Low-energy (0-20 eV) Electron Beam for Chemical Control in Surface Modification (for chemically controlled modification of supported organic films)

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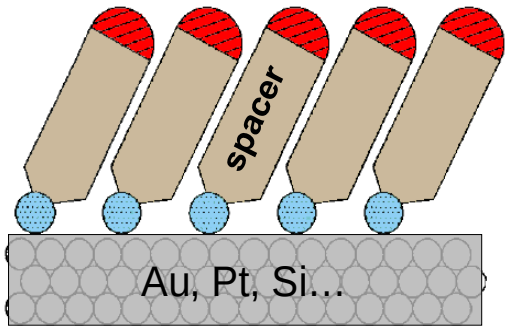
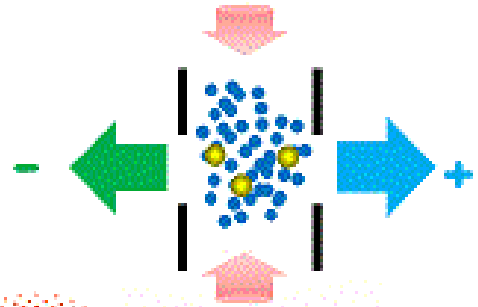
CNRS - Université Paris-Sud, Orsay, France





Contents

Motivations & model aromatic SAMs

Low-energy (0-20 eV) electron induced dissociative processes
Experimental procedure using a very rustic electron gun...

Terphenylthiol SAMs
Identification of an electron attachment resonance at 6 eV
Electron processing
- induced chemical modification
- involved mechanisms

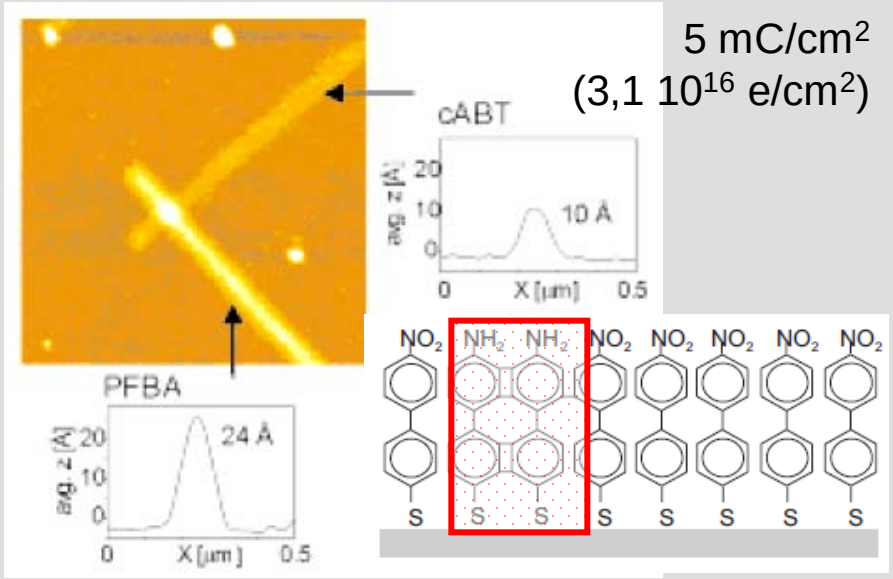
Conclusions & Perspectives

Electron processing for structuration of substrates

Development of molecular platforms for chemical or biological devices
Response to irradiation (standard probing techniques & lithography) of resist materials (contrast, sensitivity, defects)

Cyganik J.Phys.Chem.B 2005 Heister Langmuir 2000

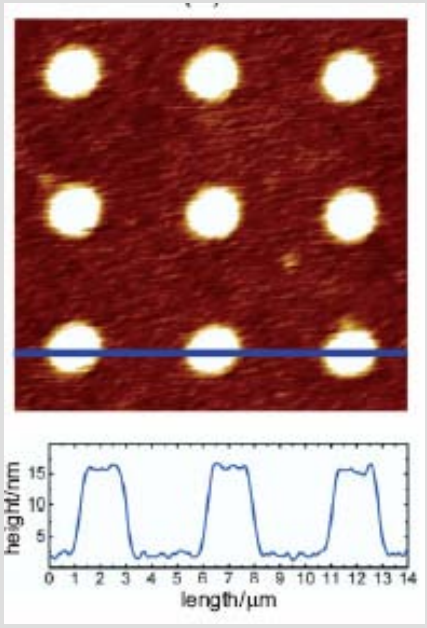
At high energy (2-20 keV)
Electron microscope (EBL)
Nanometer scale (20-200 nm)



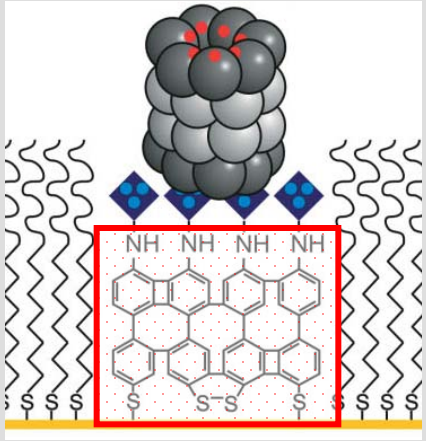
5 mC/cm^2
(3,1 10^{16} e/cm^2)

Gölzhäuser Adv. Mat. 2001
Ballav AngewChem 2008, JPhysChem 2007

At low energy (~50-100 eV)
Electron irradiation through masks
Micrometer scale (2 µm)



10-40 mC/cm^2
(6-26 10^{16} e/cm^2)

