

ELCASS Meeting

Palermo

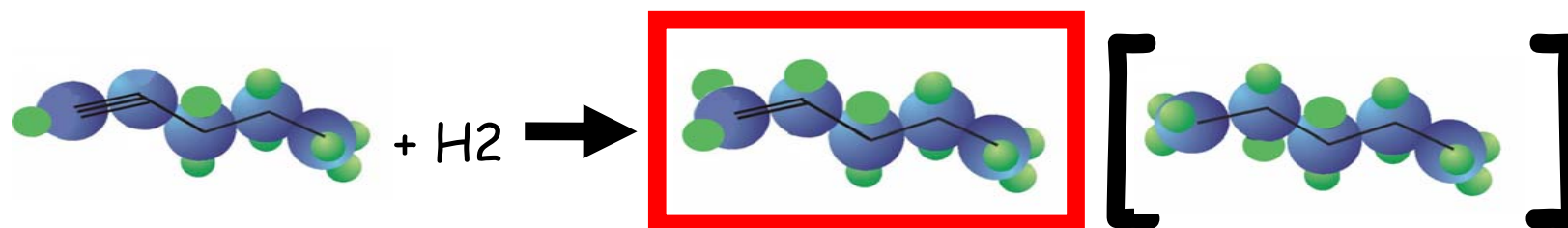
December 3-5, 2006

Does subsurface carbon influence the selectivity of Pd catalysts in the hydrogenation of pentynes?

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P. Schnörch, R. Schlögl

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Introduction



Literature

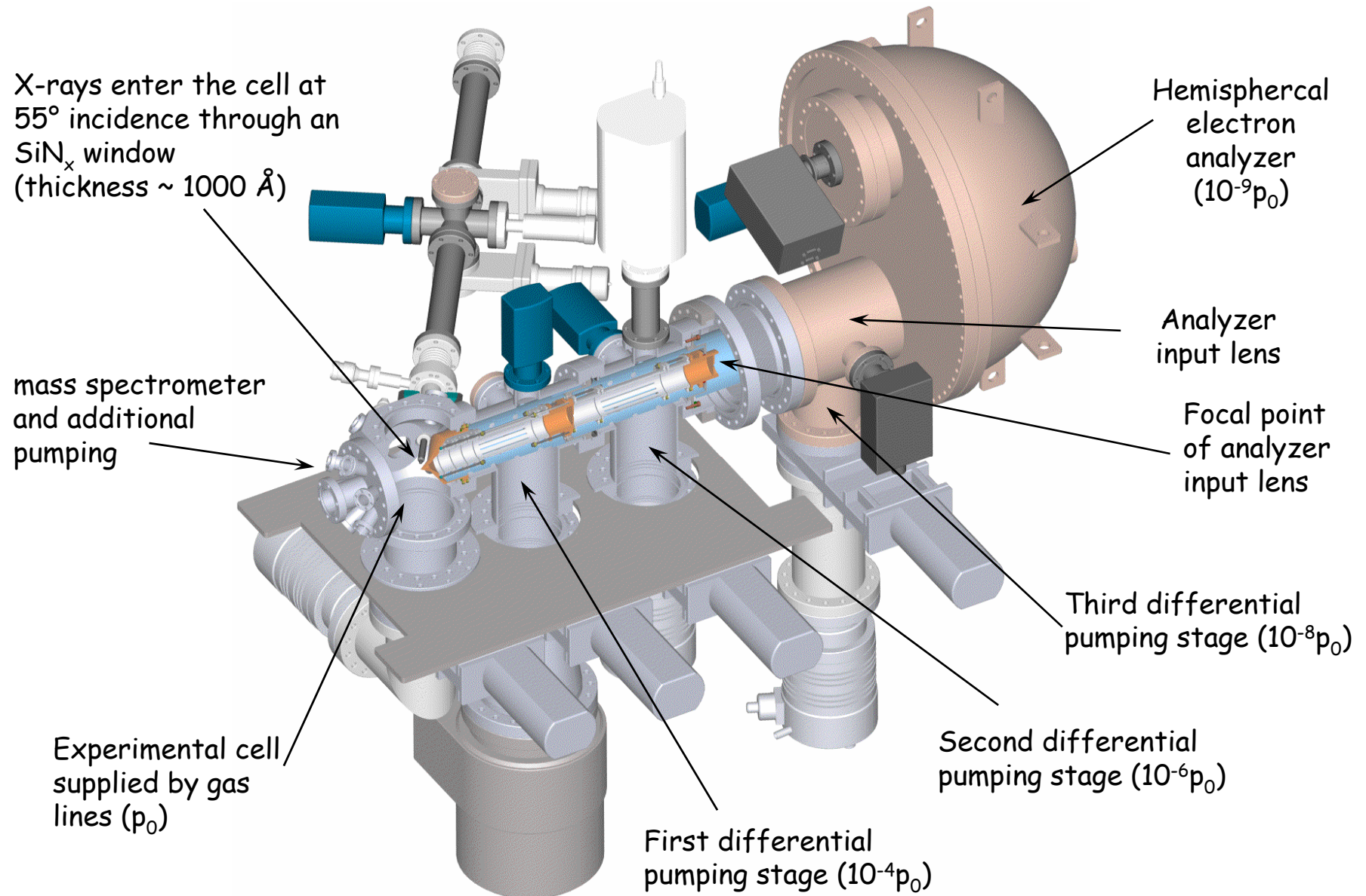
carbon laydown \longrightarrow selective hydrogenation
"similar" catalysts \longrightarrow different activity & selectivity
(structure sensitivity?)

Selectivity issue: what defines selectivity?

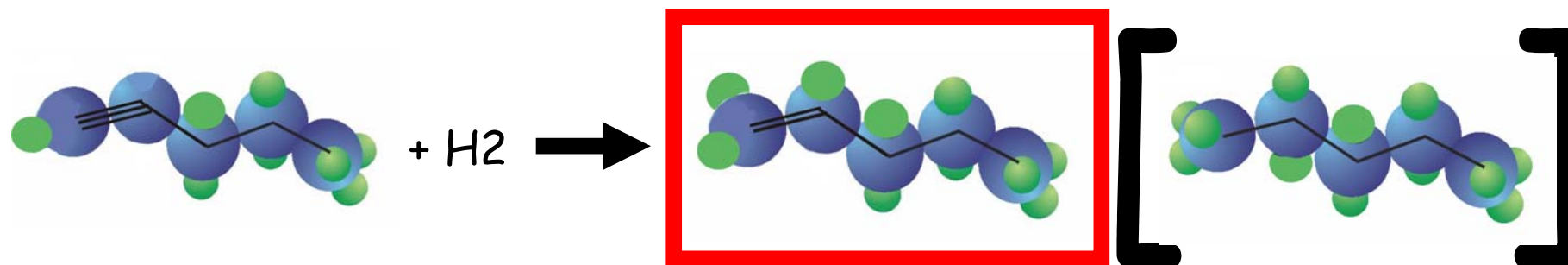
Summary

1. Subsurface H: effective for alkene-to-alkane but also for alkyne-to-alkane transformation
2. Surface H: could be selective (spillover)
3. Different reaction orders in the different selectivity regimes & Abrupt changes between regimes
4. C uptake is significantly more in the selective regime

