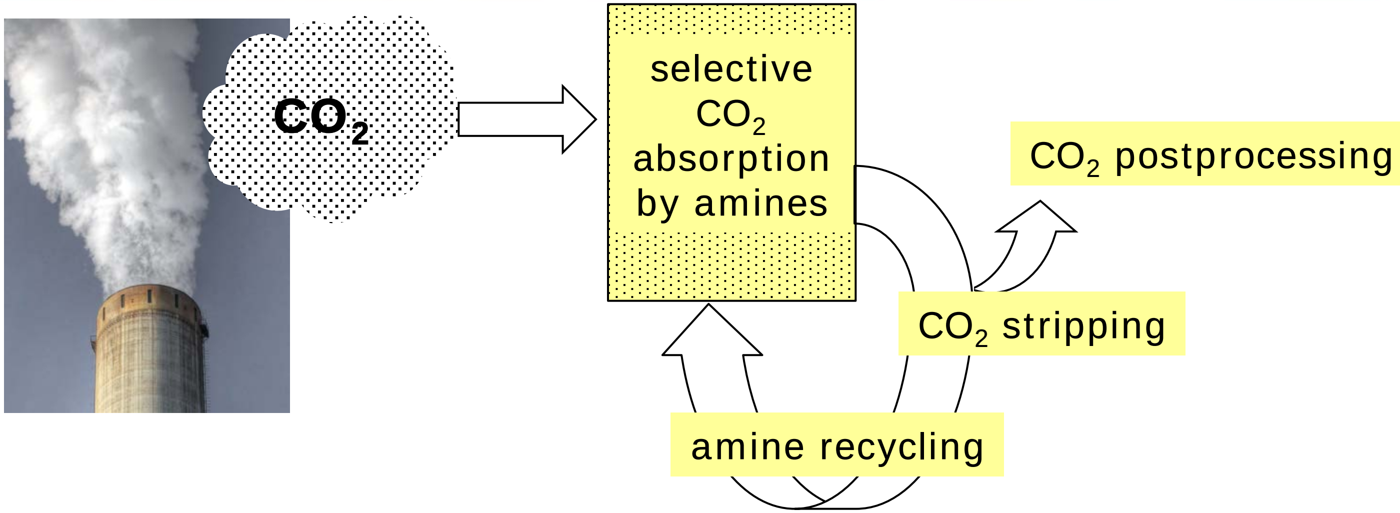
1. Surface composition of ILs

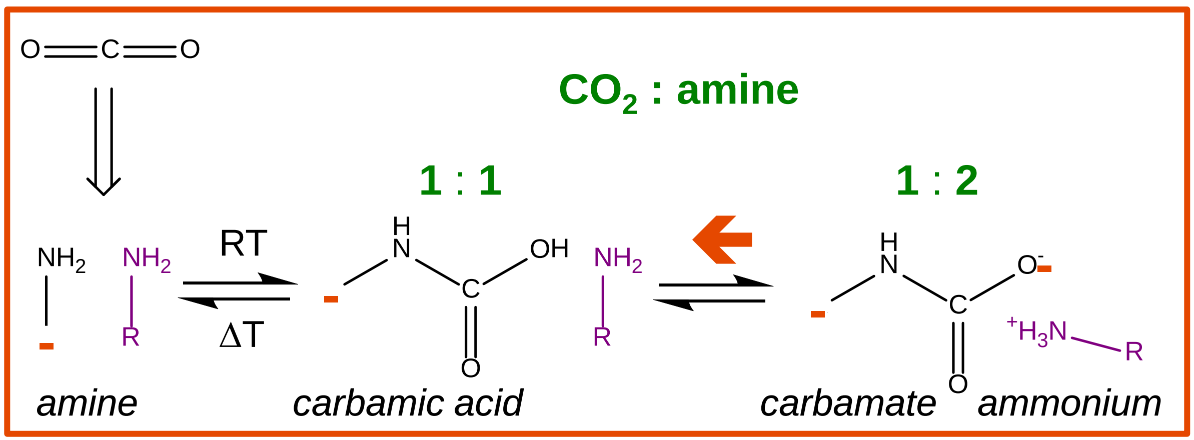
2. „Bulk“, *in situ* reactions

- **CO_2 capture by amines**

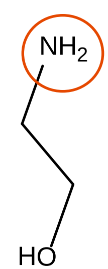
3. IL - solid interfaces

In-situ XPS: amine reaction with CO_2

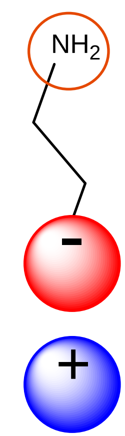




MEA (mono-ethanolamine)



amine-functionalised IL

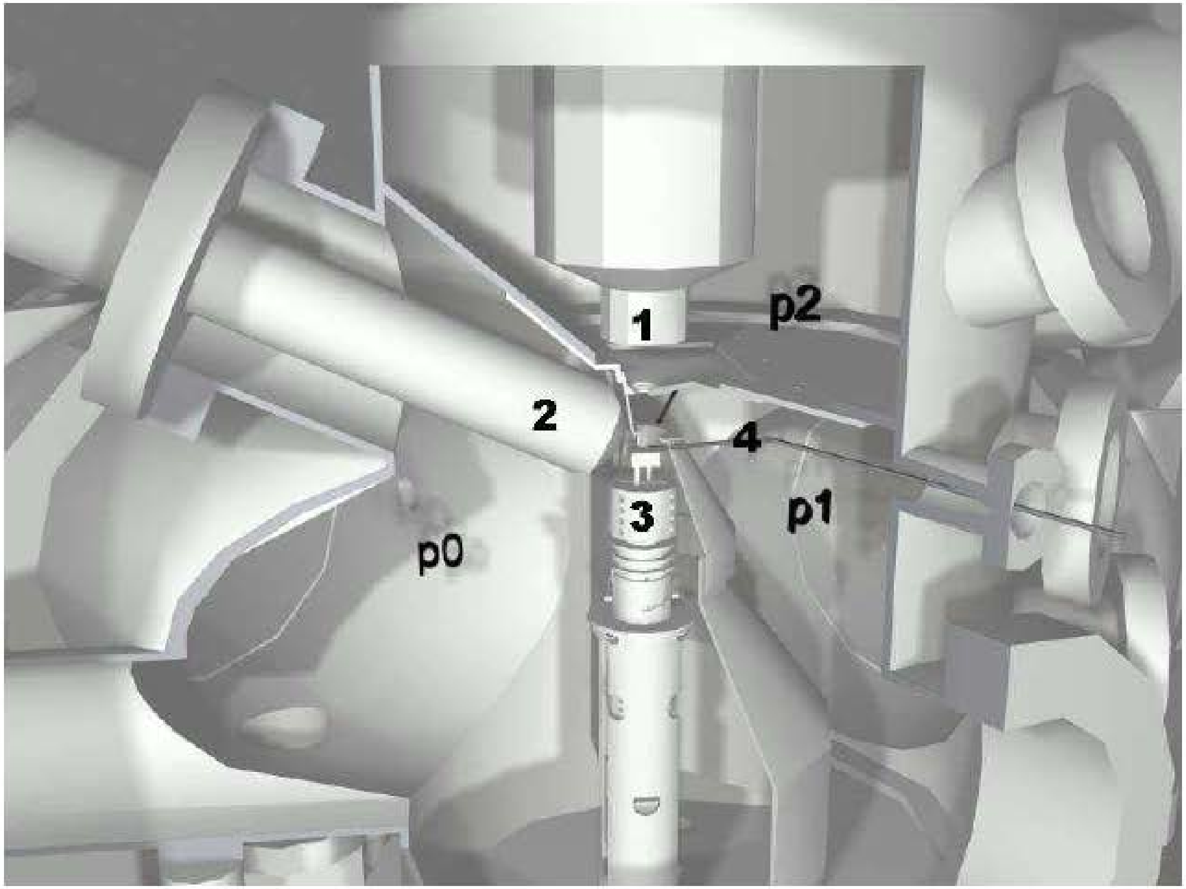


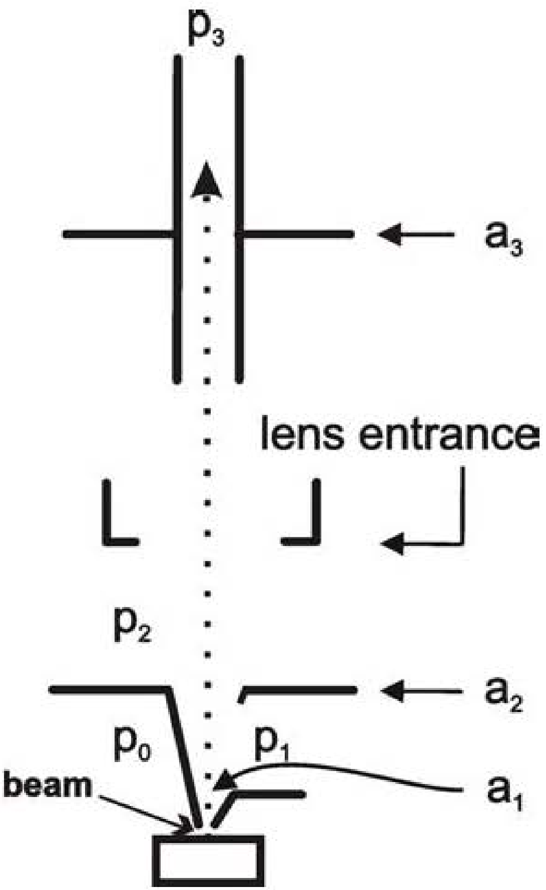
Joan Brennecke (Notre Dame)

→ B. Gurkan et al., J. Am. Chem. Soc. ***2010****, 132, 2116–2117*

In-situ XPS: amine reaction with CO_2

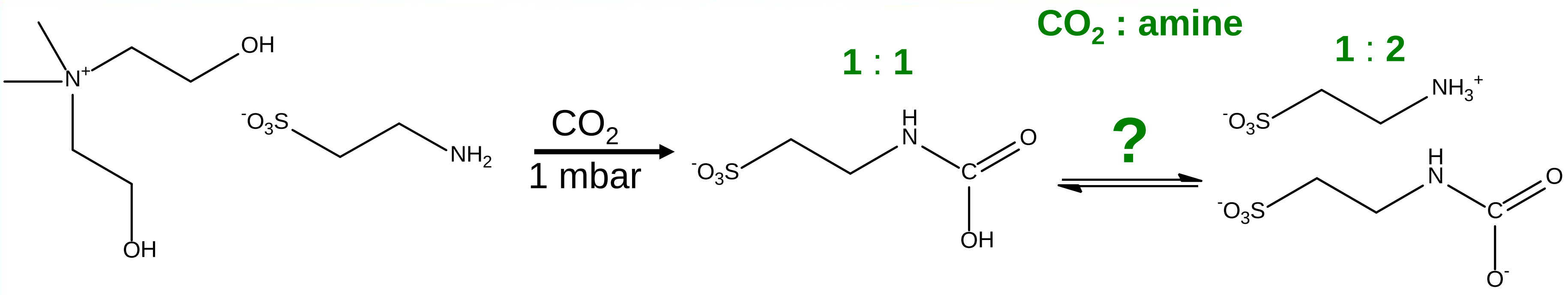
near-ambient pressure XPS: 0.9 mbar CO_2
(atmosphere: ~0.4 mbar partial pressure)





J. Pantförder, *Photoelektronenspektroskopie im „Pressure Gap" – Aufbau einer neuen Apparatur für Messungen im Druckbereich von 10-10 bis 1 mbar*, PhD thesis, **2004**, Uni Erlangen-Nürnberg

Surface (in situ) vs. bulk (ex situ)

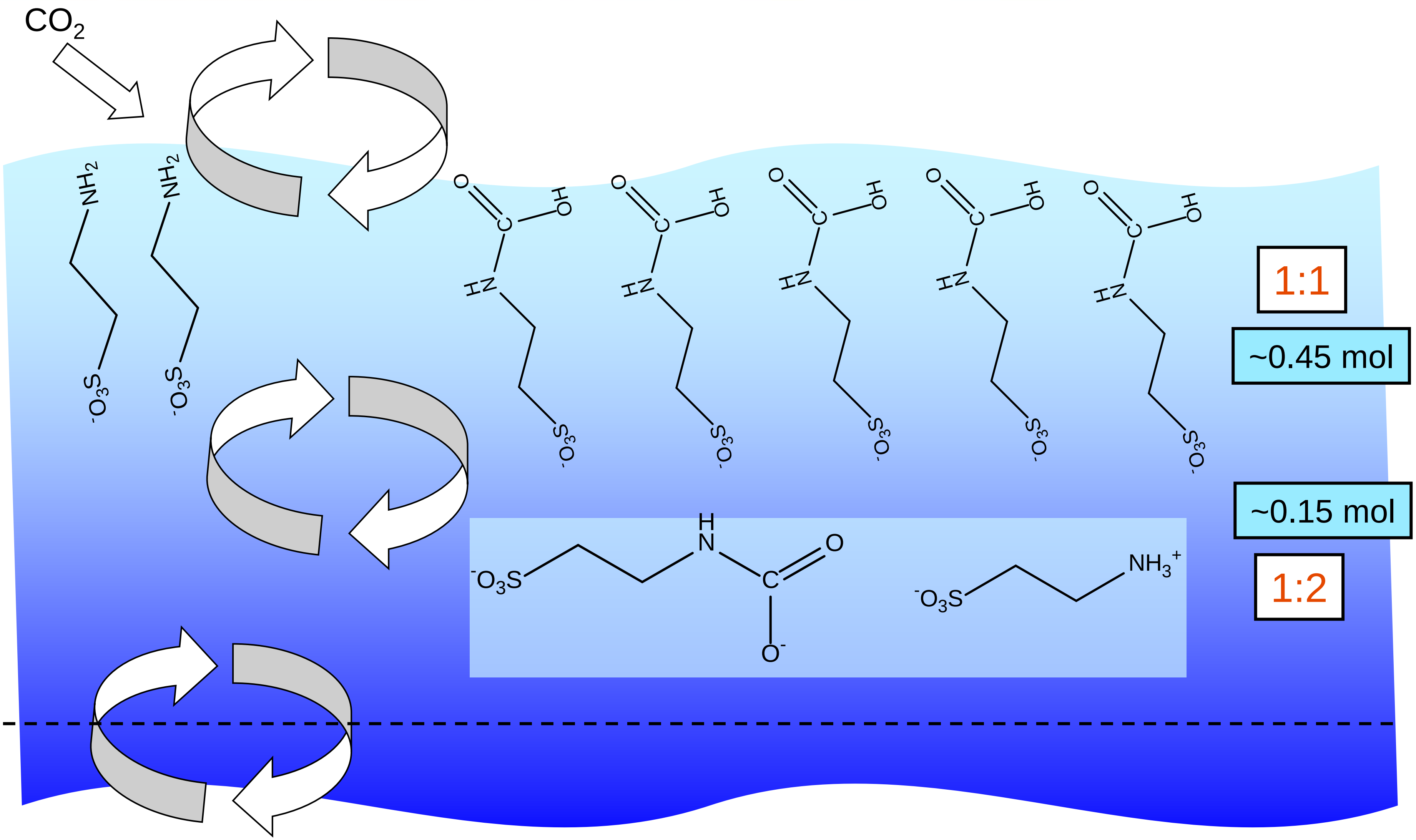


→ ***at surface (1mbar): 0.6 CO_2 per 1 IL***
(mainly 1:1 carbamic acid)

→ ***in bulk (1 mbar): no CO_2***
in bulk (1bar): 0.15 CO_2 per IL
(only 1:2 carbamate)

→ *Niedermaier, Bahlmann, J. Am. Chem. Soc., 2014, 136, 436*

Carbamic acid stabilised at surface (singly charged)



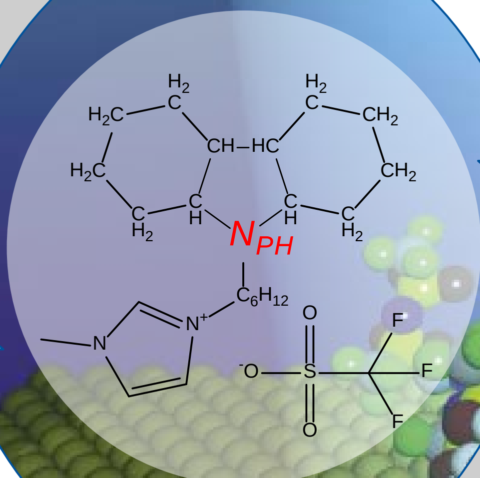
→ *Niedermaier, Bahlmann, J. Am. Chem. Soc., 2014, 136, 436*

Surface and Interface Science of Ionic Liquids

1. Surface composition of ILs

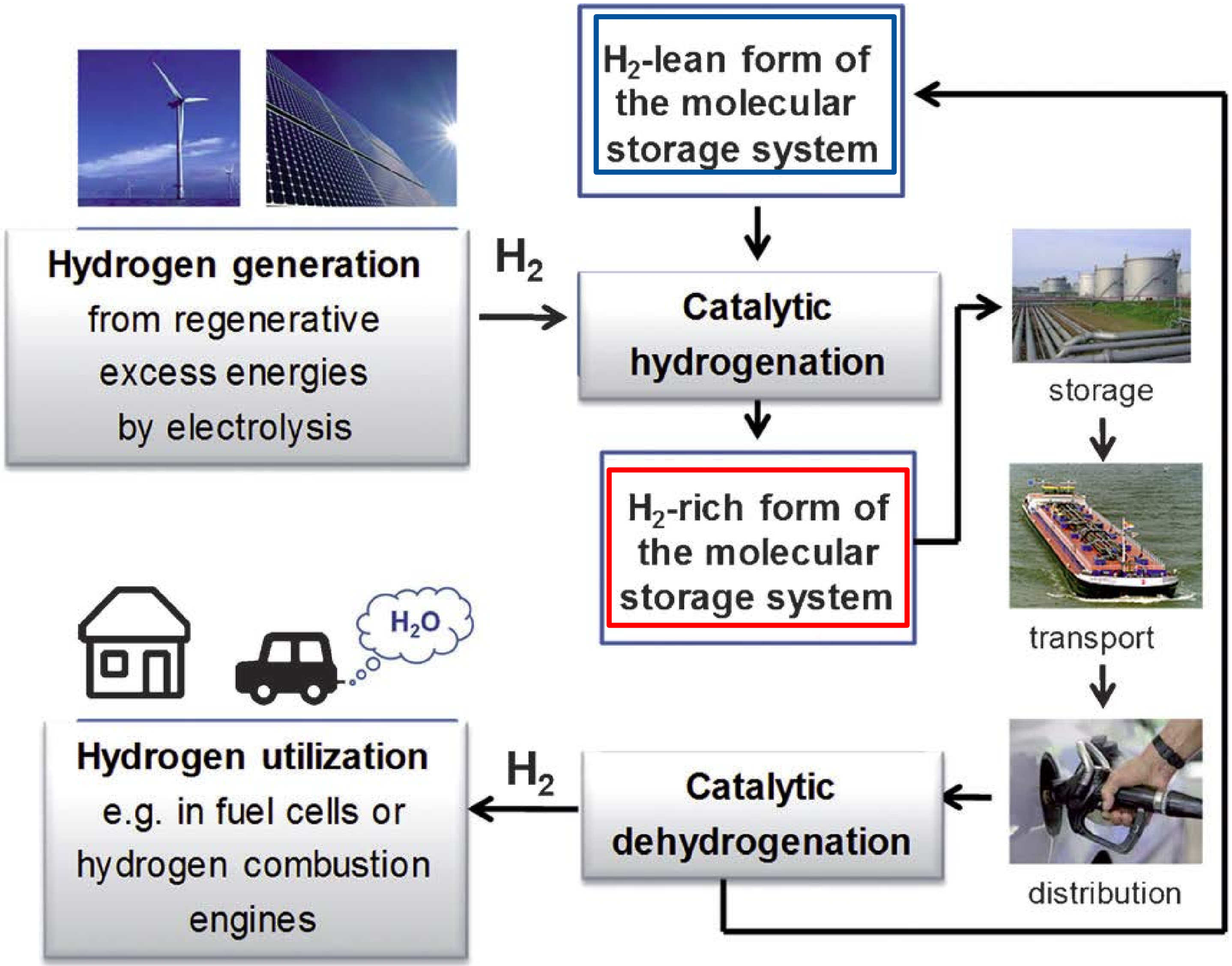
2. *in-situ* reactions

- CO_2 capture by amines
- IL-solid reaction
  → LOHC dehydrogenation



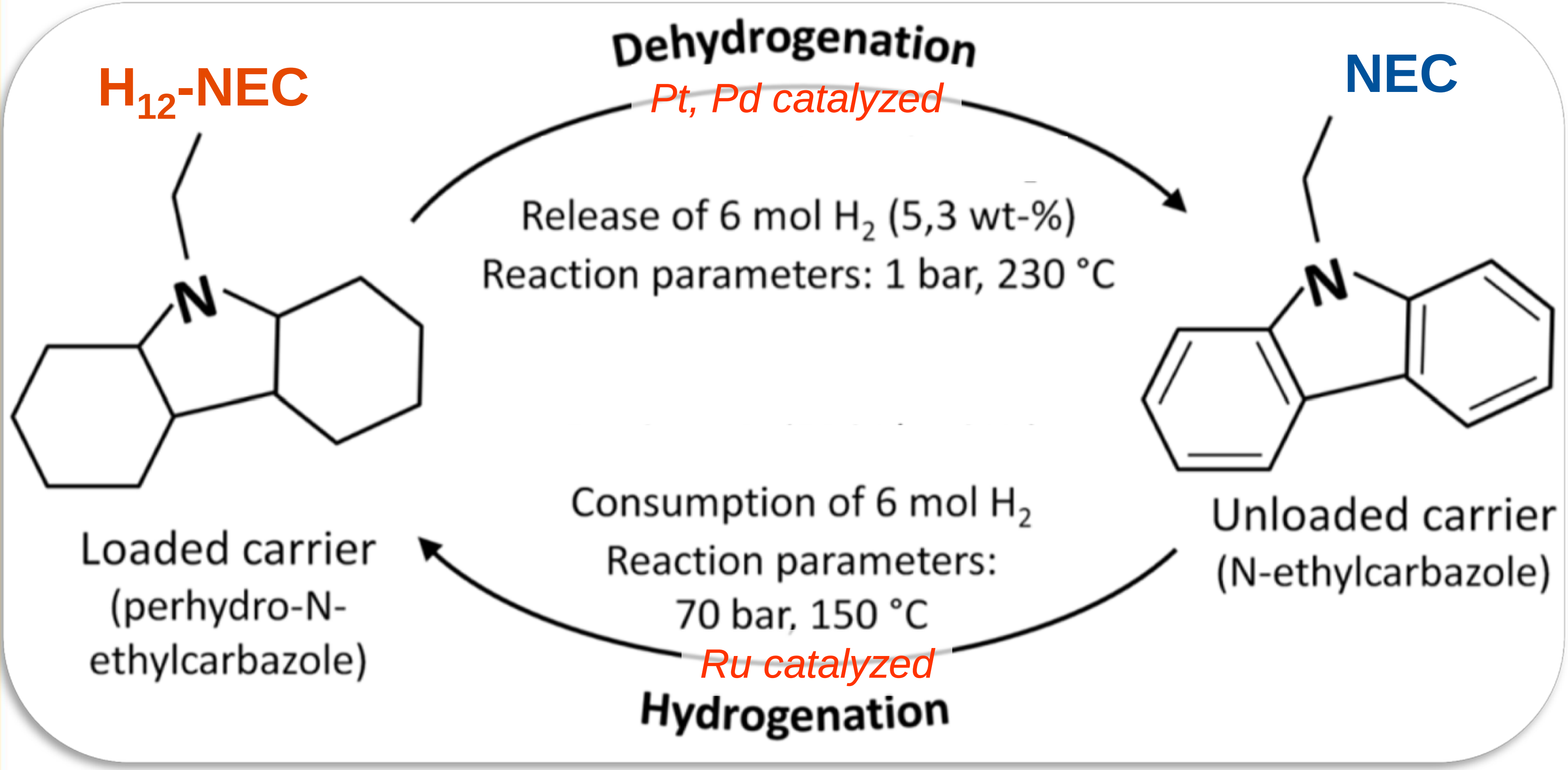
3. IL - solid interfaces

Liquid organic hydrogen carrier (LOHC)