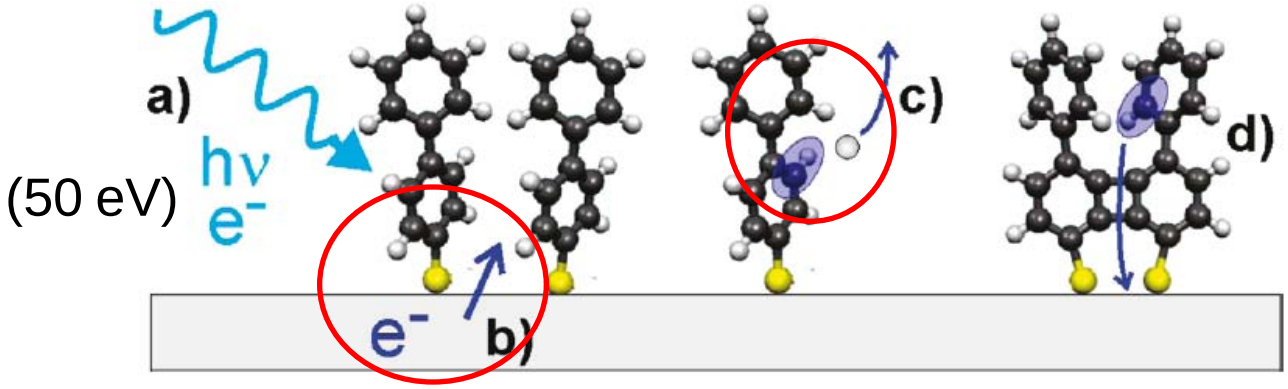


Eck Adv. Mater. 2000
Turchanin Adv. Mater. 2008

Stabilization by cross-linking & Model aromatic SAM

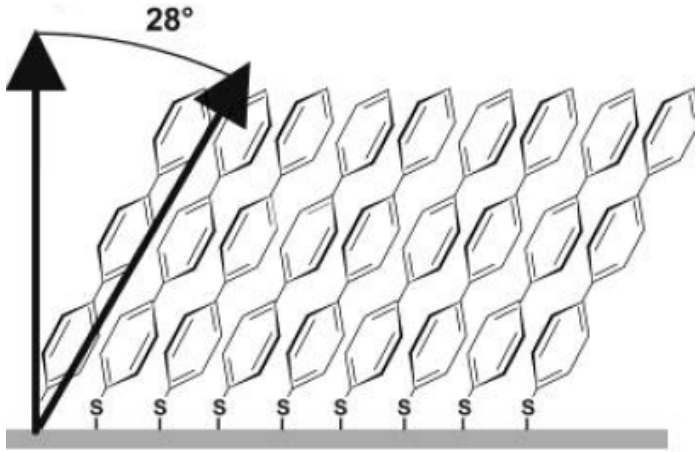
Aromatic SAMs - **Improved stability** by irradiation induced cross-linking

Among the proposed mechanisms: secondary electron induced chemistry



Turchanin
Langmuir 2009

Terphenylthiol (TPT) on gold



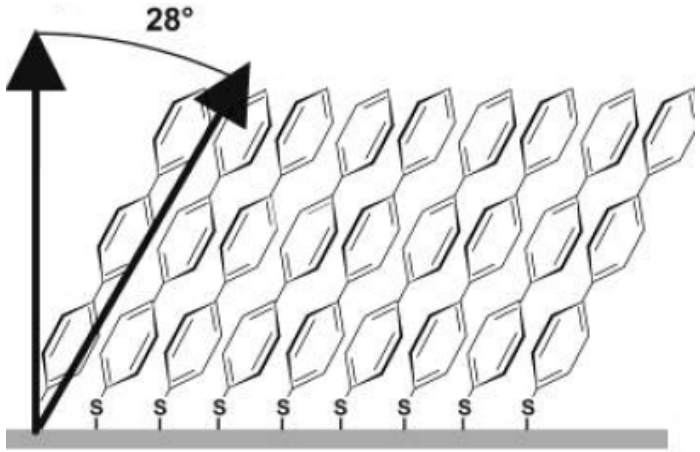
V. Humblot
C.-M. Pradier

Frey Langmuir 2001 /
Fuxen Langmuir 2001

Stabilization by cross-linking & Model aromatic SAM

- To investigate the contribution of low-energy 2nd electrons to the modifications induced within the supported molecular layer
- To understand the primary interaction mechanisms of low-energy electrons with film of molecular species
- To control and orientate per electron irradiation the chemistry induced in the supported interface and at the substrate surface