In situ XPS system



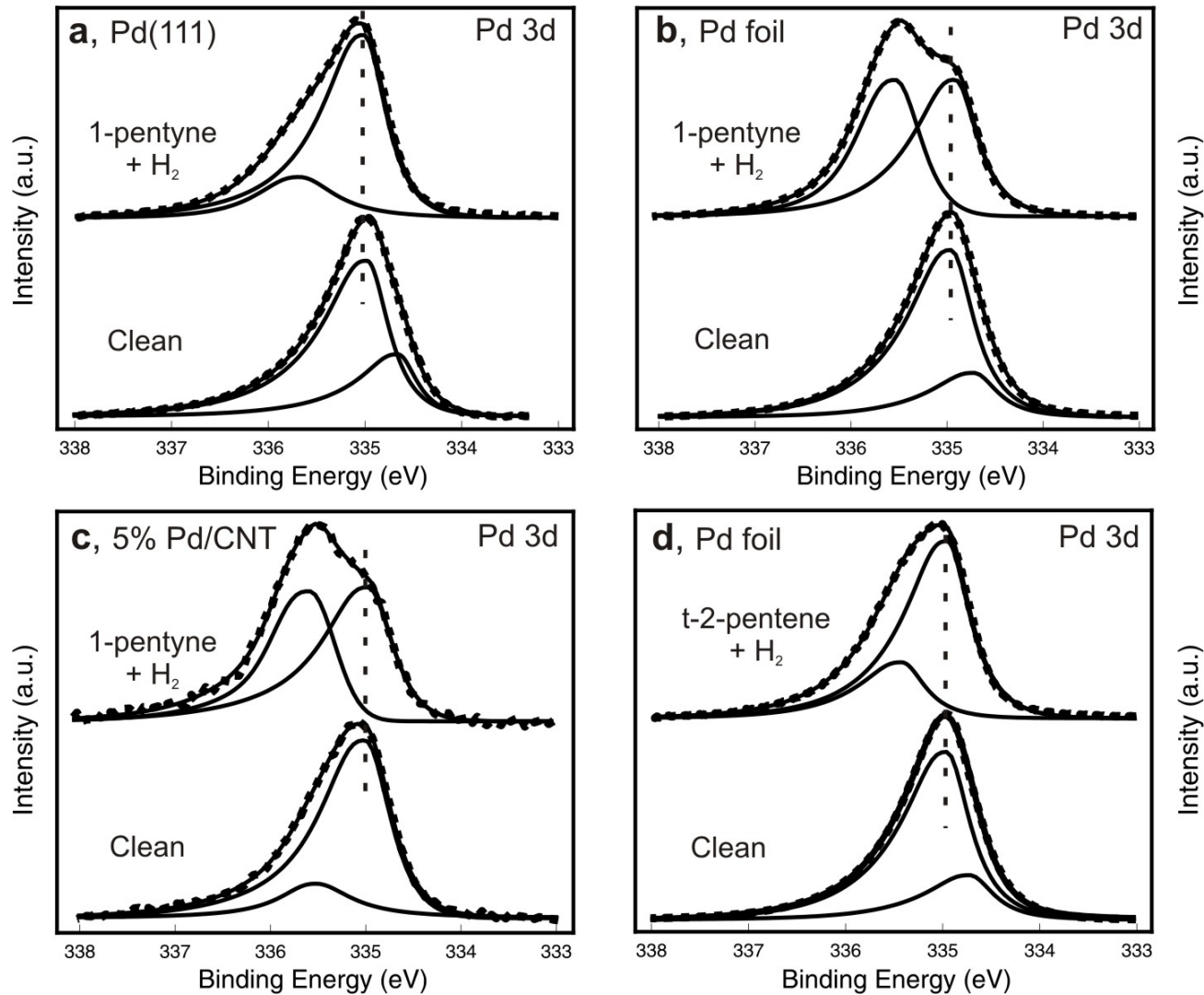
Reaction in the mbar p region (in-situ XPS)



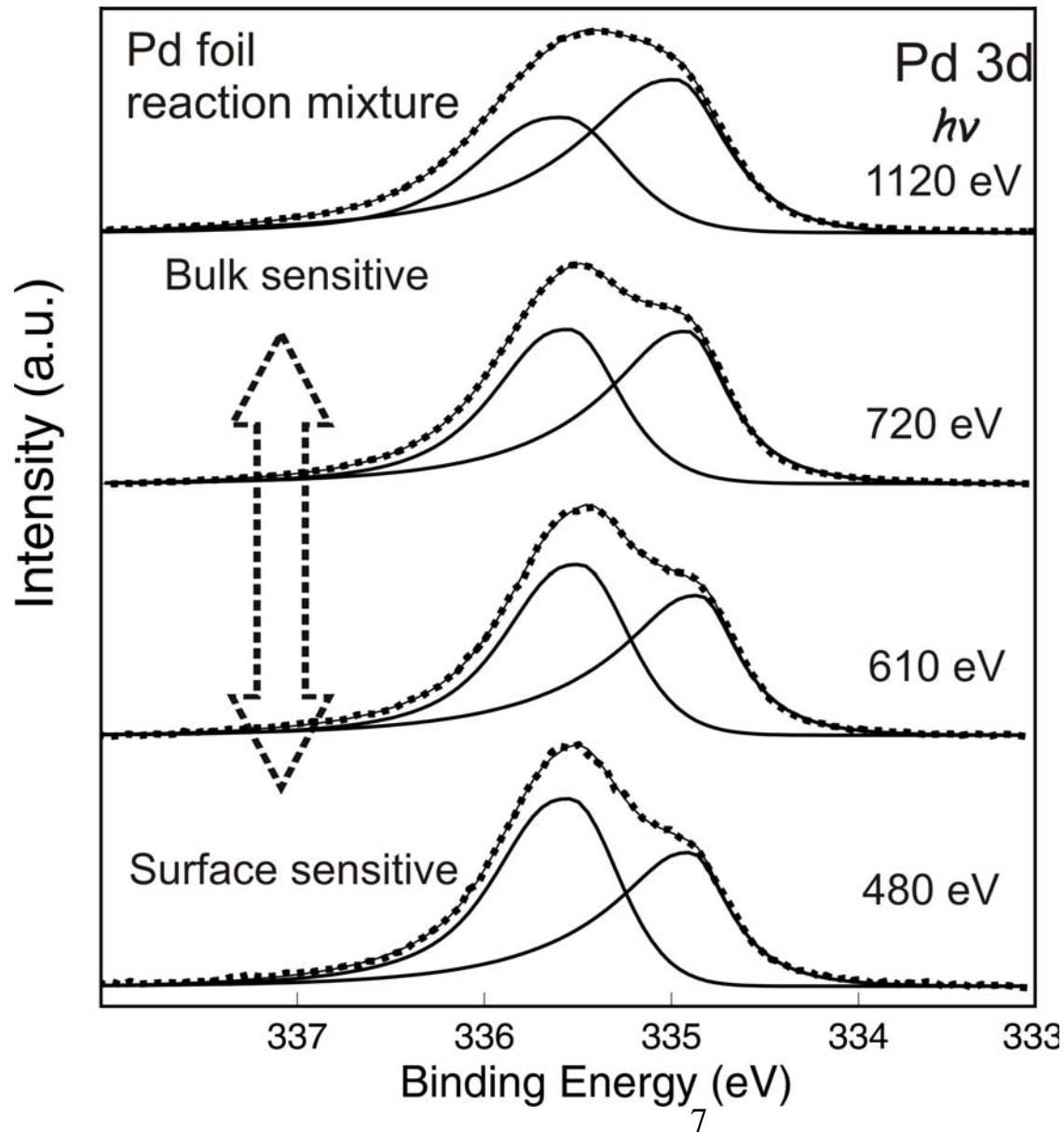
	5% Pd/CNT	3% Pd/Al ₂ O ₃	Pd foil	Pd(111)
Conversion [%]	~ 10	~5	~2.5	<1
Selectivity Pentene [%]	~95	~80	~98	100
Selectivity Pentane [%]	~5	~20	~2	-

Reaction conditions: C₅/H₂ = 1:9, 1 mbar, 358 K

In-situ XPS: Pd 3d ($h\nu$: 720 eV)