Brückner *et al.*, ChemSusChem **2014**, 7, 229

Liquid organic hydrogen carrier (LOHC)

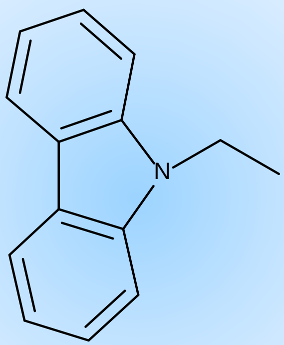


Reversible hydrogenation (Ru) and dehydrogenation (Pt, Pd) of N-ethylcarbazole (NEC) and perhydro-N-ethylcarbazole (H_{12}-NEC)

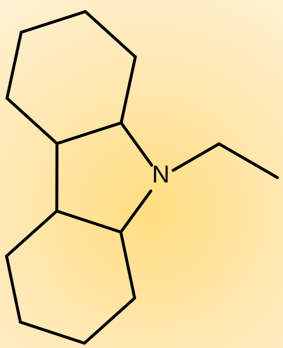
➔ not observable in UHV (multilayer desorption > -30°C)

Synthesis of carbazole functionalized IL

ENGINEERING OF ADVANCED MATERIALS
IONIC LIQUIDS
DFG – SPP 1191



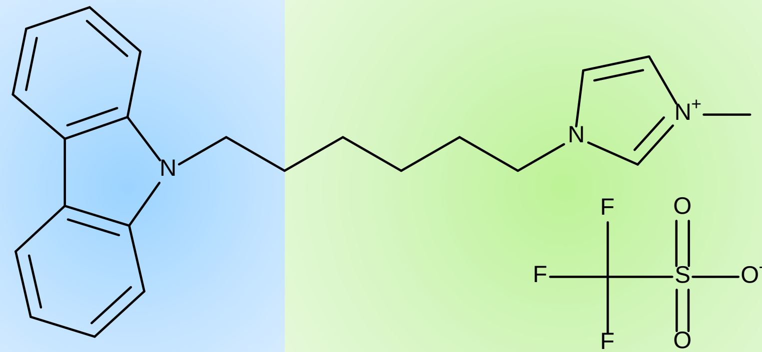
NEC



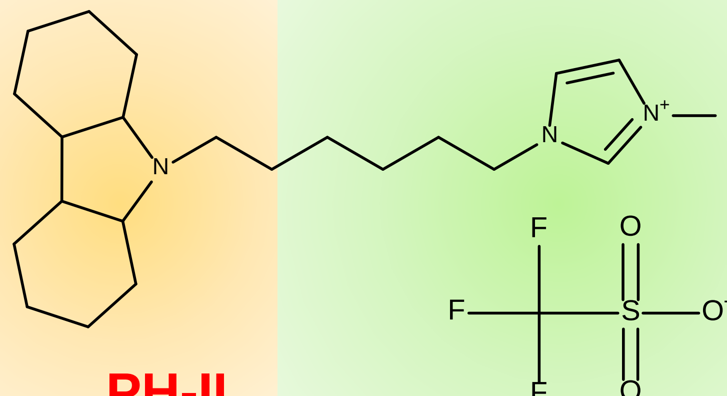
H_{12}-NEC

DeHydrogenated IL

1-[6-(N-Carbazole)hexyl]-3-methylimidazolium trifluoromethanesulfonate



DH-IL

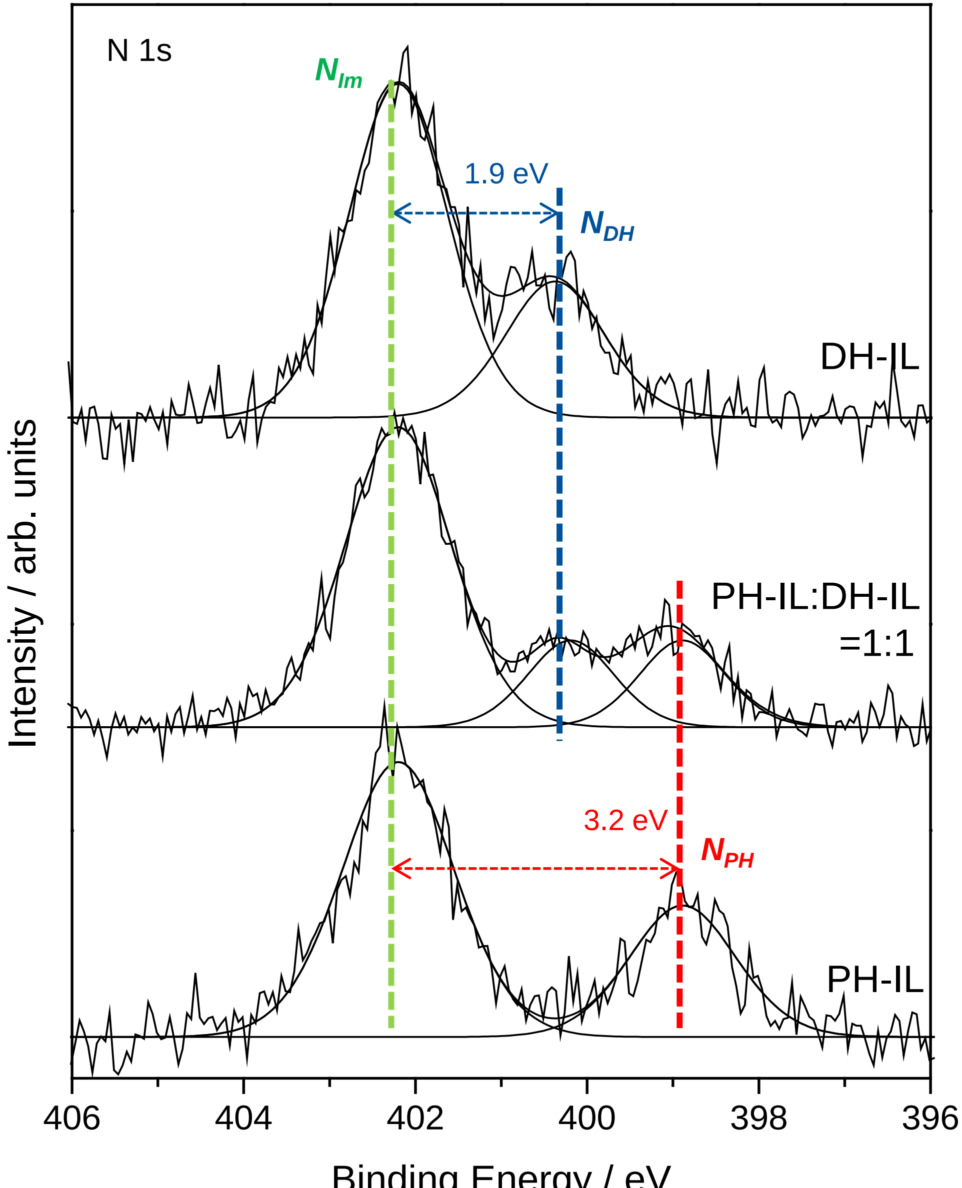


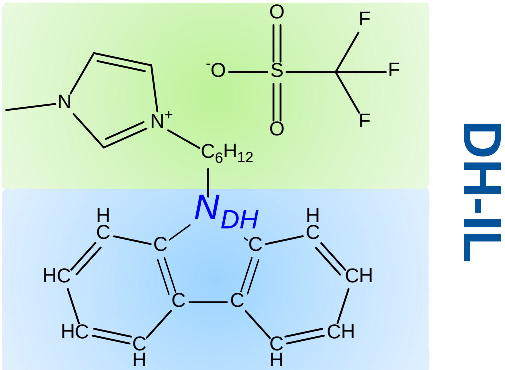
PH-IL

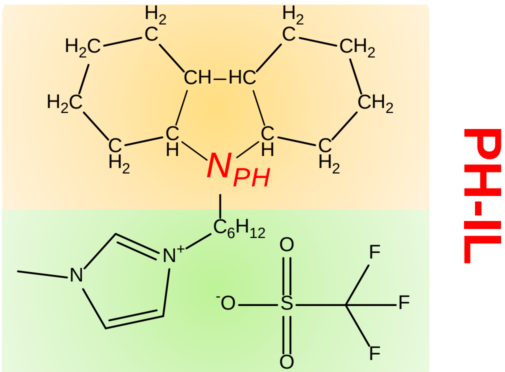
PerHydrogenated IL

1-[6-(N-dodecahydrocarbazole)hexyl]-3-methylimidazolium trifluoromethanesulfonate

XP spectra of PH-IL and DH-IL (350 K)







➔ N 1s spectrum reflects hydrogenation state of carbazole unit

X-ray Photoelectron Spectroscopy (XPS) and Thermal Desorption Spectroscopy (TDS)

ENGINEERING OF ADVANCED MATERIALS
IONIC LIQUIDS DFG – SPP 1191

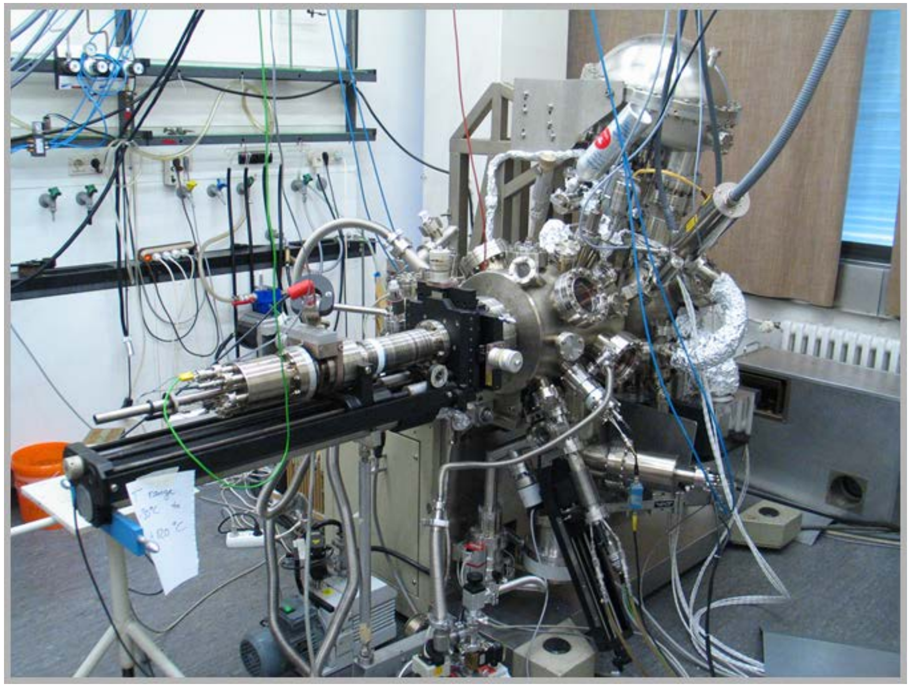
Experimental:

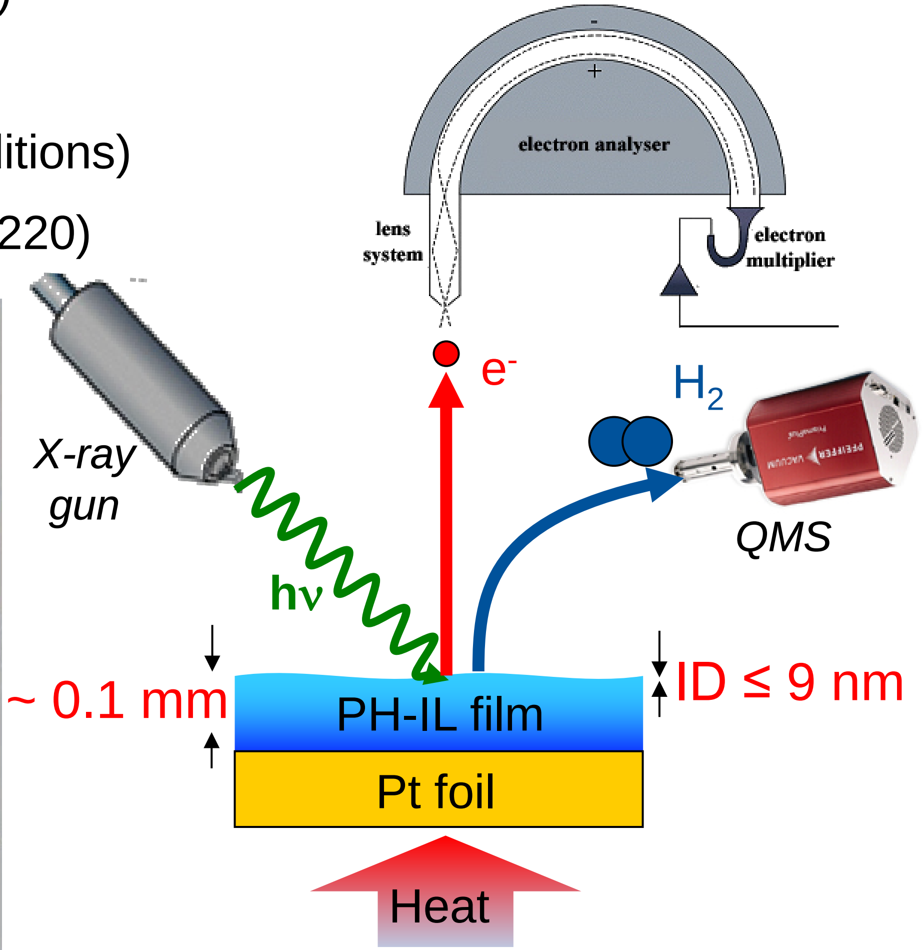
→ VG-ESCALAB 200 (Al K_α, $\Delta E = 0.9$ eV)

→ Sample transfer system

→ Pressure $<10^{-8}$ mbar (clean UHV conditions)

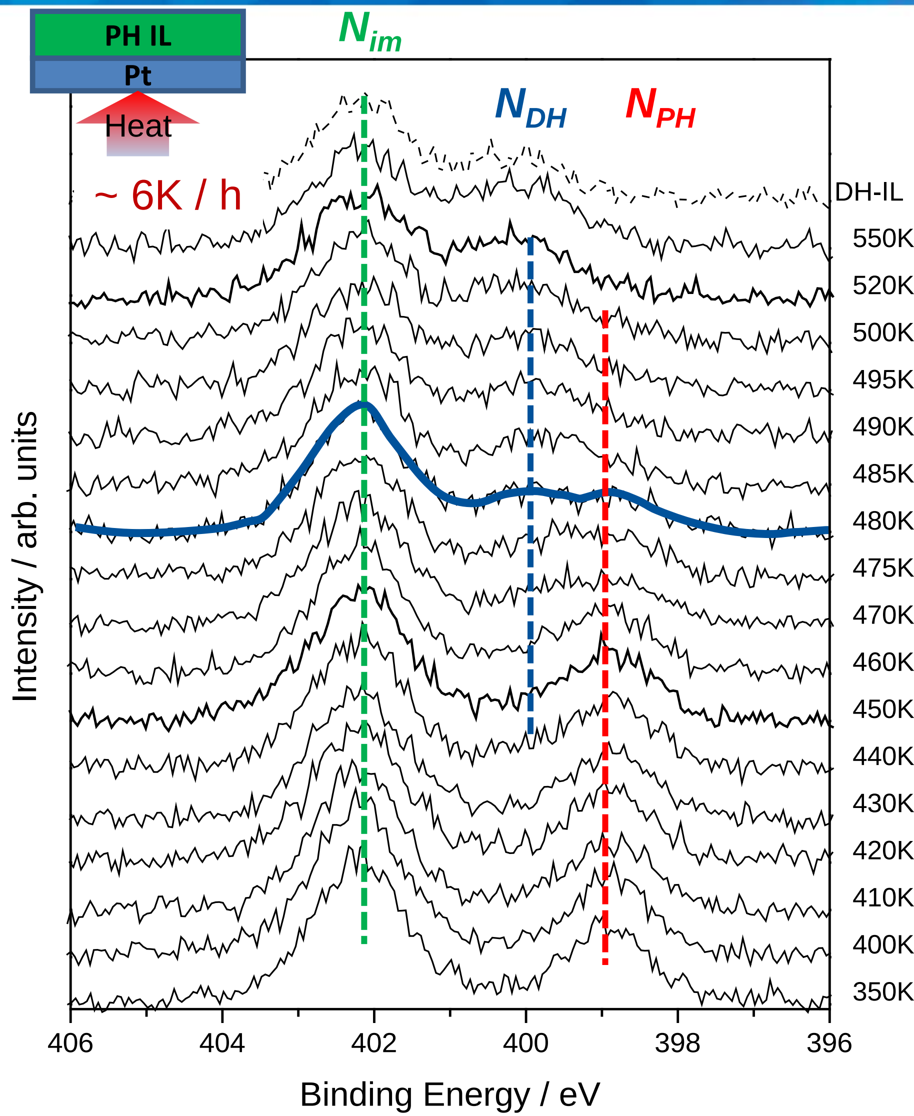
→ Equipped with QMS (PFEIFFER QMG220)