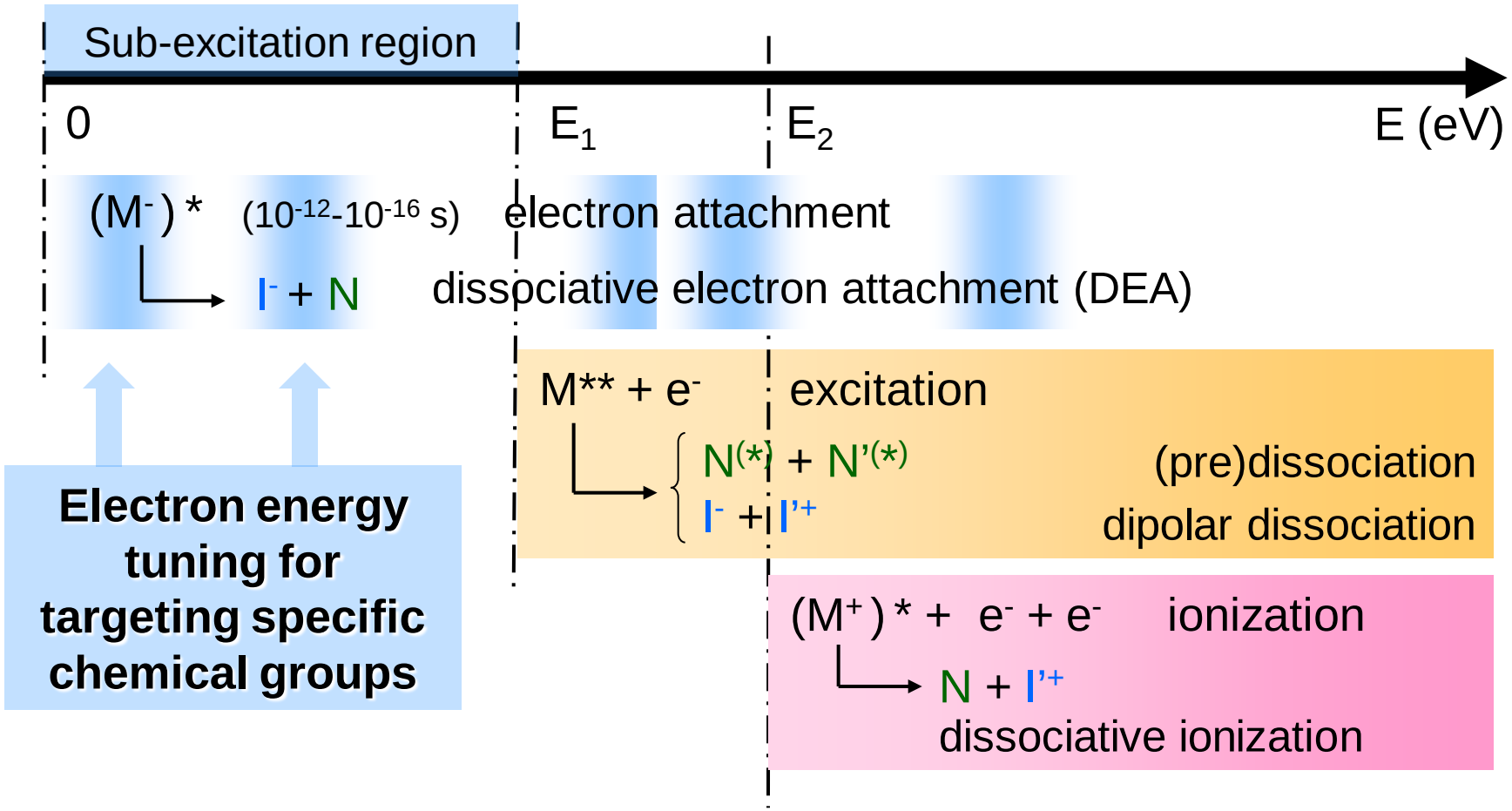
Terphenylthiol (TPT) on gold



Frey Langmuir 2001 /
Fuxen Langmuir 2001

V. Humblot
C.-M. Pradier

e^- + M – Dissociative processes induced by electron impact



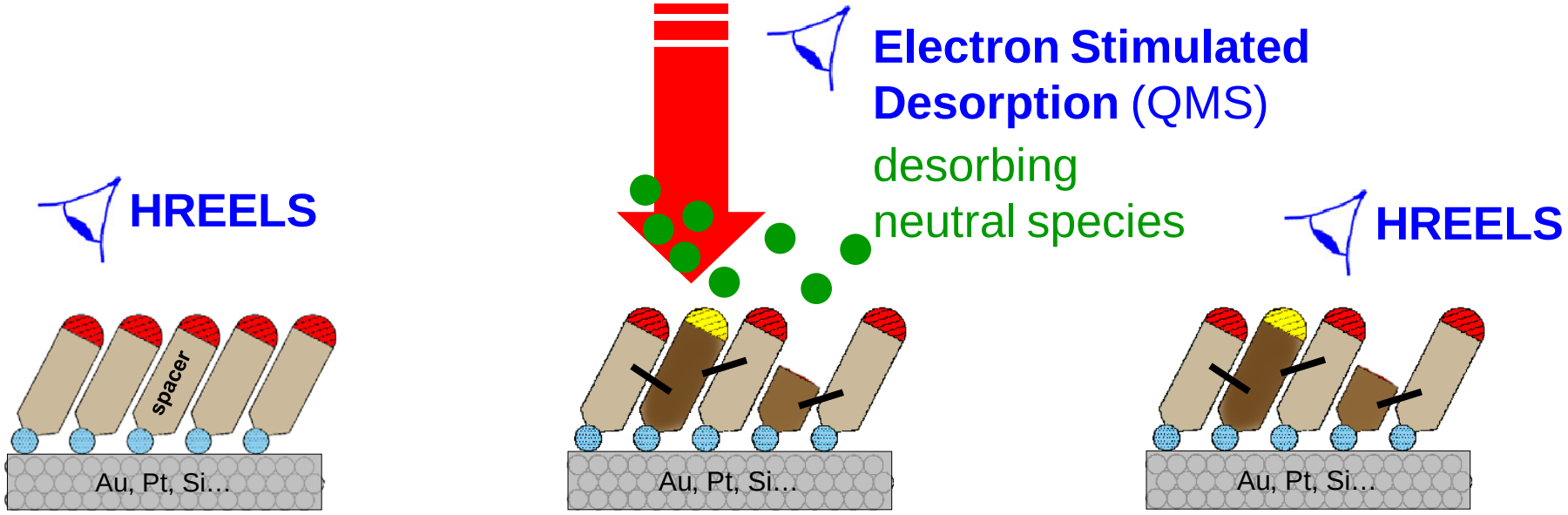
G.J. Schulz Rev. Modern Phys. 1973

E. Illenberger, in Adv. Series in Phys.Chem10B 2000

I. Bald Int. J. Mass Spectrom. 2008