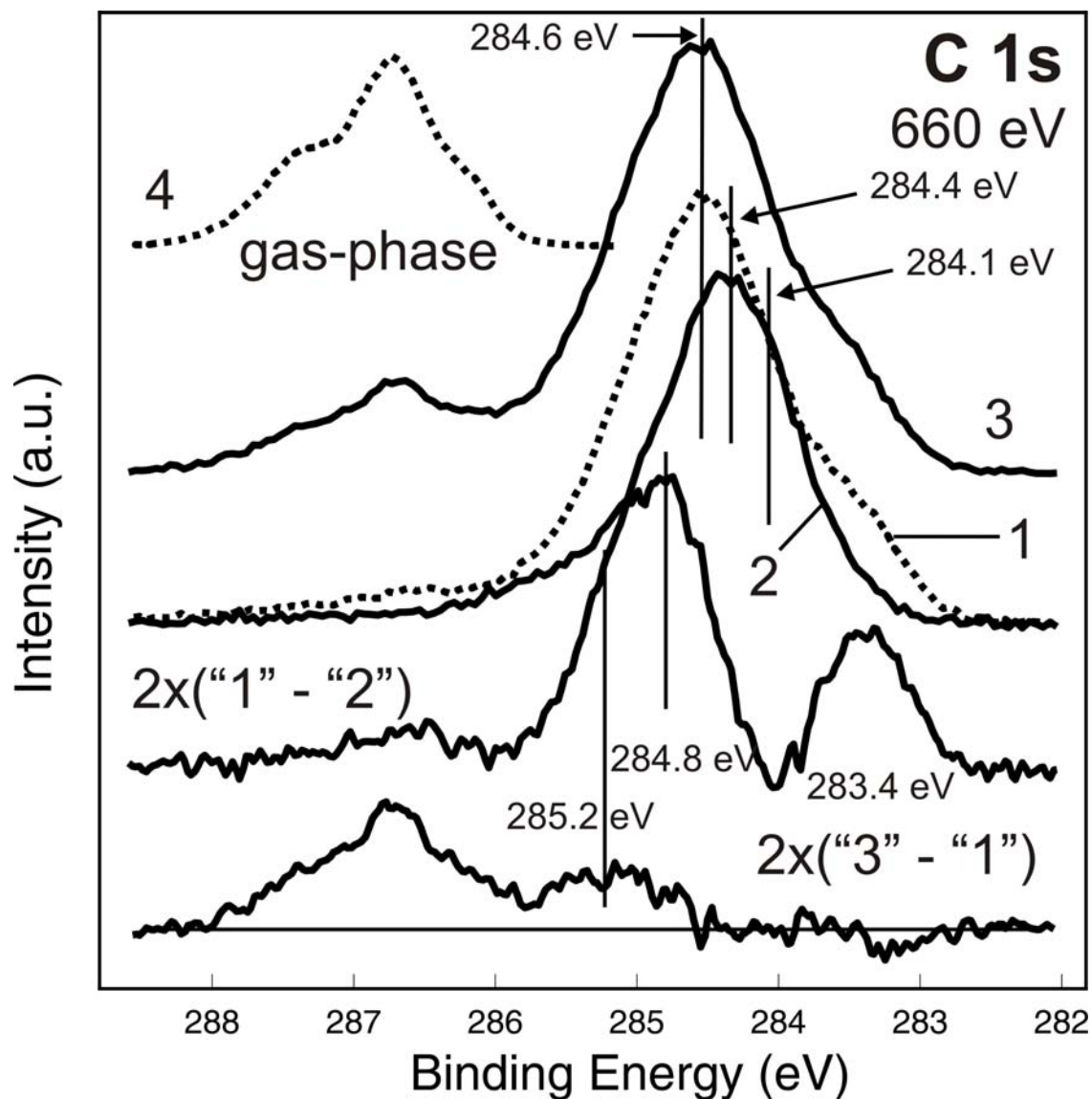
In-situ XPS: Pd 3d depth profiling



Not only
adsorbate-induced
surface core level
shift!

But on-top location!

In-situ XPS: C1s (Switching off experiments)

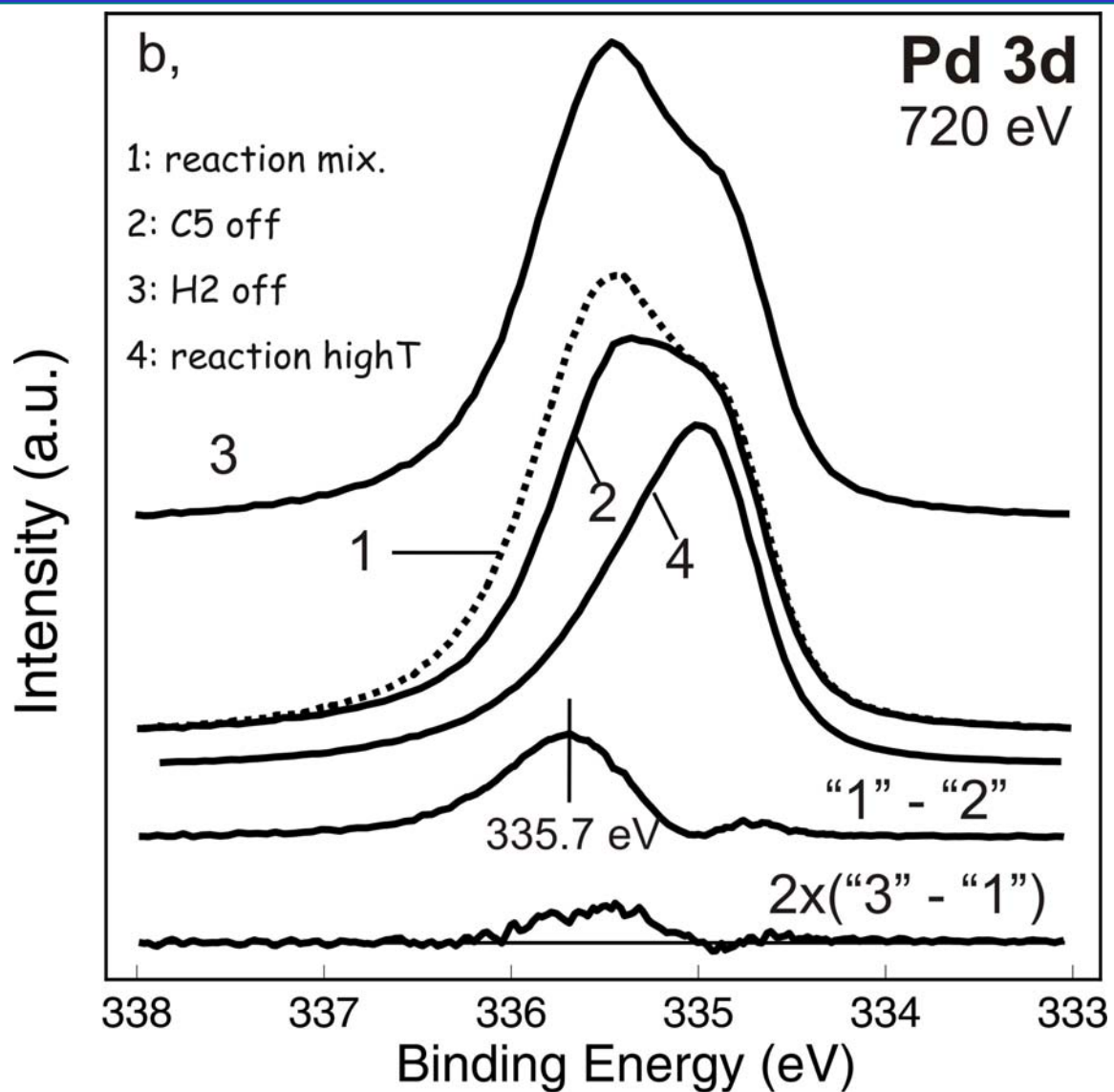


- 1: reaction mix.
- 2: C5 off
- 3: H2 off
- 4: C5 gas-phase

Teschner et al.

J. Catal. 242 (2006) 26-37

In-situ XPS: Pd 3d (Switching off experiments)



1: reaction mix.

2: C5 off

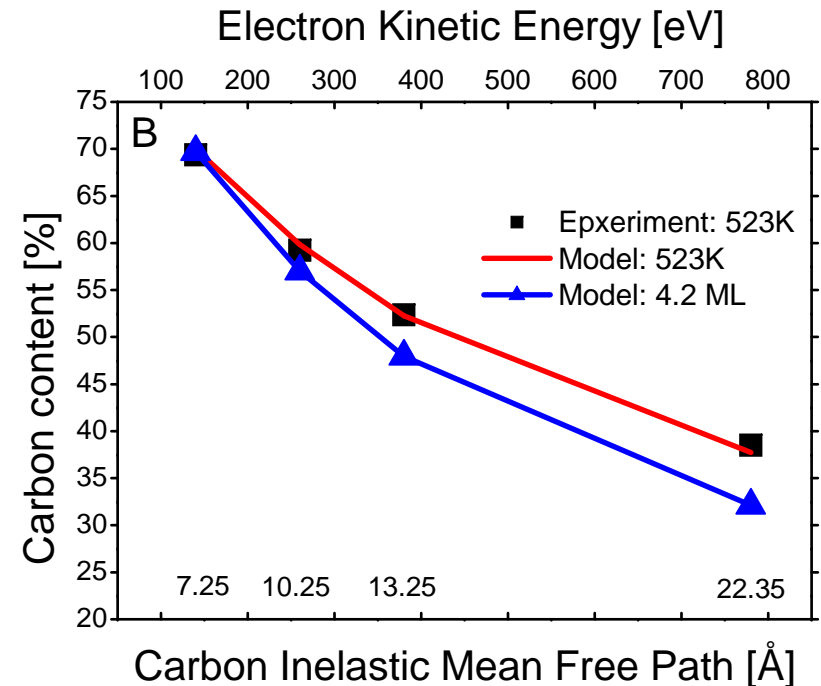
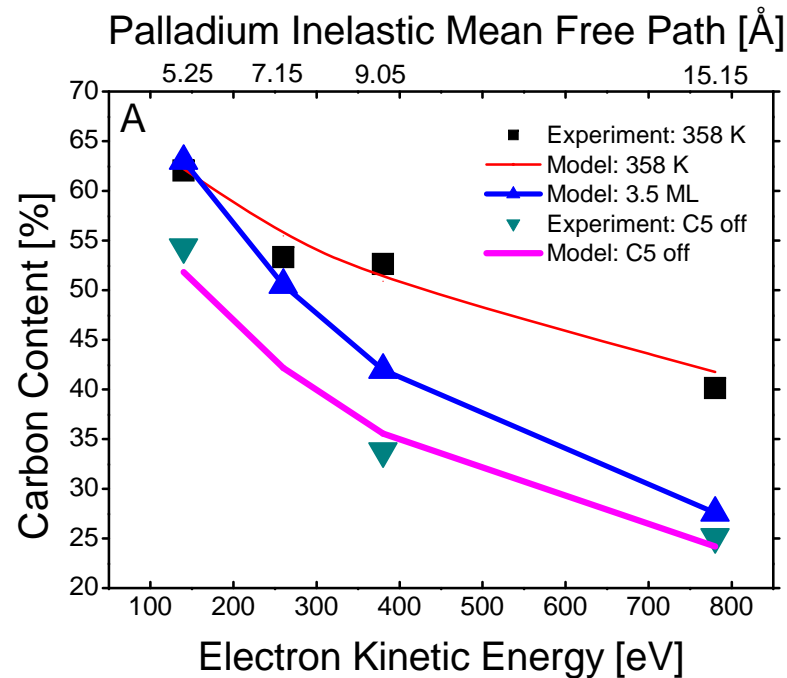
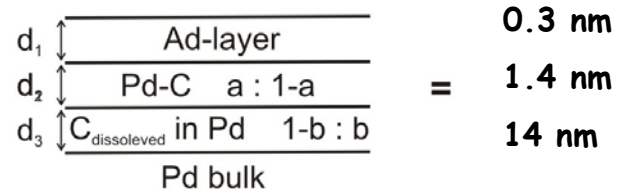
3: H2 off