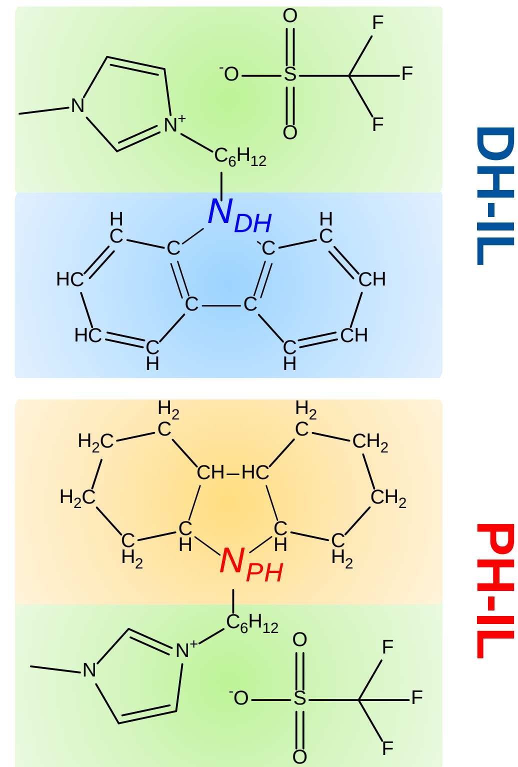


*Matsuda, Taccardi, Schwegler et al., ChemPhysChem, **2015**, 16, 1873-1879*

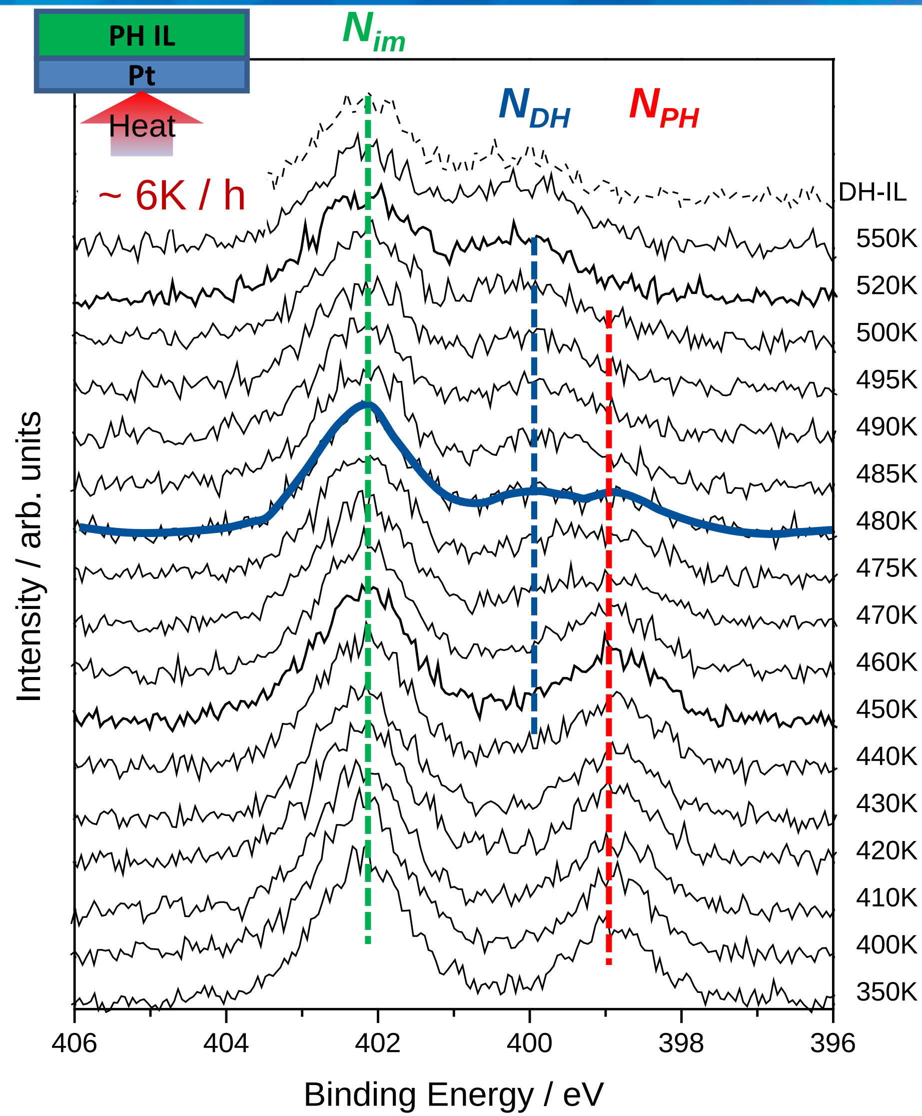
XPS of PH-IL on Pt

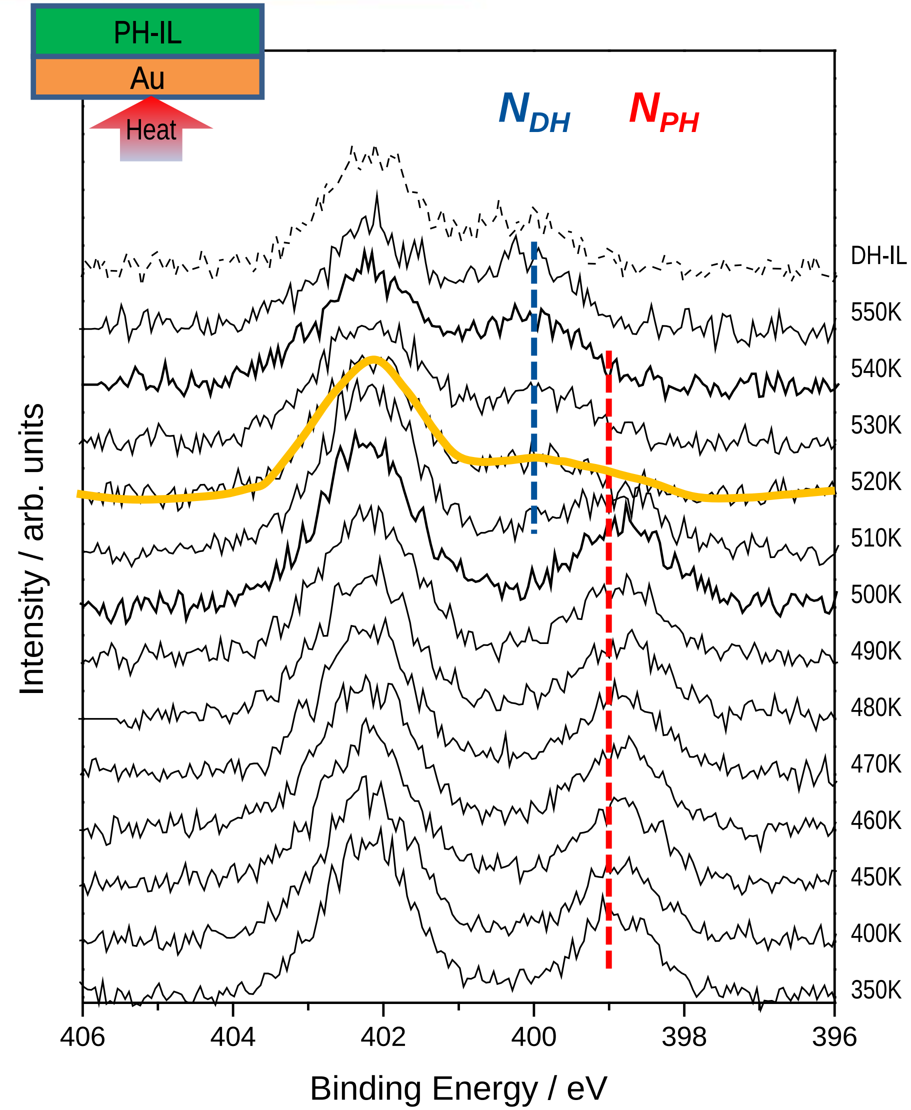


@ Pt-foil: 440 – 520 K



XPS of PH-IL on Pt or on Au



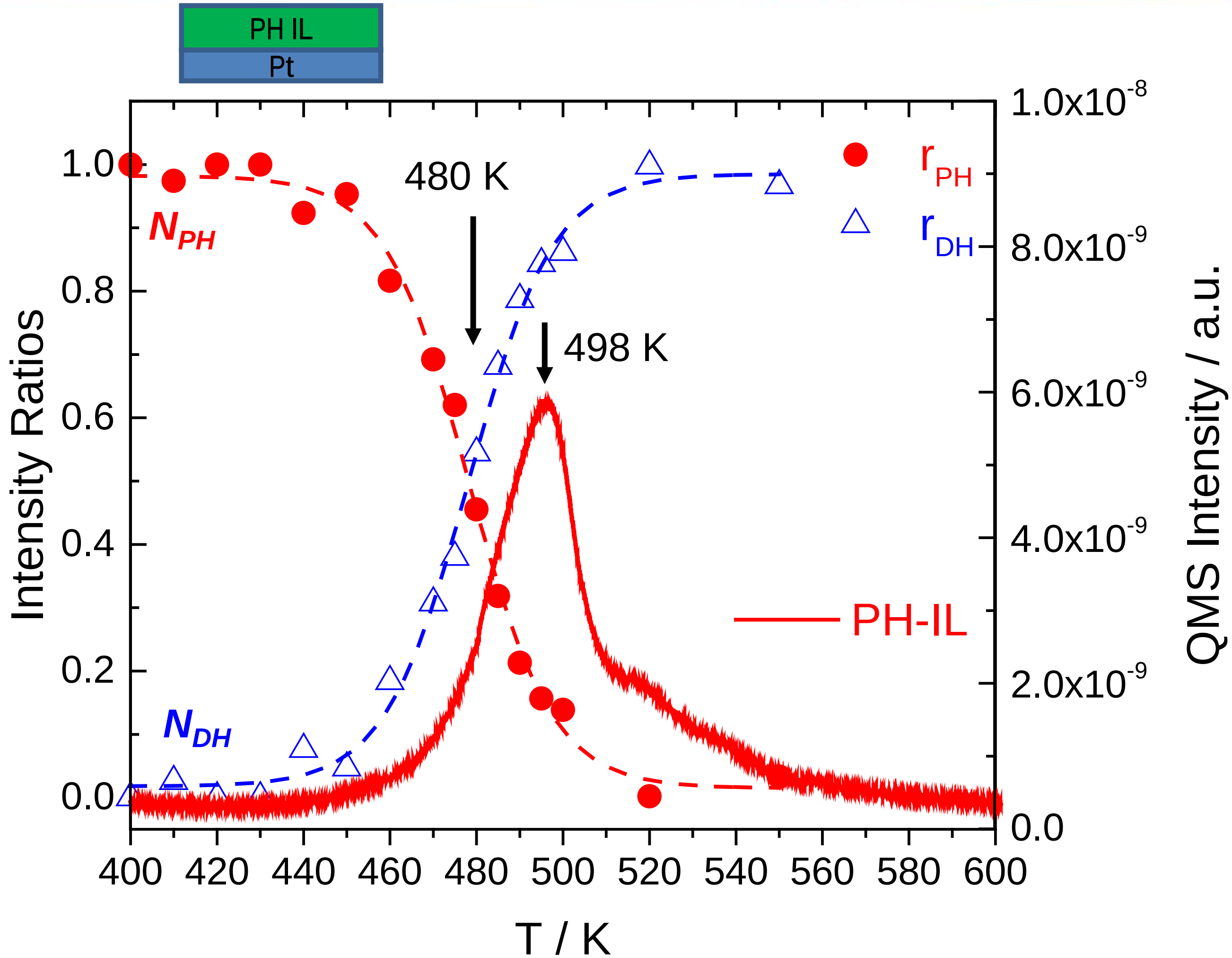


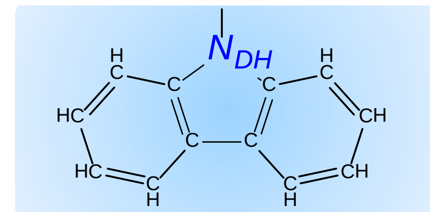
@ Pt-foil: 440 – 520 K

@ Au-foil: 500 – 550 K (decomp.)

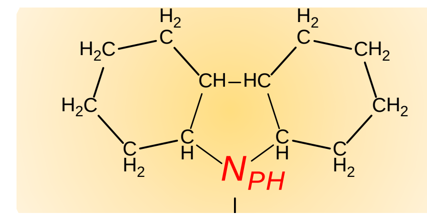
→ no catalyst (Au support): dehydrogenation & decomposition at T ≥ 510K

XPS of PH-IL on Pt





DH-IL

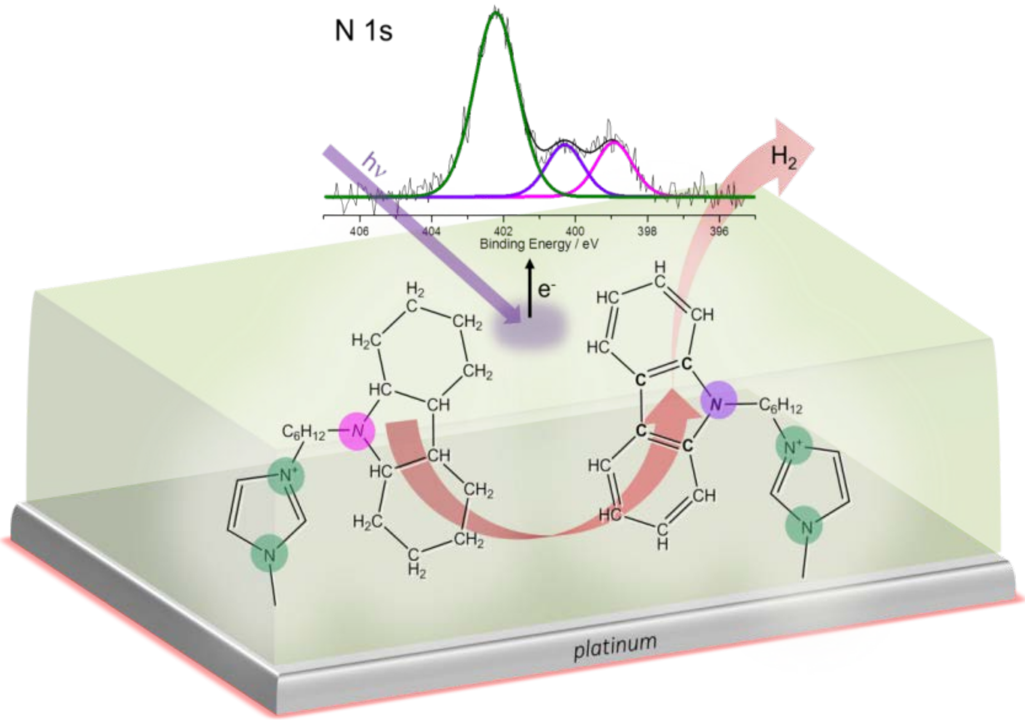


PH-IL

→ dehydrogenation liquid H_{12}-NEC (supported Pt @ 500K)

Relative intensity: $r_{PH} = N_{PH}/(N_{PH} + N_{DH})$, $r_{DH} = N_{DH}/(N_{PH} + N_{DH})$ Mean heating rate: 0.002 K/s (XPS), 0.04 - 0.14 K/s (TDS)

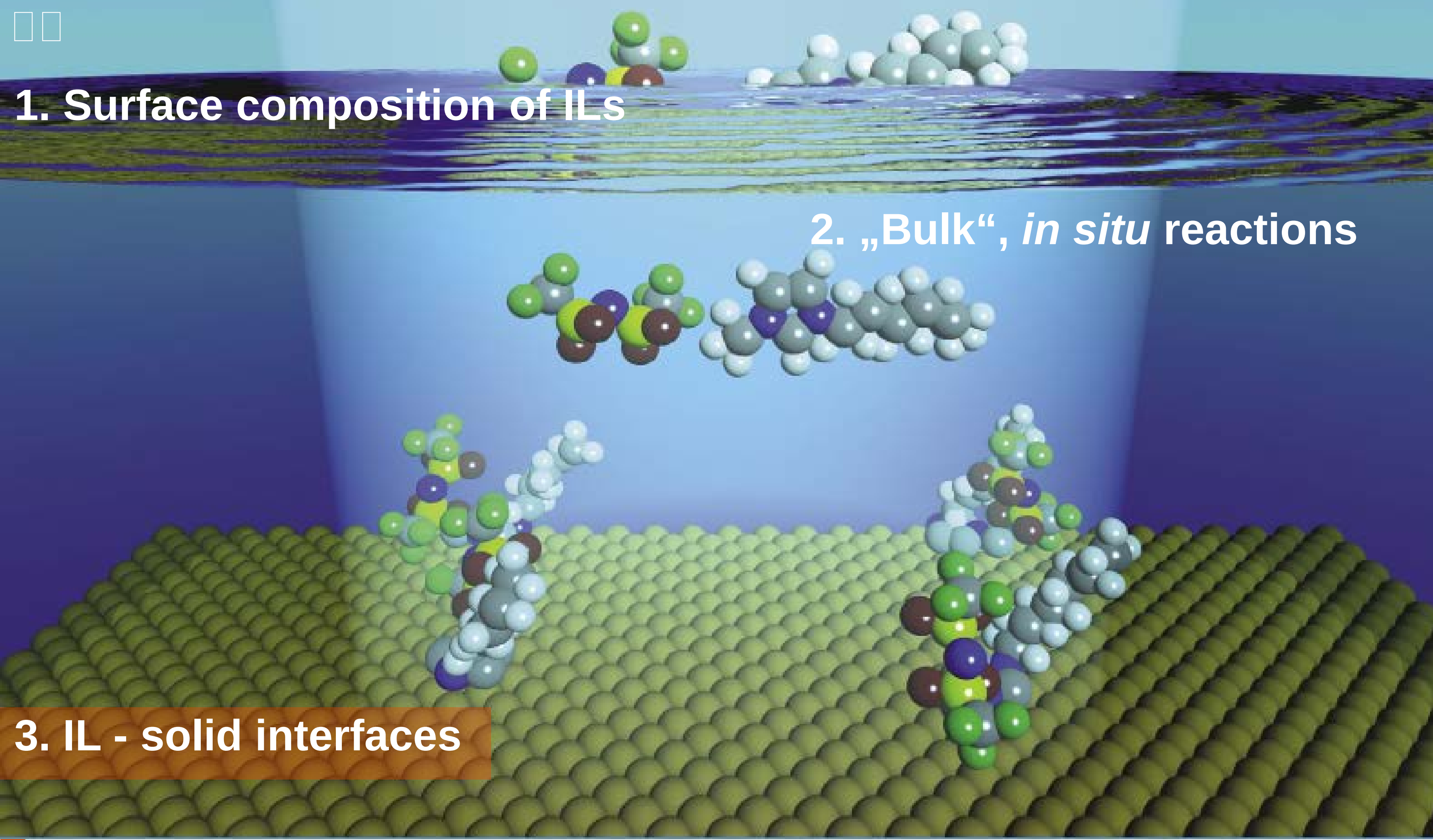
LOHC – IL: Summary



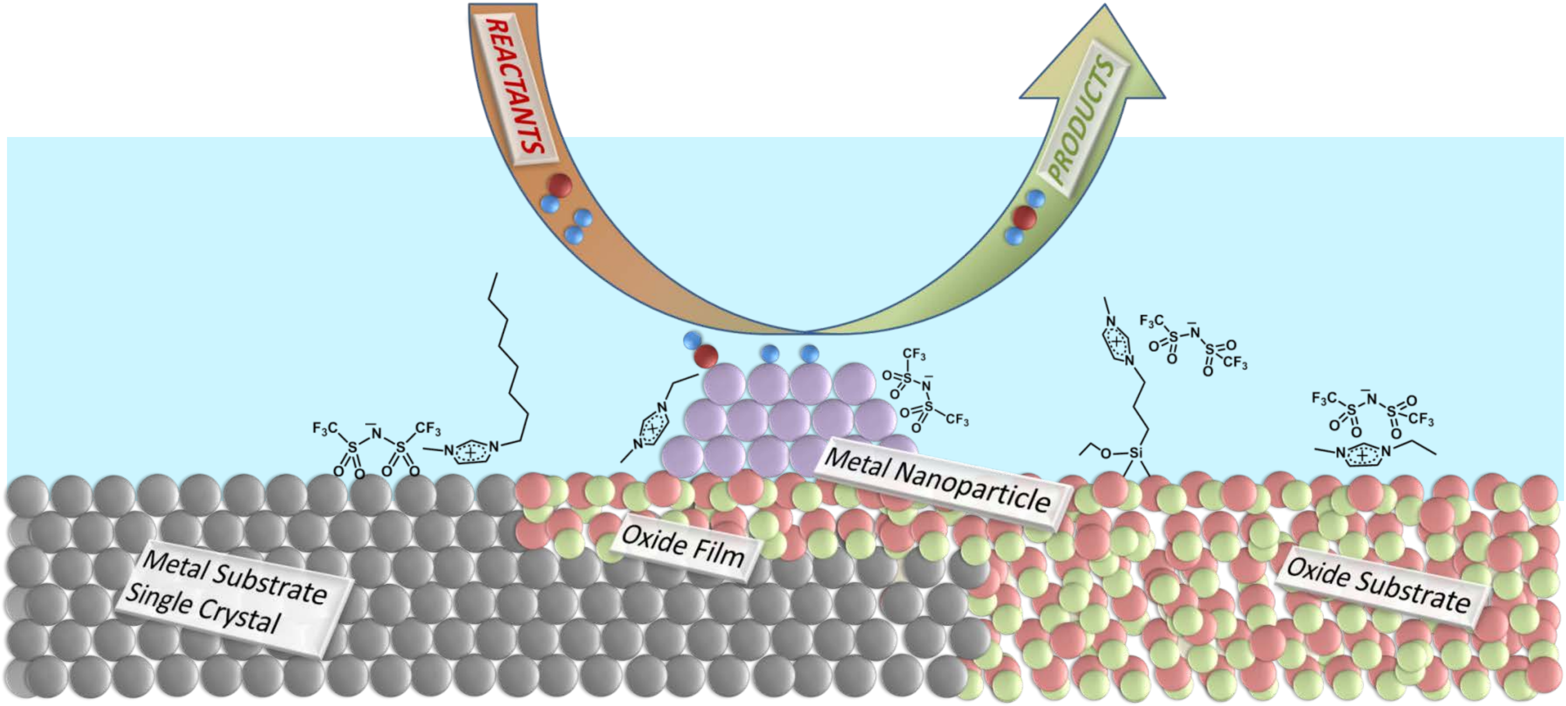
- LOHC linked to non-reactive IL-tag to reduce vapor pressure
- *in situ* reaction monitored (XPS, TDS) at equilibrium under UHV
- catalyzed dehydrogenation close to techn. conditions
- on Au dehydrogenation / decomposition at higher T (+30K)

