Mapping Surface Chemistry and Molecular Orientation with Combinatorial Near Edge X-ray Absorption Fine Structure

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Review Paper: D.A. Fischer, K. Efimenko, R.R. Bhat, S. Sambasivan, and J. Genzer Macromolecular Rapid Communications, 25, 141 (2004)

NIST
National Institute of Standards and Technology
Technology Administration, U.S. Department of Commerce

NC STATE UNIVERSITY

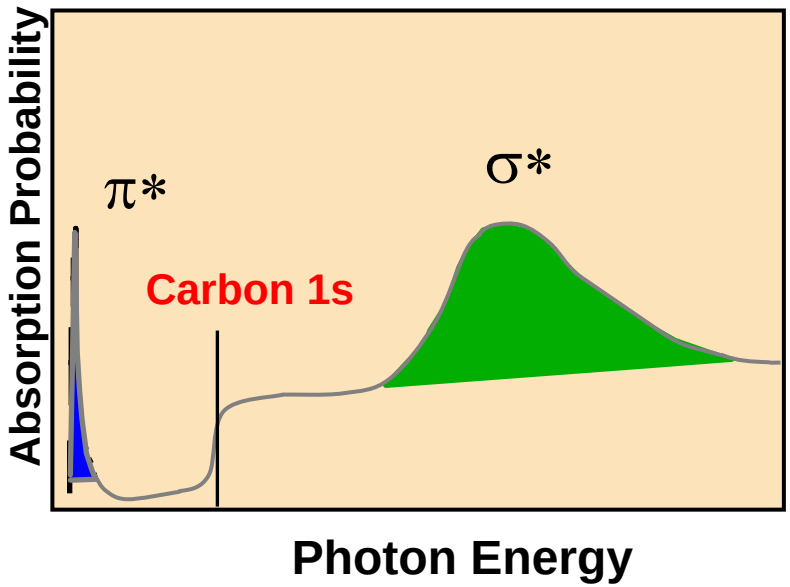
Outline

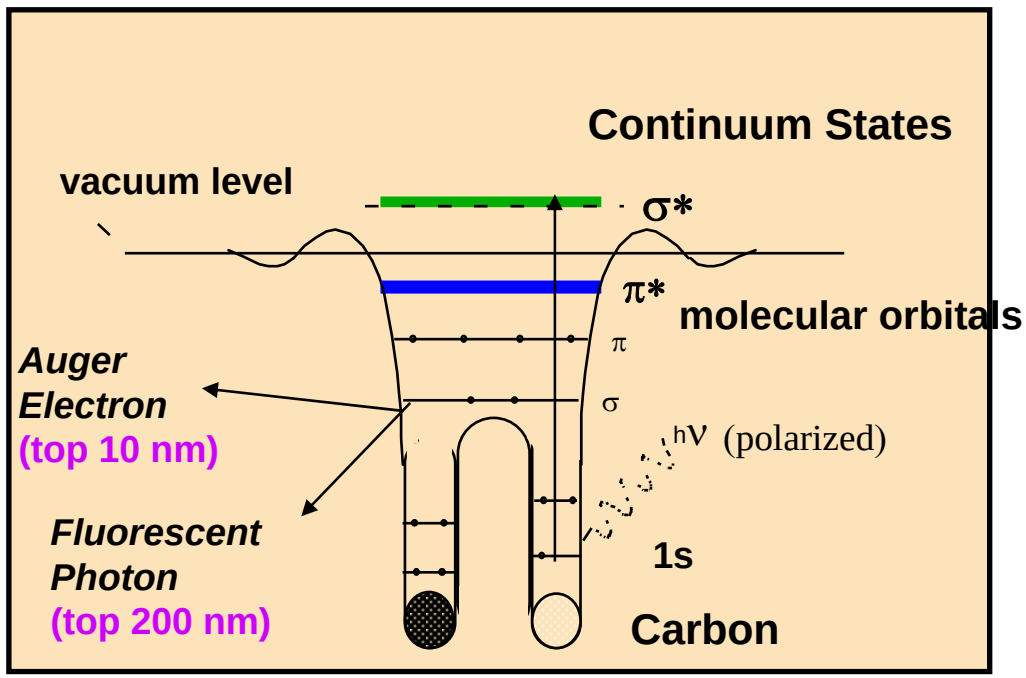
- What is NEXAFS?
- What is combinatorial NEXAFS?
- Mapping molecular bond concentration and orientation
  - Molecular gradients (1D and 2D)
  - Validation of molecular gradients for nanoparticle templates
- Mapping the rehybridization of propylene on zeolite catalyst arrays (prototypical catalyst discovery experiment)
- What's next?
  - Parallel process imaging: Combi-NEXAFS pictures and movies
  - Nanomovie! "When monolayers collide"

NIST / Dow Soft X-ray Beamline (U7A); National Synchrotron Light Source (NSLS) @ Brookhaven National Laboratory (DOE)

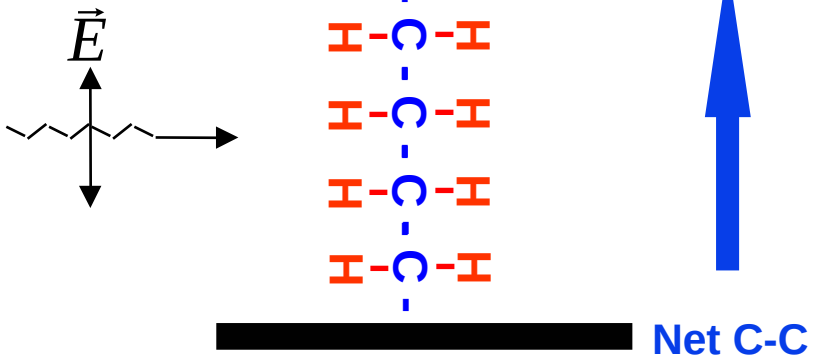
NEXAFS
(Near Edge X-ray Absorption Fine Structure)

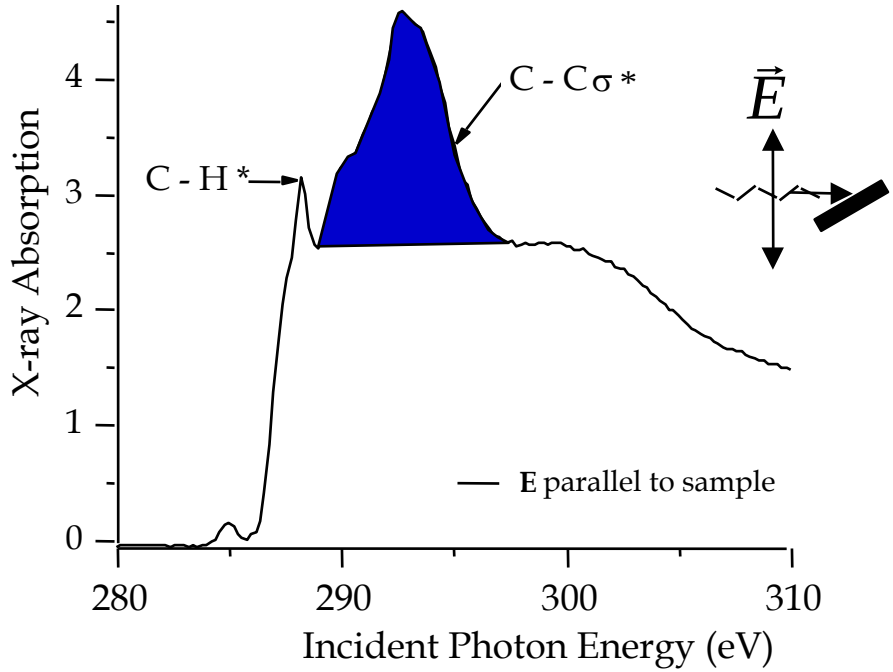
- **Elemental selectivity**
- **Chemical bond sensitivity**
- **Orientation Information**
- **Depth selectivity**

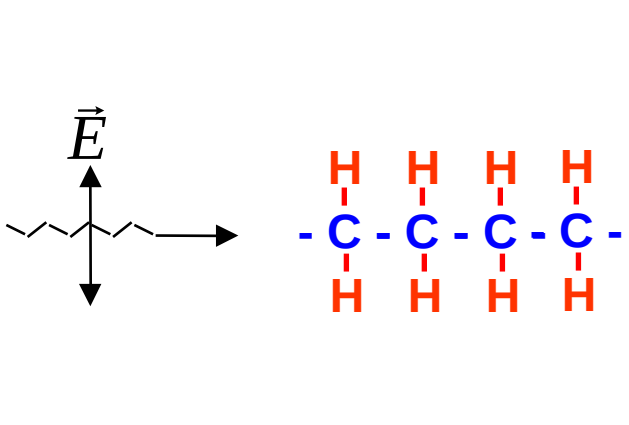


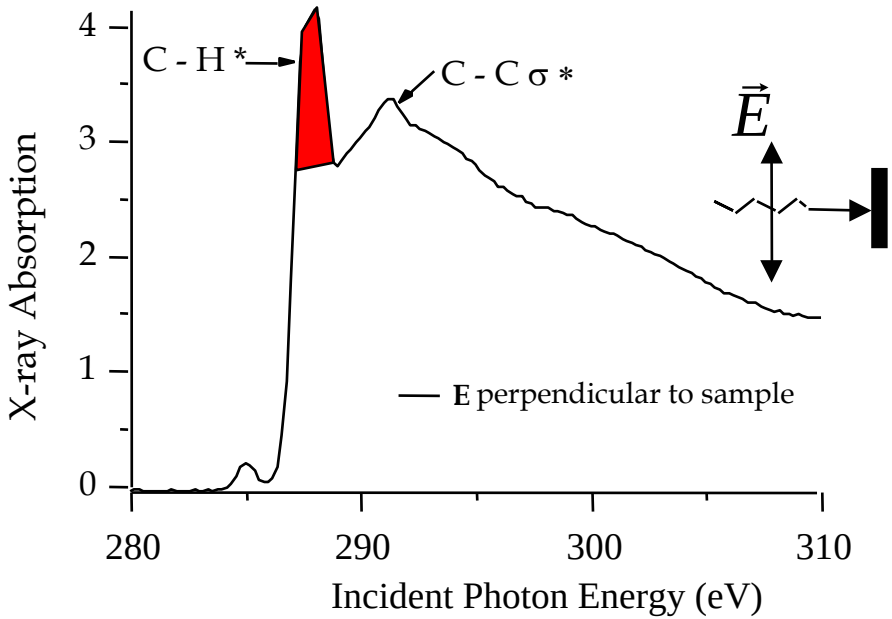


Molecular Orientation: NEXAFS Polarization Anisotropy

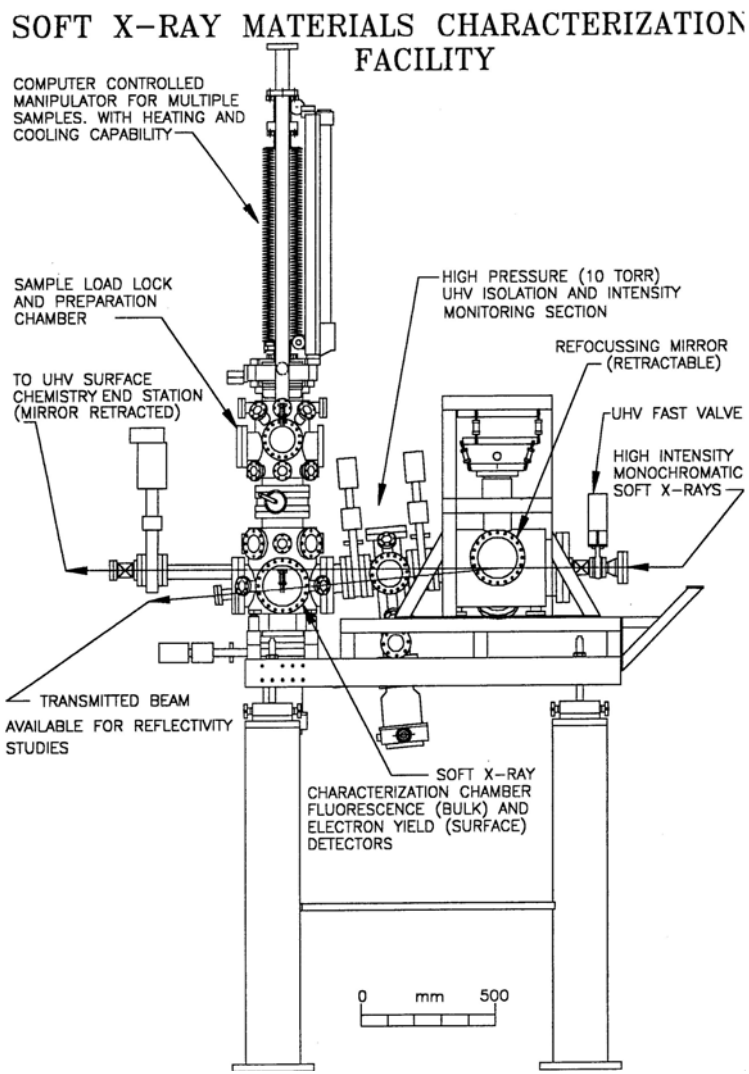


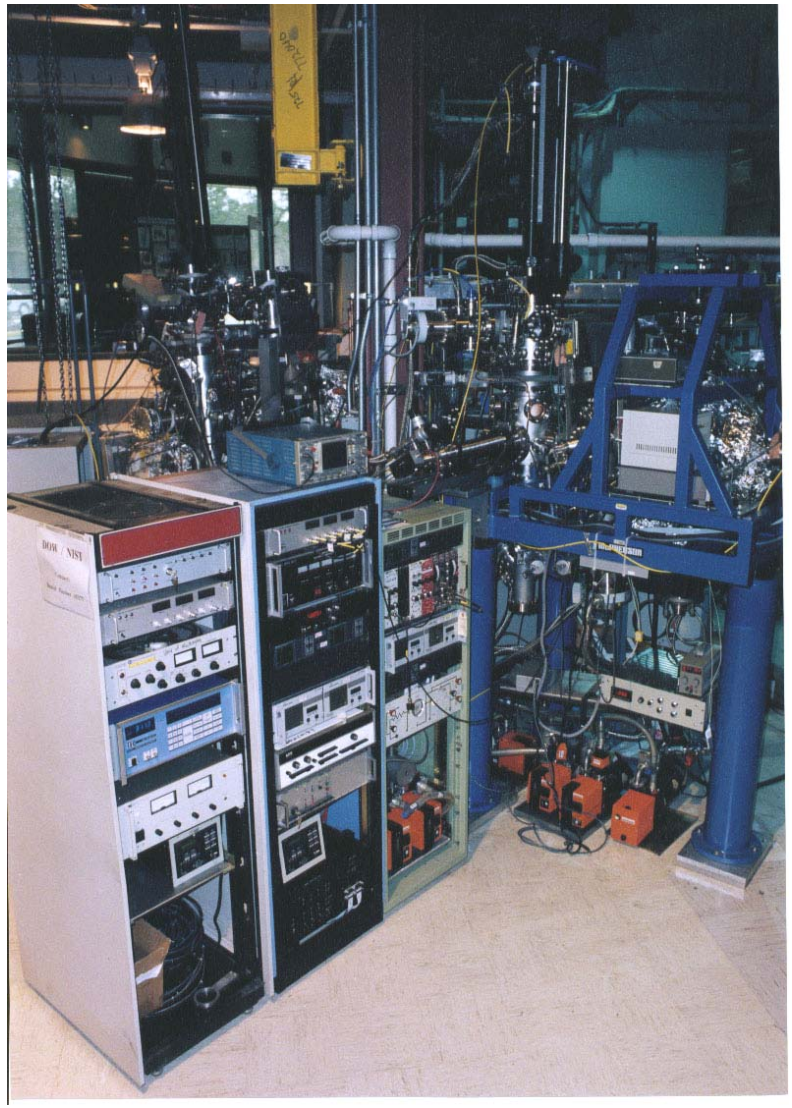






Mapping molecular concentration and orientation : Combinatorial NEXAFS, Pictures & Movies