4: reaction; high T

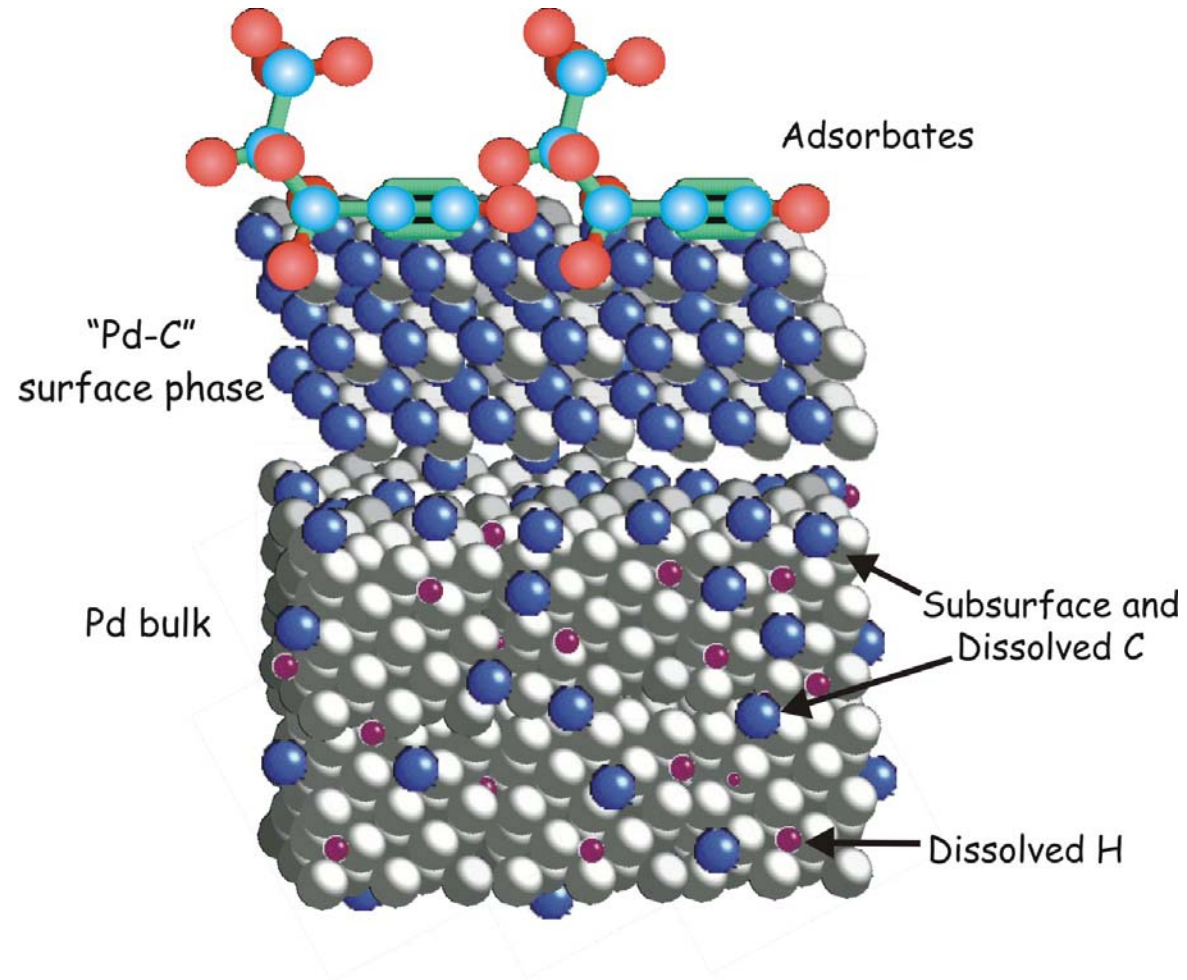
523 K

In-situ XPS: Pd vs. C depth profiling

Model



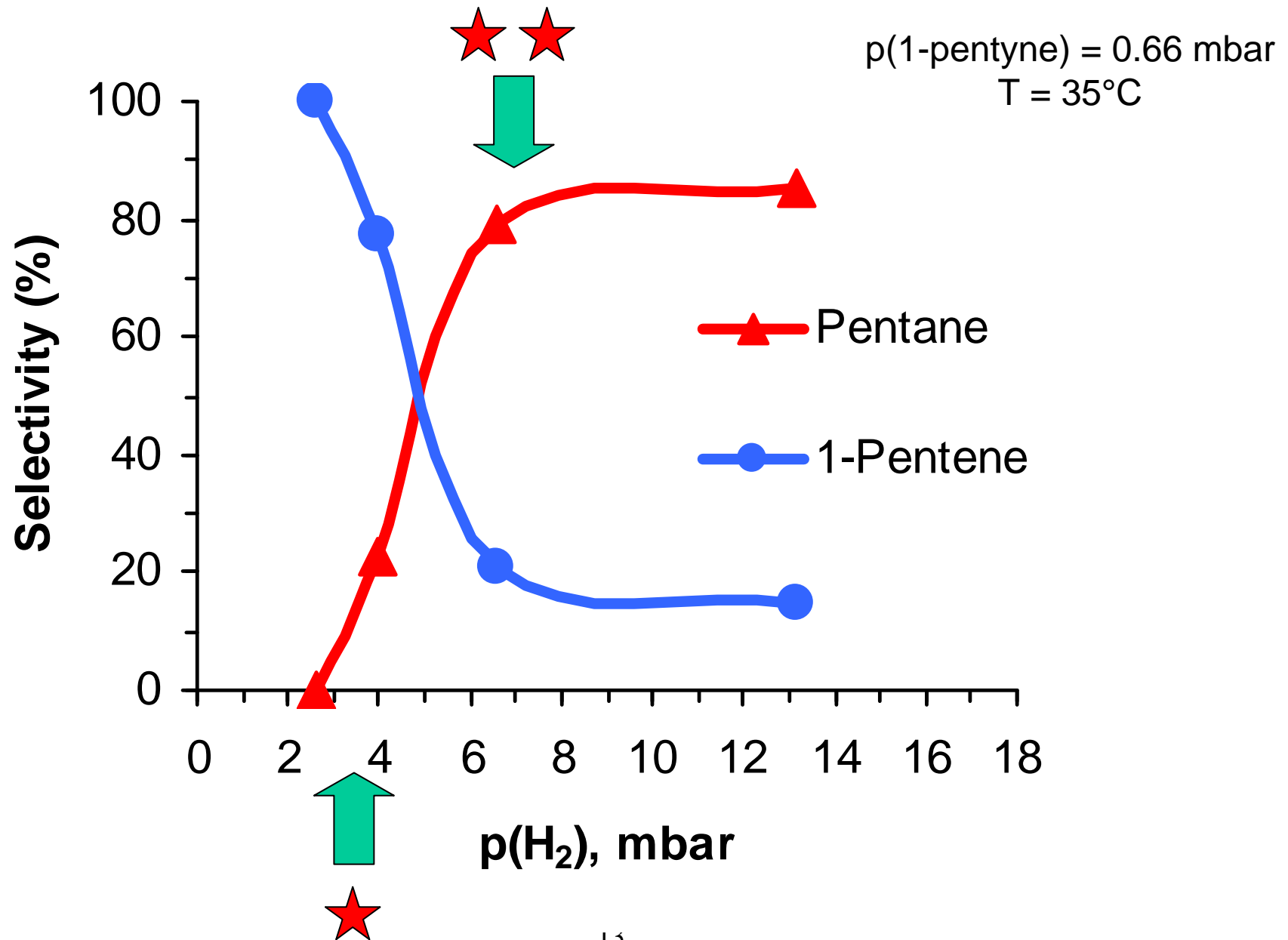
Model (during the reaction)