Vacuum surface science meets heterogeneous catalysis:
Dehydrogenation of a liquid organic hydrogen carrier in the liquid state
*T. Matsuda, N. Taccardi, J. Schwegler et al., ChemPhysChem, **2015**, 16, 1873-1879*

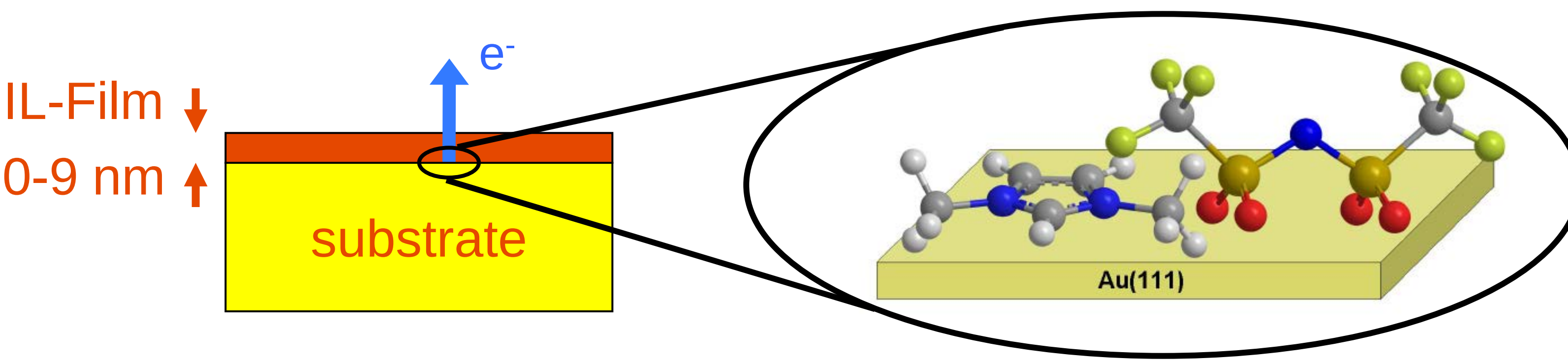
Surface and Interface Science of Ionic Liquids



IL – solid interfaces studied by ARXPS



access to IL-solid interface: ultrathin IL layers required

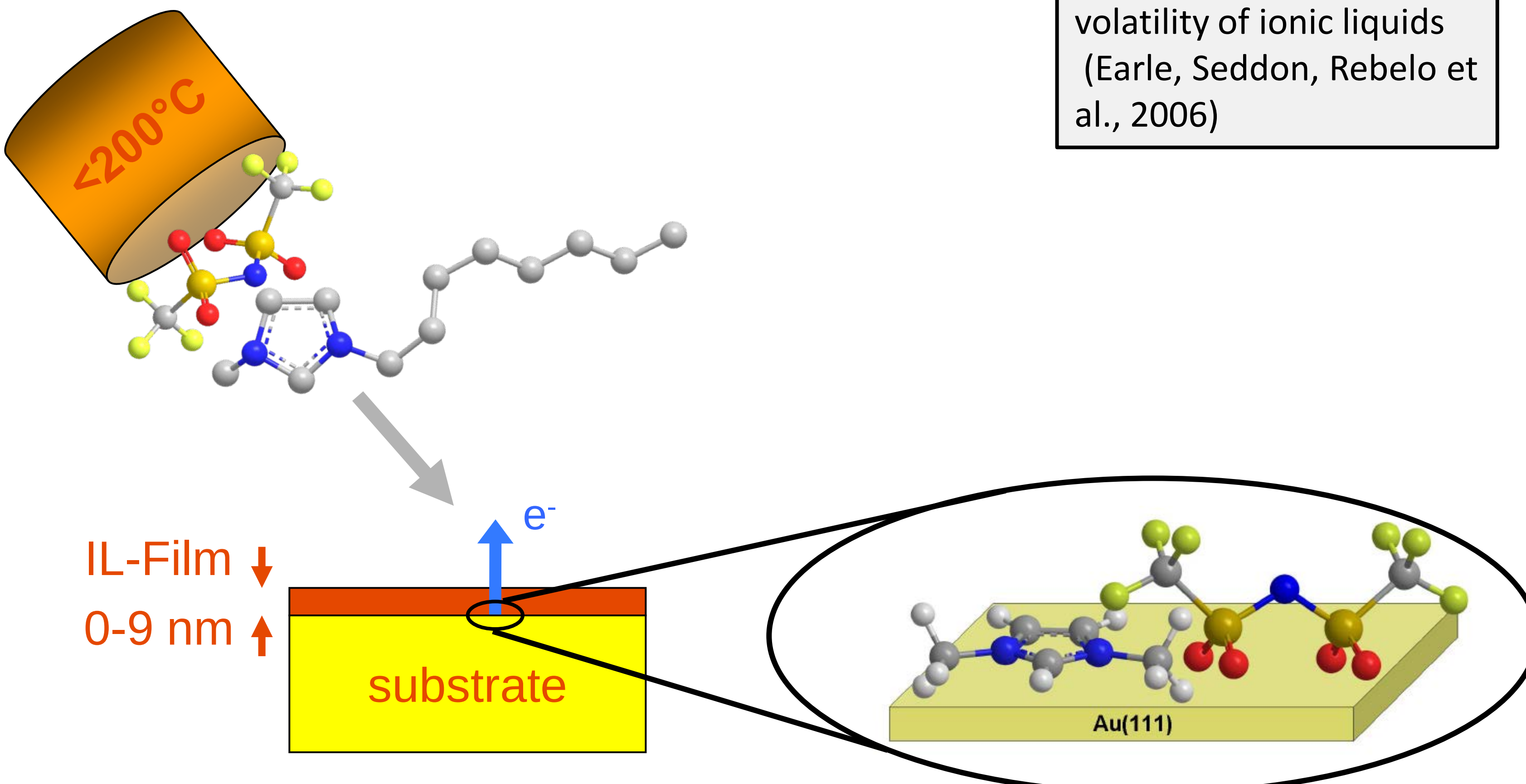


IL – solid interfaces studied by ARXPS

- in-situ preparation in UHV: <u>physical vapor deposition</u> of IL (ion pairs)
- sub-monolayer dosing (typically ~0.3 ML IL / min at 400 – 450 K)

➔ deposition of well-defined amount of clean IL on clean support

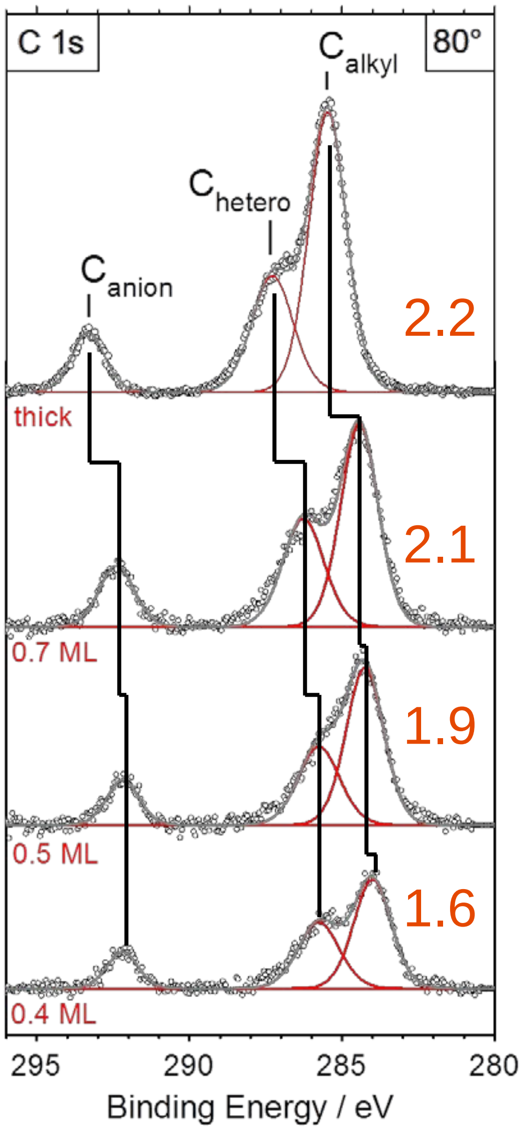
The distillation and volatility of ionic liquids (Earle, Seddon, Rebelo et al., 2006)

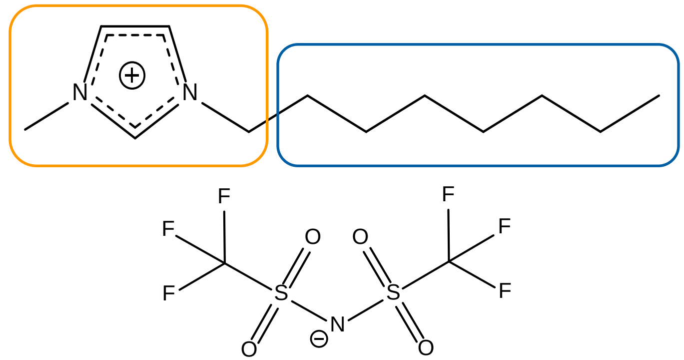


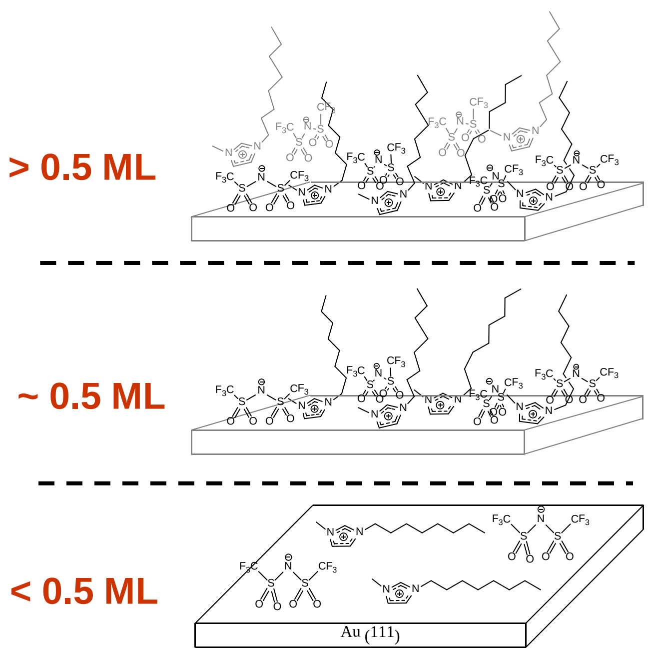
*T. Cremer et al., ChemPhysChem, **2008**, 9, 2185*

Interface $[C_8C_1Im][Tf_2N]$ / Au(111)

C_{alkyl} / C_{hetero} (nom. 1.4)



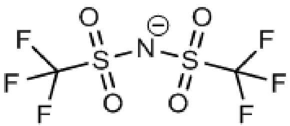




- Subsequent IL multilayers
- Restructuring at d = 0.5 ML
- Checkerboard-like structure

Cremer *et al.*, *Langmuir,* **2011**, 27, 3662

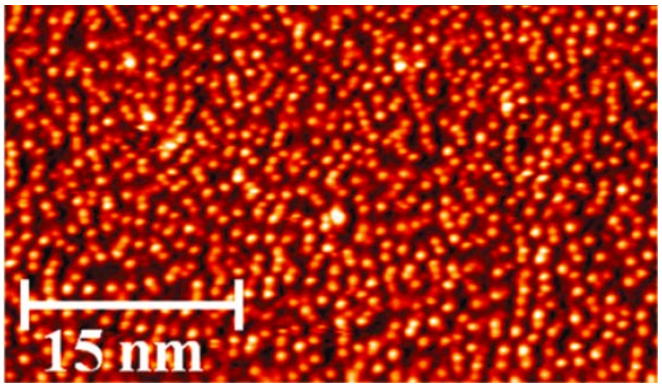
Interface $[C_4C_1Pyr][Tf_2N]$ „BMP-TFSA“ / Au(111)

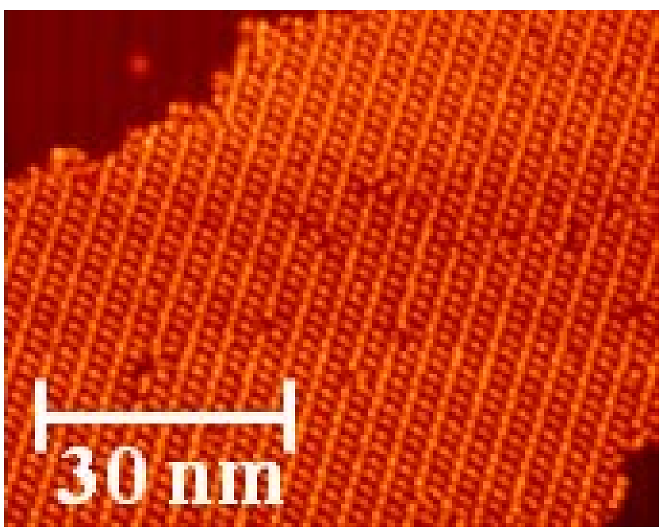


$[C_4C_1Pyr][Tf_2N]$ layer

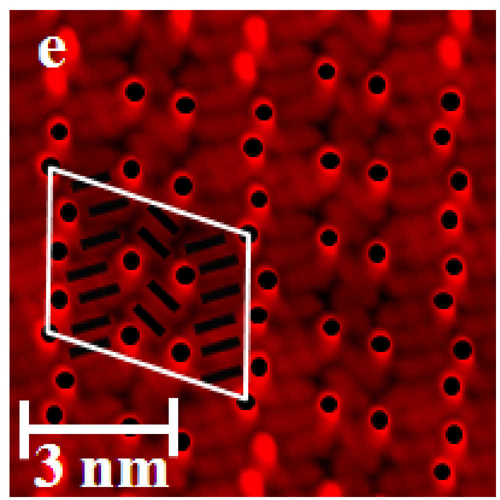
[1-butyl-1-methyl**pyrrolidinium**-bis(trifluoromethylsulfonyl)imide

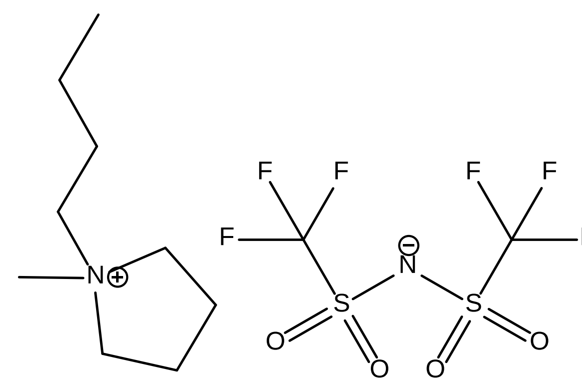
- STM: At 300 K highly mobile 2D liquid phase
- Disordered 2D amorphous phase next to well ordered 2D crystalline layer at T < 200 K
- XPS & STM: checkerboard-like structure
  - → cations and anions in contact with surface
  - → alkyl chains sticking out
  - → anion in cis-conformation (CF_3 groups towards vacuum)





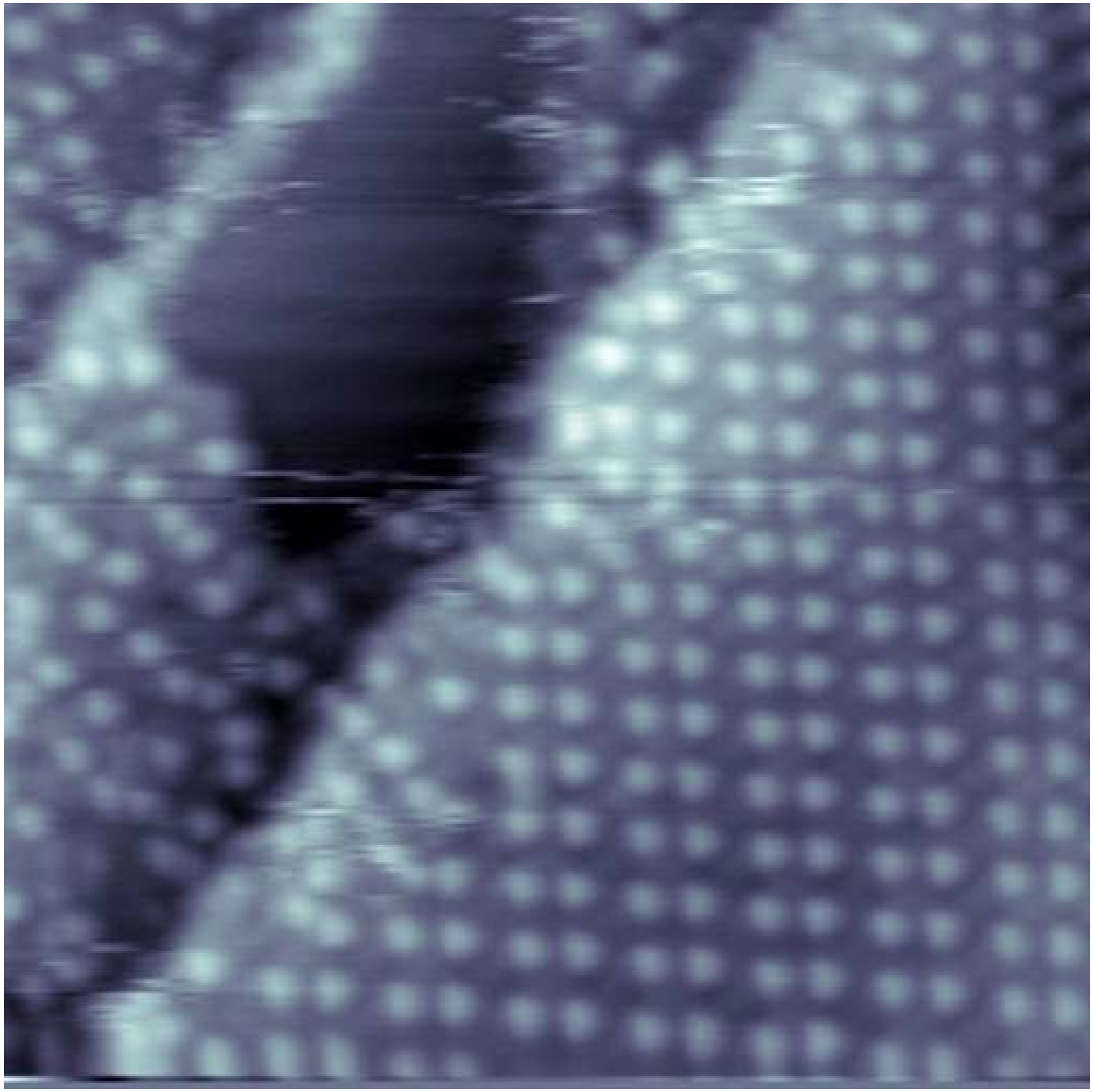
U = -1.8 V, I = -0.060 nA, T = 102 K





Uhl, Cremer, Maier, Steinrück, Behm, *PCCP*, **2013**, 15, 17295

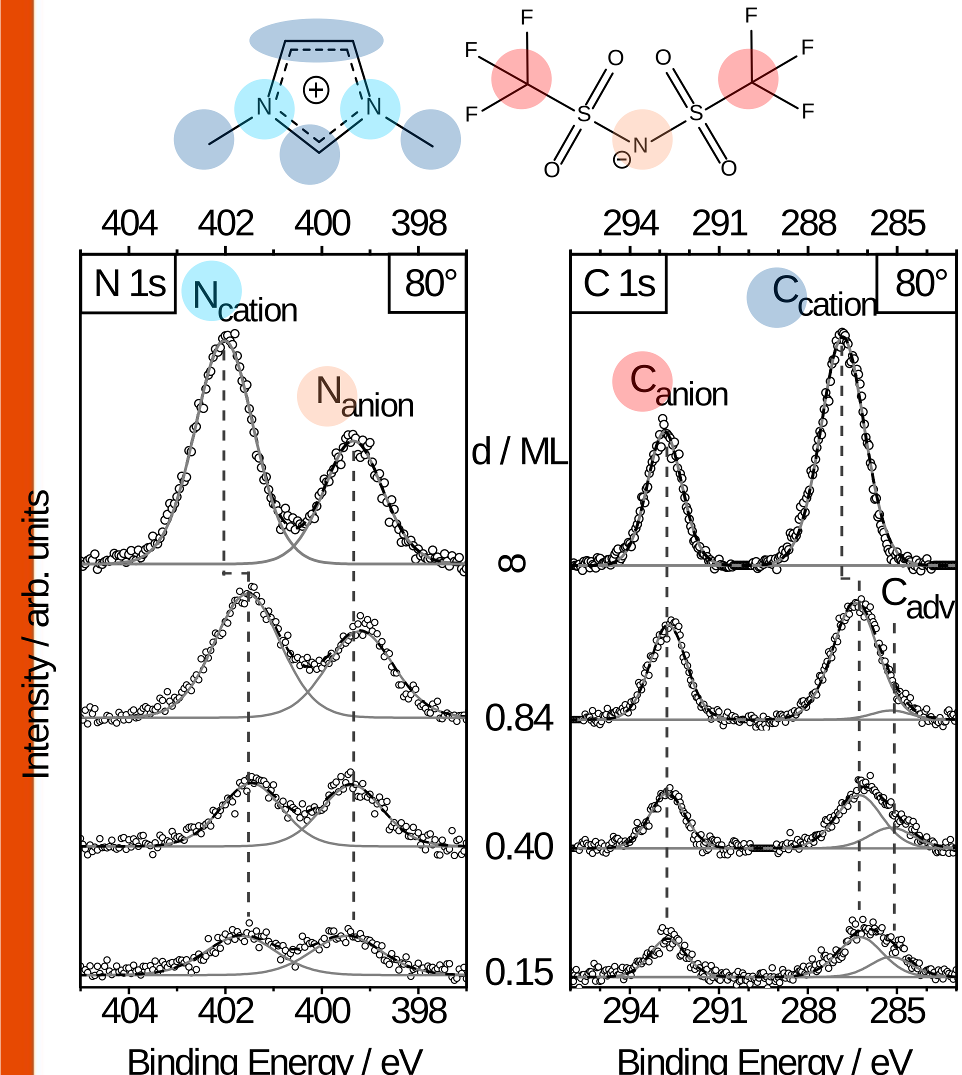
Interface $[C_4C_1Pyr][Tf_2N]$ „BMP-TFSA“ / Au(111)