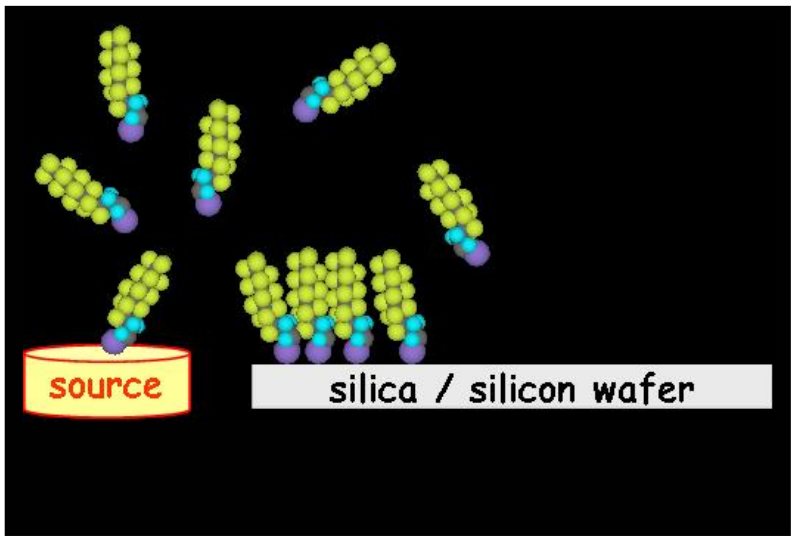




Molecular Gradients

The need: measuring bond concentration and orientation

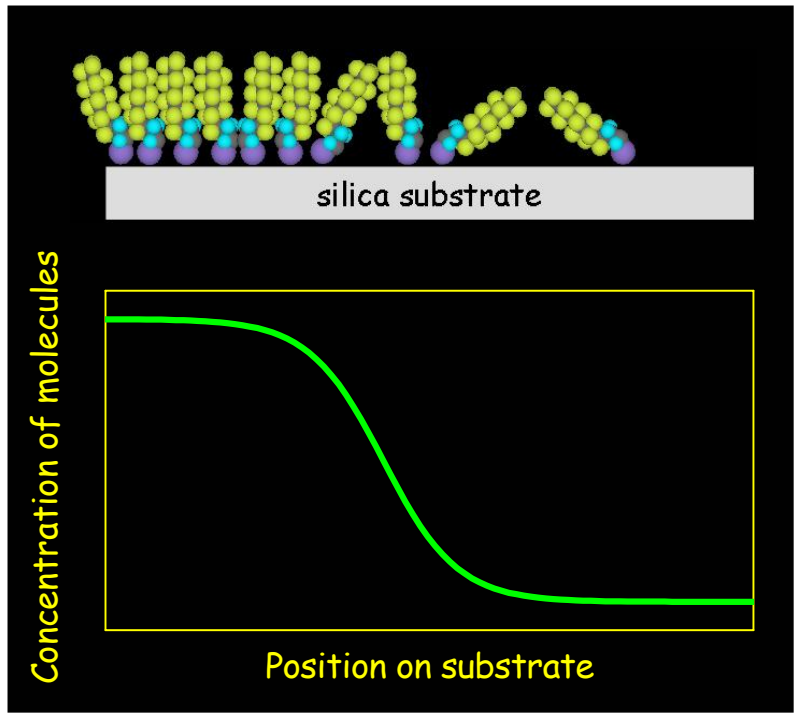
- For some applications, it is desirable that the physico-chemical characteristics, such as wetting (CF_3 end groups) of the substrate, change gradually;
- Nanoscale templates (NH_2 end groups) for fabricating nanoparticle gradients



Vapor source ≡ chlorosilane/paraffin oil mixture
(e.g. semi fluorinated alkane chlorosilane)

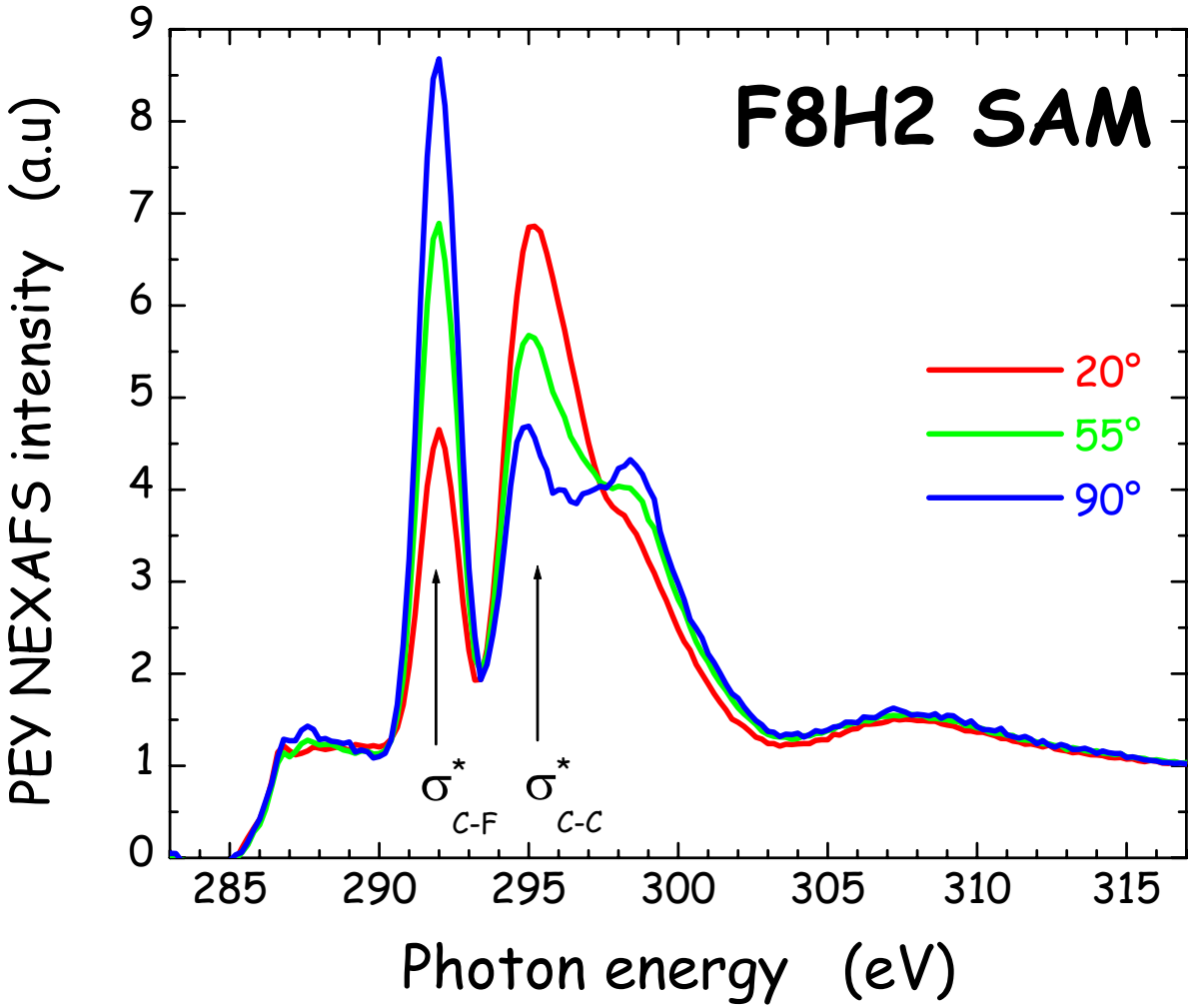
By controlling chlorosilane/paraffin oil ratio, one can control the vapor flux of the silanes

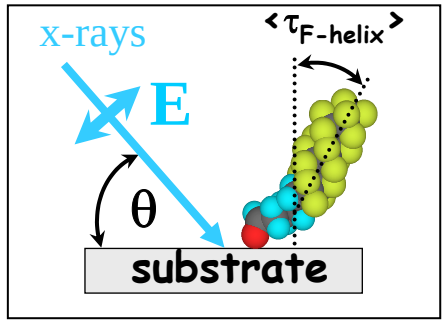
Gradient SAM



NEXAFS of semifluorinated SAMs

(Vapor deposition of semifluorinated alkyl tri-chlorosilane)



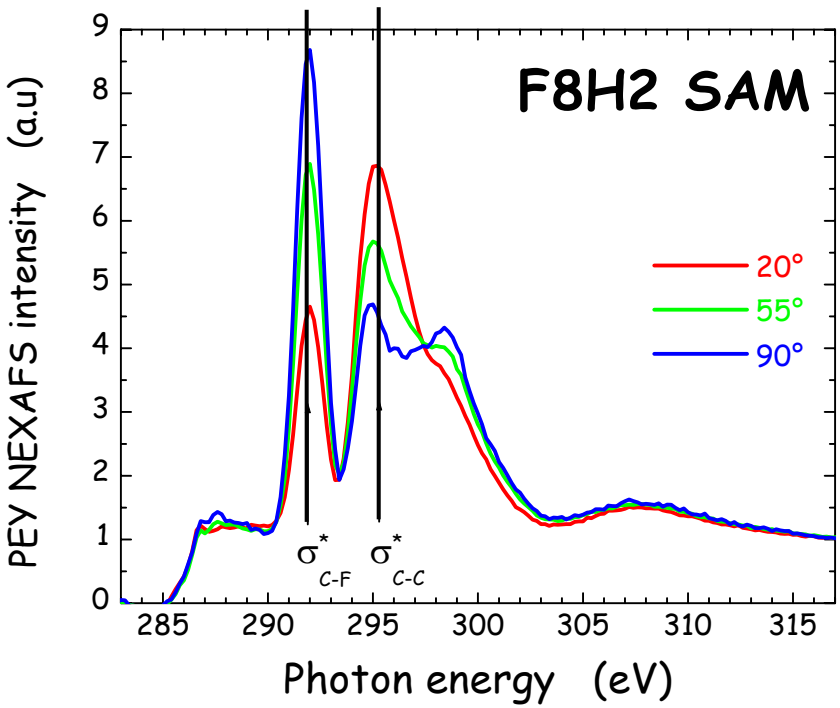


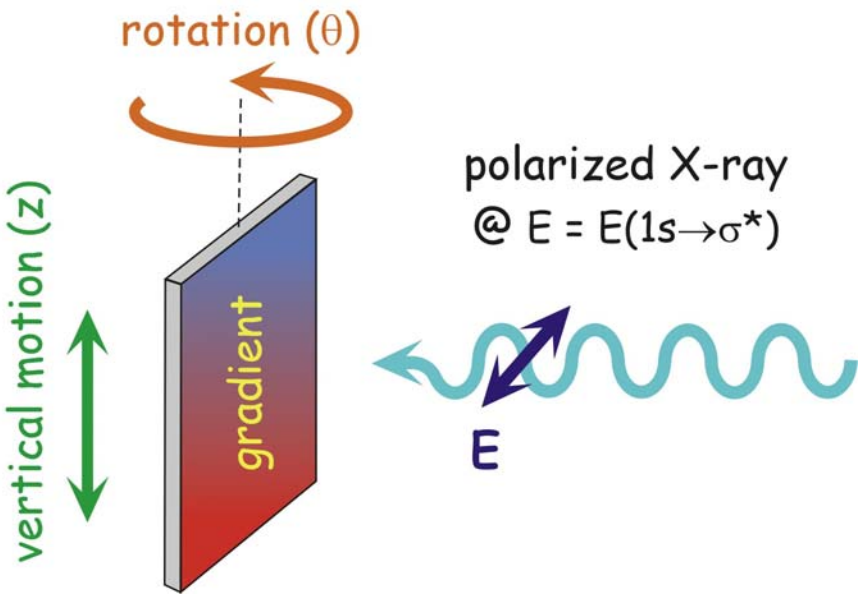
Experiments on F8H2-SAMs show that the F8H2 molecules stand almost ⊥ in dense SAMs

Extension to one-dimensional molecular gradients

Combinatorial NEXAFS

Enables exploring the gradient properties in a multivariate manner…





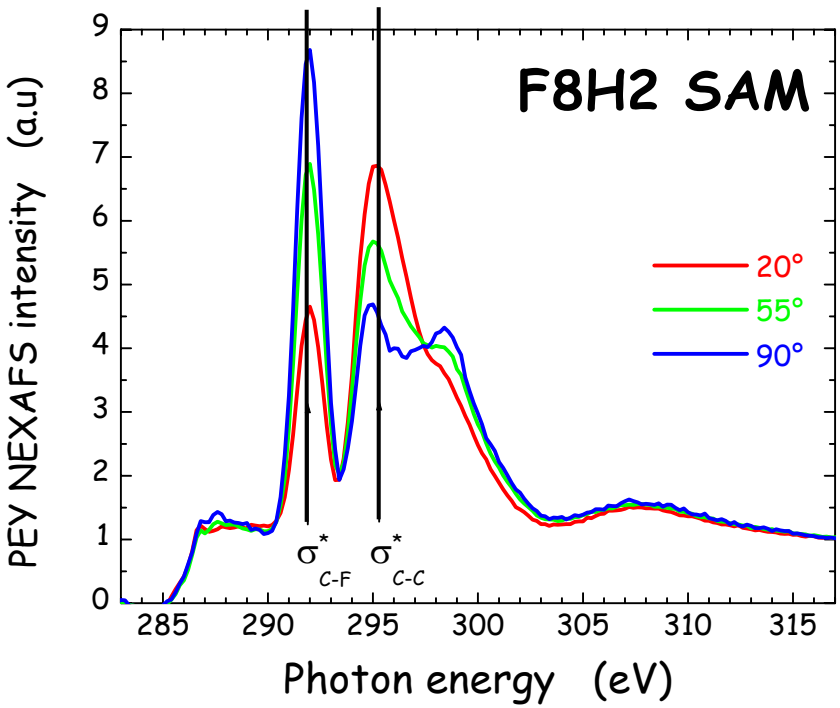
Approach:

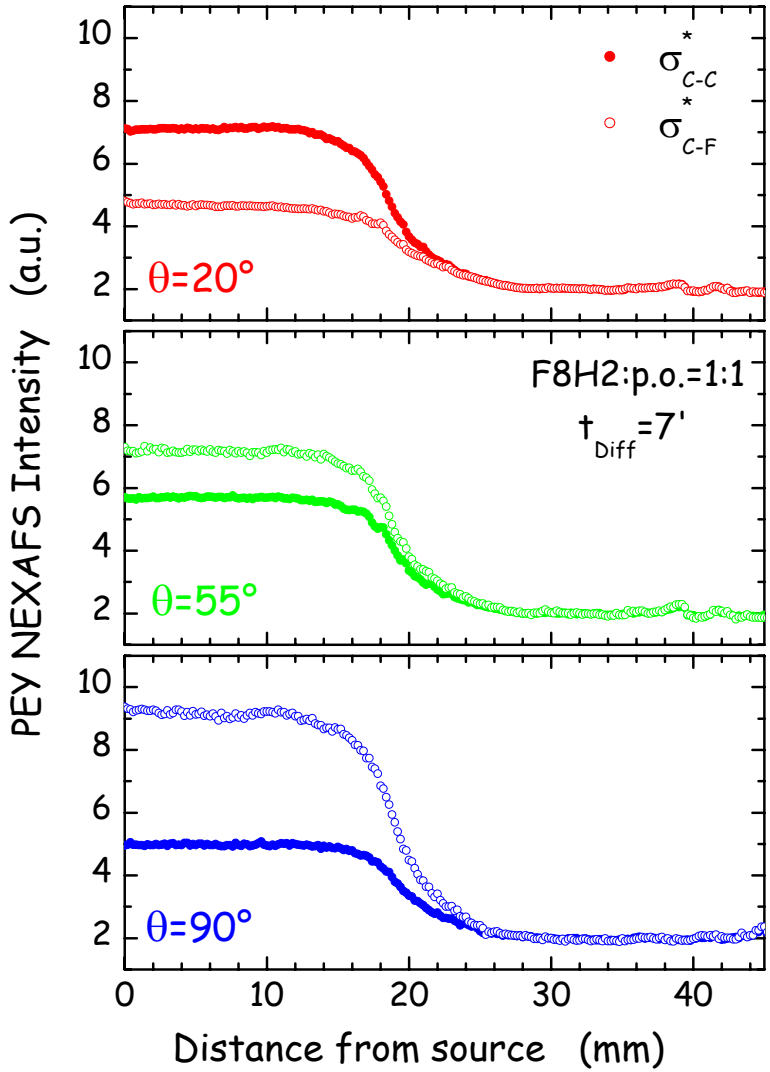
Fix E @ $\sigma^*_{C\text{-}C}$ (and $\sigma^*_{C\text{-}F}$) and perform a position scan across the gradient by moving the sample vertically