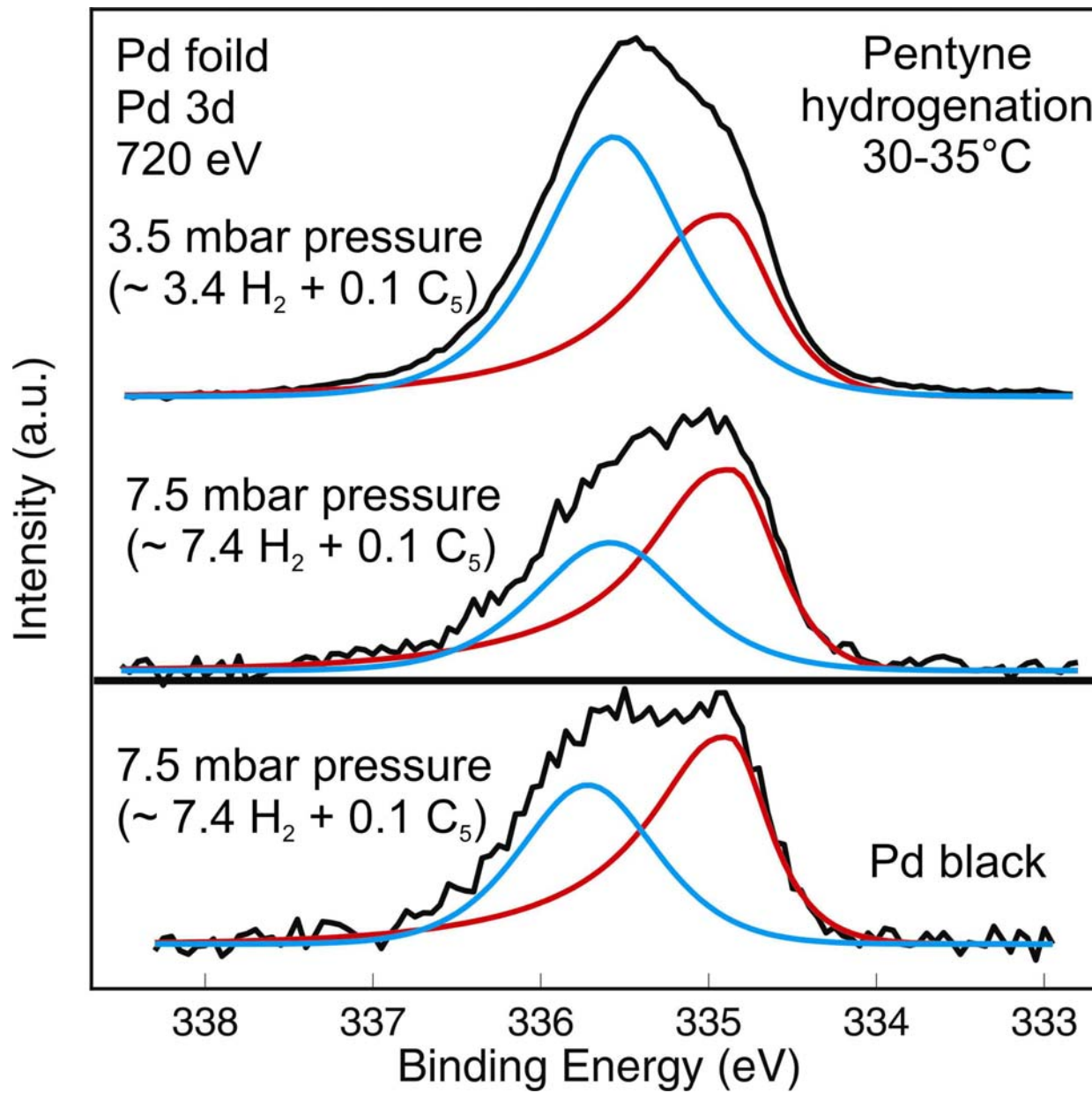
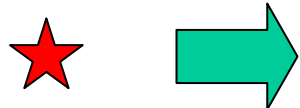
Summary

1. Subsurface H: effective for alkene-to-alkane but also for alkyne-to-alkane transformation
2. Surface H: could be selective (spillover)
3. Different reaction orders in the different selectivity regimes & Abrupt changes between regimes
4. C uptake is considerably more in the selective regime
5. Pd-C surface phase forms during selective hydrogenation of pentyne & there is significant amount of subsurface C below of it
6. Dynamic behaviour of Pd-C and subsurface C

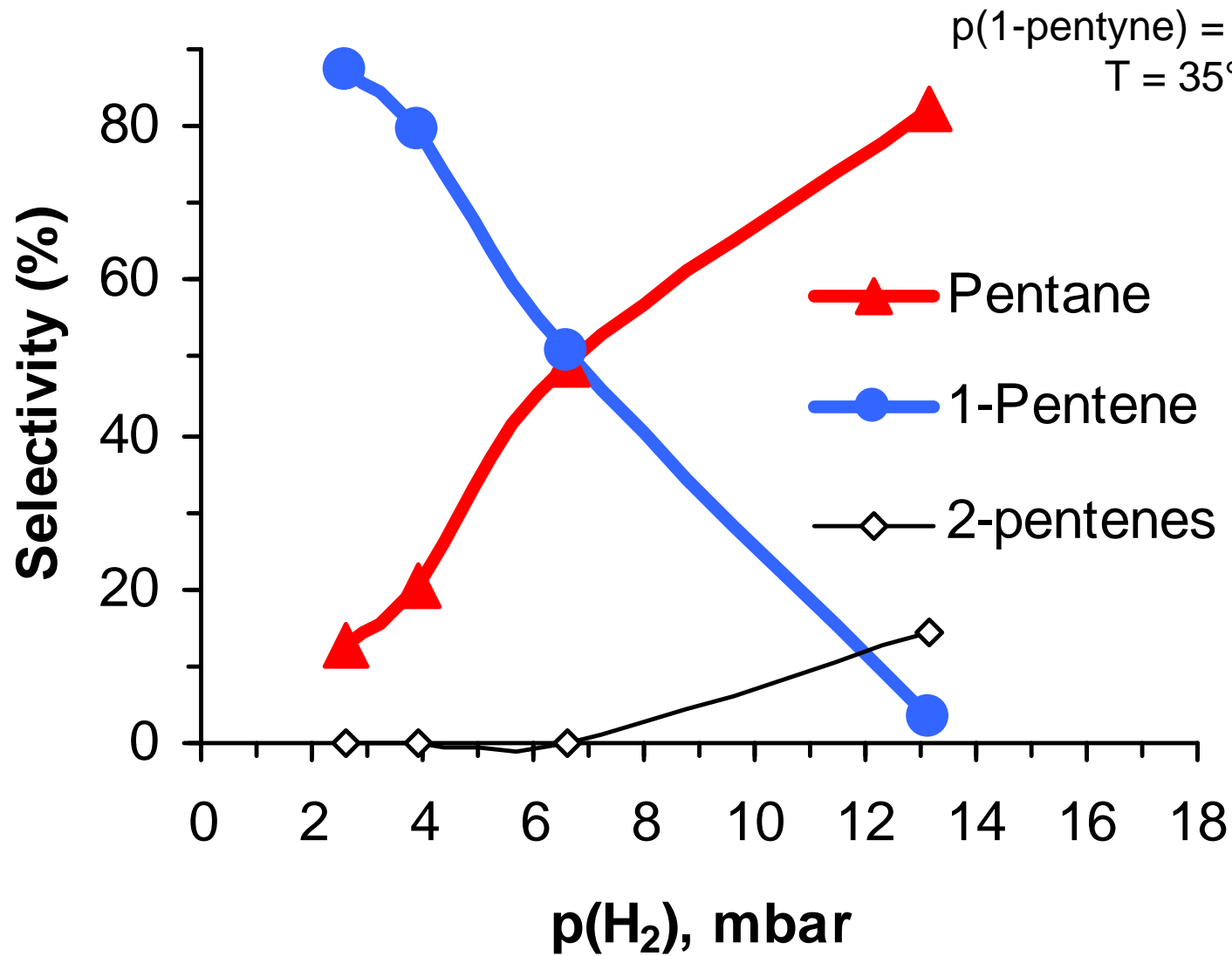
1-pentyne hydrogenation on Pd Black (done in Budapest)



And at Bessy?