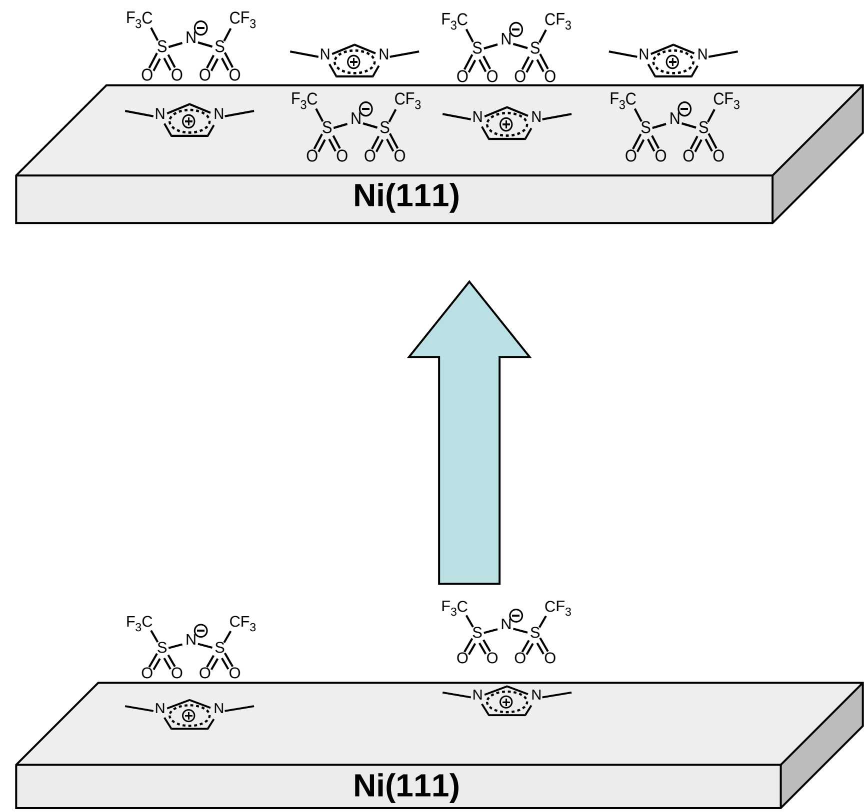


Buchner, Uhl, Behm *et al.*, *ACS Nano*, **2015**, 7, 7773

Interface $[C_1C_1Im][Tf_2N]$ / Ni(111)

➔ Enhancement of anion-related species for d < 1ML



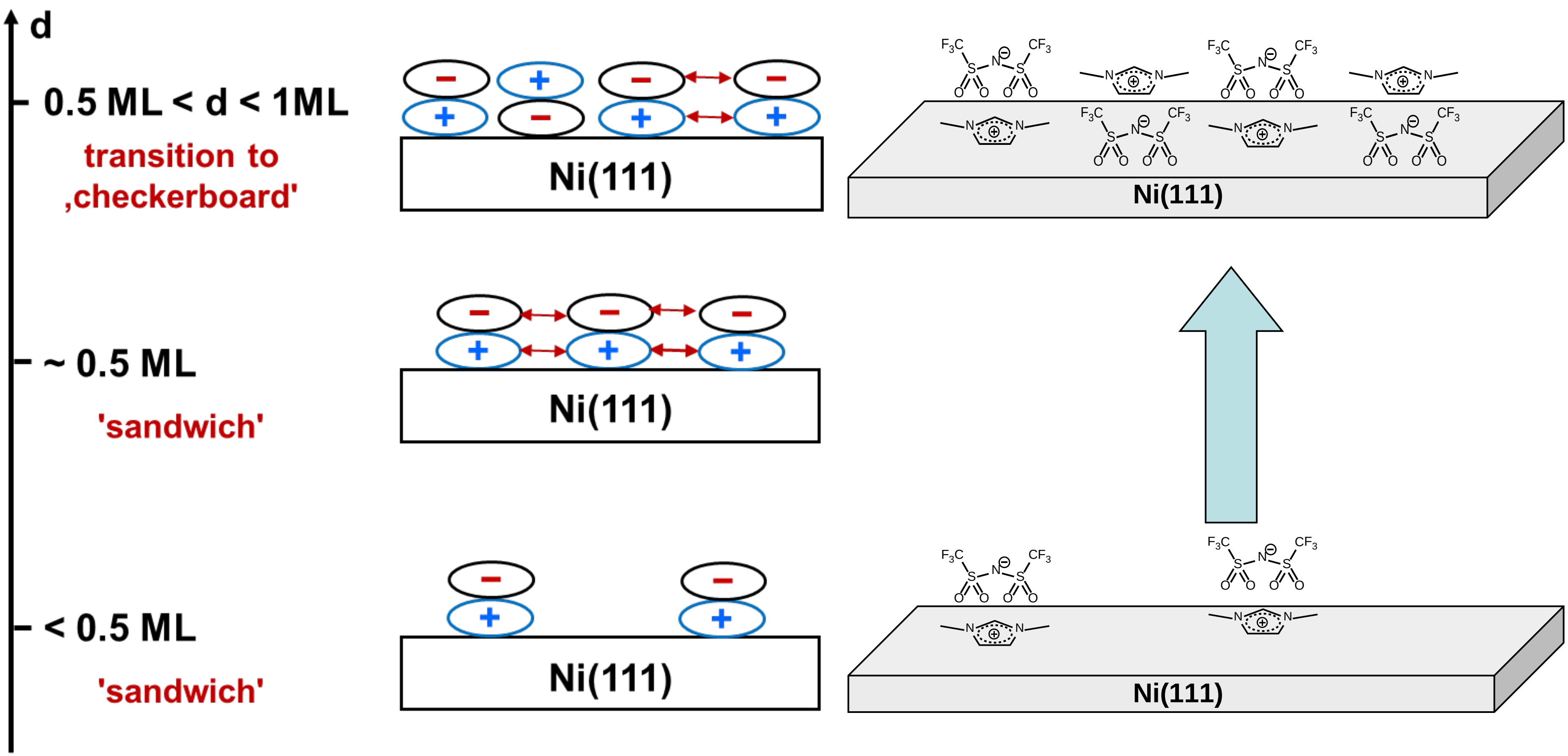


→ Rearrangement to **checkerboard** structure at higher film thickness

Cremer *et al.*, *PCCP*, 14 (2012) 5153

Interface $[C_1C_1Im][Tf_2N]$ / Ni(111)

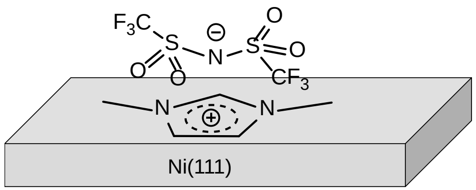
➔ Rearrangement from **bilayer** to **checkerboard** structure with coverage

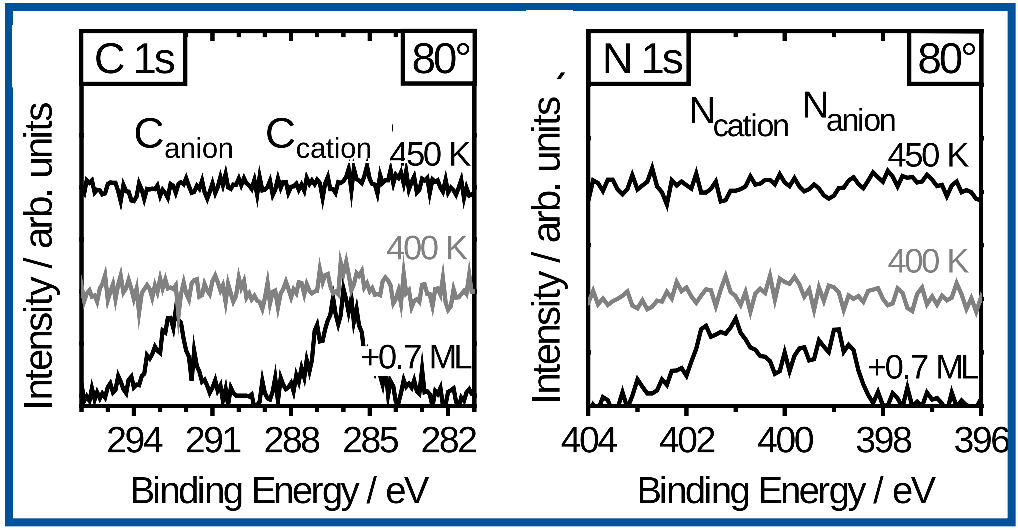


Cremer *et al.*, *PCCP*, **2012**, 14, 5153

Reactions of ultrathin IL layers on solid surfaces

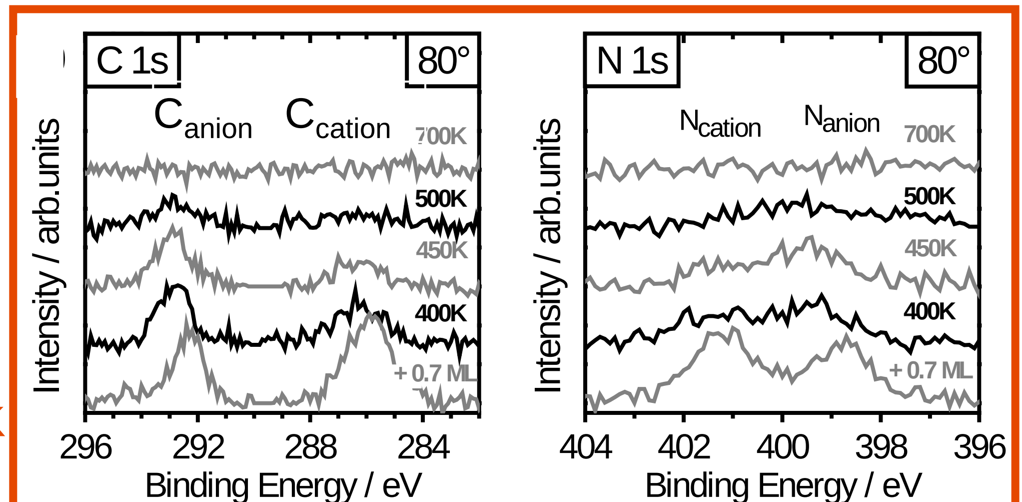
0.7 ML $[C_1C_1Im][Tf_2N]$





0.7 ML $[C_1C_1Im][Tf_2N]$ on Ni(111) + Heating:

- Cation + anion thermally desorbs as neutral ion pairs at ~400K



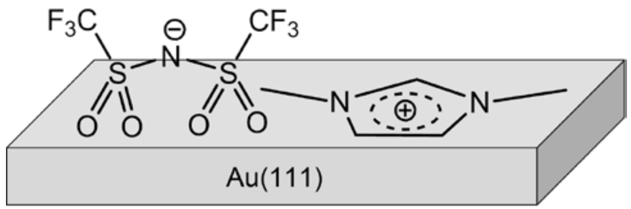
0.7 ML $[C_1C_1Im][Tf_2N]$ on NiO + Heating

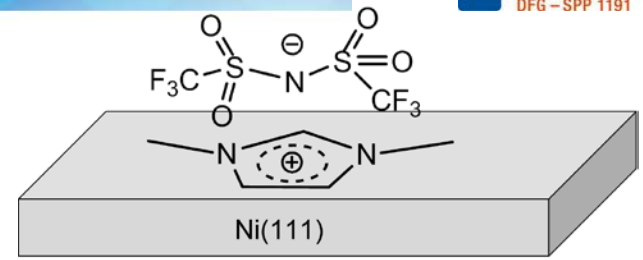
- Cation desorbs first, starting at 400K
- Anion + decomposition of NiO at T>500K

➔cation with OH^- surface groups (volatile), $[Tf_2N]^-$ at Ni^{2+} site still stable

Cremer *et al.*, *PCCP*, **2012**, 14, 5153

IL growth behaviour: Au(111) vs Ni(111)

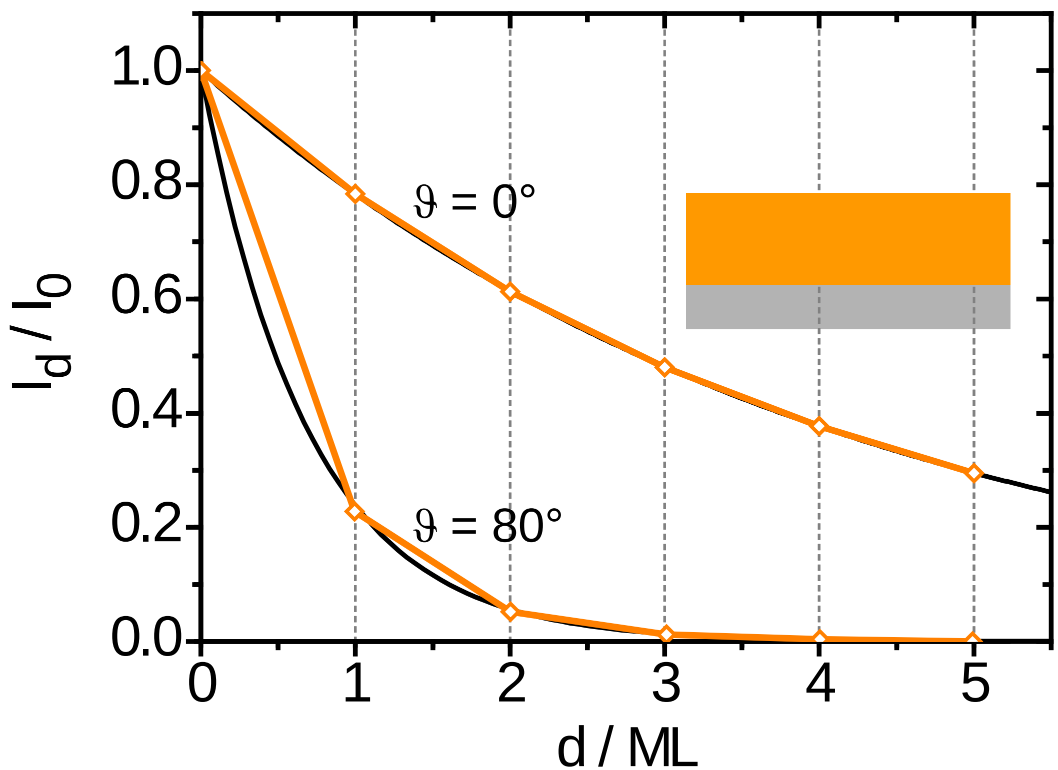




Initially: *C&A at Au (checkerboard)* *C at Ni (sandwich)*

➔ Differences in growth for multilayers?

Attenuation of substrate signal



For ideal layer-by-layer growth:

- Linear decay with monolayer breaks intersecting with exponential line

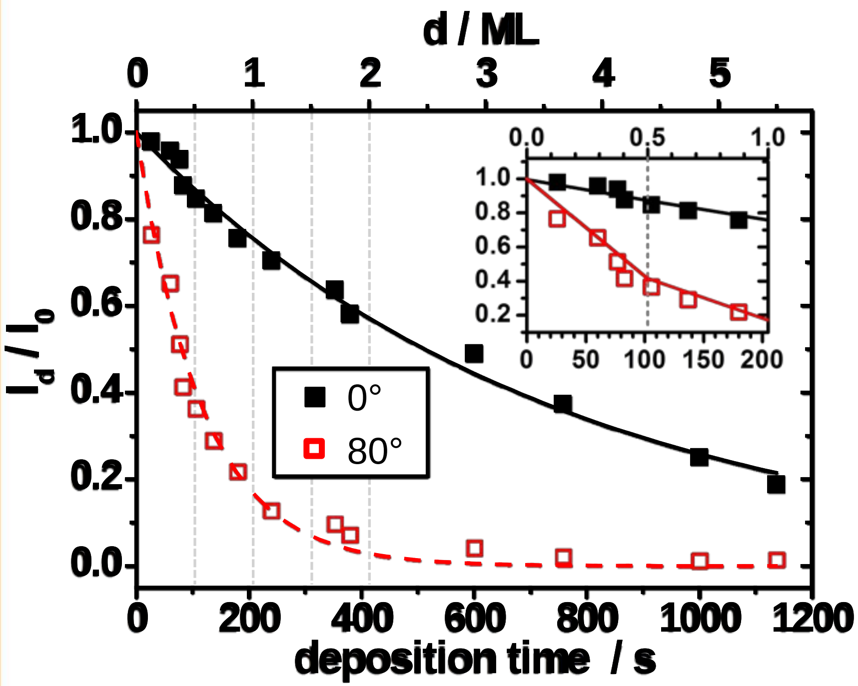
$$\frac{I_d}{I_0} = e^{-d/\lambda(E_{kin})\cdot\cos\vartheta}$$

$[C_1C_1Im][Tf_2N]$ on Au(111):
λ = 3 nm
d_{ML} = 0.73 nm

IL growth behaviour: Au(111) vs Ni(111)

ENGINEERING OF ADVANCED MATERIALS
IONIC LIQUIDS DFG – SPP 1191

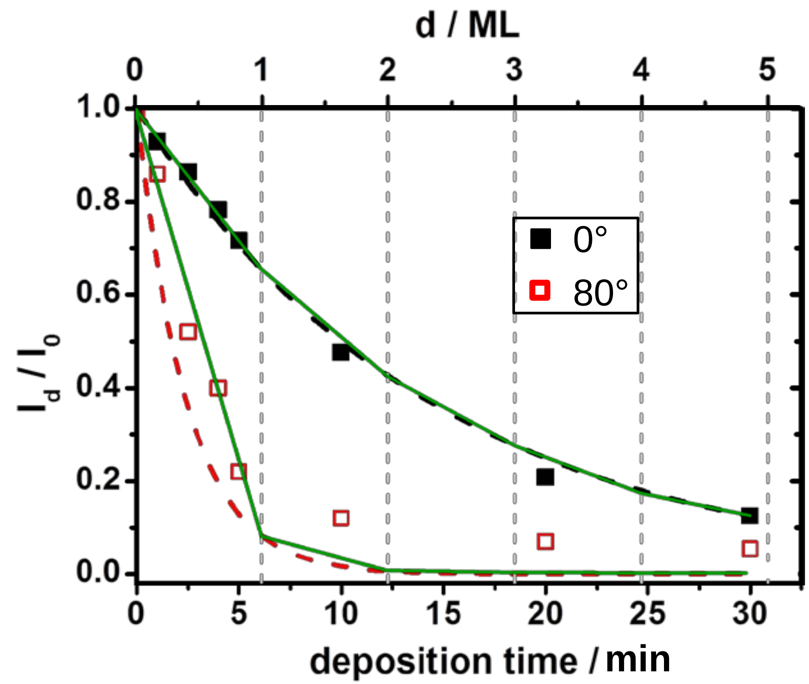
$[C_8C_1Im][Tf_2N]$ on Au(111)



- Perfect agreement between 0° and 80°
- Sectionwise decay not resolved (layer completed at 0.5 ML)

→ Layer-by-layer growth

$[C_1C_1Im][Tf_2N]$ on Ni(111)

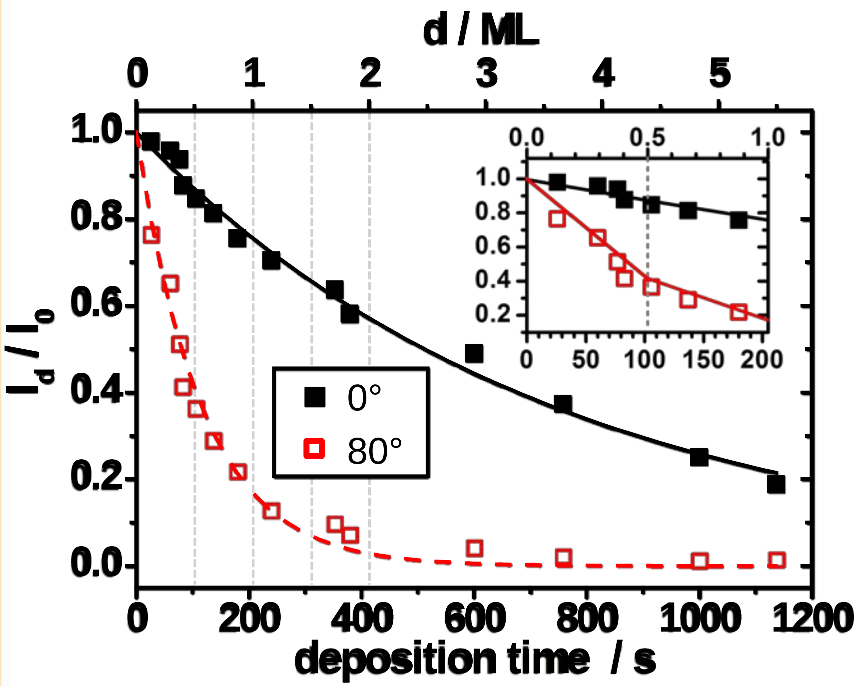


- Sectionwise decay resolved within first monolayer
- 80° data deviates from calculated damping curve