One-dimensional molecular gradient semifluorinated SAMs

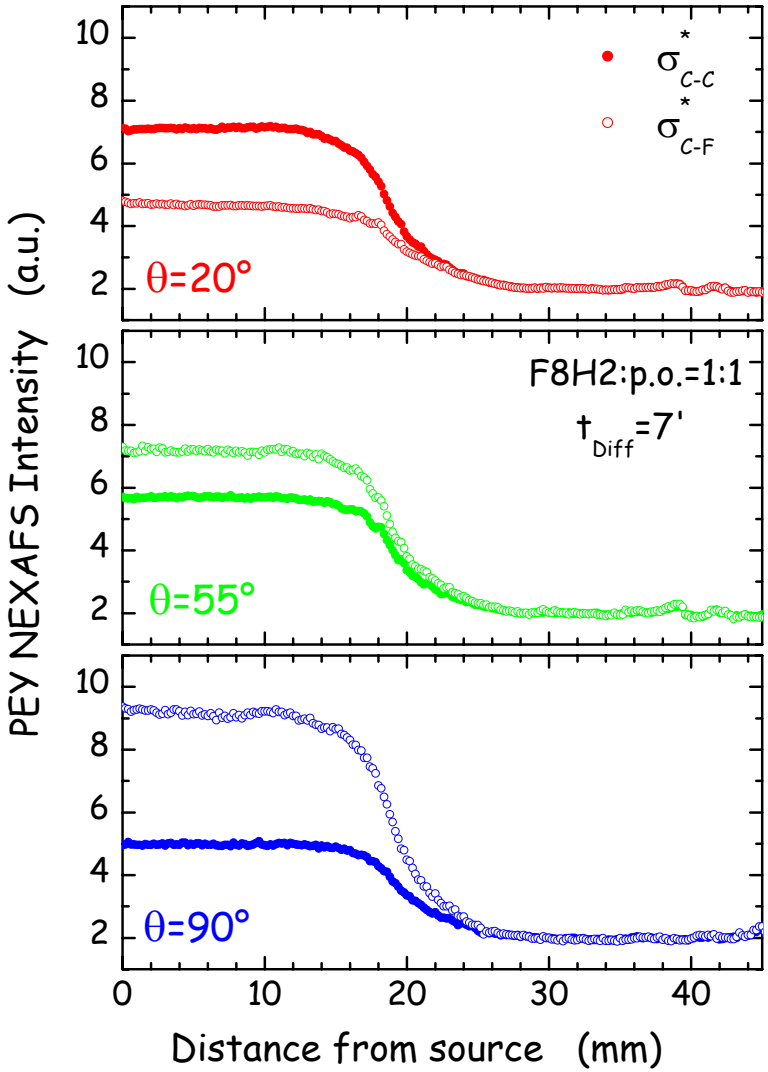
Approach:

Fix E @ $\sigma^*_{C\text{-}C}$ (and $\sigma^*_{C\text{-}F}$) and perform a position scan across the gradient by moving the sample vertically



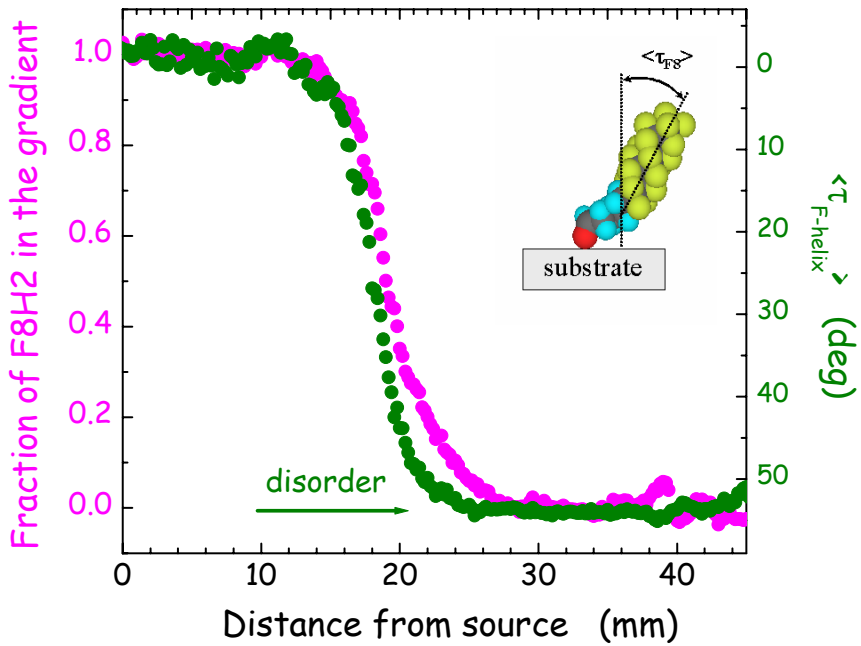


Analysis of Combi-NEXAFS molecular 1D gradient data

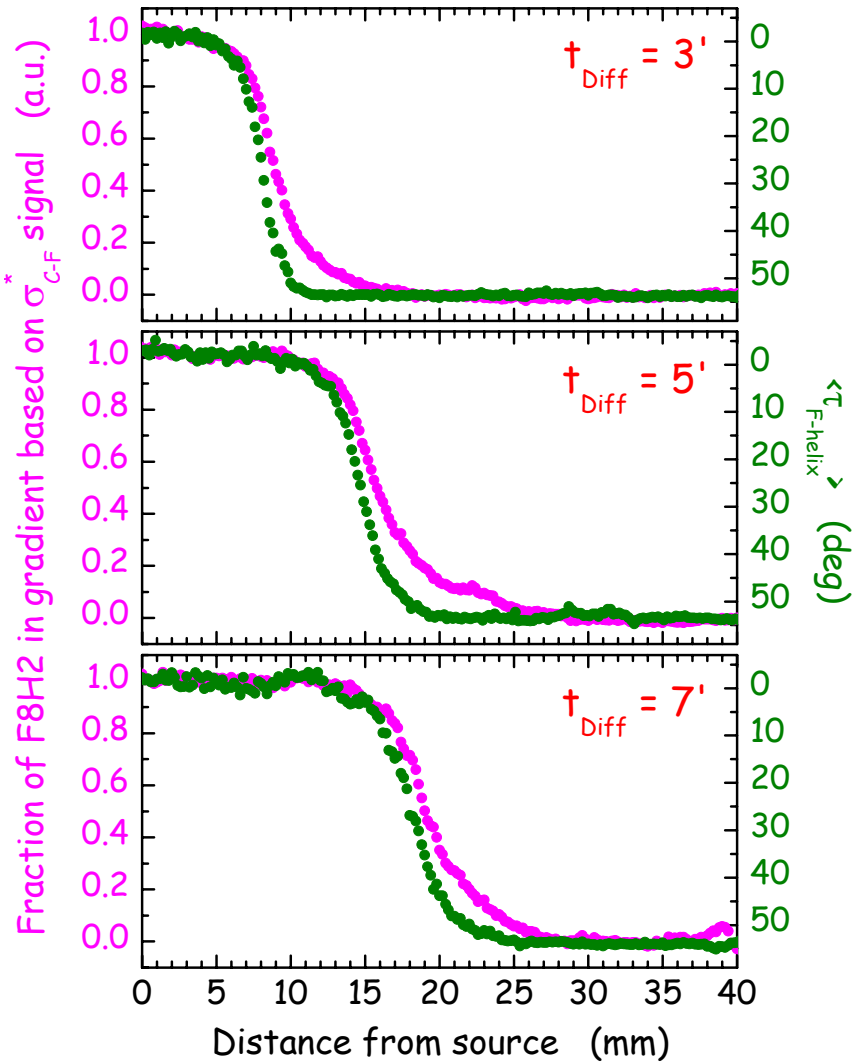


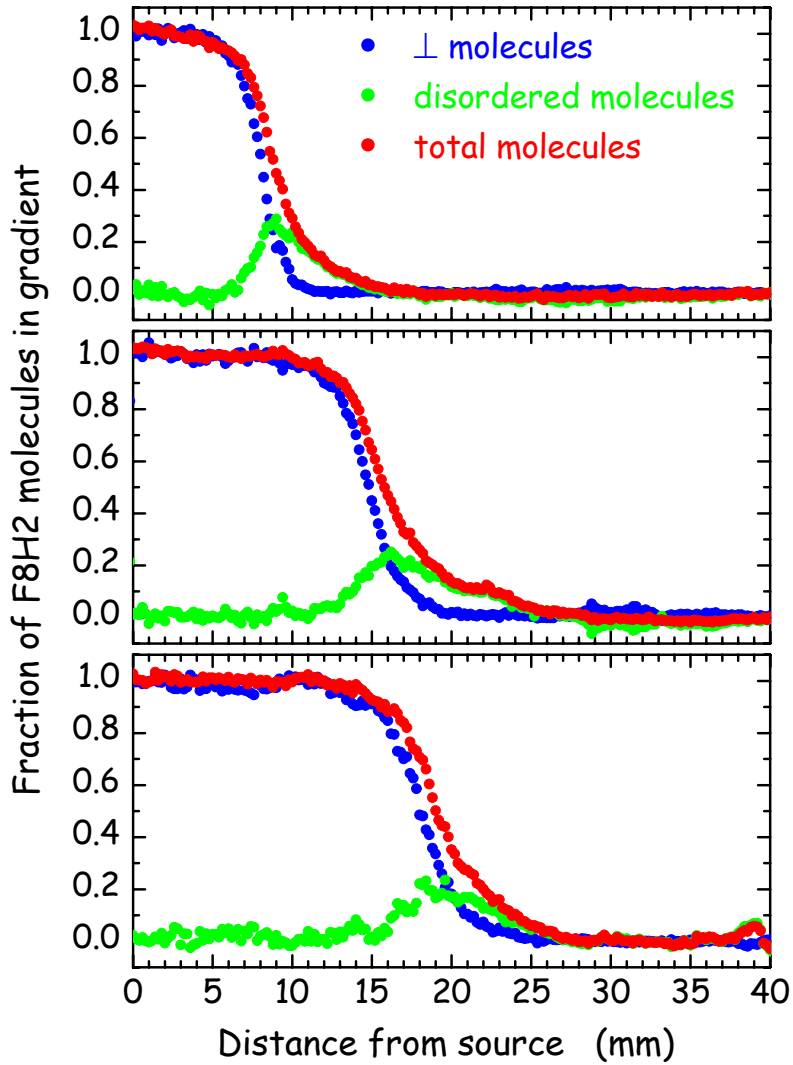
NEXAFS spectroscopy provides (simultaneously) information about:

- **Concentration of F8H2 (from θ=55° data)**
- **Orientation of F8H2 (from all angles)**

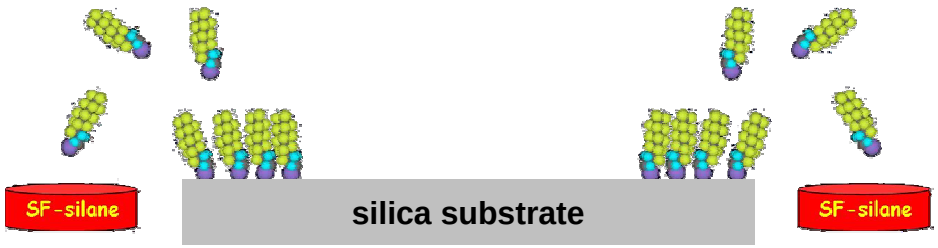


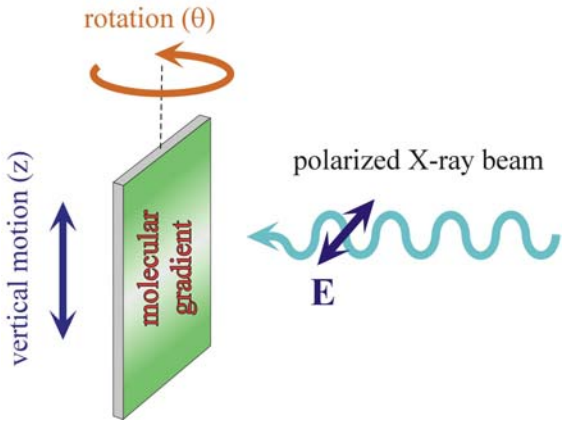
Mapping molecular concentration and orientation: Gradient diffusion times 3, 5, 7 minutes



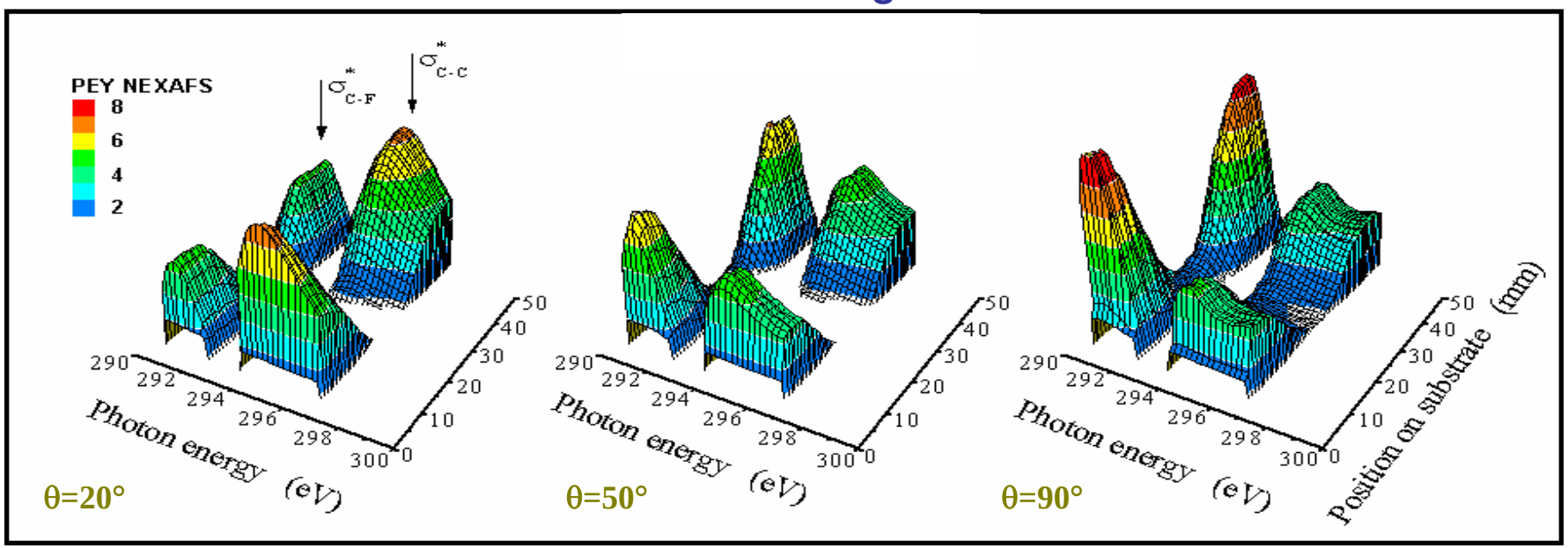


Mapping molecular concentration and orientation: One dimensional double gradient SAM



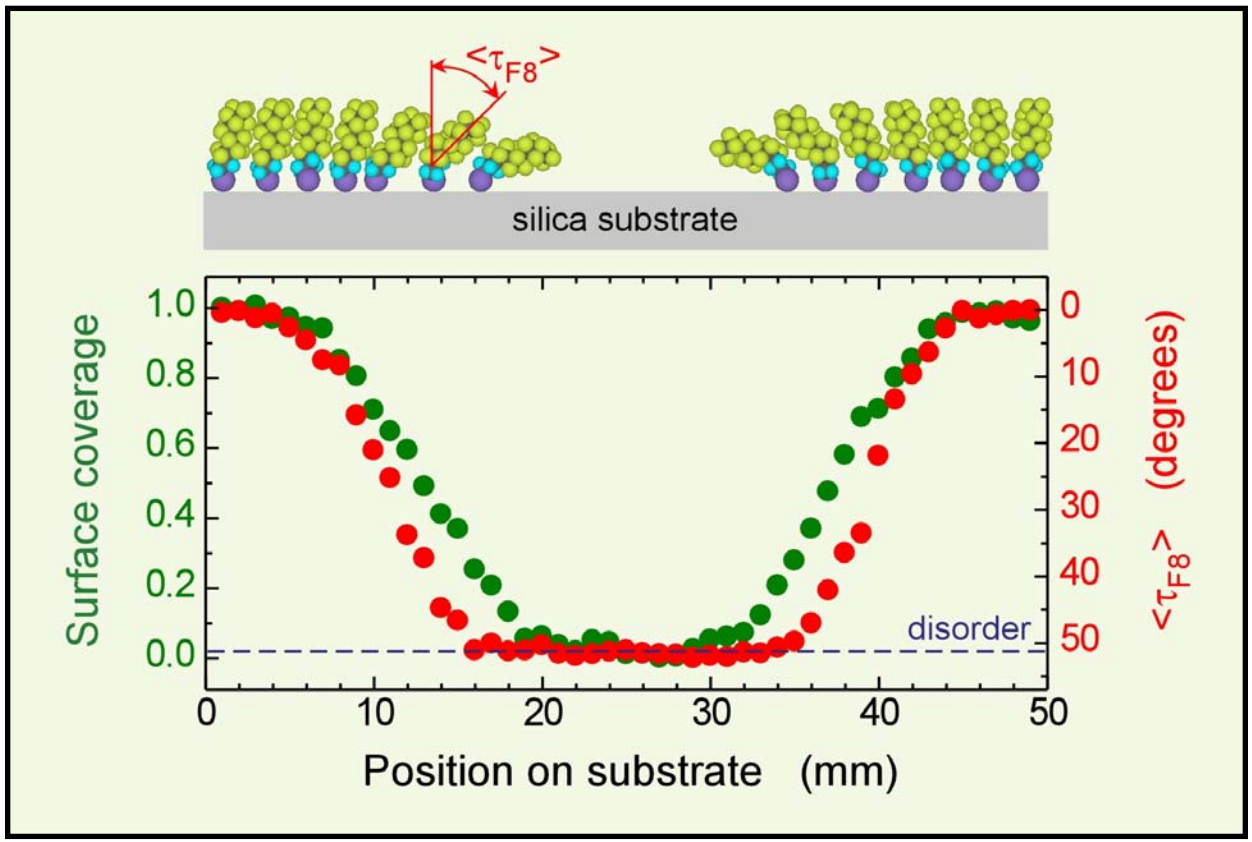


Combi-NEXAFS 1D double gradient SAM data



Mapping molecular concentration and orientation: One dimensional double gradient SAM