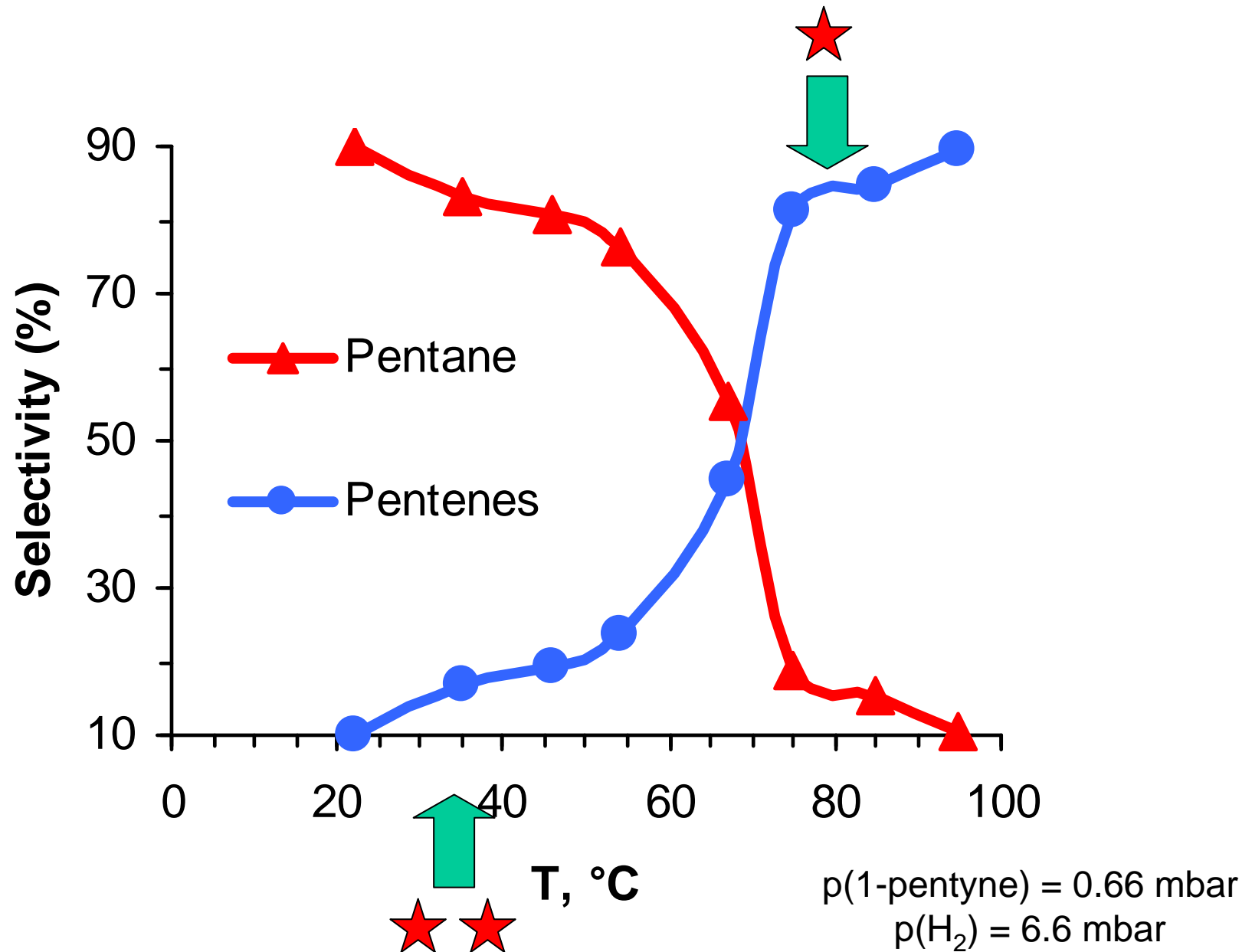


1-pentyne hydrogenation on 1%Pd/Al₂O₃ (done in Budapest)

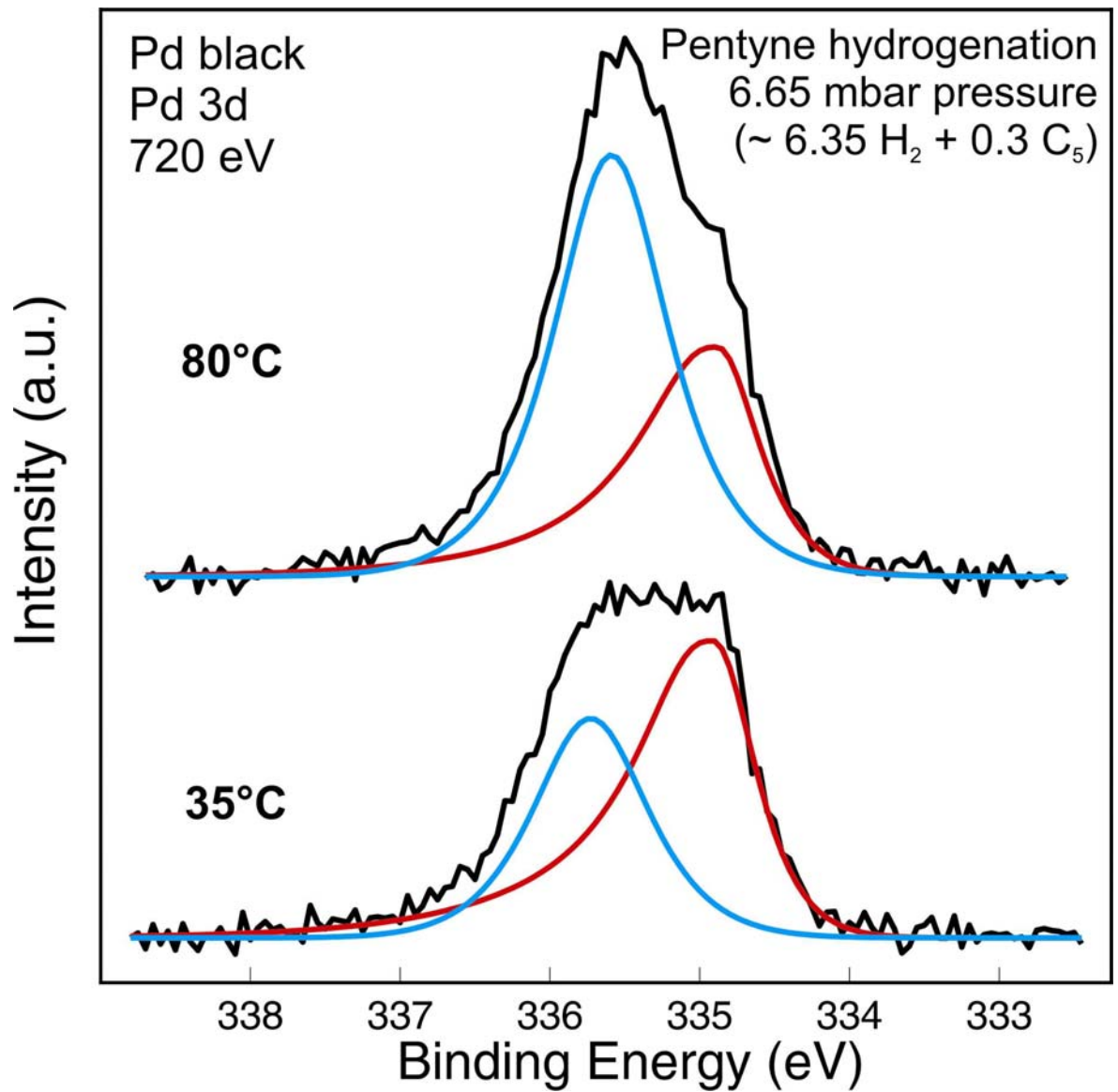
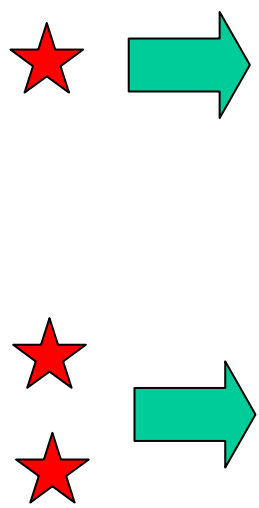


Generally **similar trend** was observed as with bulk Pd

1-pentyne hydrogenation on Pd Black (done in Budapest)