→ Wetting layer followed by mixed growth (2D → 3D)

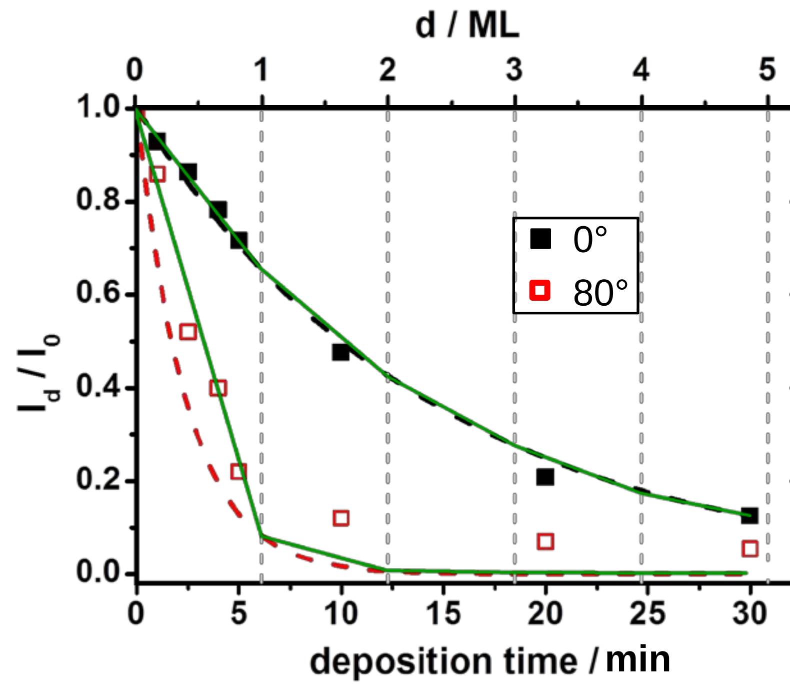
IL growth behaviour: Au(111) vs Ni(111)

$[C_8C_1Im][Tf_2N]$ on Au(111)



→ Layer-by-layer growth

$[C_1C_1Im][Tf_2N]$ on Ni(111)



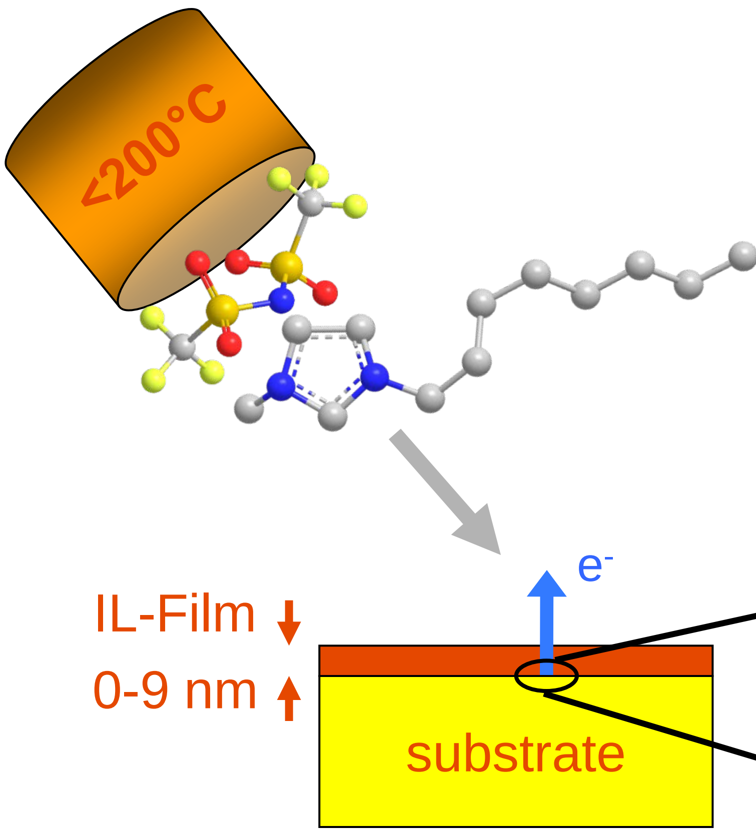
→ Wetting layer followed by mixed growth (2D → 3D)

Unstable ILs: alternative deposition methods

ENGINEERING OF ADVANCED MATERIALS
IONIC LIQUIDS
DFG – SPP 1191

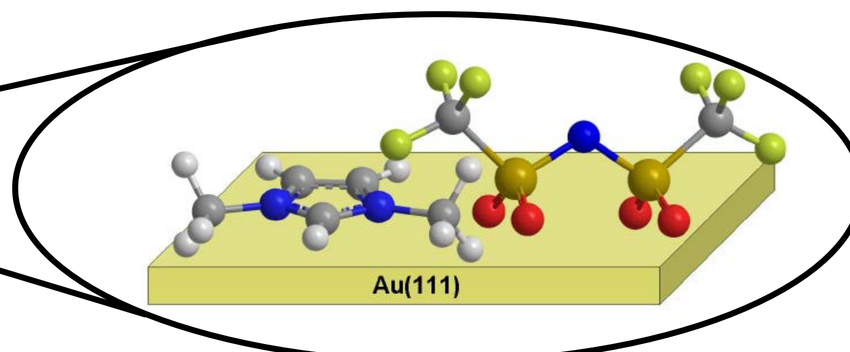
- in-situ preparation in UHV: physical vapor deposition of IL (ion pairs)
- sub-monolayer dosing (typically ~0.3 ML IL / min at 400 – 450 K)

➔ deposition of well-defined amount of clean IL on clean support



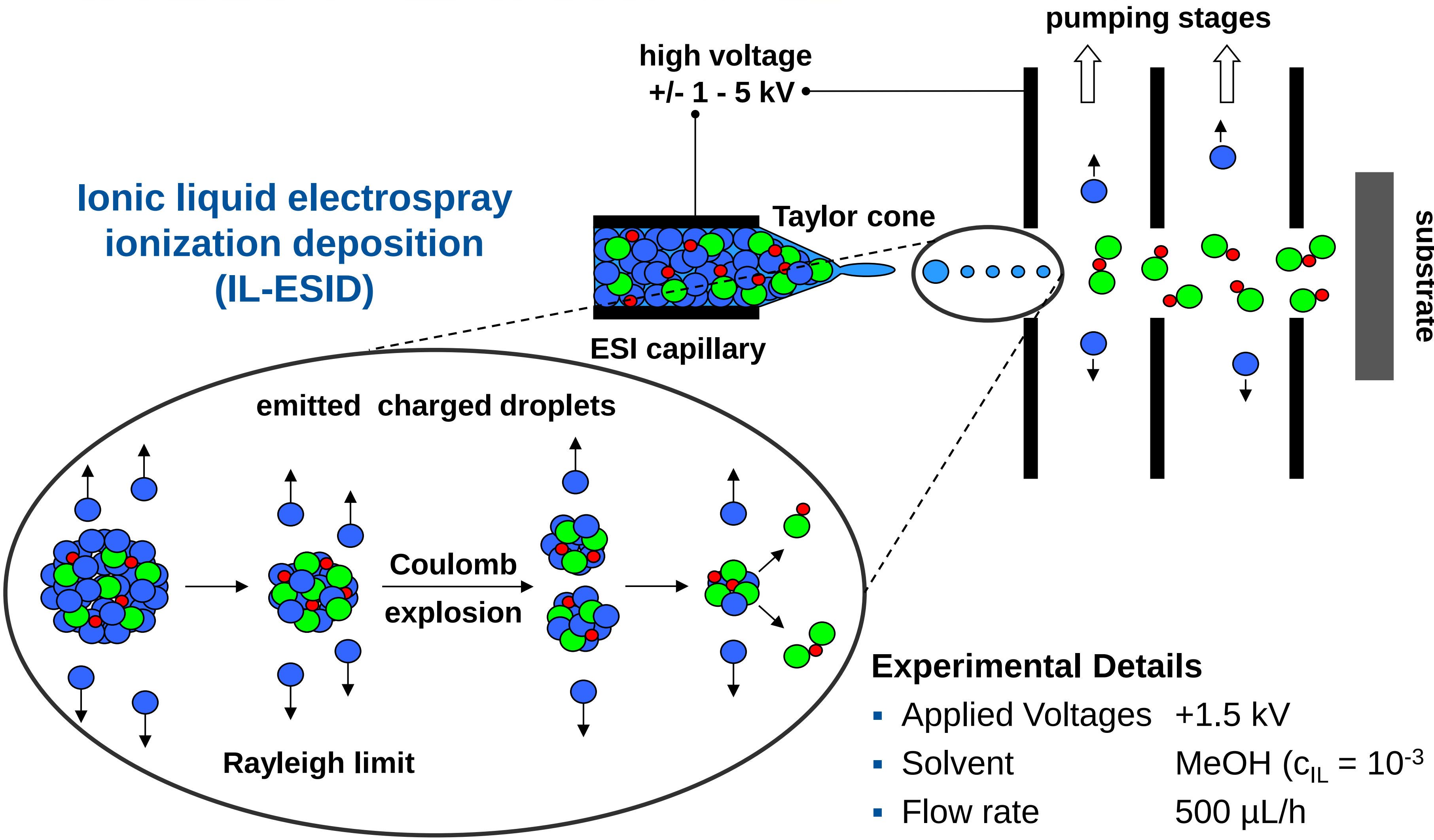
➔ PVD requires thermally stable IL

For non-evaporable ILs (e.g. halide ILs) different in-situ method required
➔ **electrospray deposition (ESID)**



IL-ESID concept

Ionic liquid electrospray ionization deposition (IL-ESID)



Experimental Details

- Applied Voltages +1.5 kV
- Solvent MeOH ($c_{IL} = 10^{-3}$ M)
- Flow rate 500 µL/h
- Distance to sample: ~ 0.7 m

→ Time for 1ML / 1cm^2 : ~1h

F. Rietzler *et al.*, *Langmuir*, **2014**, *30*, 1063

IL-ESID: $[C_8C_1Im]Cl$ / Au(111)

Growth behaviour $[C_8C_1Im]Cl$ on Au(111)

θ **< 1st closed layer**

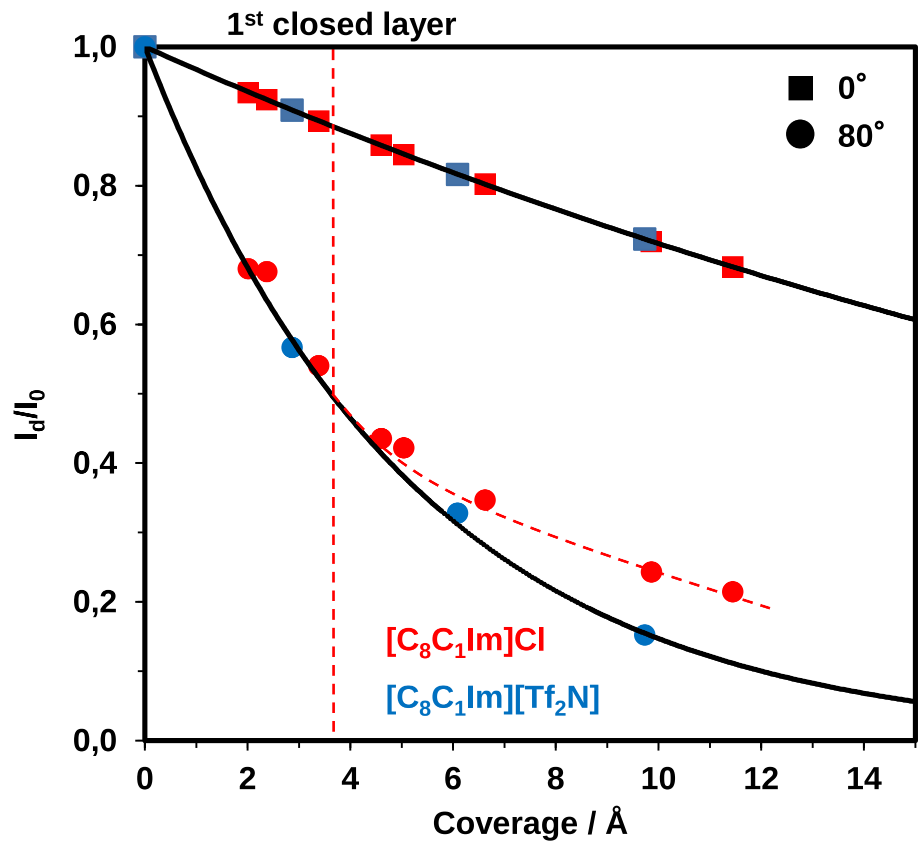
data agree with ideal 2D growth

→ formation of a wetting layer

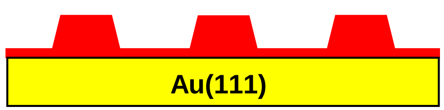
θ **> 1st closed layer**

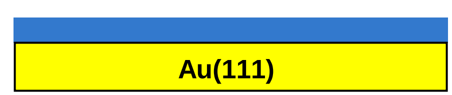
80° data above ideal curve

→ indication for 3D growth



$[C_8C_1Im]Cl$





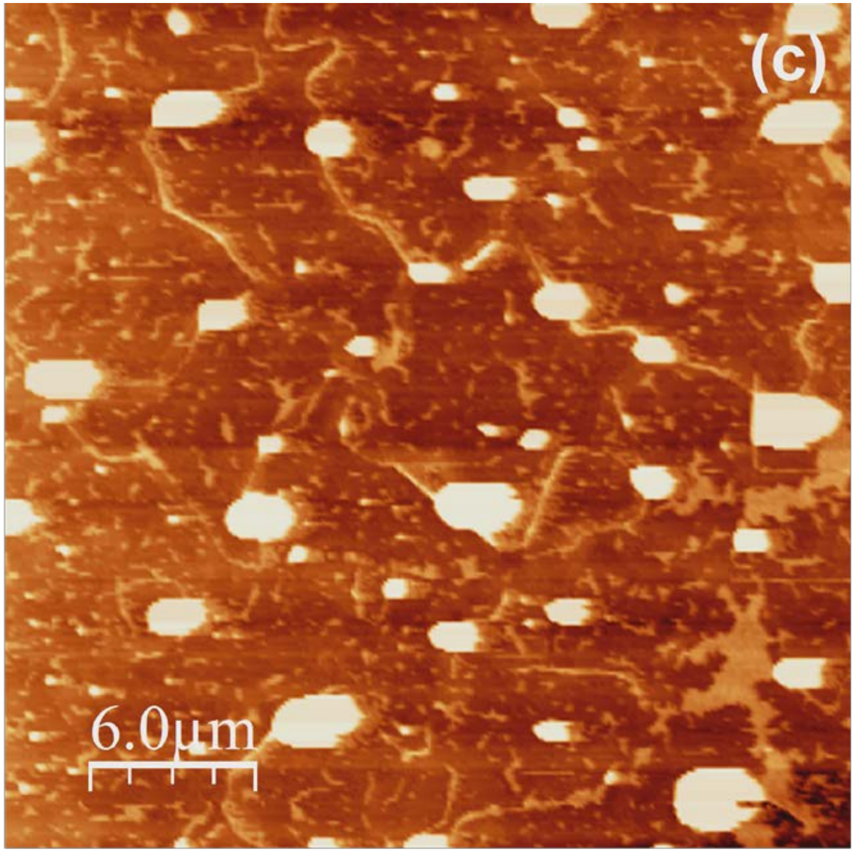
$[C_8C_1Im][Tf_2N]$

F. Rietzler *et al.*, *Langmuir*, **2014**, *30*, 1063

IL-ESID: $[C_8C_1Im]Cl$ / Au(111)

Atomic force microscopy (AFM) measurements

- nominal IL coverage: ~ 50 ML on epitaxial Au(111)/mica
- ex-situ AFM measurements (ambient conditions)



$[C_8C_1Im]Cl$

F. Rietzler *et al.*, *Langmuir*, **2014**, *30*, 1063

Influence of interionic interactions on growth mode

- stronger interionic interactions (particularly stronger hydrogen bonding) between an imidazolium cation and Cl^- compared to Tf_2N^- ,

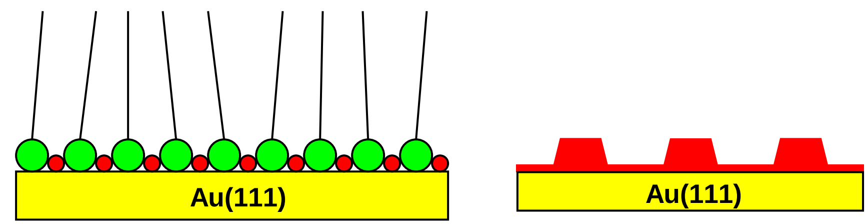
Influence of IL / solid interface on growth mode

$[C_8C_1Im]Cl^-$

non-polar outer surface of the wetting layer due to densely packed octyl chains

→ weak bonding of further deposited IL molecules to wetting layer

→ island nucleation



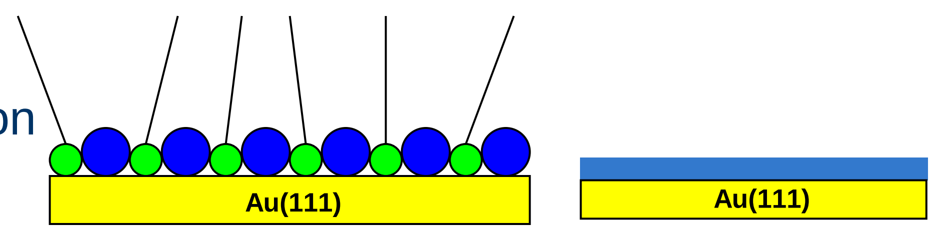
$[C_8C_1Im][Tf_2N]$

lower packing density of octyl chains

→ more open structure

→ prevention of early island nucleation

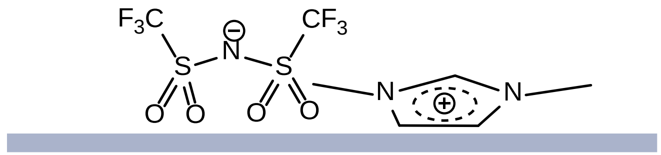
→ layer-by-layer growth



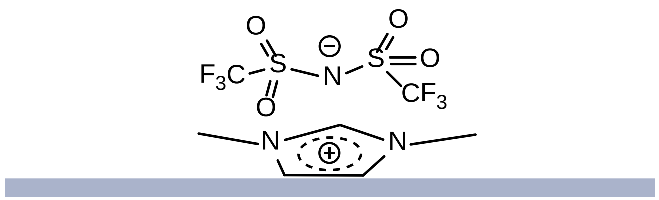
Summary: Surf. Sci. gives ”close look at the interface”

ENGINEERING OF ADVANCED MATERIALS
IONIC LIQUIDS
DFG – SPP 1191

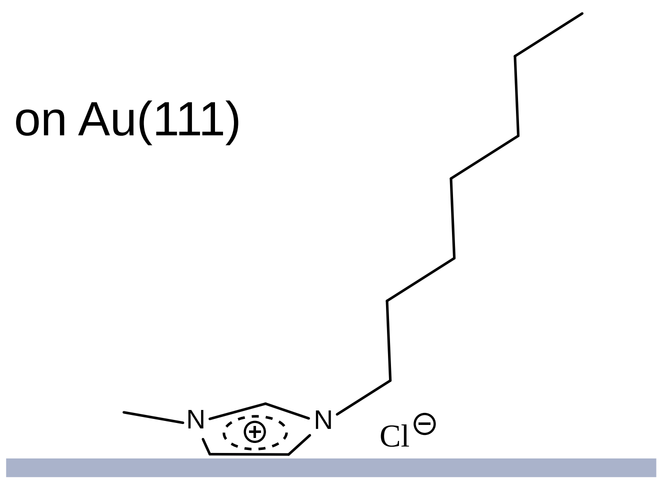
$[C_nC_1Im][Tf_2N]$, $[C_4C_1Pyr][Tf_2N]$ on Au(111)



$[C_1C_1Im][Tf_2N]$ on Ni(111)