Analysis of Combi-NEXAFS 1D double gradient SAM data



J. Genzer, D. A. Fischer, and K. Efimenko Appl. Phys. Lett., 82, 266 (2003)

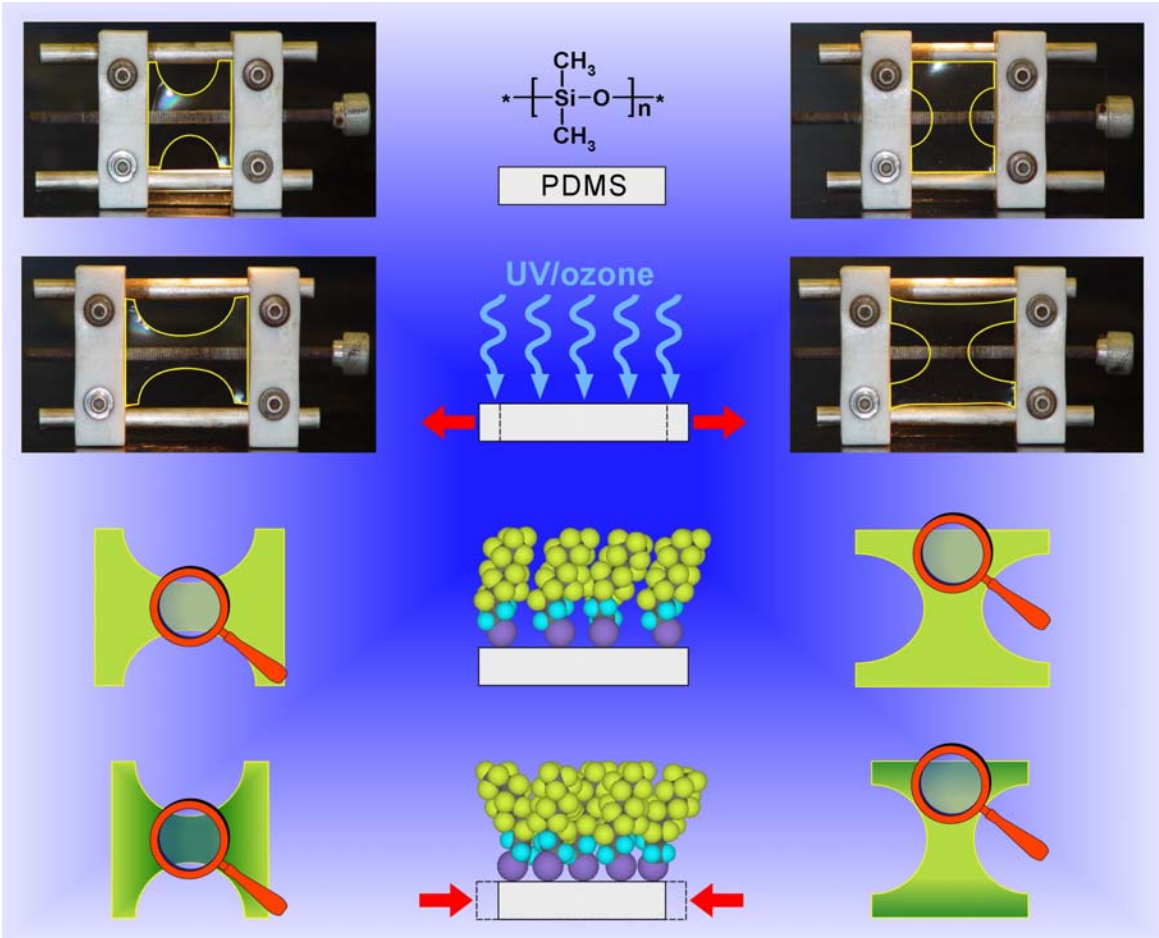
Mapping molecular concentration: Creating two-dimensional molecular gradients

"Dog bone" (PDMS) substrates

Asymmetric stretching (2 dog bones)

Vapor deposition of t-F8H2 (Uniform SAM)

Results in 2D gradient concentration of t-F8H2



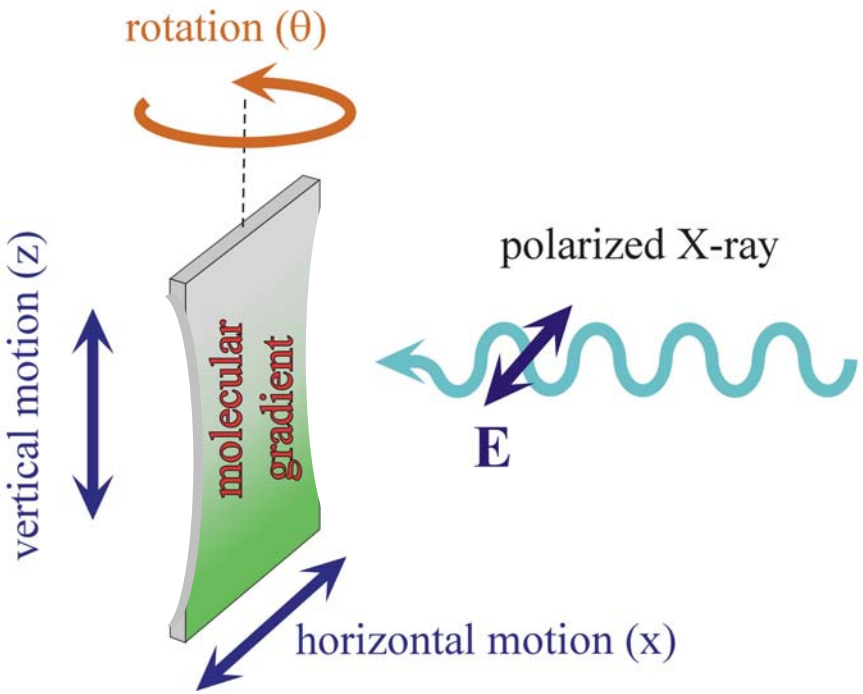
Mechanically assembled monolayers (MAMs)*

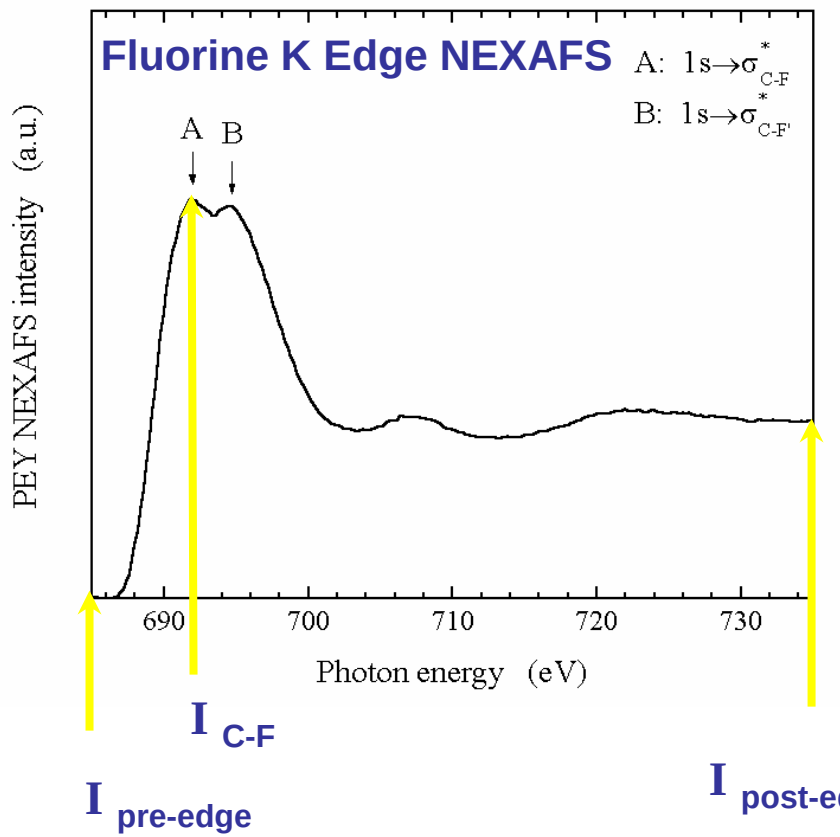
*J. Genzer et al Science, 290, 2130-2133 (2000)

Mapping molecular concentration: Two-dimensional molecular gradients

2D mapping C-F bond concentration using combinatorial NEXAFS

$$I_{C\text{-}F,norm} = (I_{C\text{-}F} - I_{pre\text{-}edge}) / (I_{post\text{-}edge} - I_{pre\text{-}edge})$$



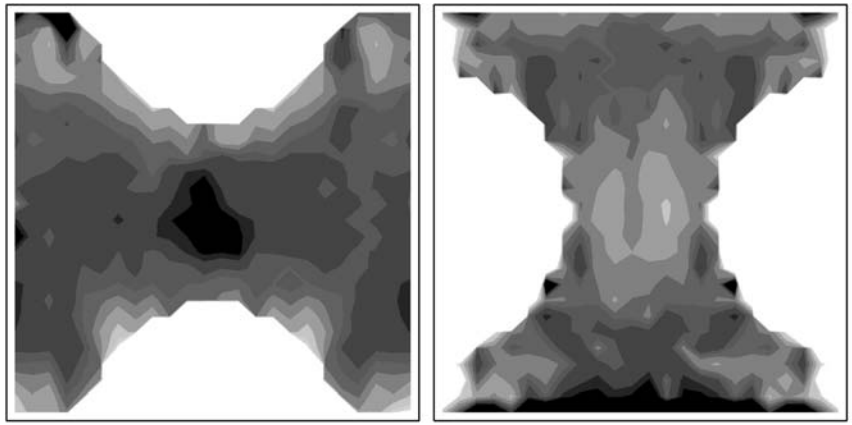


"Dog bone" (PDMS) substrate
2D gradient of F8H2

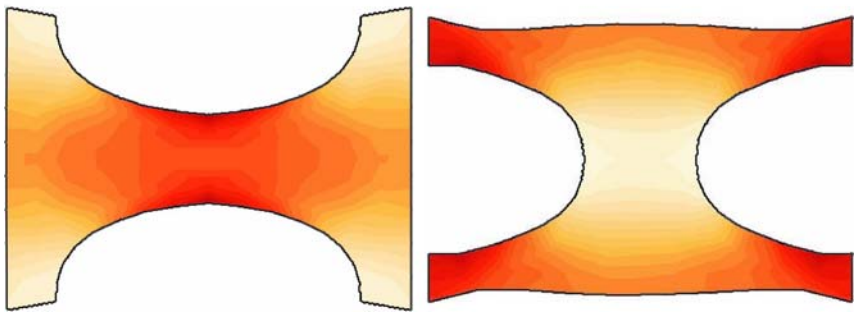
Mapping molecular concentration: Two-dimensional molecular gradients

"Relaxed dog bones after MAM"

Combinatorial NEXAFS
C-F bond concentration maps
Max / Min: 1.35/1 and 1.25/1



Calculated strain maps of stretched PDMS "dog bones"



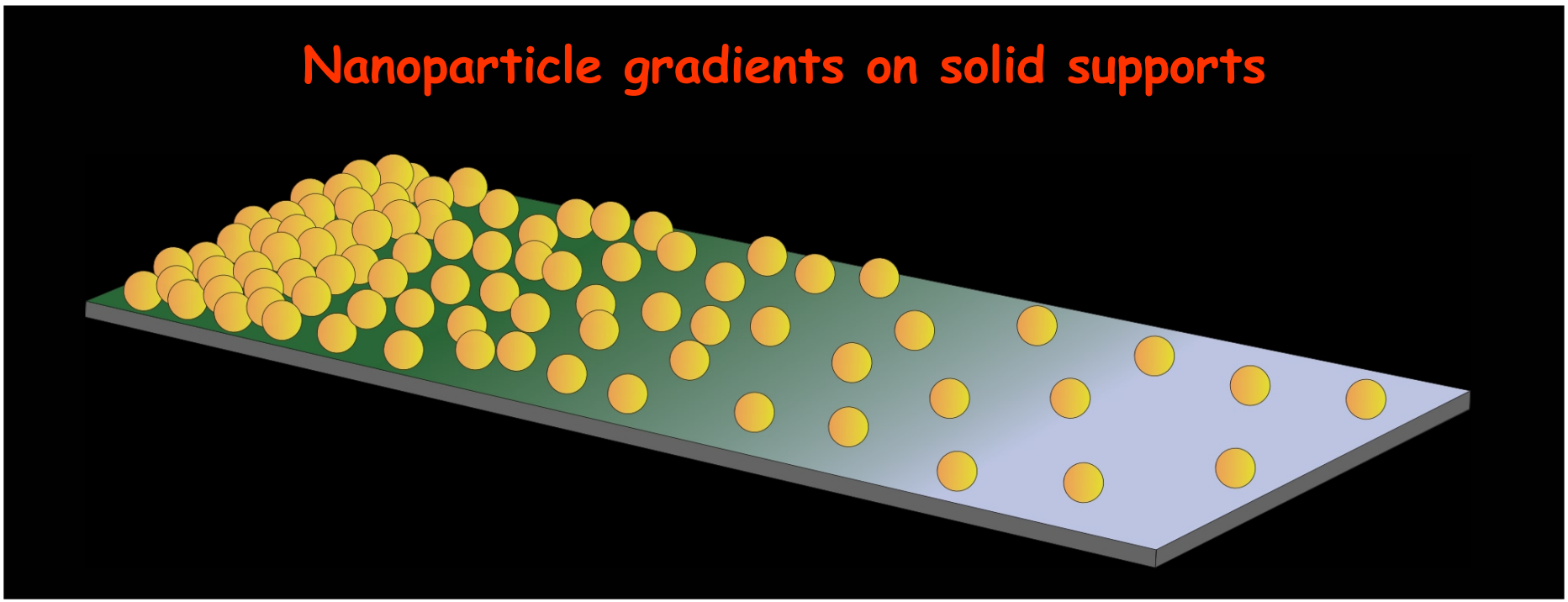
F8H2 density highest at maximum dog bone initial strain

J. Genzer, K. Efimenko, D.A. Fischer Advanced Materials, 15, 1545 (2003)

Validation of molecular gradients for nanoparticle templates

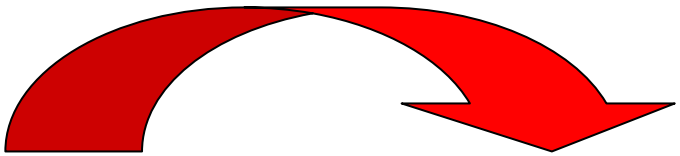
Templating using gradients

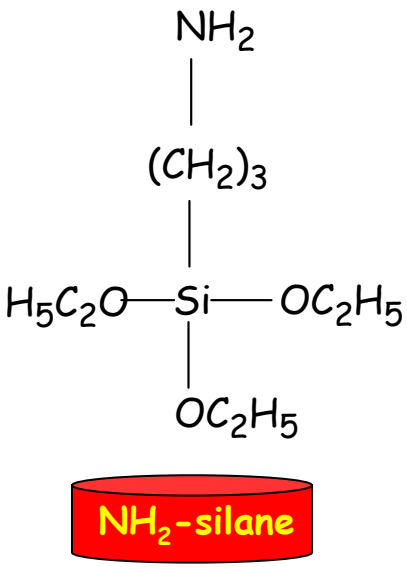
- Molecular gradients are envisioned as intriguing templates for creating materials assemblies;
- The dual nature of molecular gradients (discrete on molecular scales, continuous on meso scales) endows them with unique characteristics;



Forming nanoparticle gradients

"Molecular gradient template"

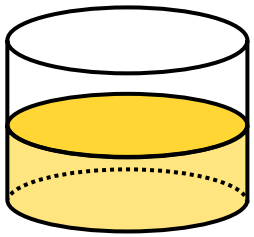




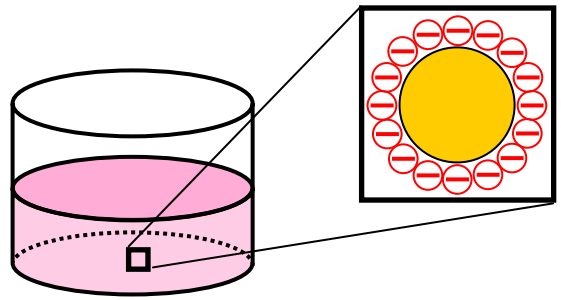
✓ 1. Create molecular a gradient of NH_2-terminated silane (APTES) on silica substrate (3–5 minutes)

(APTES - aminopropyl triethoxysilane, in paraffin oil)

Nanoparticles details
"Gold(-) solution"