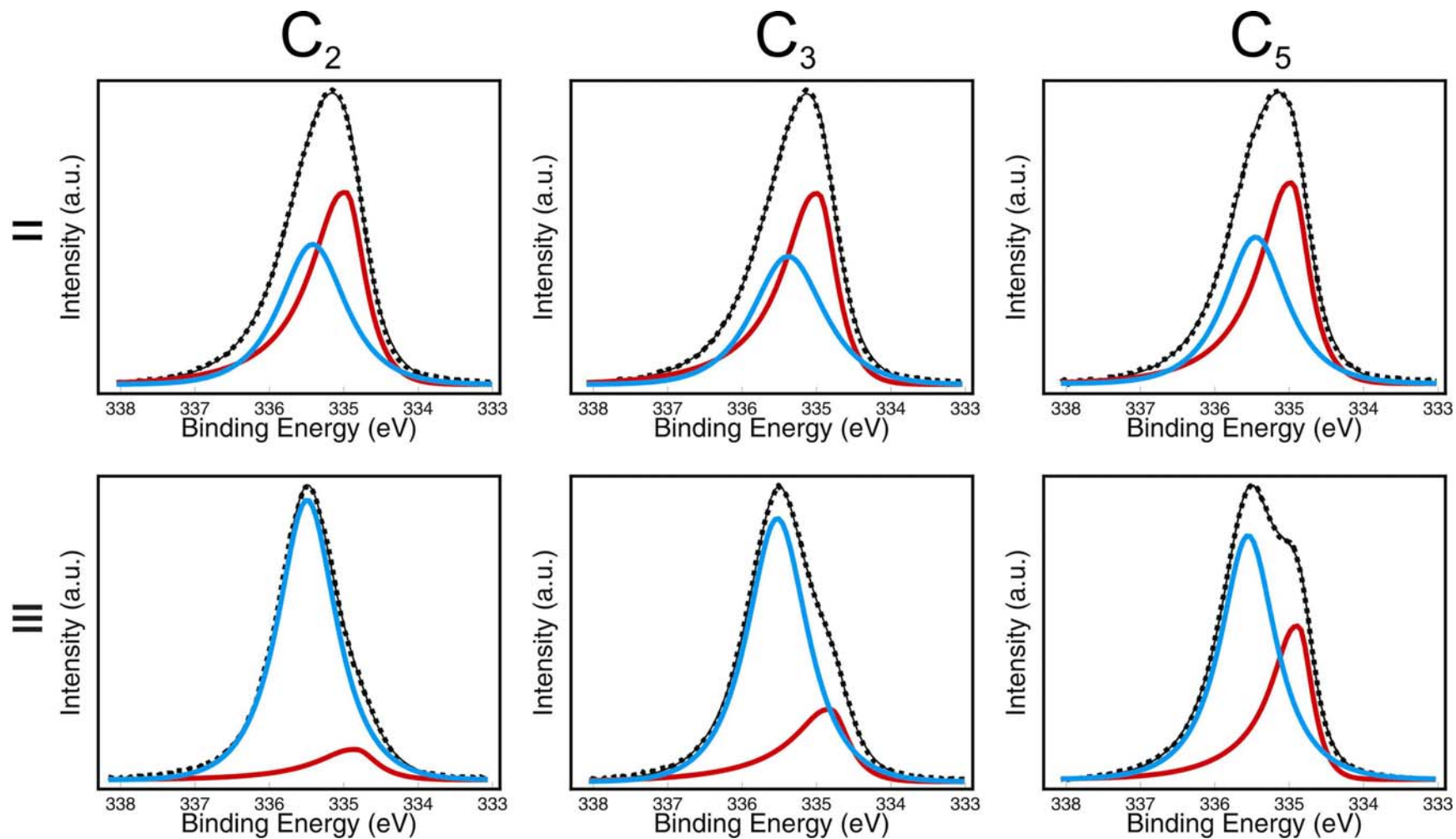


And at Bessy?



Alkene and alkyne hydrogenation at BESSY

Pd foil, $\sim 70^\circ\text{C}$, 1mbar ($0.1\text{ mbar C}_x\text{H}_y + 0.9\text{ mbar H}_2$)





MAX-PLANCK-GESELLSCHAFT

Outlook: In situ XPS / XAS The future at BESSY



ISISS:



Innovative Station for In Situ Spectroscopy

A project of BESSY and the Dep. Inorganic Chemistry, Fritz-Haber-Institut

- ▶ Installation of a beamline exclusively used for in situ spectroscopy in the soft X-ray range
- ▶ Installation of infrastructure optimized for these kind of experiments on site (e.g. chemical lab, gas supply, gas analytics)
- ▶ Later, further implementation of other in situ spectroscopy techniques: multi wavelength Raman, UV-Vis, fluorescence yield ?!
- ▶ Start of user operation of the beamline: 2007

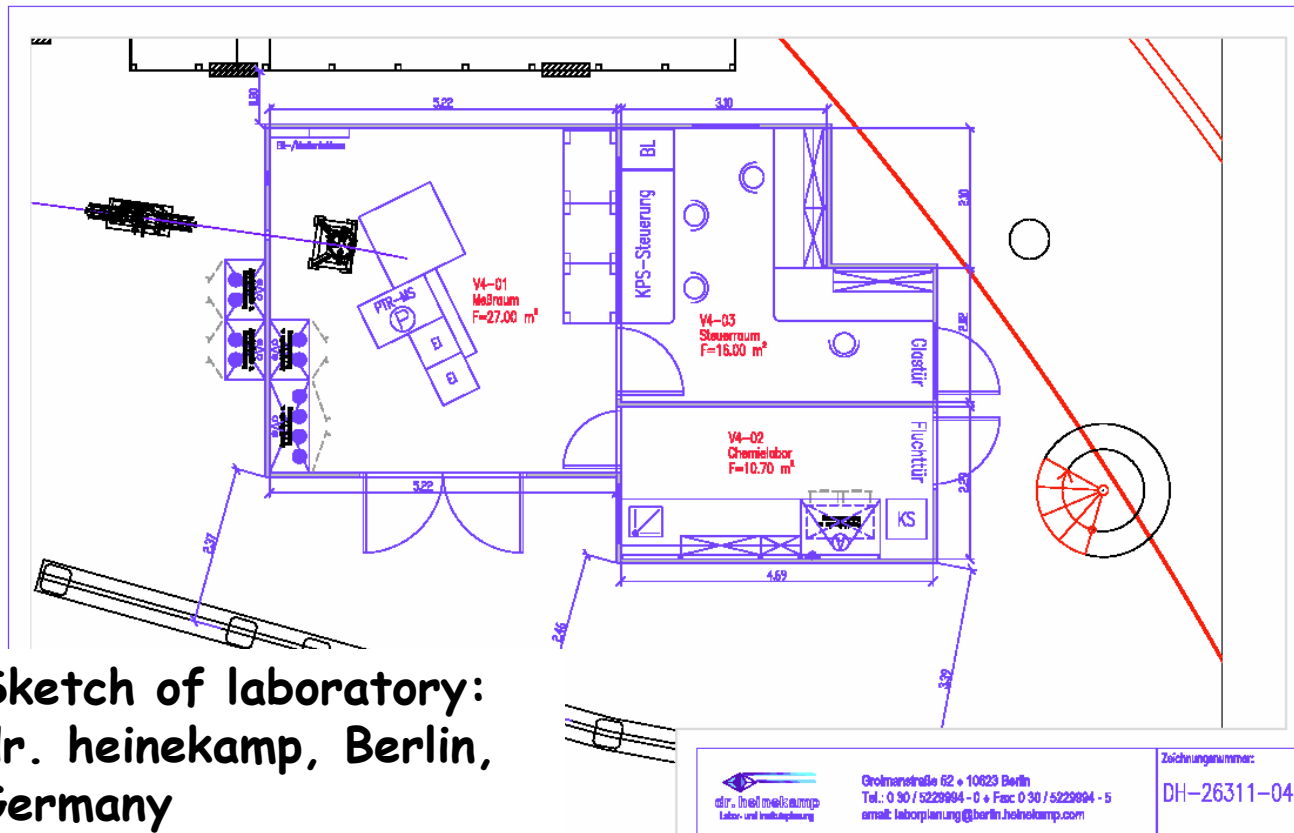


MAX-PLANCK-GESELLSCHAFT

Outlook: In situ XPS / XAS The future at BESSY

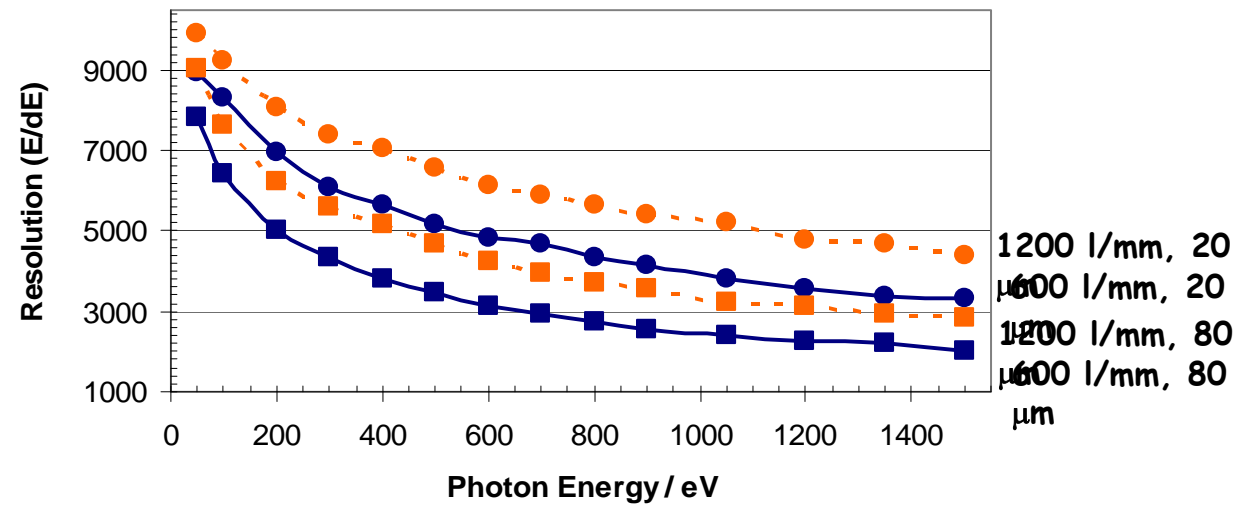
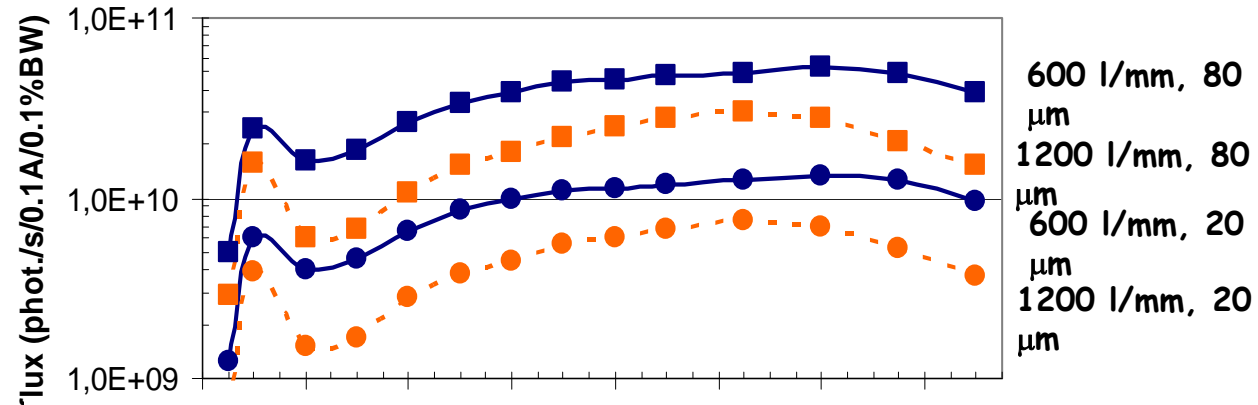