Experimental procedure - Induced chemistry at RT in UHV

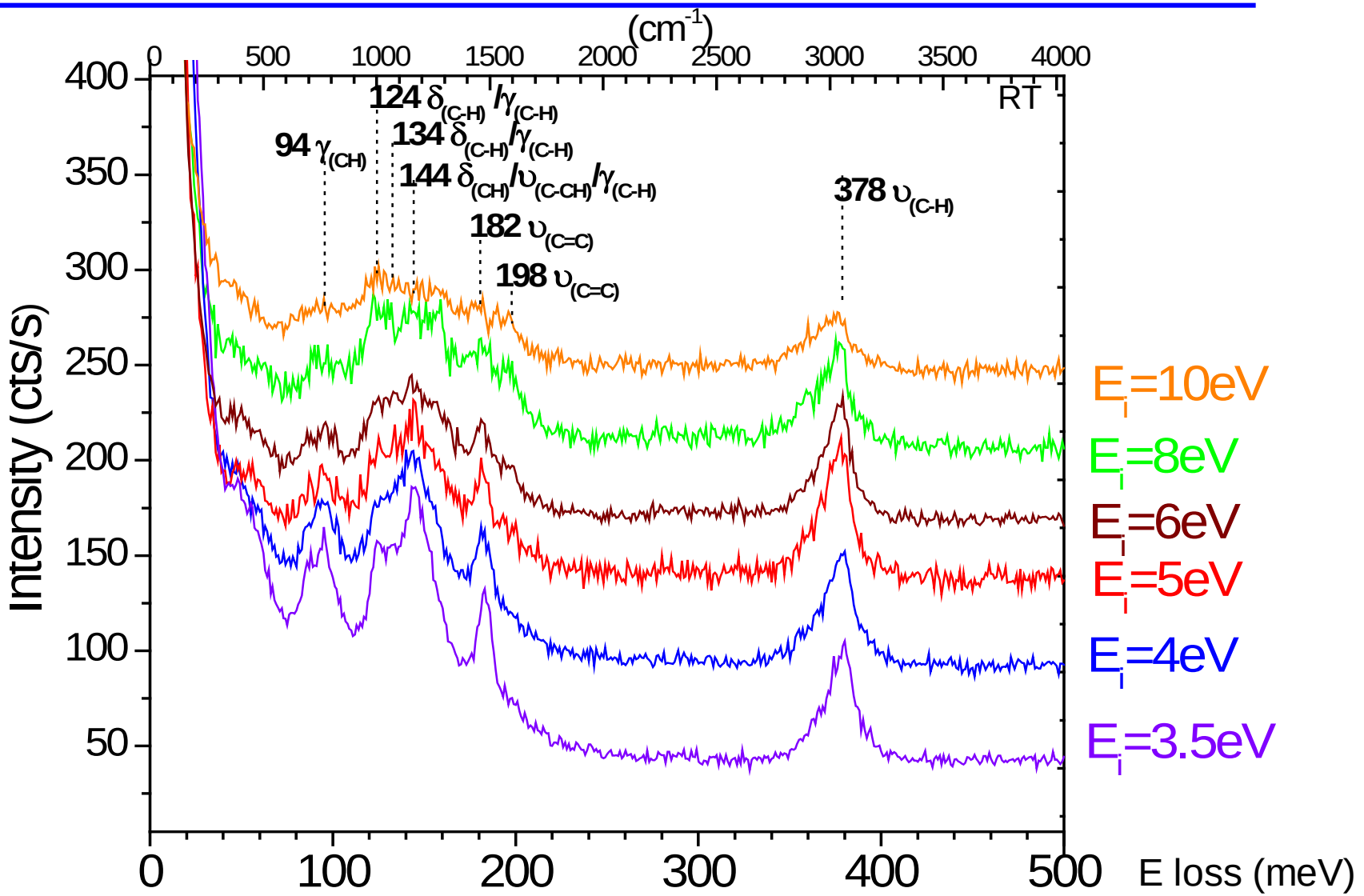
Low-energy electron PROCESSING
Commercial electron gun
E ~ 0.5-20 eV ø ~ 2-7 mm I ~ 0,02 – 1,60 μA
D ~ 30-500 e/molecule



Supported layer CHARACTERIZATION by vibrational spectrocopy
High Resolution Electron Energy Loss Spectroscopy (HREELS)