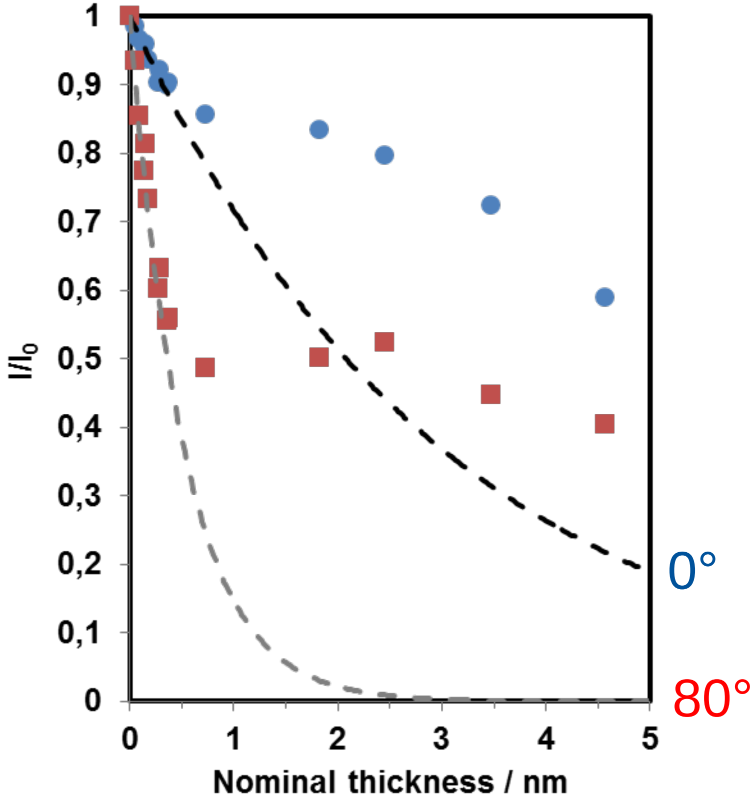


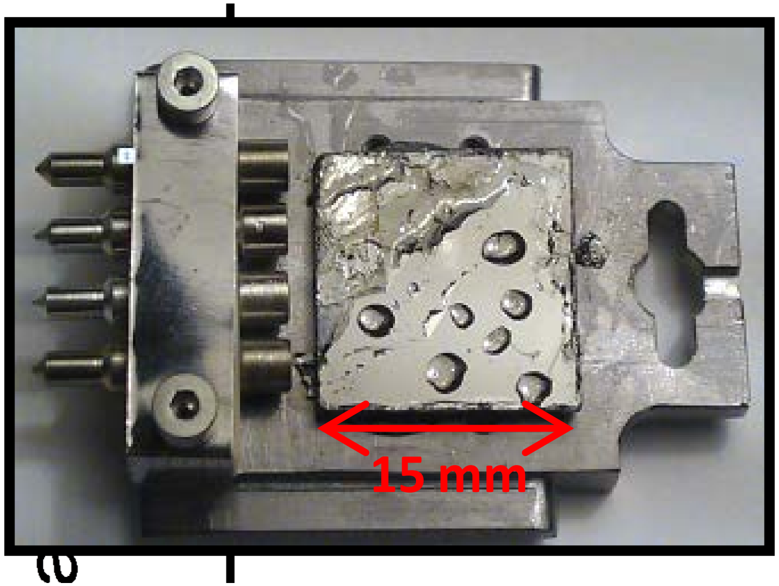
$[C_8C_1Im]Cl$ on Au(111)

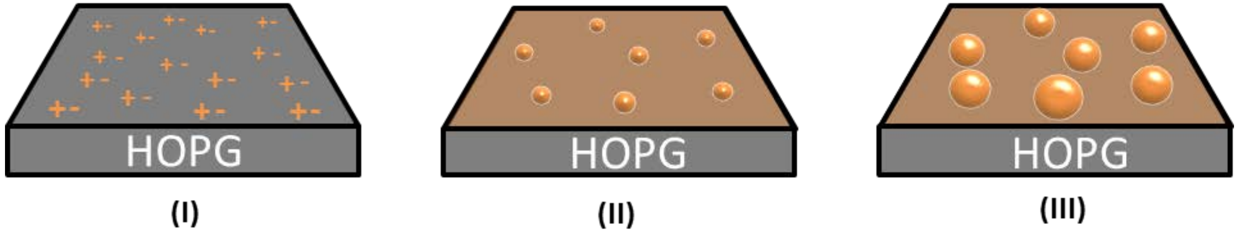


$[C_1C_1Im][Tf_2N]$ on HOPG

- no wetting for macroscopic amounts





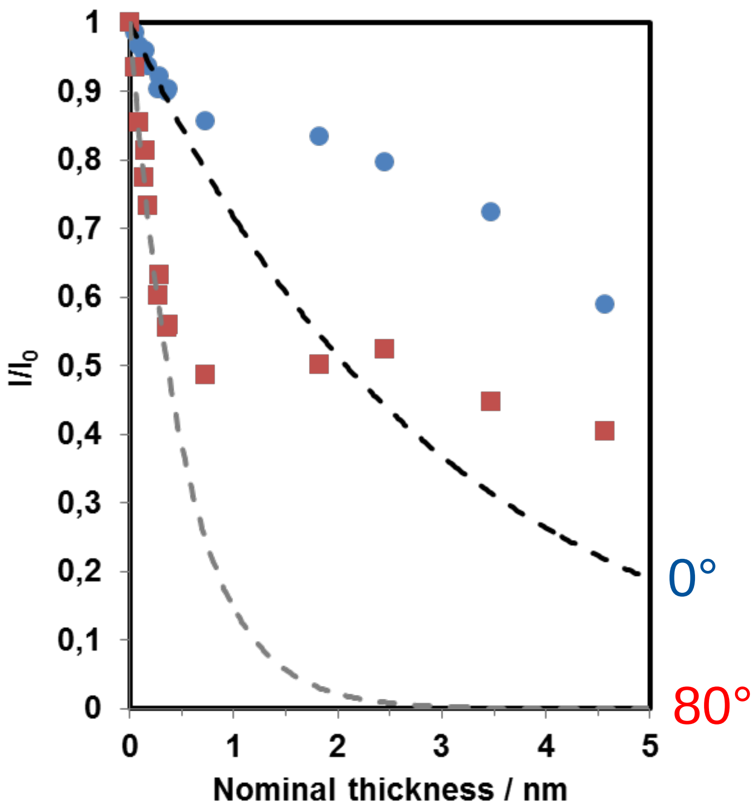


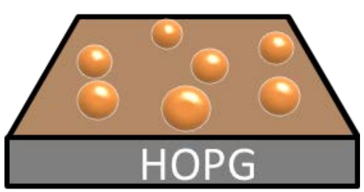
Role of carbon for IL film growth

ENGINEERING OF ADVANCED MATERIALS
IONIC LIQUIDS
DFG – SPP 1191

$[C_1C_1Im][Tf_2N]$ on HOPG

- no wetting for macroscopic amounts

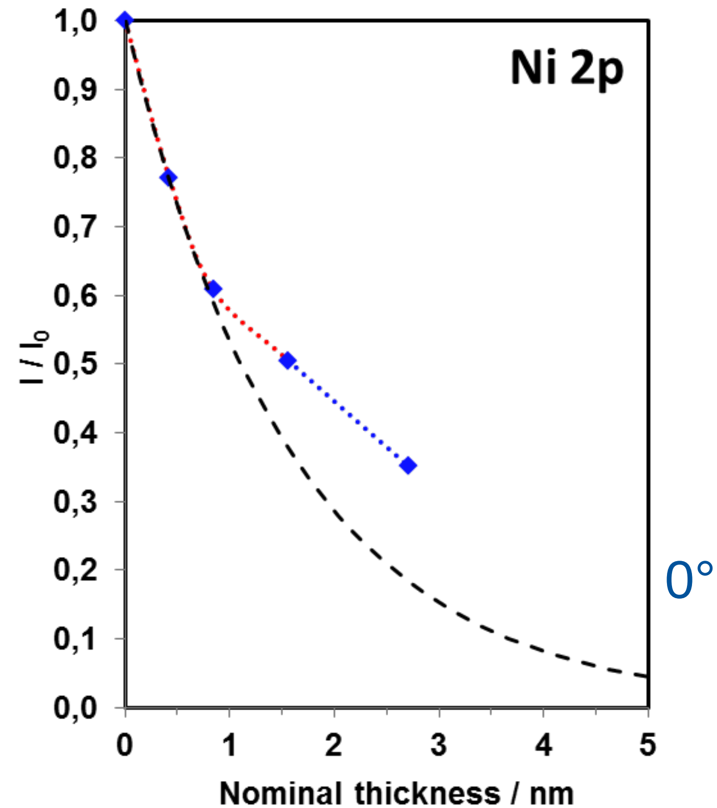




(III)

onto 1ML graphene / Ni(111)

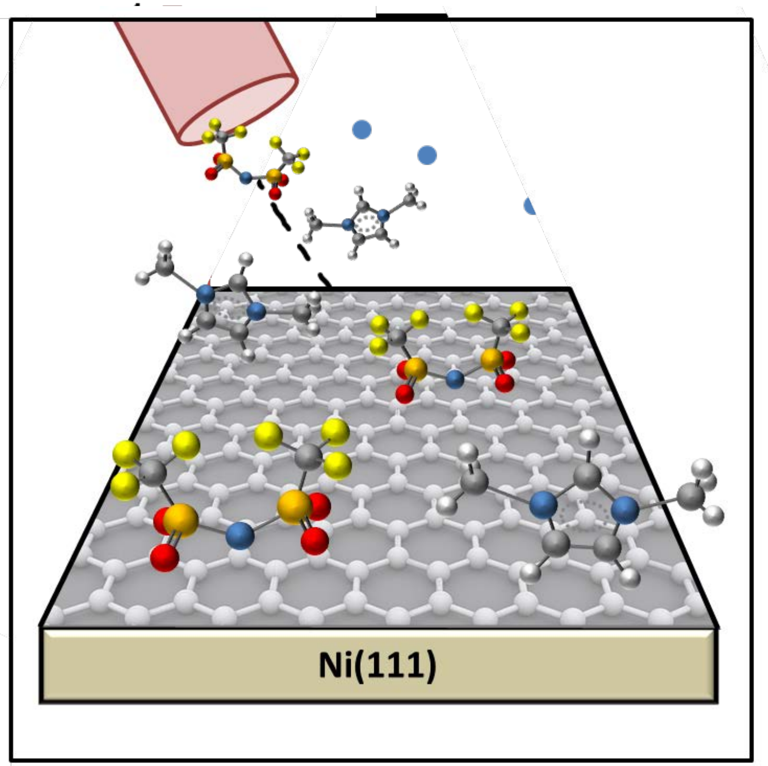
medium wetting, checkerboard ads.

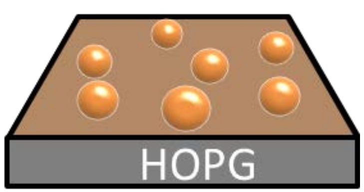


Role of carbon for IL film growth

[C_1C_1Im][Tf_2N] on HOPG

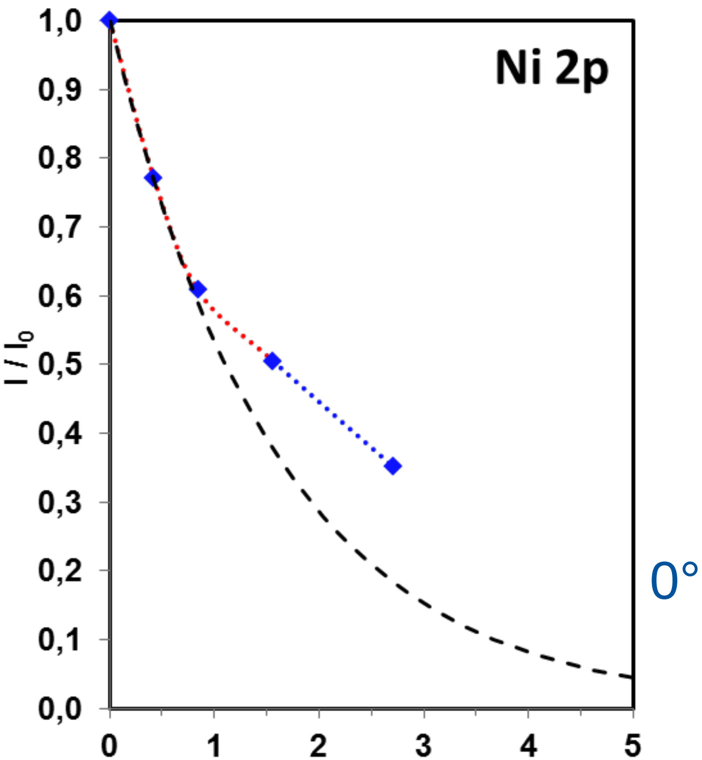
- no wetting for macroscopic amounts



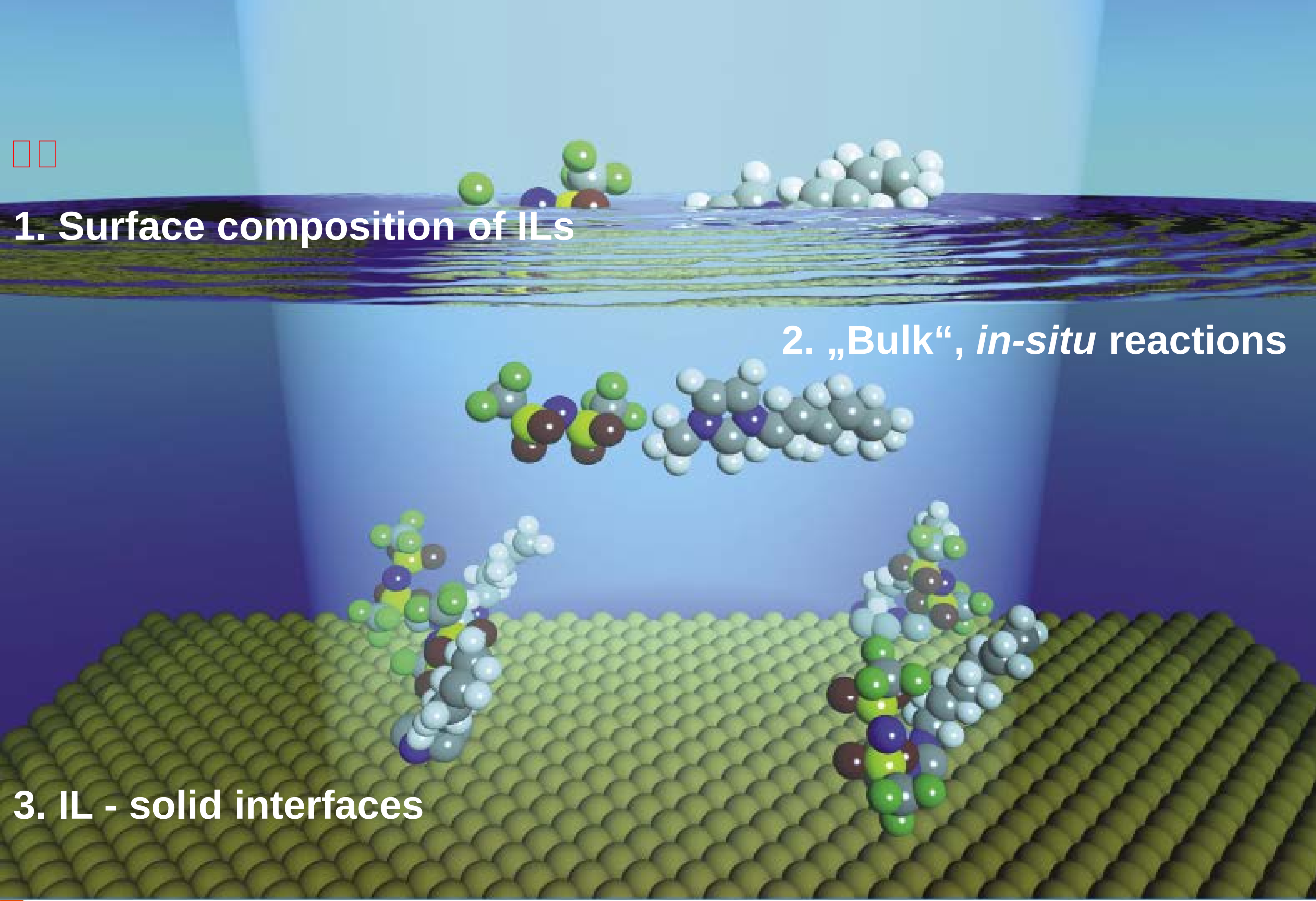


onto 1ML graphene / Ni(111)

medium wetting, checkerboard ads.

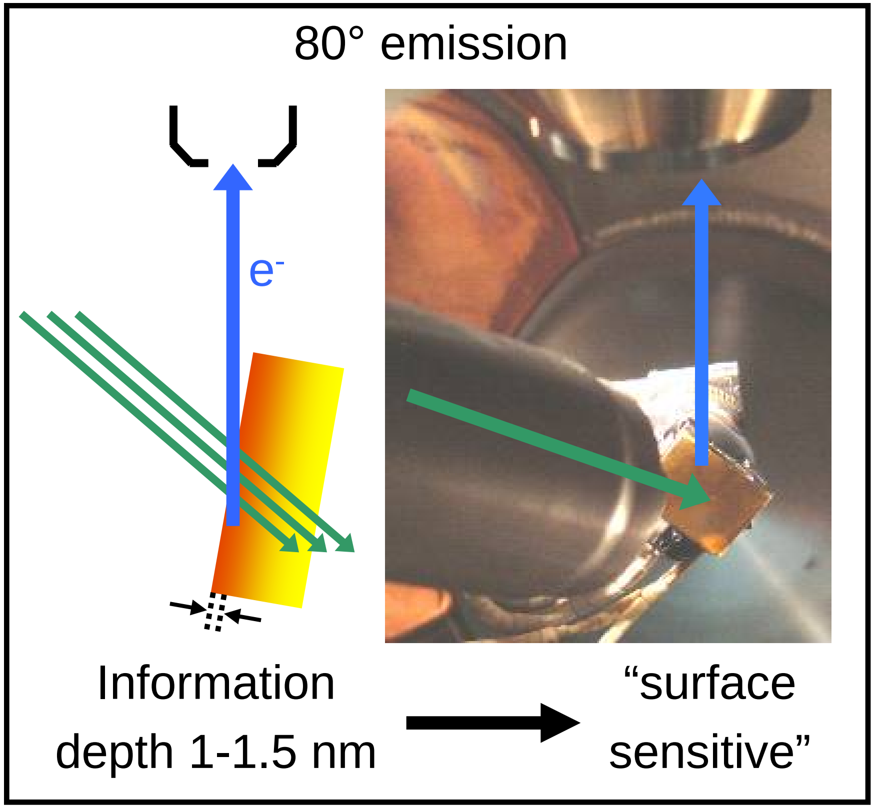


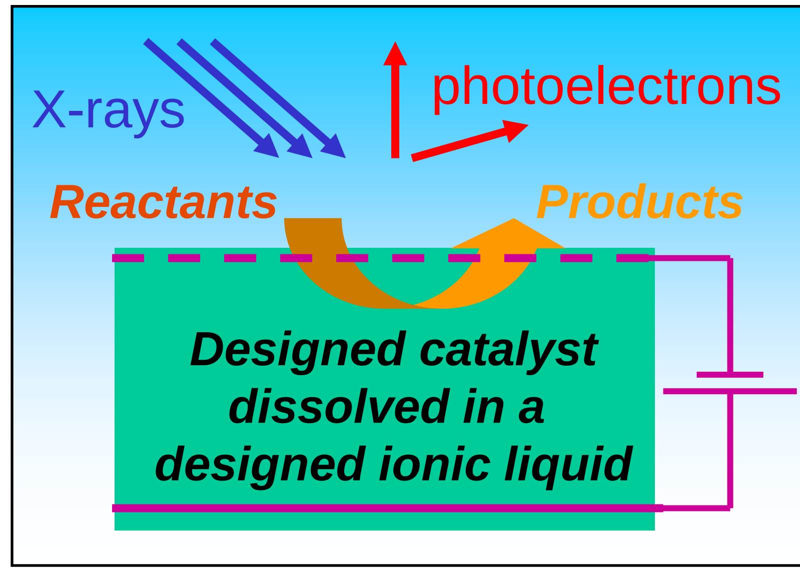
Surface and Interface Science of Ionic Liquids



Angle-resolved XPS (ARXPS)

variation of surface sensitivity by varying electron detection angle

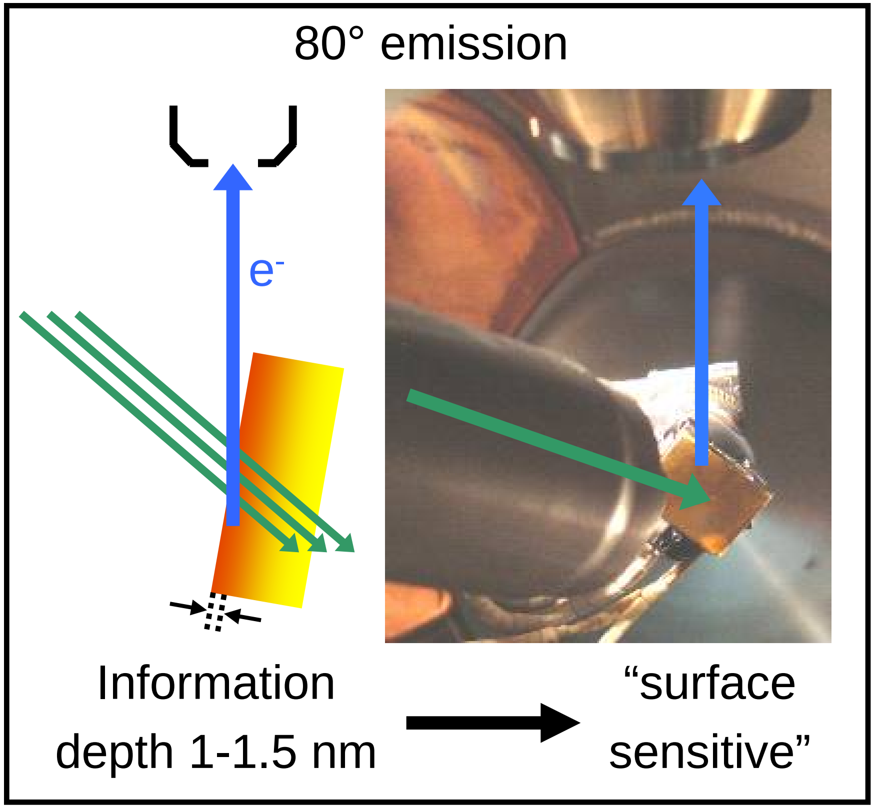


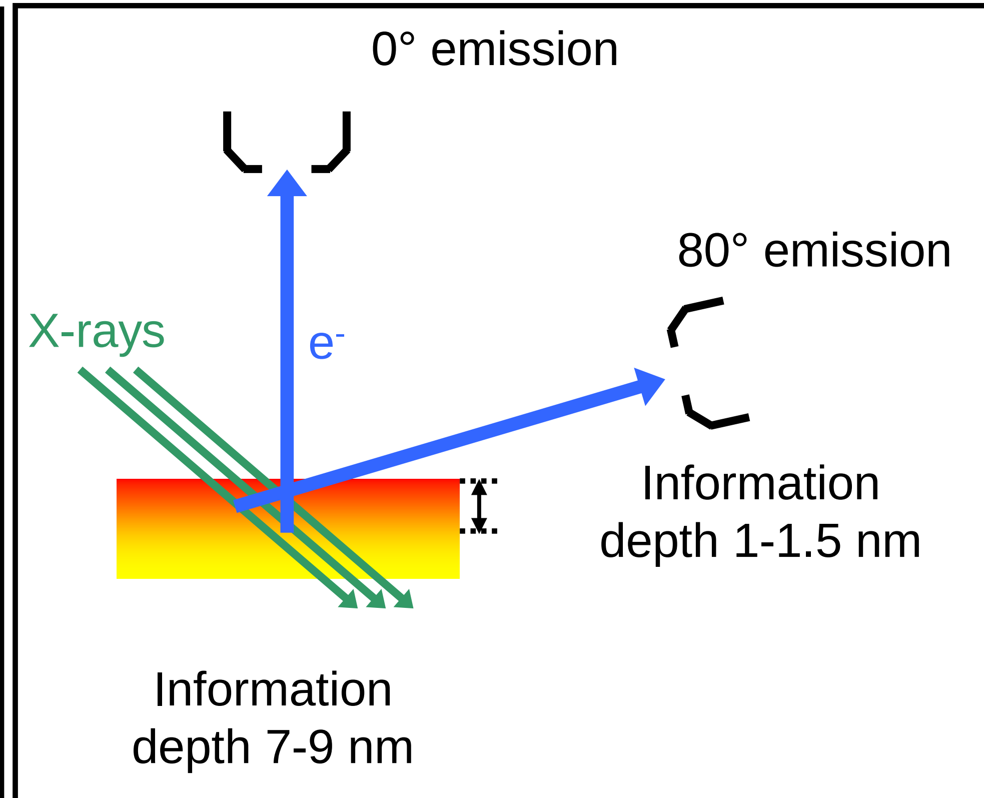


How to measure ARXPS without tilting a liquid sample?