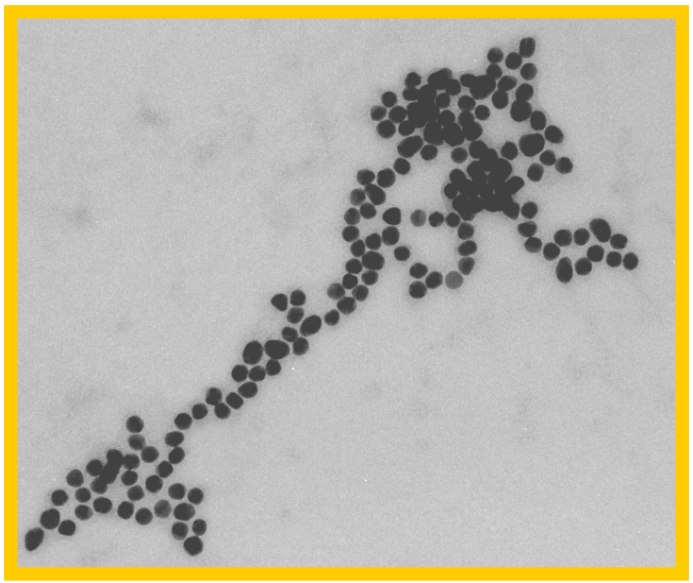


+ $Na_3Citrate$ ☛



solution of $HAuCl_4$

Aq. solution of Au nanoparticles
(pH ≈ 6.5)



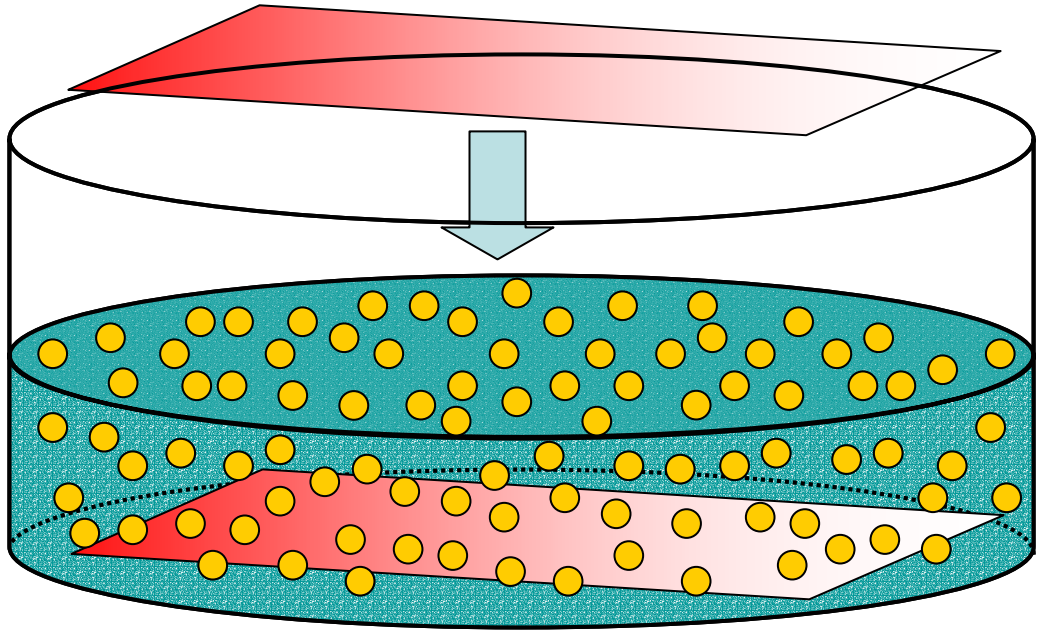
gold nanoparticles are uniform in size (17±2) nm

pH < 7.5 template $-NH_2$ strongly positively charged (forming $-NH_3^+$)

Hence for pH < 7.5 the adhesion between the APTES and the negatively charged Au nanoparticles is strong

Forming nanoparticle gradients

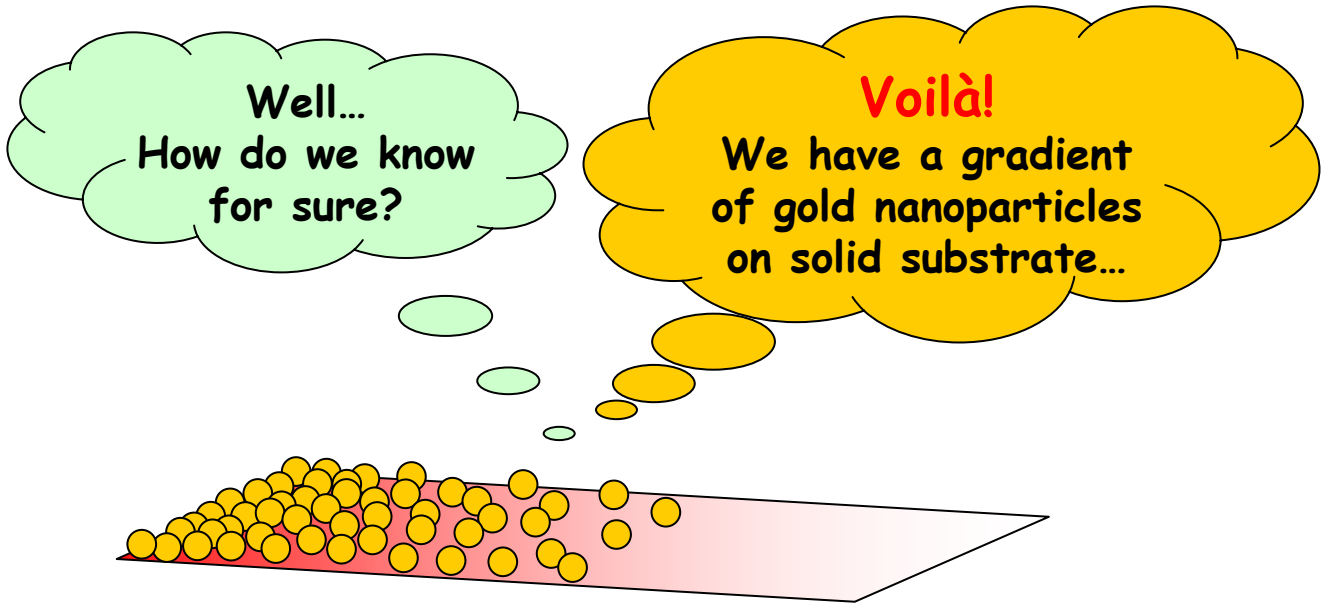
"Electrostatic attraction"



✓ 1. Create molecular a gradient of NH_2-terminated silane (APTES) on silica substrate (3–5 minutes)

✓ 2. Immerse (24 hours) NH_3^+ template in solution containing gold nanoparticles (neg. charged)

Forming nanoparticle gradients

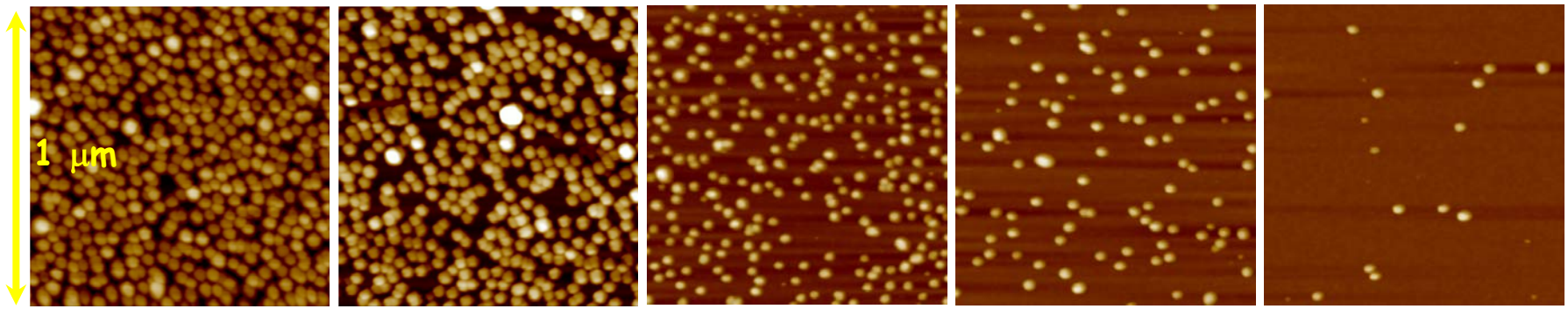


✓ 1. Create molecular a gradient of NH_2-terminated silane (APTES) on silica substrate

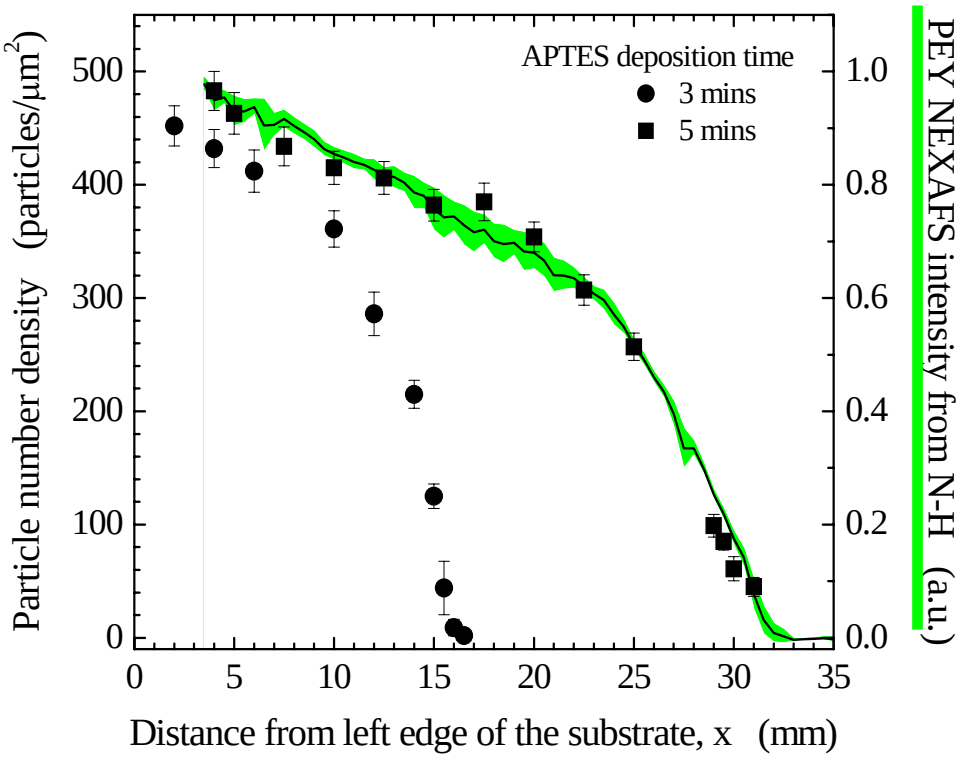
✓ 2. Immerse into solution containing gold nanoparticles

✓ 3. Remove from solution and wash any physisorbed molecules and weakly bound nanoparticles

Validation of molecular gradients for nanoparticle templates



(x=4) (x=15) (x=25) (x=29) (x=30)



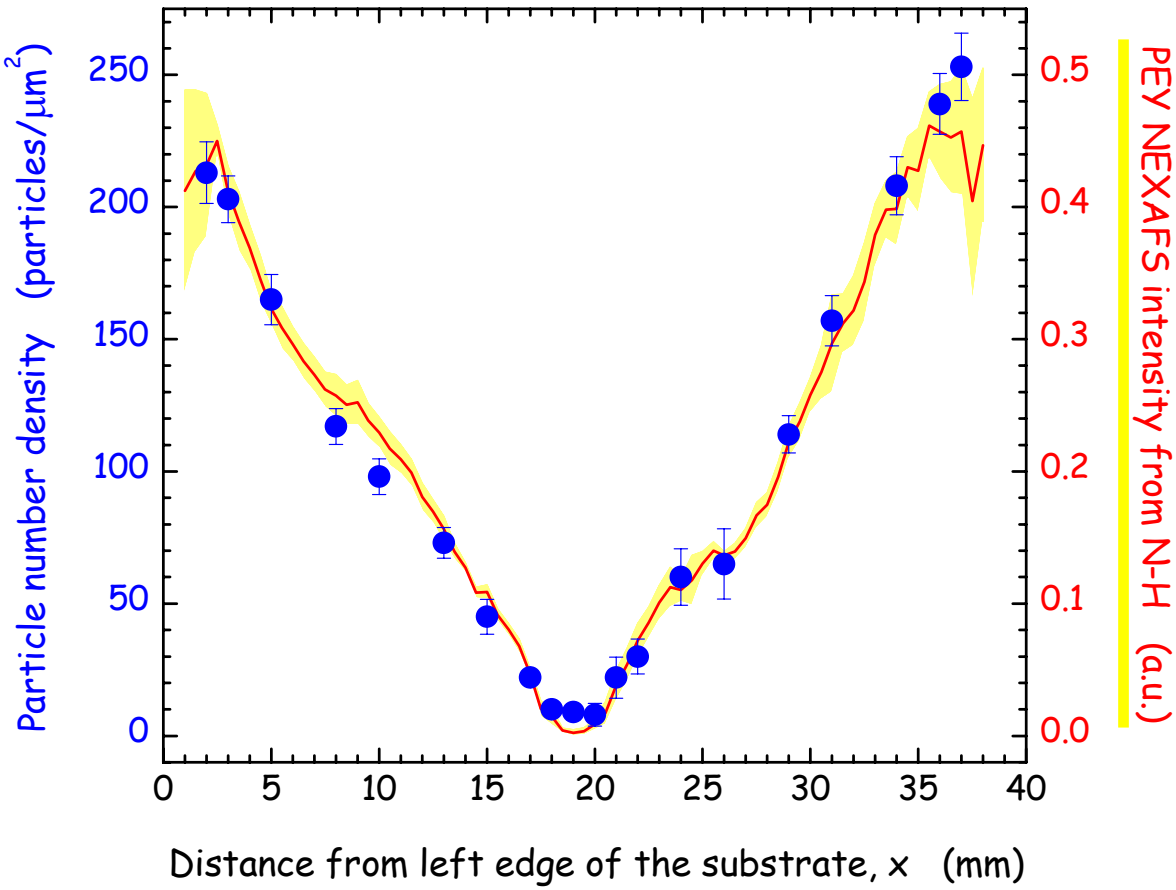
- **Number density of Au nanoparticles (by AFM) follows a gradient profile dictated by the APTES SAM template (by N-H NEXAFS)**
- **Increasing (decreasing) diffusion time of APTES results in broader (narrower) nanoparticle gradient**

(APTES - aminopropyl triethoxysilane)

Validation of molecular gradients for nanoparticle templates

How about multiple gradients of nanoparticles?