Energy Loss spectra $I = I_{E0}(\Delta E)$ & Excitation functions $I = I_{\Delta E}(E_0)$

Amiaud Submitted to PCCP

TPT – Vibrational excitation



Assignments: Barnes Surf. Rev. Lett. 1999; Shen Surf. Sci. 1993; Arnold Langmuir 2001; Shaporenko J .Phys. Chem. 2004

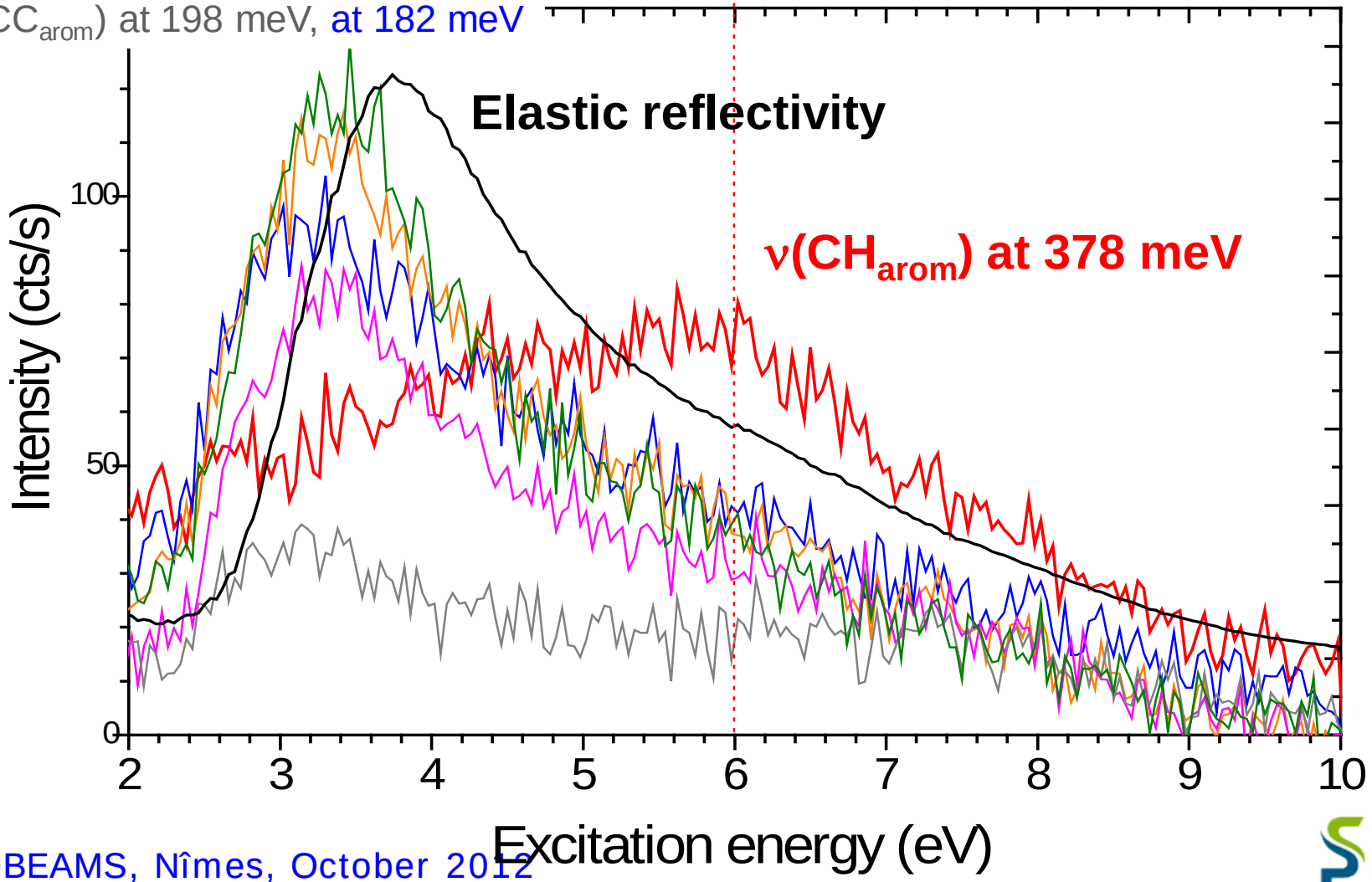
TPT- Selective resonance at 6 eV for $\nu(CH_{arom})$