ISSI:





Outlook: In situ XPS / XAS The future at BESSY





MAX-PLANCK-GESELLSCHAFT

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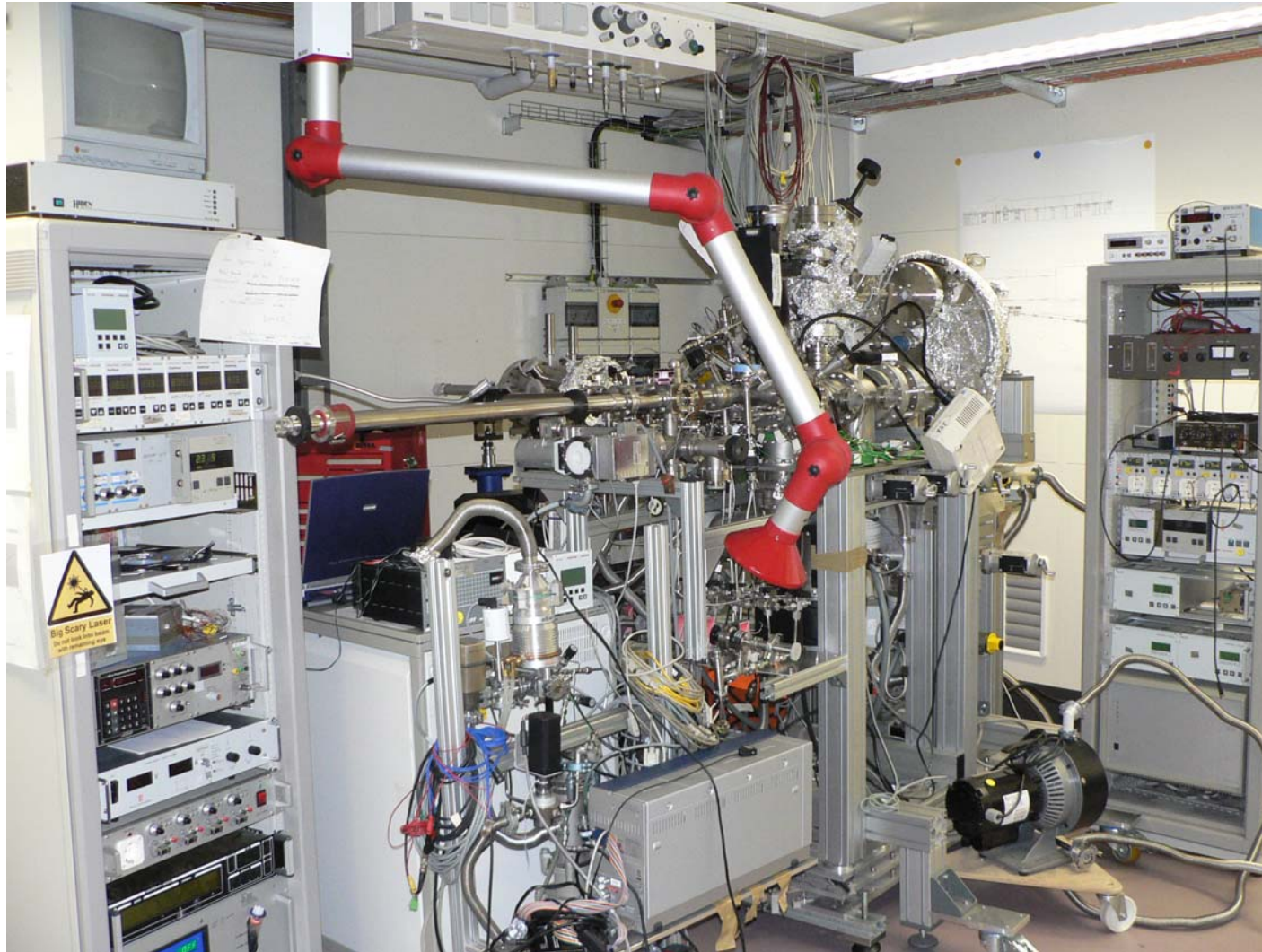
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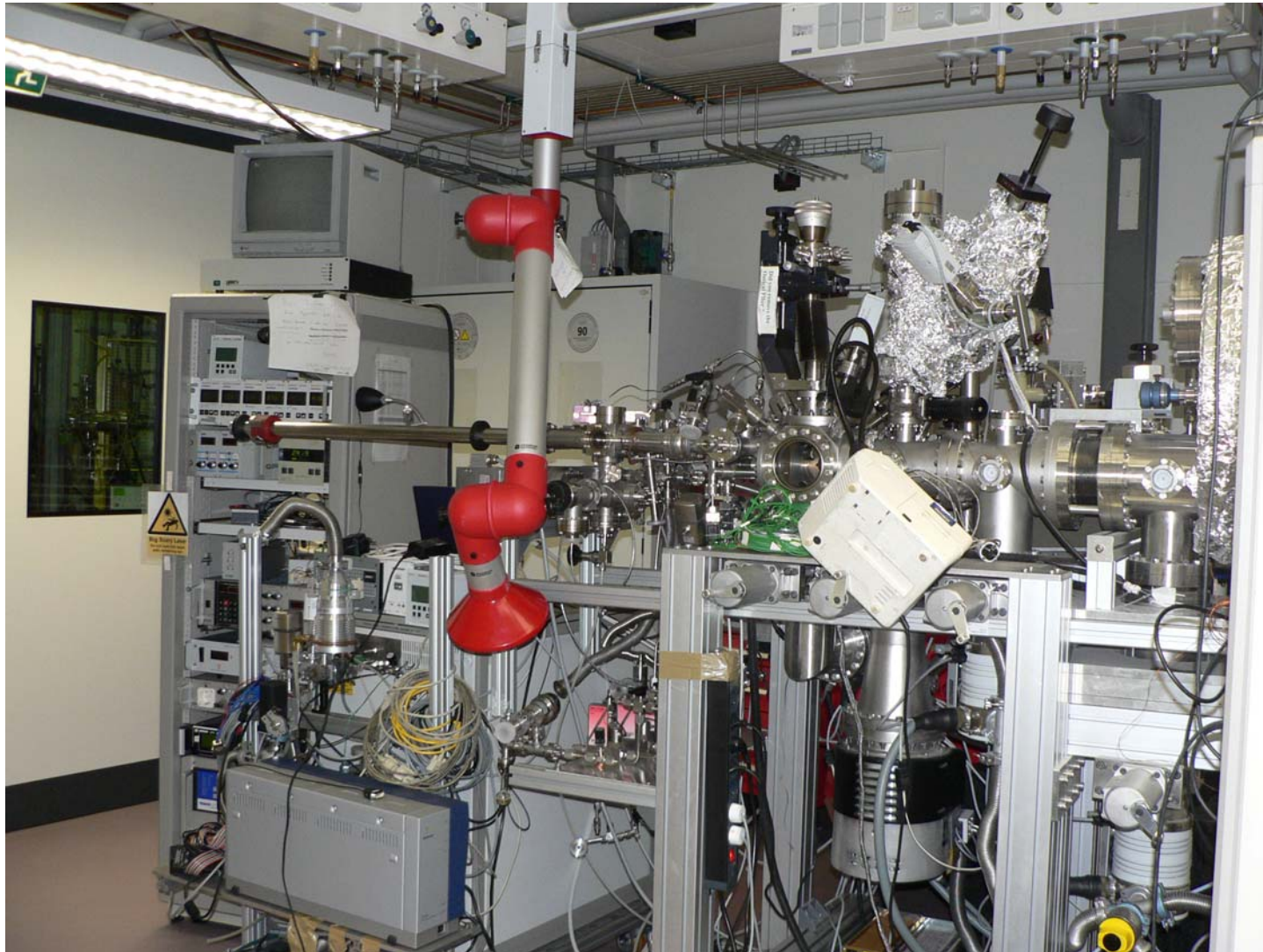
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