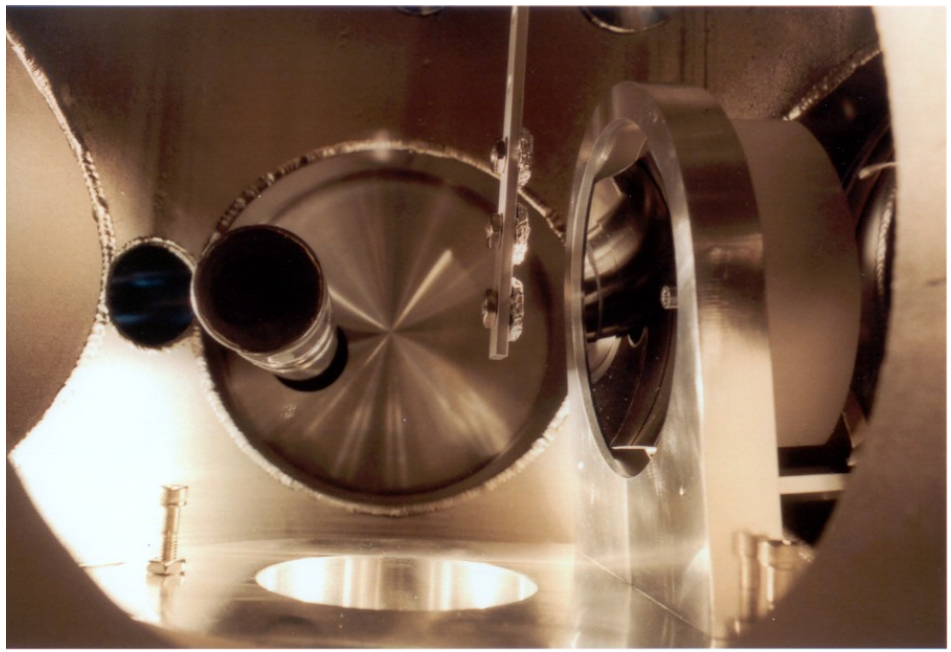
2 Sources of APTES in paraffin oil, 3 minute deposition



R. R. Bhat, D. A. Fischer, J. Genzer Langmuir, 18, 5640-5643 (2002)

Mapping the rehybridization of propylene on zeolite catalyst arrays (prototypical catalyst discovery)

Focusing multilayer mirror fluorescence detection system: Photon-in photon-out in-situ catalytic carbon K-edge NEXAFS*



- Catalyst library: five ZSM-5 zeolites
- Silica to alumina ratio: 31.6 (highest acidity) to 280 (lowest acidity)
- Propylene dosing (10 kPa for 10 minutes at room temperature)

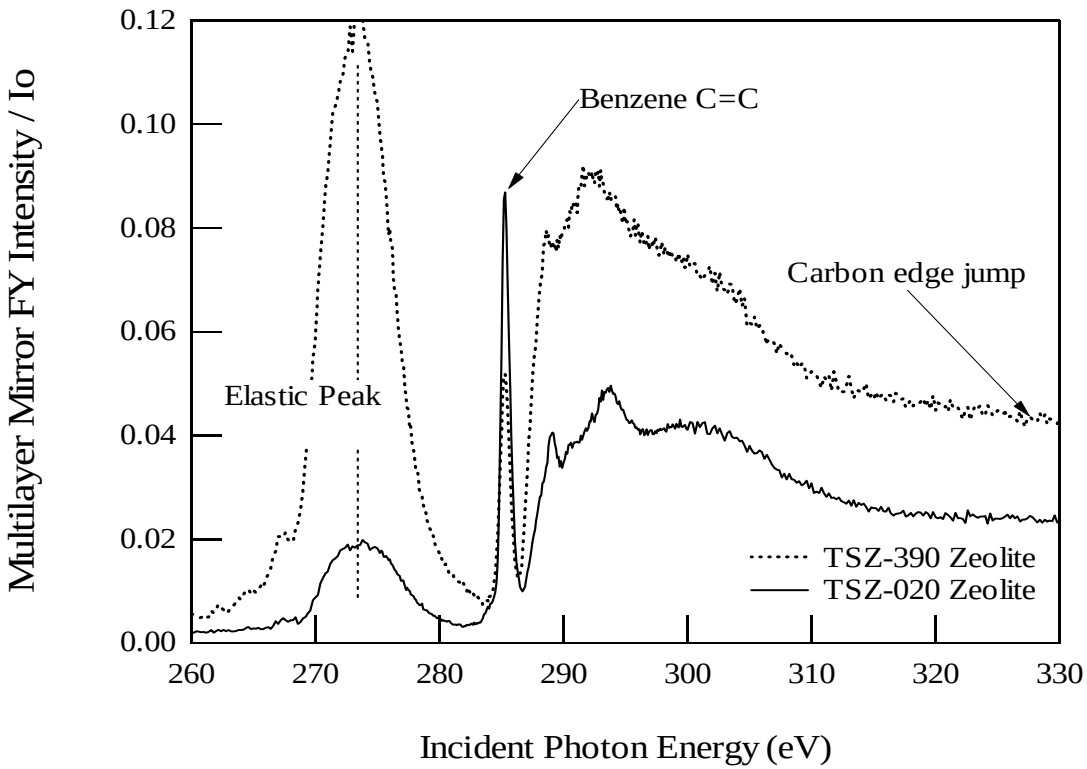
*D.A. Fischer, S. Sambasivan, A. Kuperman, Y. Platonov and J.L. Wood Rev. of Sci. Instruments, 2002(73)1469-1475

Mapping the rehybridization of propylene on zeolite catalyst arrays (prototypical catalyst discovery)

Fluorescence yield carbon K-edge NEXAFS
Benzene dosed zeolites: TSZ-20 (solid) and a TSZ-390 (dashed)

•Near zero background

•Direct in-situ observation of catalytic reaction intermediates



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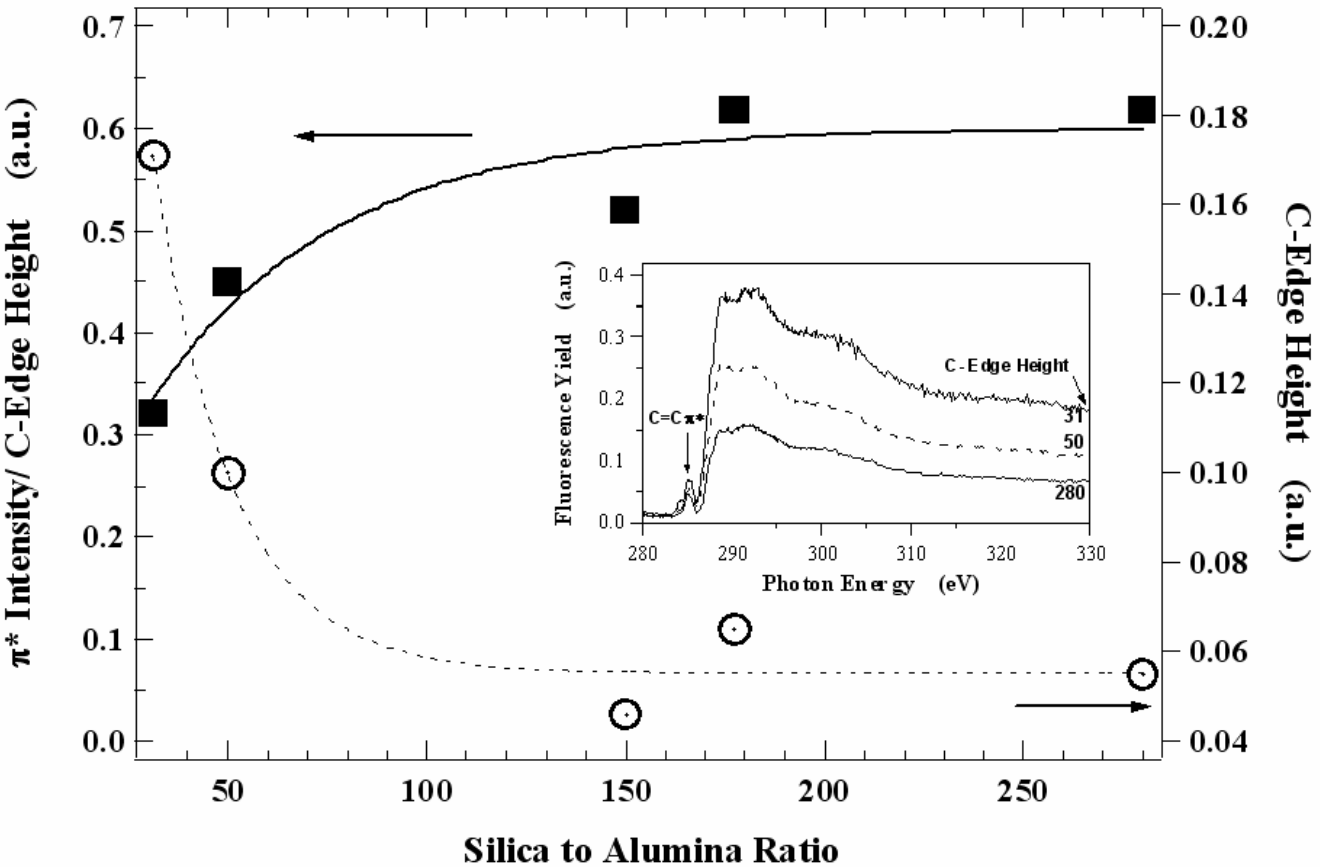
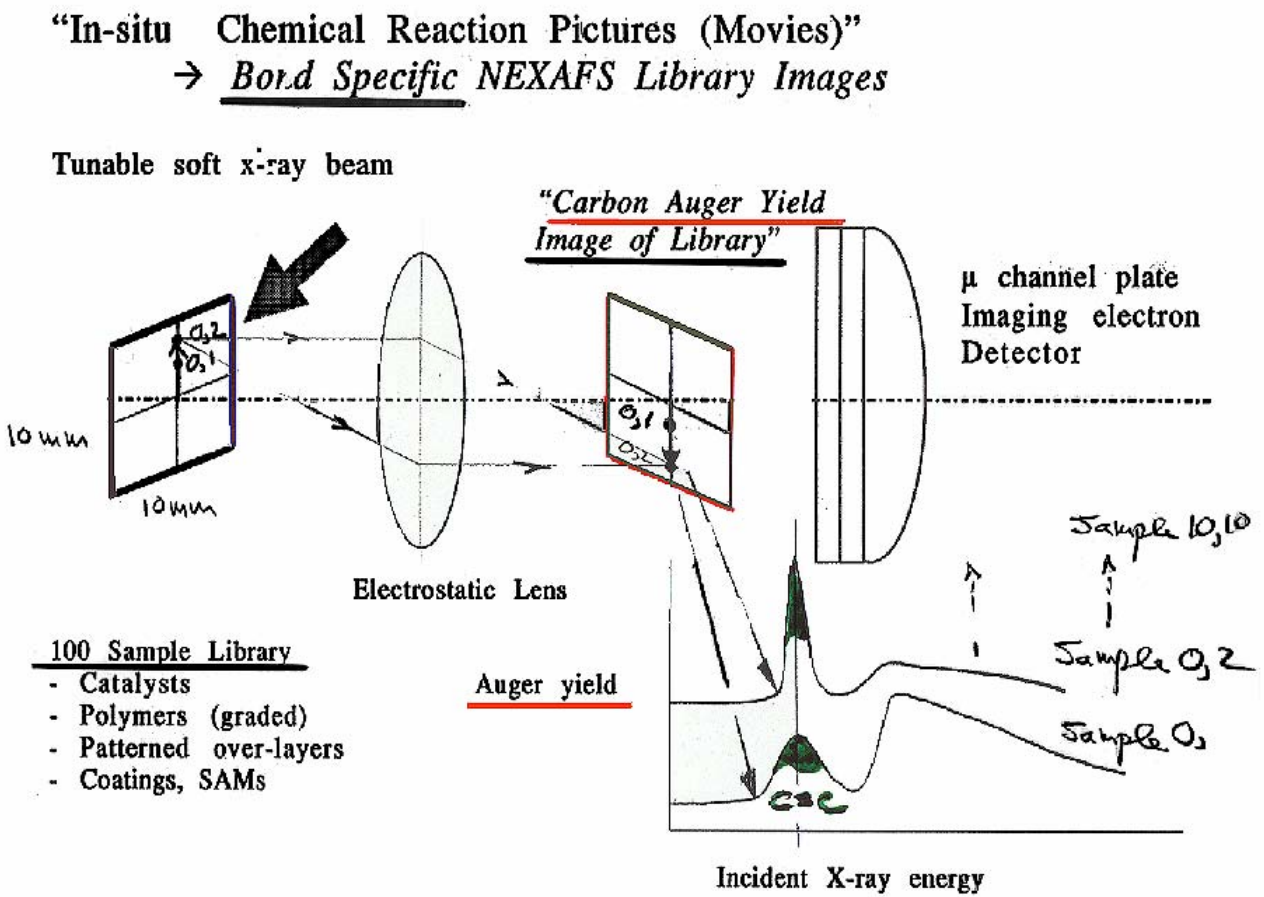


Most acidic ZSM-5 has highest activity

What's next?

Parallel process imaging: Combi-NEXAFS pictures and movies

Nano-movie! "When monolayers collide"



NIST SBIR phase 1 (2?): Large Area Imaging Two-Dimensional Electron Energy Analyzer

WHEN MONOLAYERS COLLIDE

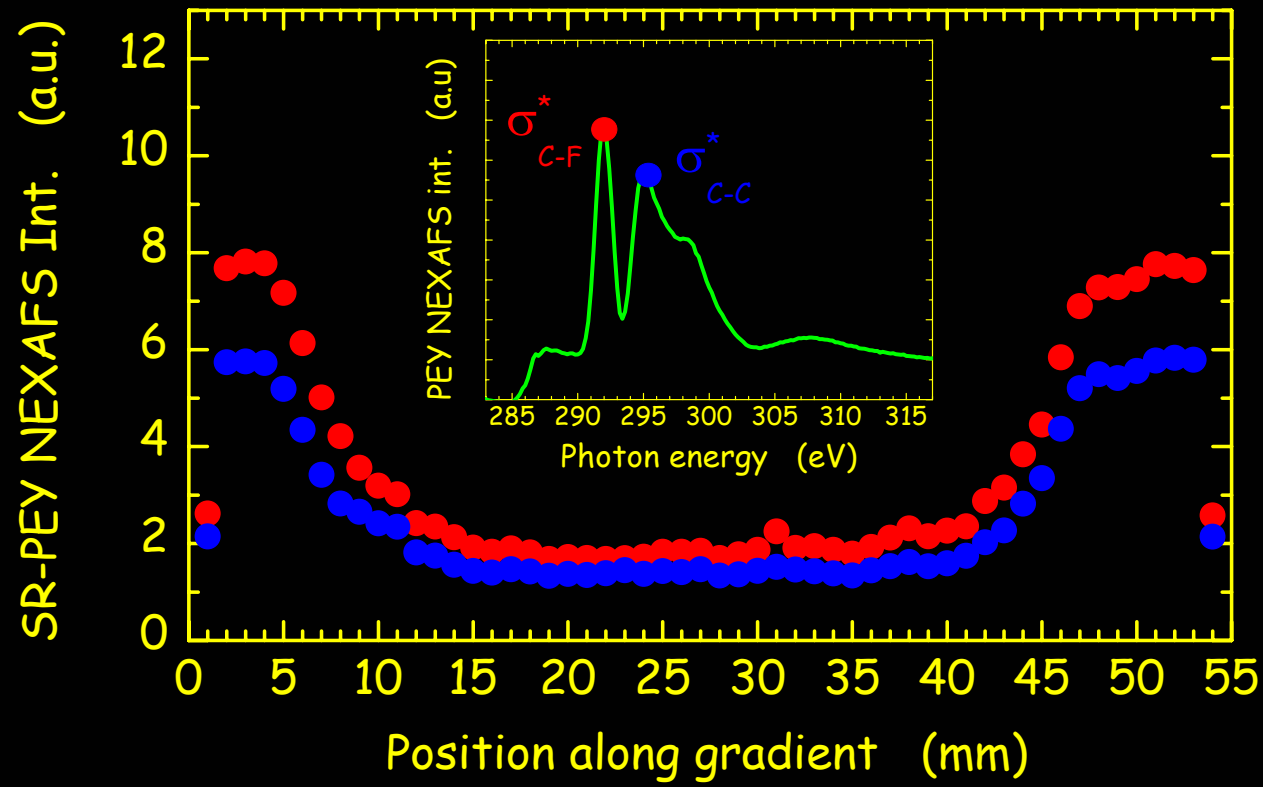
A sneak preview of a new nanomovie

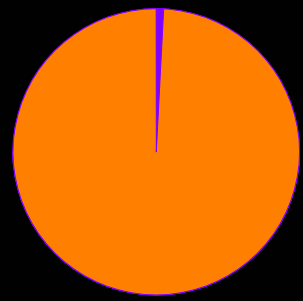
Staring very small actors with very big roles

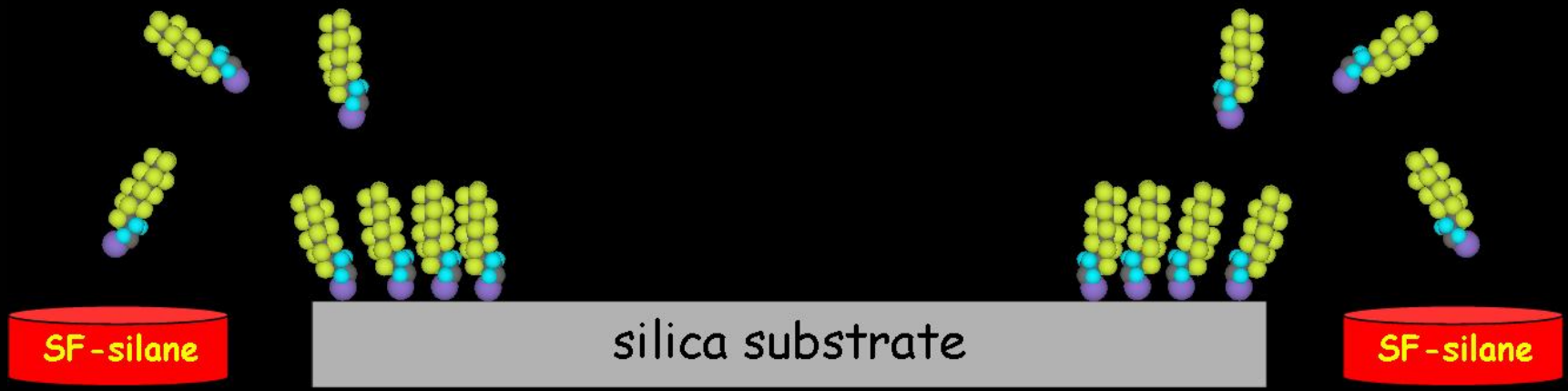
Coming soon to selected Laboratories near you!