$\gamma(CH_{arom})$ at 94 meV

$\delta(CH_{arom})$ / $\gamma(CH_{arom})$ at 124 meV

$\delta(CH_{arom})$ / ν(C-CH) / $\gamma(CH_{arom})$ at 144 meV

$\nu(CC_{arom})$ at 198 meV, at 182 meV



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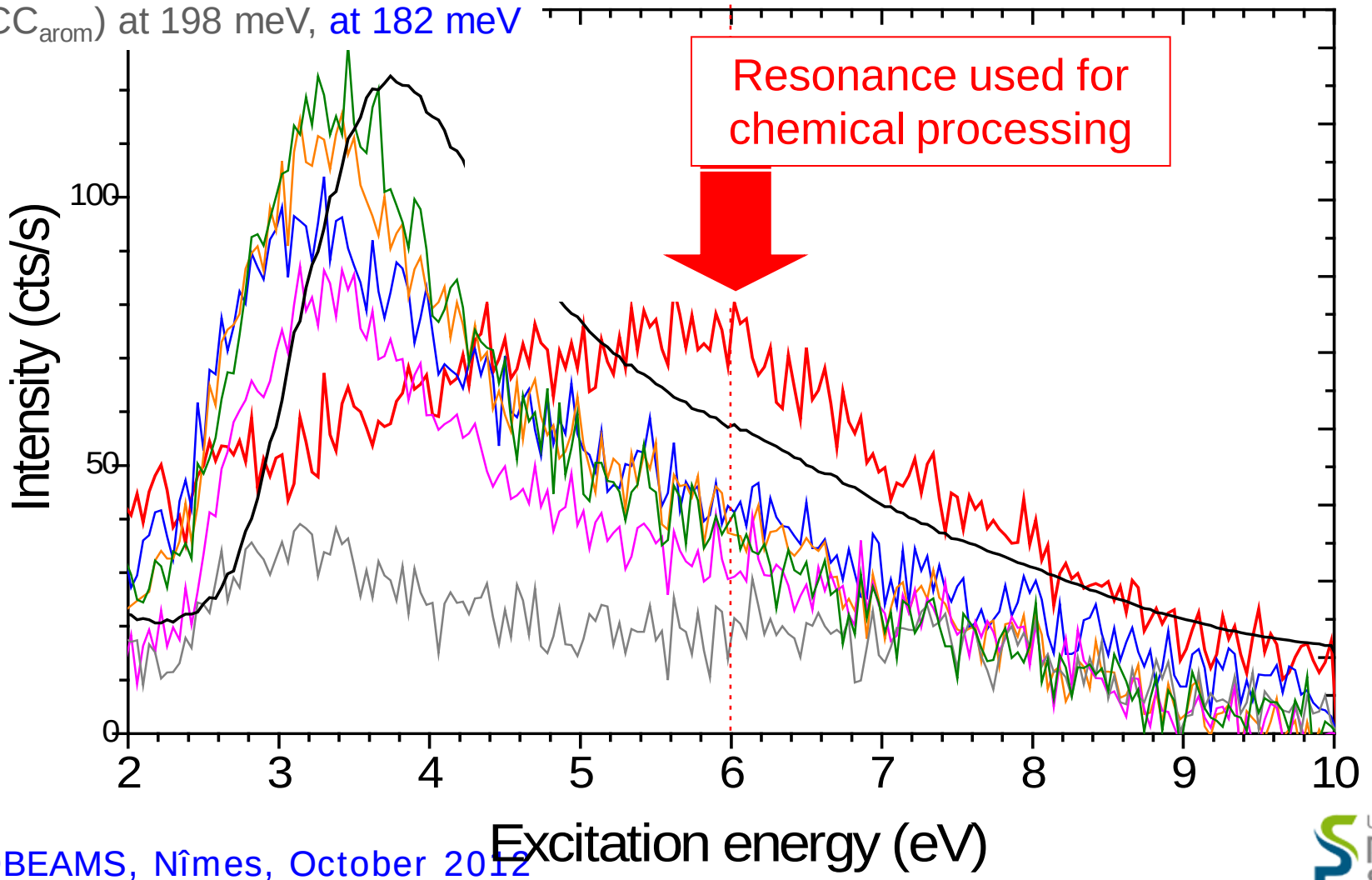
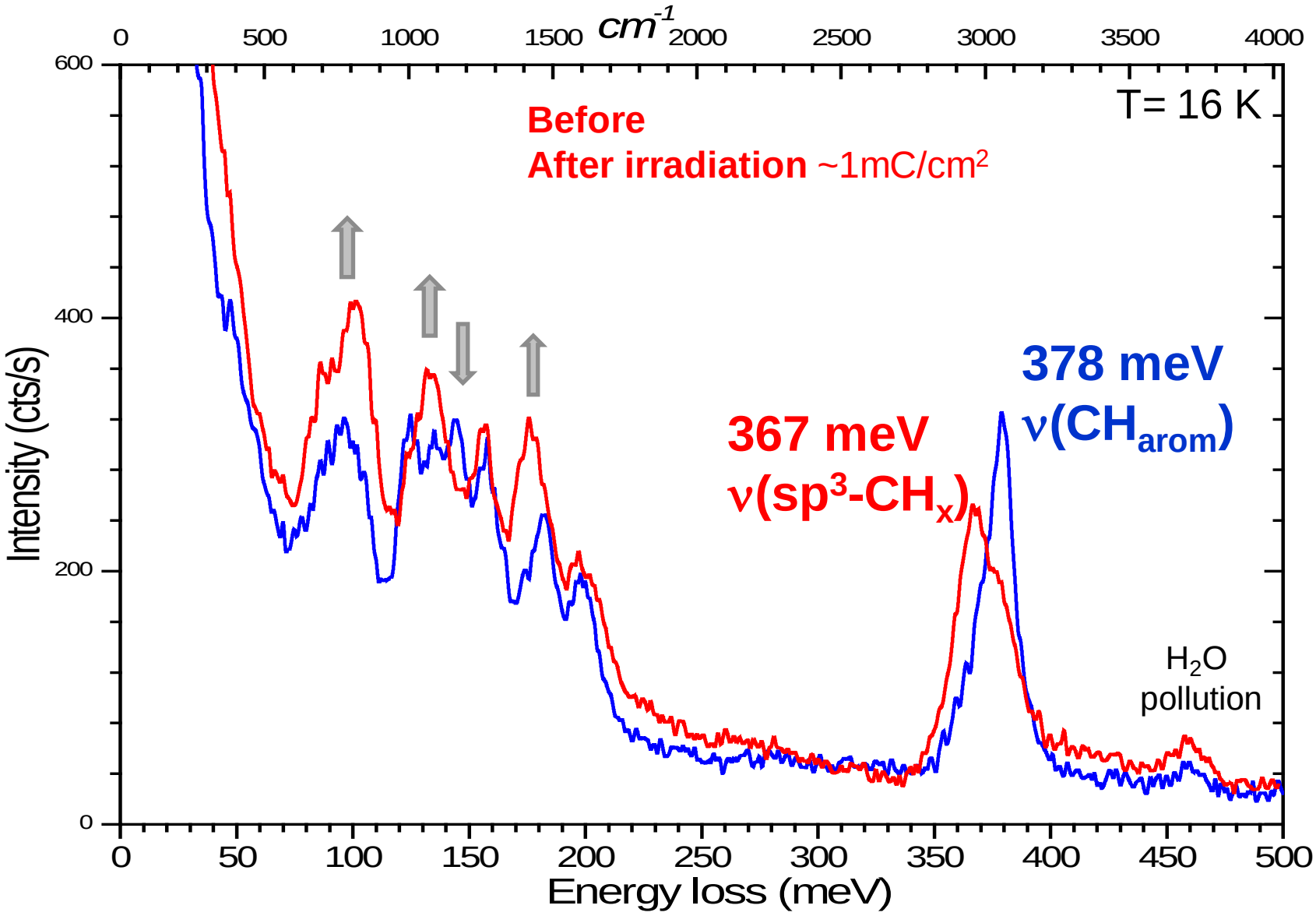