Angle-resolved XPS (ARXPS)

variation of surface sensitivity by varying electron detection angle





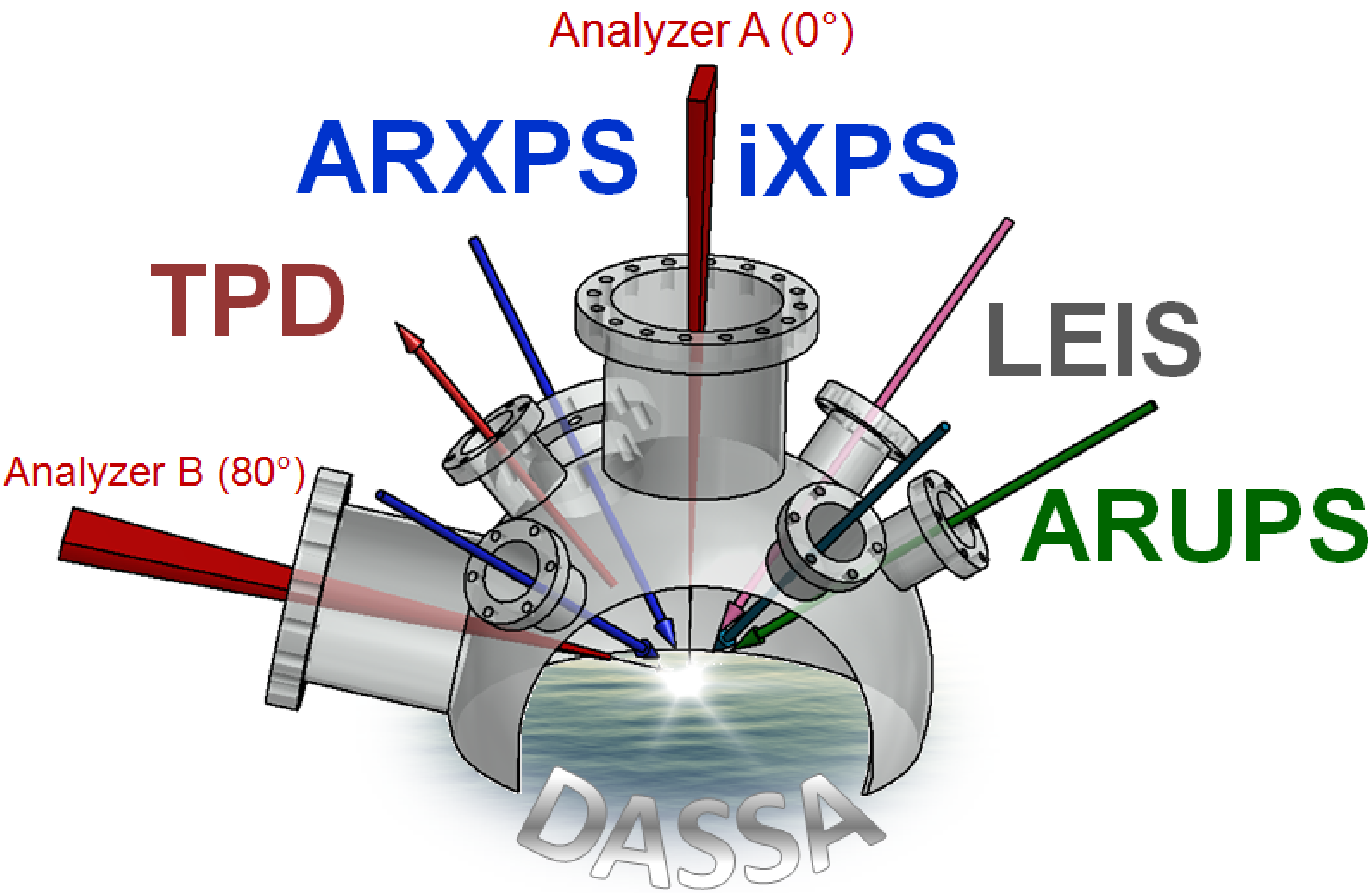
How to measure ARXPS without tilting a liquid sample?

➔ 2 analysers mounted in 0° and 80°

Dual Analyser System for Surface Analysis (DASSA)

ENGINEERING OF ADVANCED MATERIALS
IONIC LIQUIDS
DFG – SPP 1191

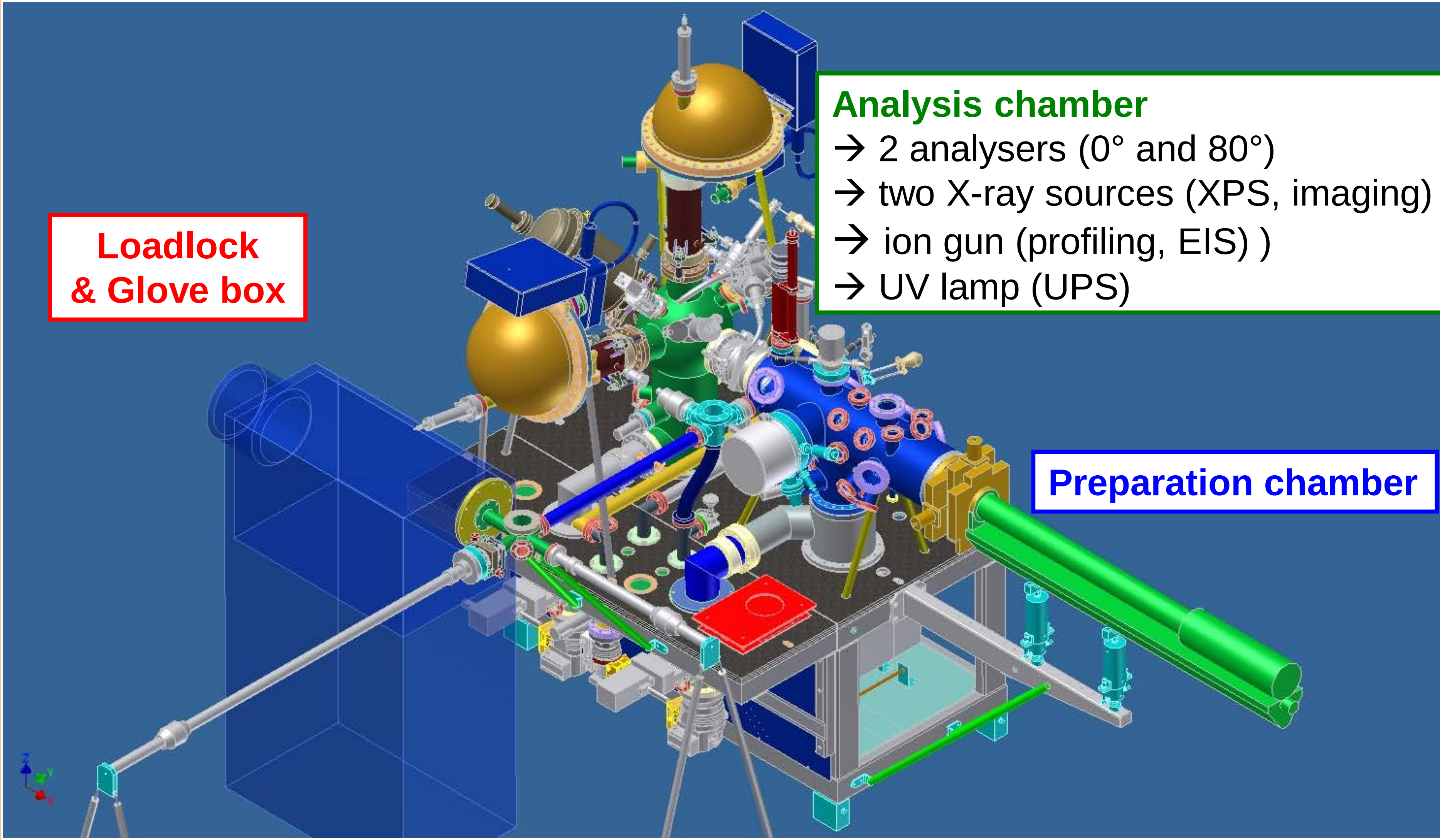
Development of a new ARXPS system 2010-2014 together with Omicron dedicated for liquid systems



Dual Analyser System for Surface Analysis (DASSA)

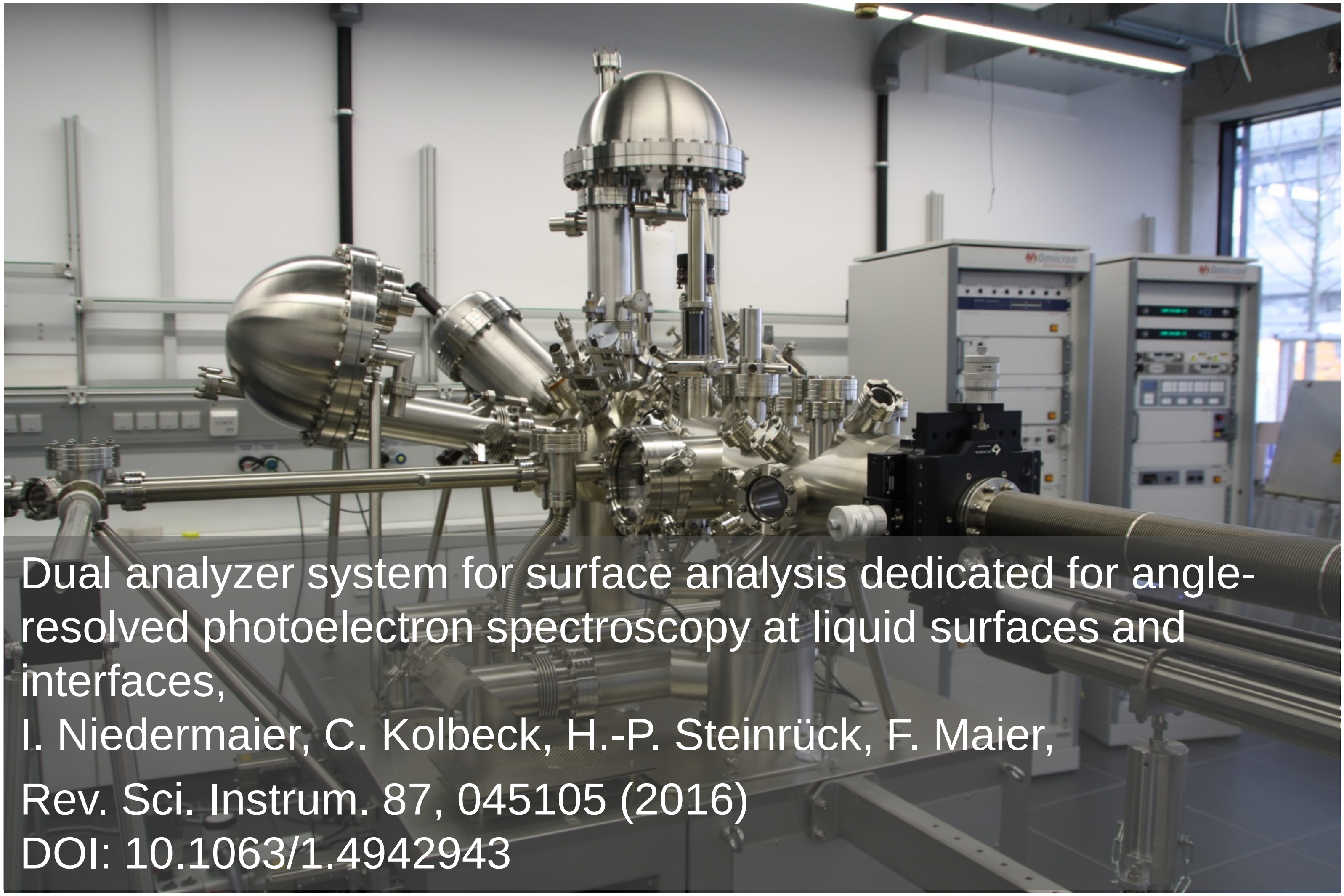
ENGINEERING OF ADVANCED MATERIALS
IONIC LIQUIDS DFG – SPP 1191

Development of a new ARXPS system 2010-2014 together with Omicron dedicated for liquid systems



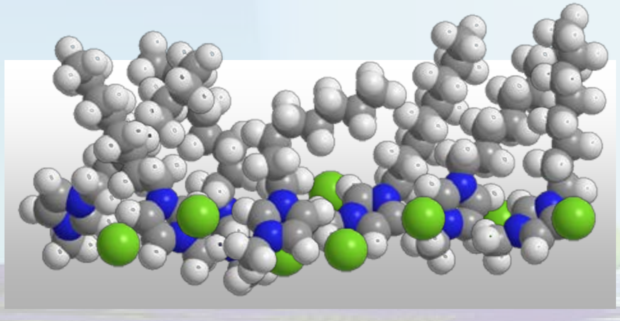
Dual Analyser System for Surface Analysis (DASSA)

Development of a new ARXPS system 2010-2014 together with Omicron dedicated for liquid systems

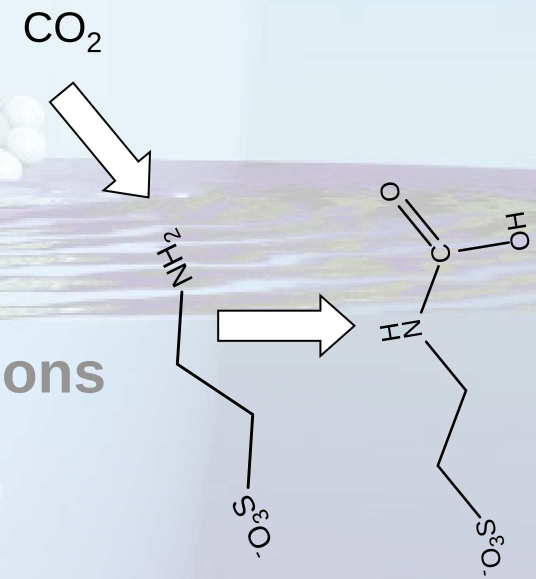


Dual analyzer system for surface analysis dedicated for angle-resolved photoelectron spectroscopy at liquid surfaces and interfaces,
I. Niedermaier, C. Kolbeck, H.-P. Steinrück, F. Maier,
Rev. Sci. Instrum. 87, 045105 (2016)
DOI: 10.1063/1.4942943

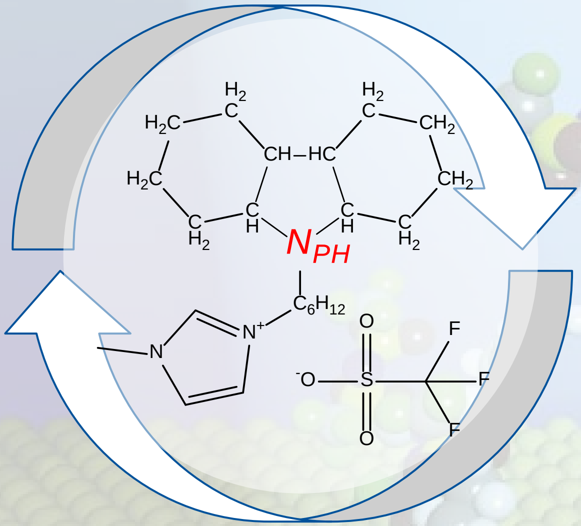
Surface and Interface Science of Ionic Liquids

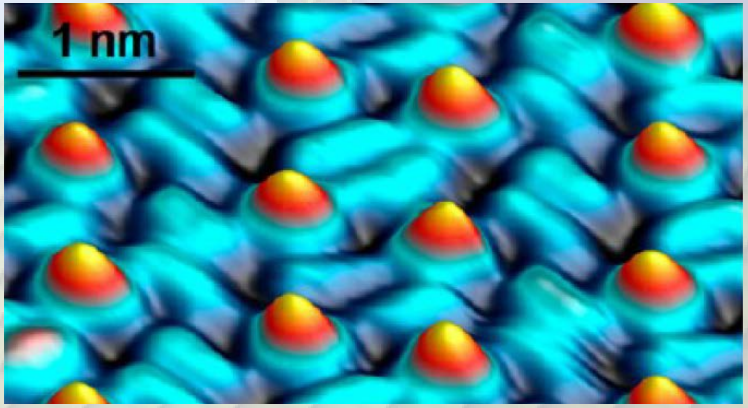


1. Surface composition of ILs



2. *in-situ* reactions





3. IL – solid interfaces

(group J. Behm, university Ulm)

Near future

ENGINEERING OF ADVANCED MATERIALS
IONIC LIQUIDS DFG – SPP 1191

5 years ERC advanced grant:

Ionic Liquid Interface **Dynamics** (H.-P. Steinrück)

(➔ Postdoc)

Who are we looking for?

a) *1 Postdoc:* General experience in UHV-based surface science, solid knowledge of one of the following methods at least: XPS, STM/AFM and molecular beam techniques

b) *2-3 PhD-Students:* MSc in chemistry (focus physical chemistry) or physics, ideally with experience in surface science and/or ionic liquids

What do we offer?

- Postdoc (full position, E13), PhD (1/2 E13); employment, payment, and social benefits are determined by the German Public Sector Collective Agreement
- Contract duration: Postdoc: initially 1 year, extendable; PhD: 3 years
- Start date: July 1, 2016 or later

Remarks

The project will be funded through an ERC Advanced Grant, embedded in the research environment of the Cluster-of-Excellence “Engineering of Advanced Materials” (EAM).

Acknowledgements

ENGINEERING OF ADVANCED MATERIALS
IONIC LIQUIDS DFG – SPP 1191

Prof. Dr. Peter Wasserscheid

crt Lehrstuhl für Chemische Reaktionstechnik

P. Schulz

N. Taccardi

N. Paape

W. Wei

M. Bahlmann

J. Schwegler

Prof. Dr. Hans-Peter Steinrück

PC-II

C. Kolbeck

I. Niedermaier

B. May

K. Lovelock

A. Deyko

T. Matsuda

T. Cremer

F. Rietzler

P. Schreiber

B. Heller

Collaborations:

P. Licence, R. Jones, B. Kirchner, A. Fröba, J. Libuda, S. Baldelli, J. Behm, J. Schatz, J. Lopes ...

Supported by: DFG (SPP 1191, CoE-EAM, STE 620/9-1), A.v.Humboldt- and Max-Buchner-Stiftung, Industry