Rating XXX – Xtremely Xciting X-rays

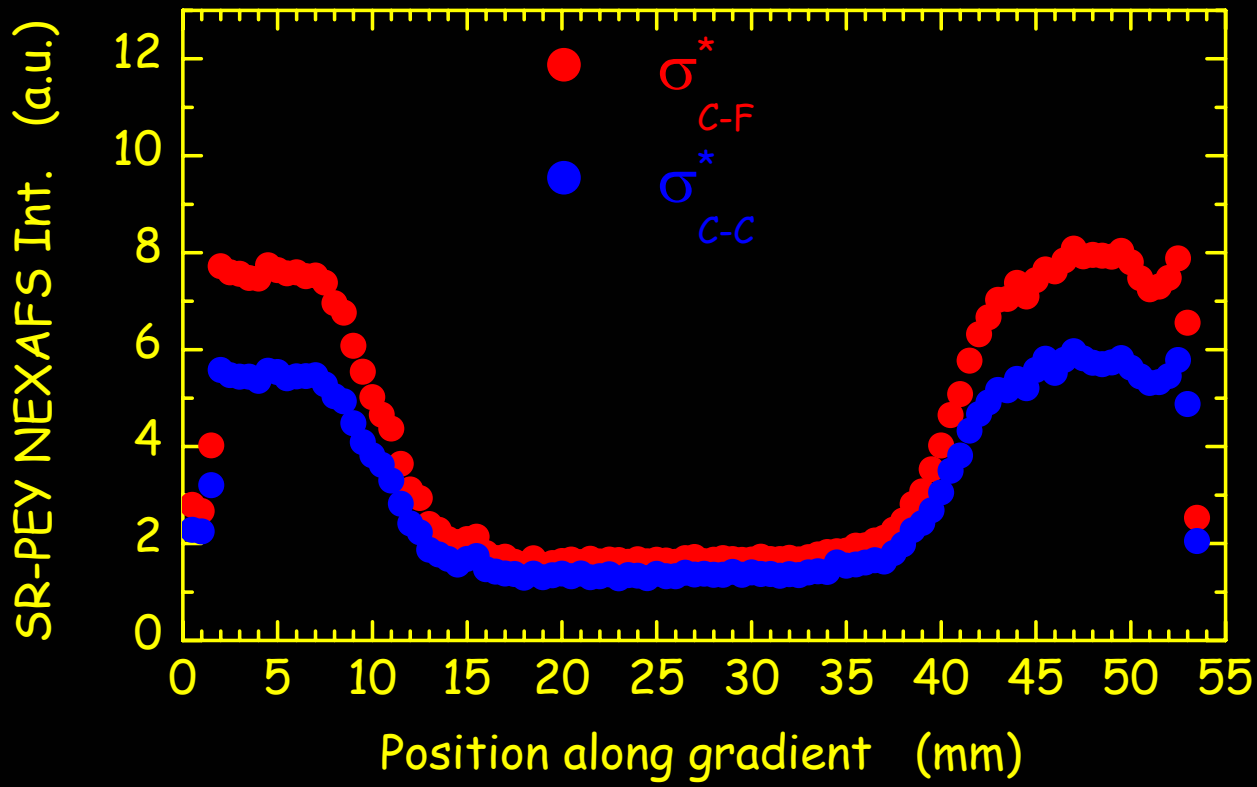
Double gradient of F8H2-SAMs on a silicon wafer

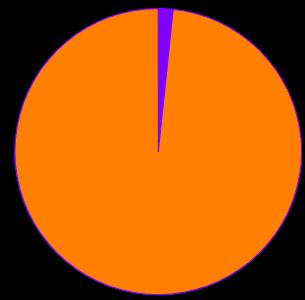


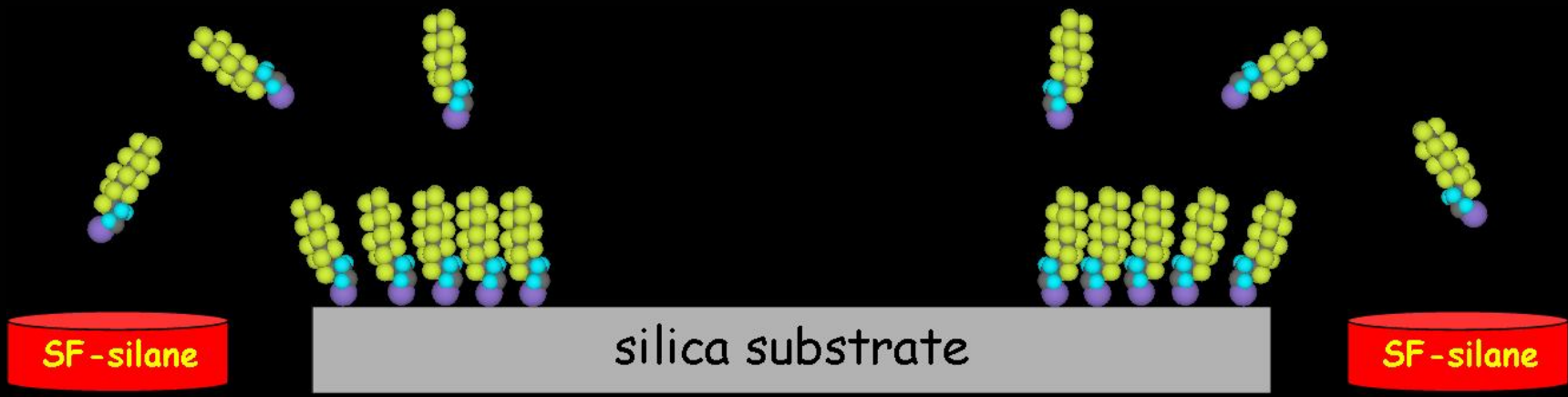




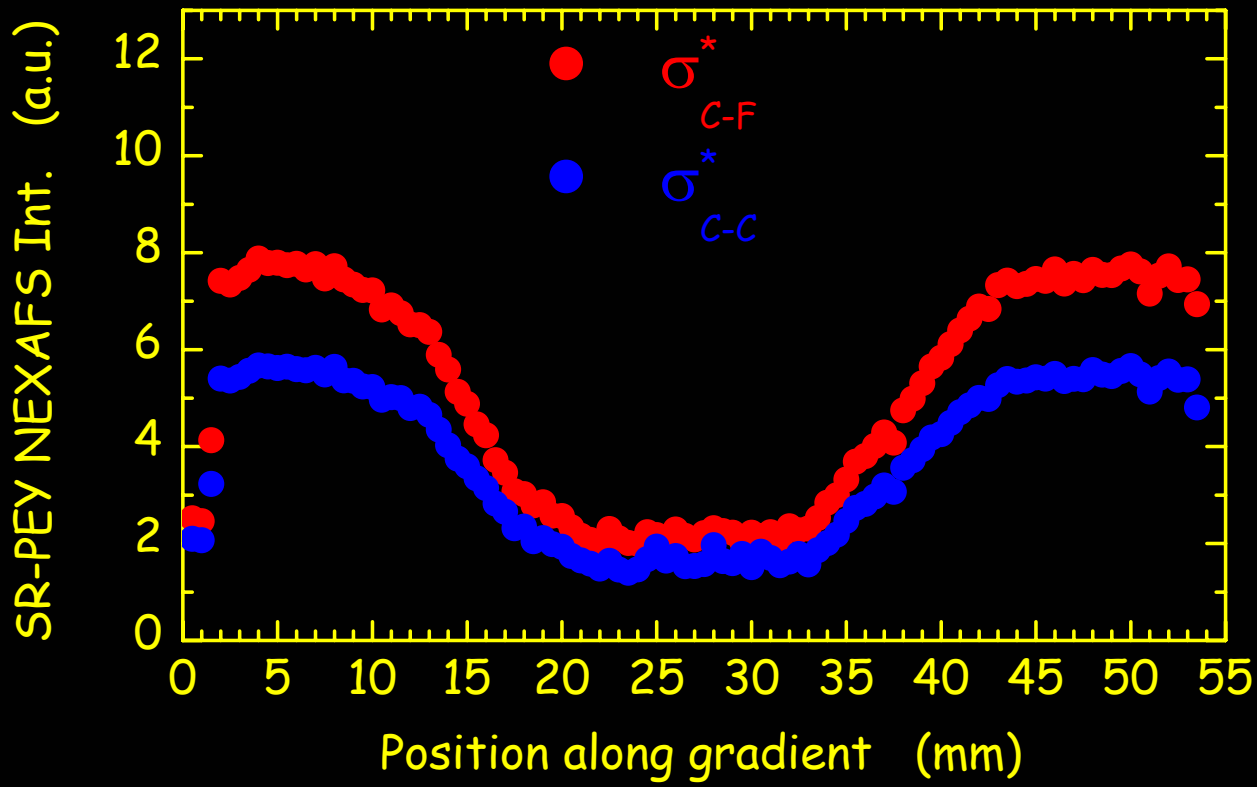
Double gradient of F8H2-SAMs on a silicon wafer

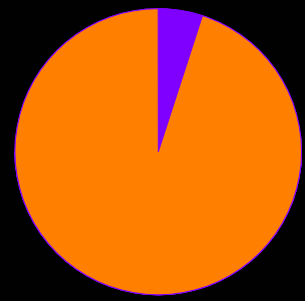


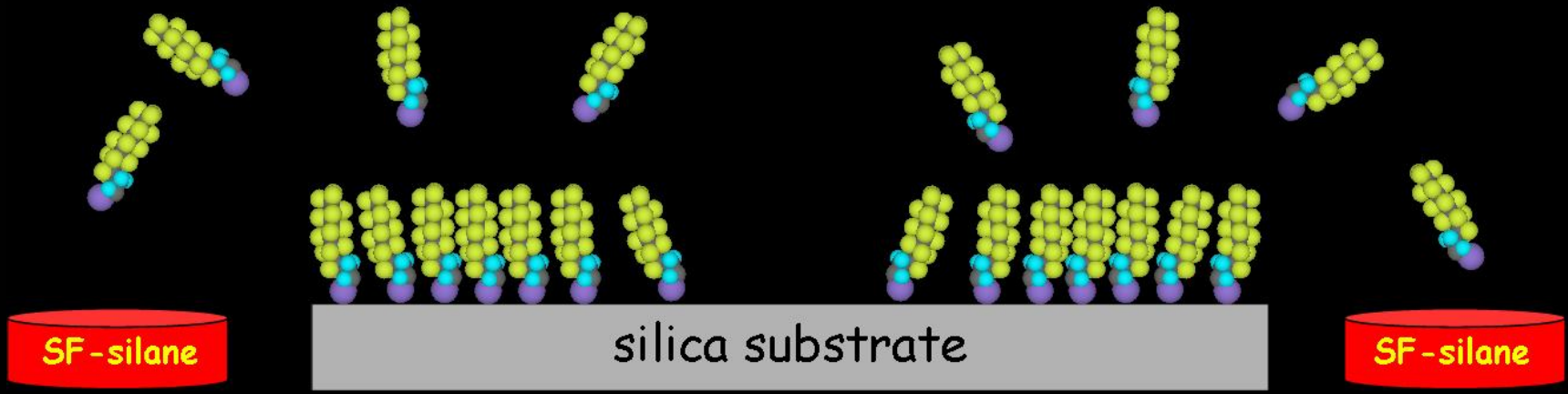




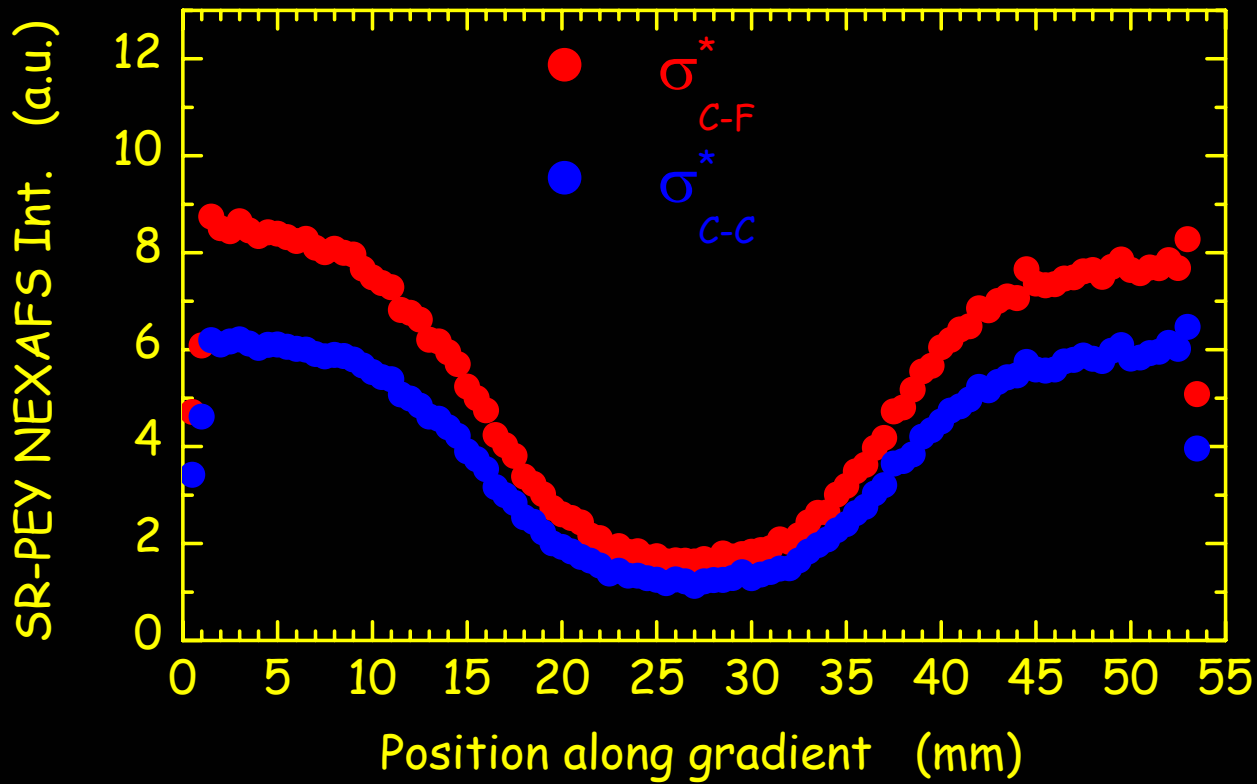
Double gradient of F8H2-SAMs on a silicon wafer