TPT – e^- induced loss of aromaticity at 6 eV



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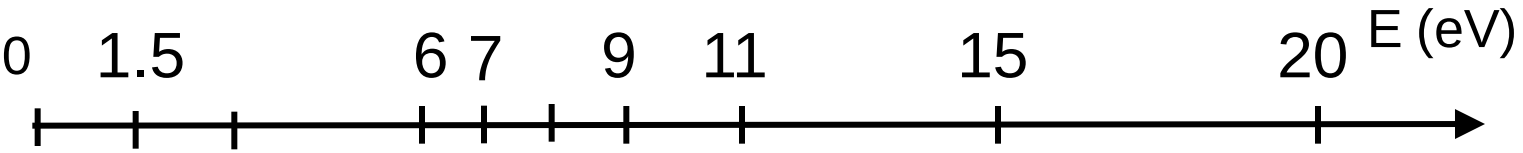
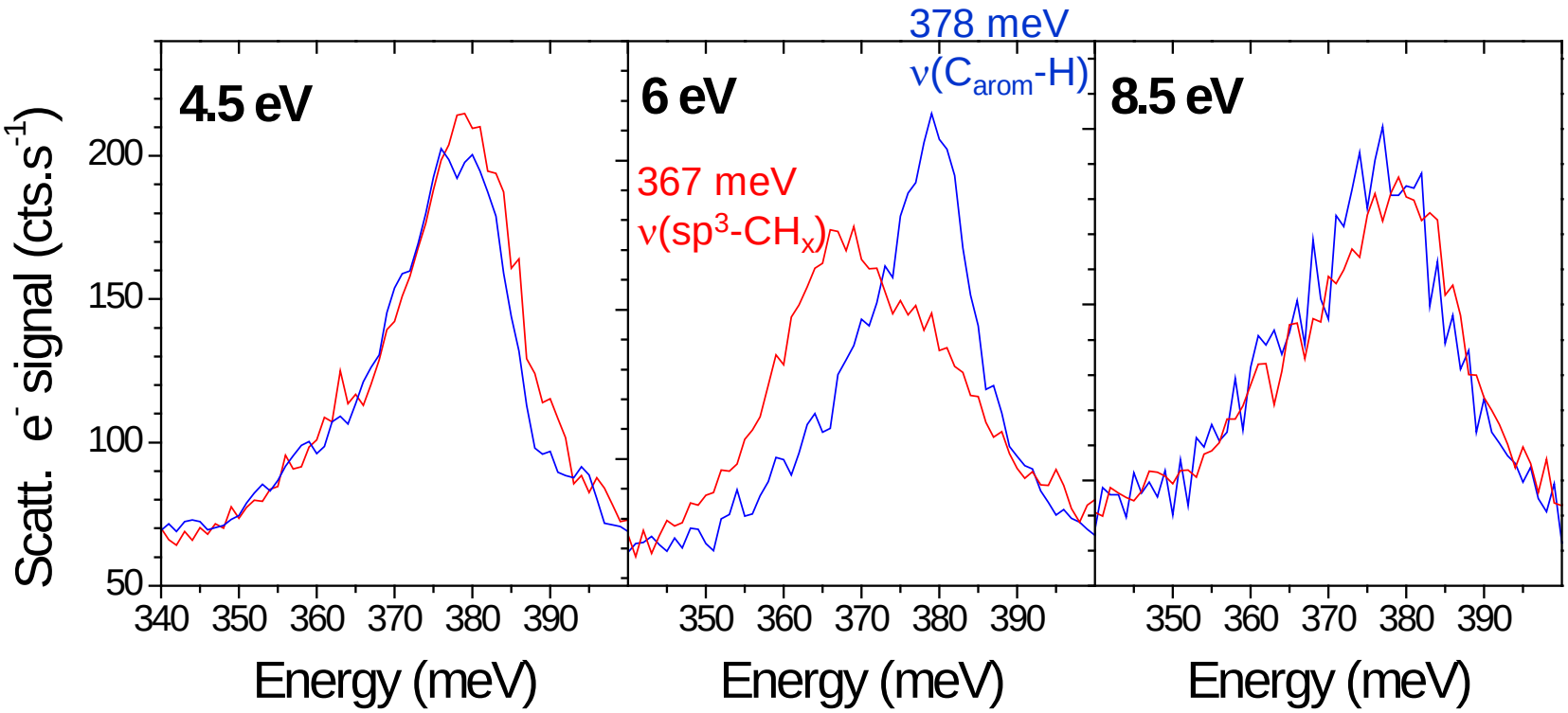
TPT - Irradiation energy effect on the induced chemistry



Aromatic



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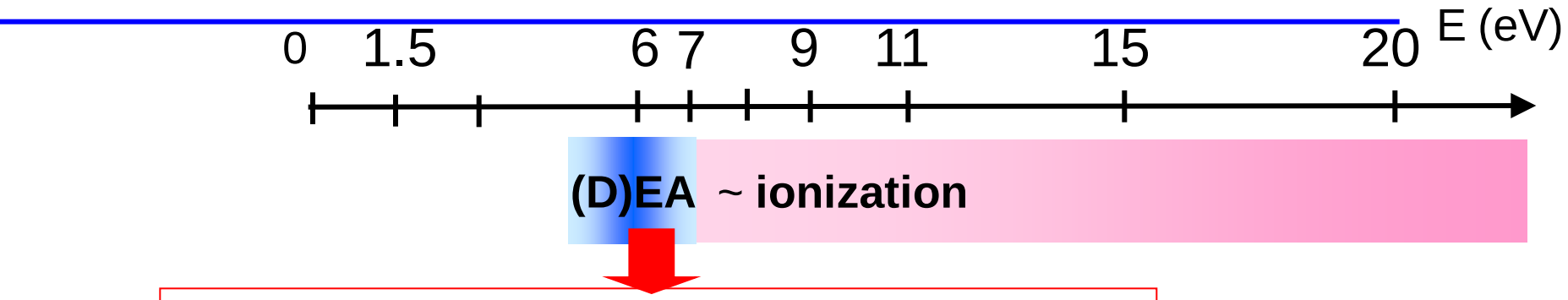
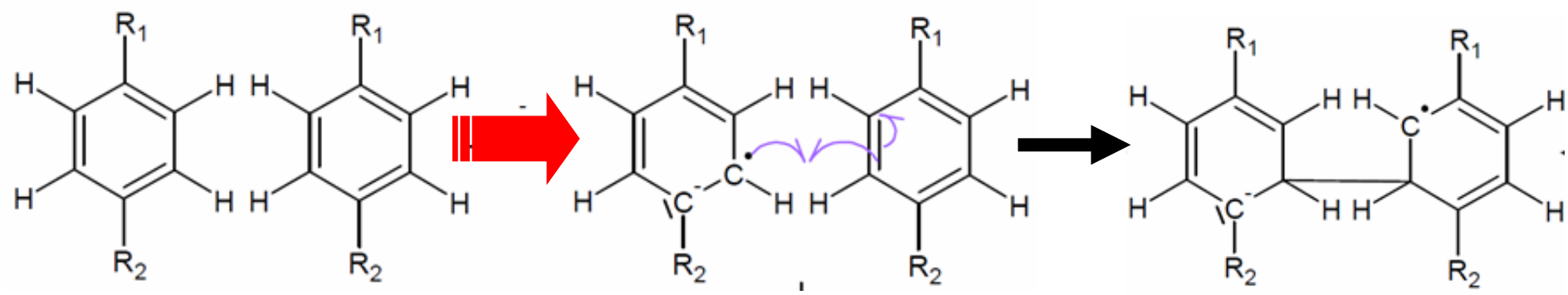
Involved processes and proposed mechanism