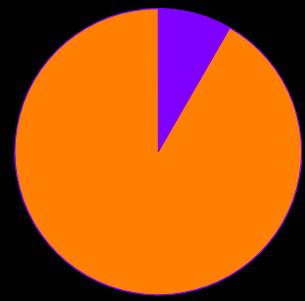


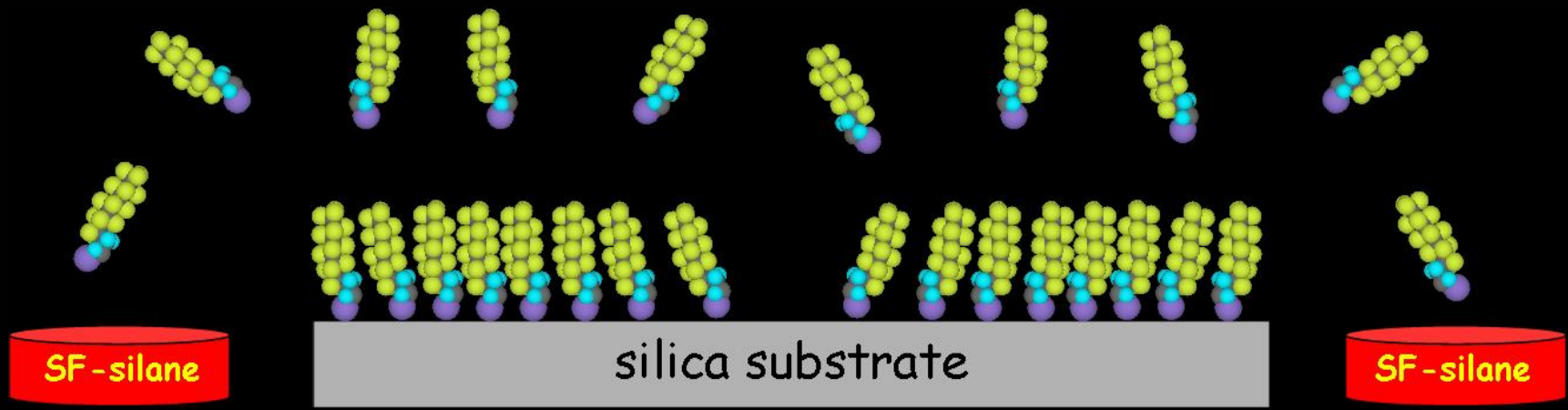




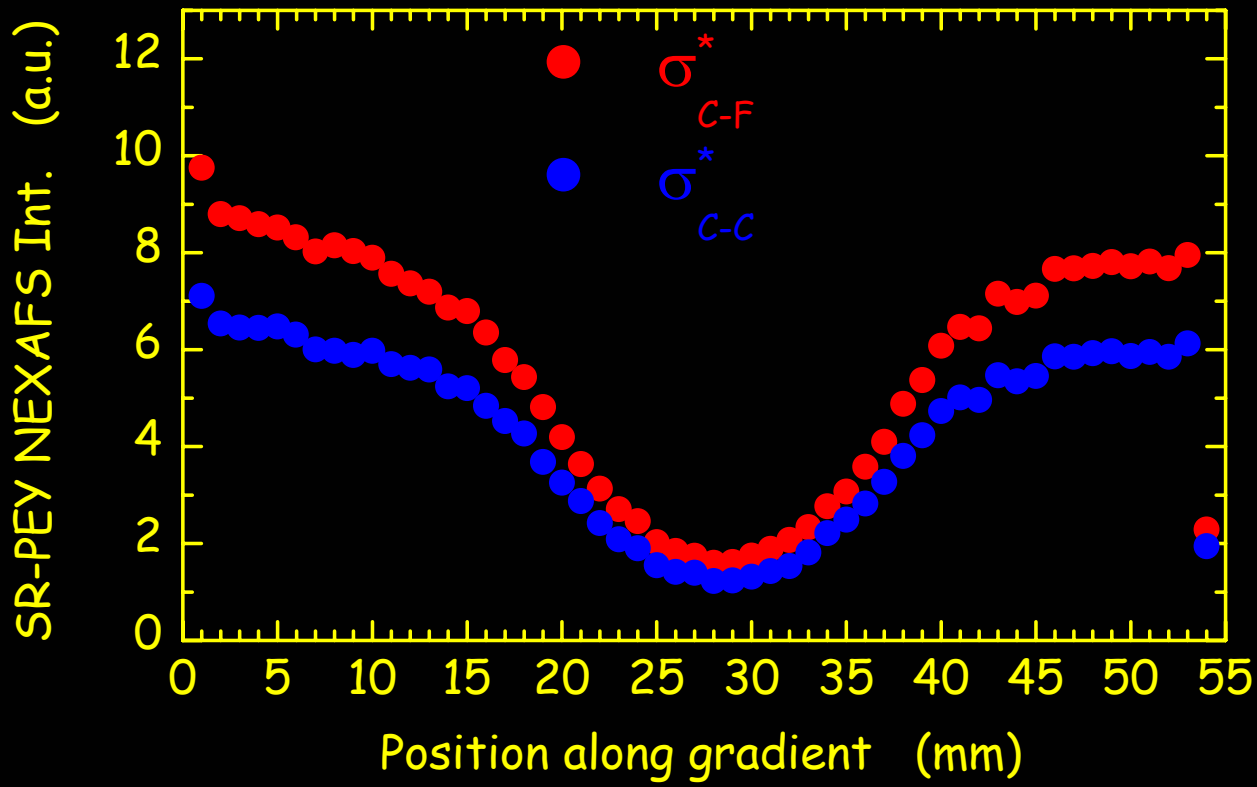
Double gradient of F8H2-SAMs on a silicon wafer

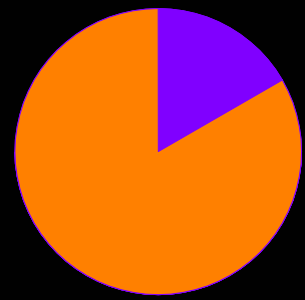




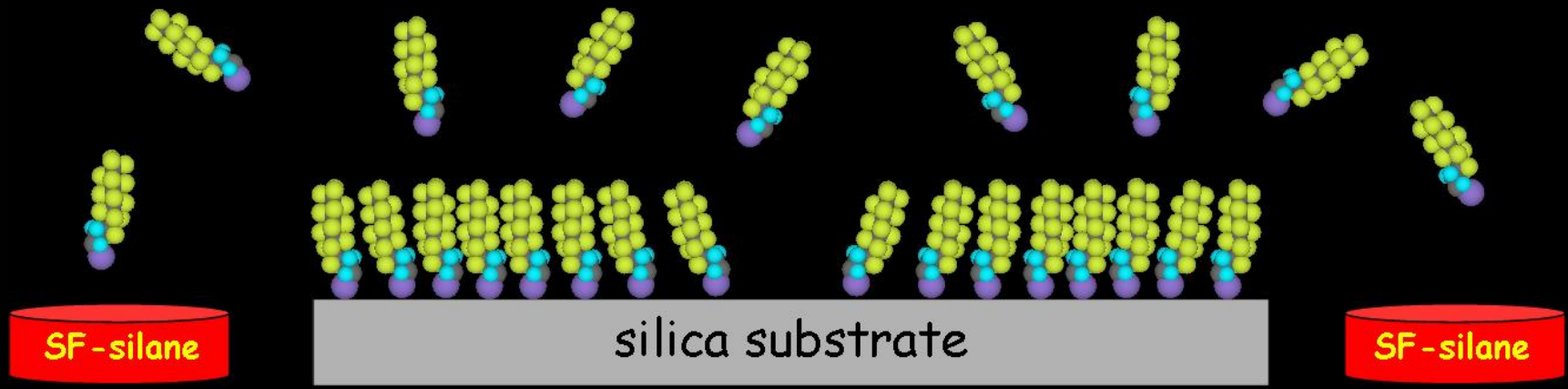


Double gradient of F8H2-SAMs on a silicon wafer

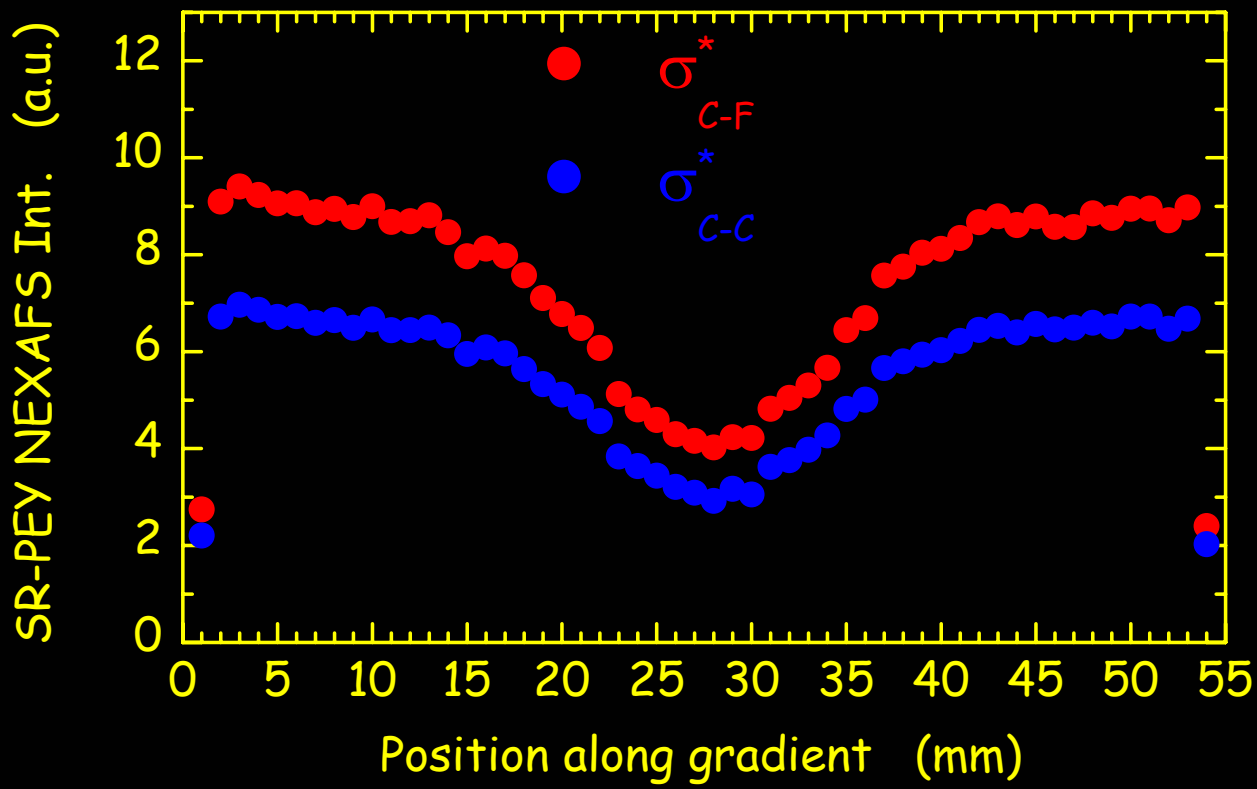


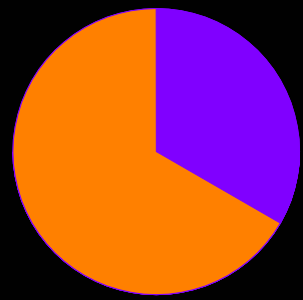


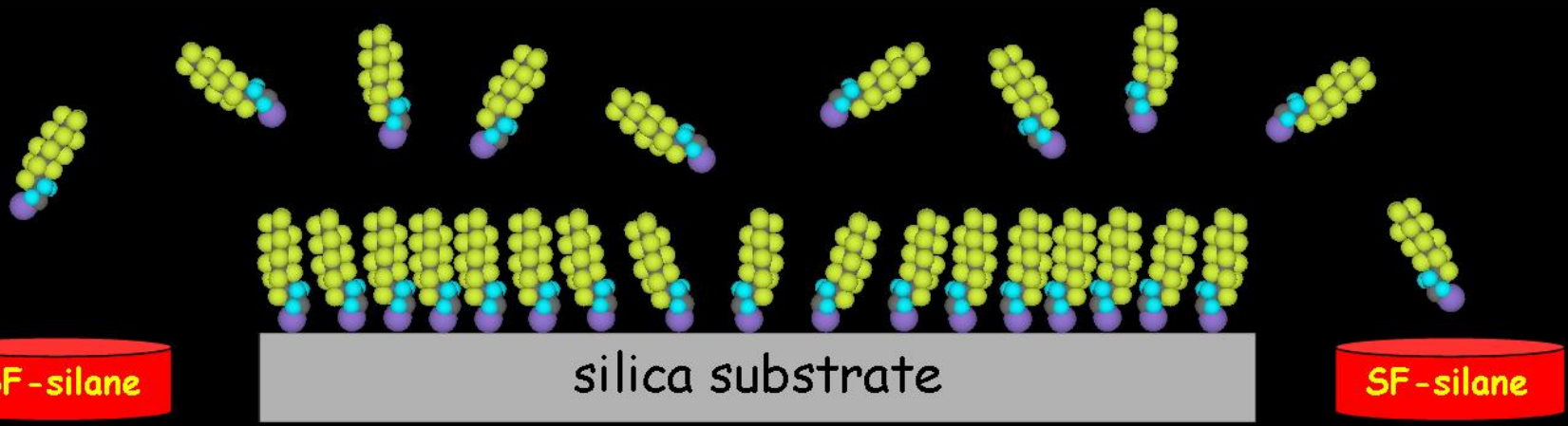
10 mins



Double gradient of F8H2-SAMs on a silicon wafer







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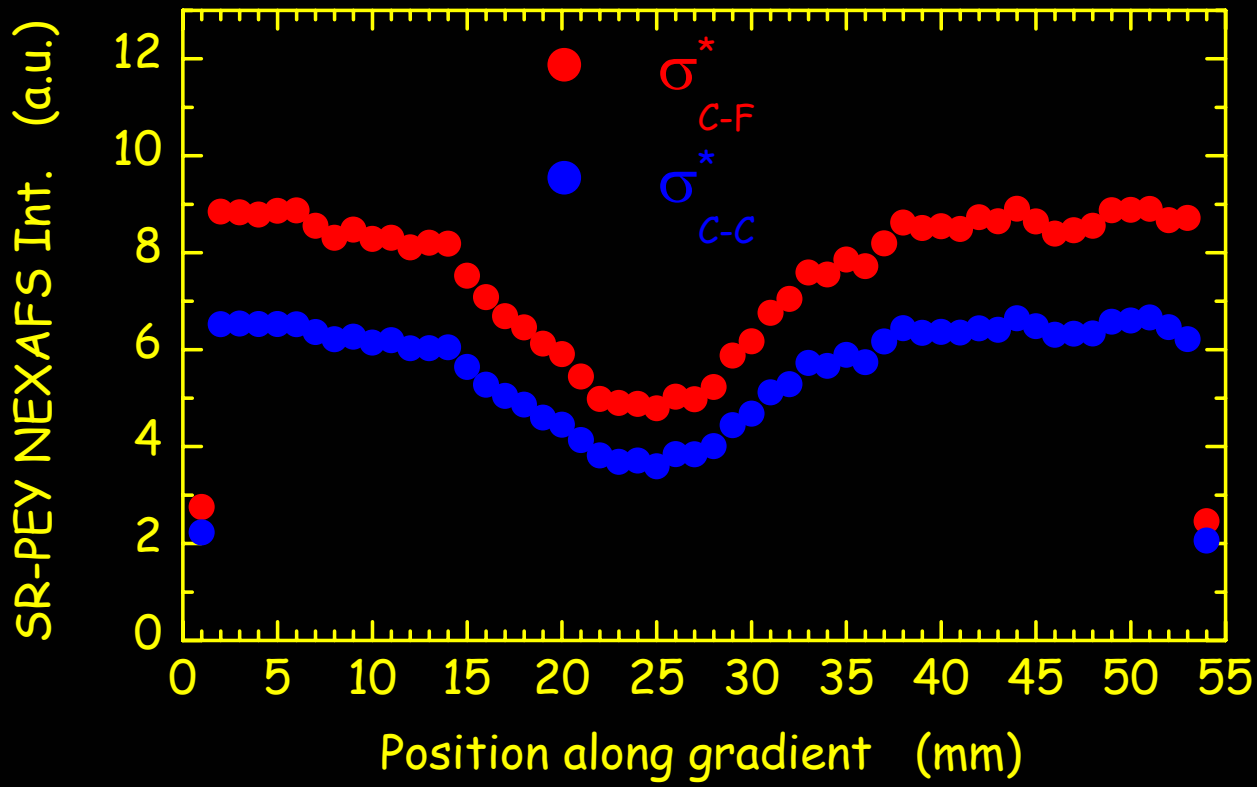

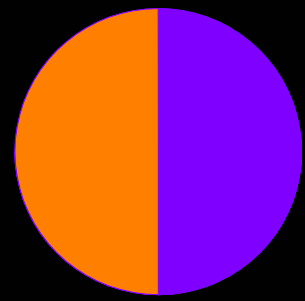

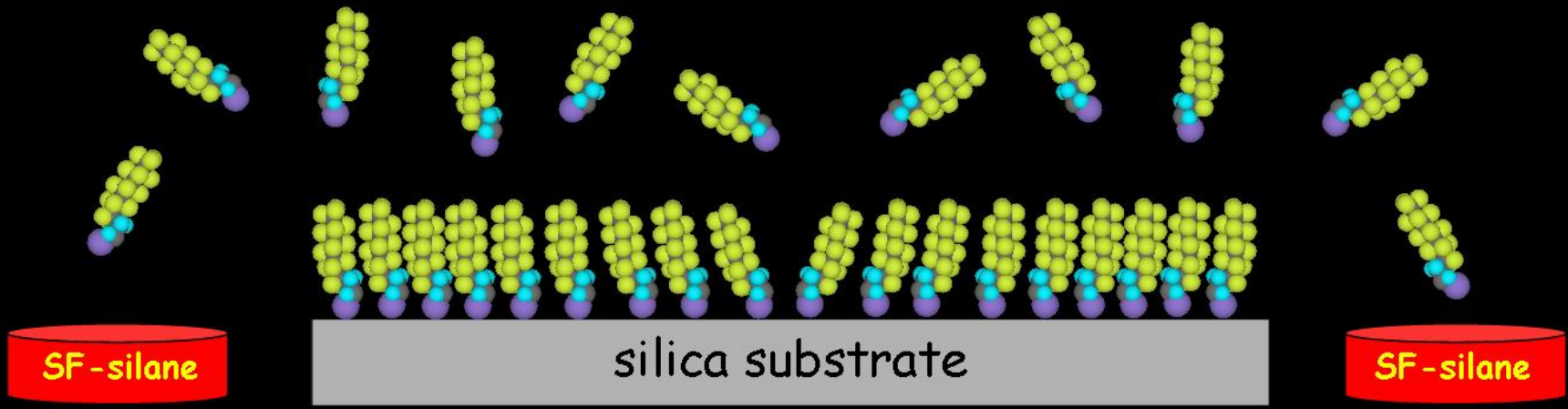

Conclusions

- **Introduction to combinatorial NEXAFS**
- **Mapping molecular bond concentration and orientation**

  Molecular gradients (1D and 2D)

  Validation of molecular gradients for nanoparticle templates
- **Mapping the rehybridization of propylene on zeolite catalyst arrays (prototypical catalyst discovery experiment)**
- ***Parallel process imaging: Combi-NEXAFS pictures and movies***
- **Review Paper: D.A. Fischer, K. Efimenko, R.R. Bhat, S. Sambasivan, and J. Genzer Macromolecular Rapid Communications, 25, 141 (2004).**