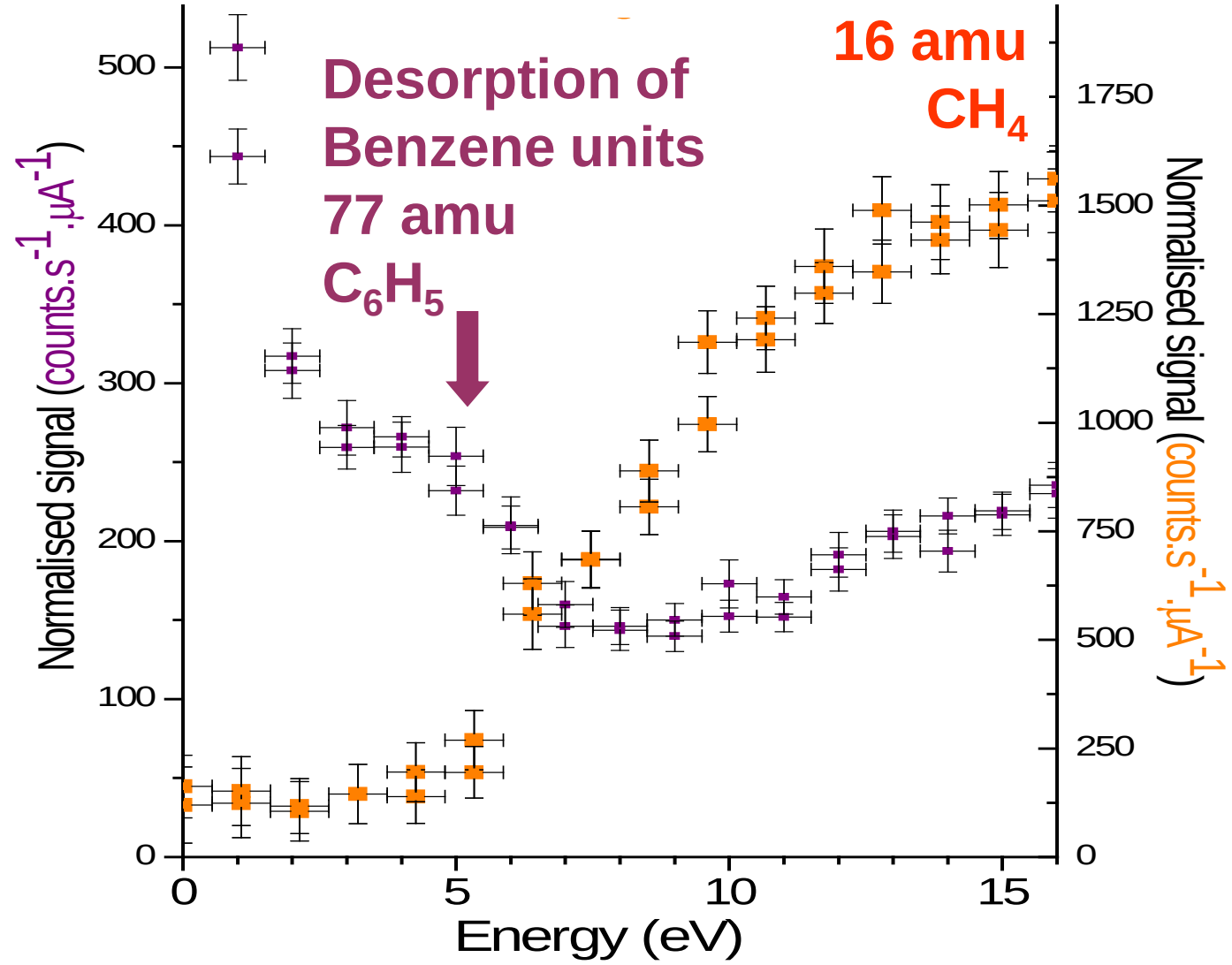
Enhanced vibrational excitation
Aromaticity loss - CH_{arom} → sp^3-CH_x conversion

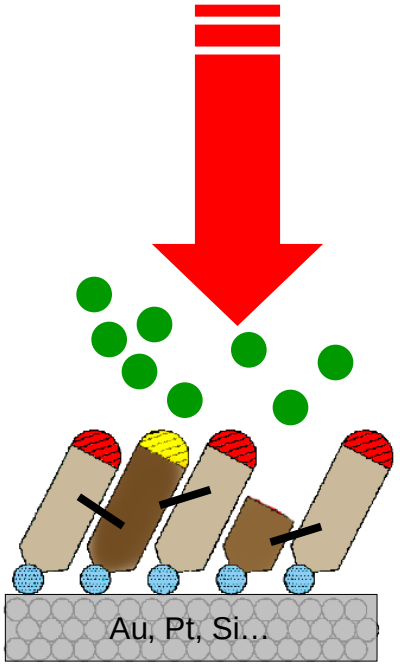
Proposed contributing mechanism

Low-energy electron attachment → formation of an activated site (radical) → radical induced loss of aromaticity → cross linking



Preliminary results - ESD of neutral fragments (QMS)





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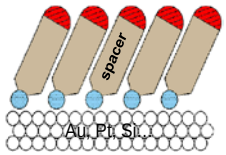
Conclusion & perspectives

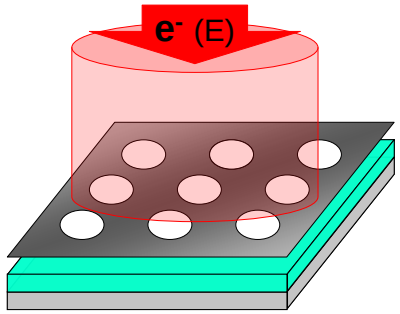
Low-energy (0-20 eV) electron processing of supported thin films studied by vibrational spectroscopy (HREELS) & ESD



→ To identify some induced chemical modifications

→ To understand the processes induced by low-energy electrons

Development of irradiation strategies using low-energy electrons as processing particles



→ Chemical control achieved through DEA

→ Towards 2D structuring
at the micrometer scale using scale using masks,
at the nanometer-scale using new low-energy electron beams…

Collaboration with Daniel Comparat's group (LAC)

Monochromatic electron source based on a Cs 2D-Magneto Optical Trap (MOT)

cf. Yoann Bruneau 's talk and Guyve Khalili 's poster

Thanks

Thank you for your attention

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