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Science and  
Technology  
Facilities Council

# Bringing X-ray photoelectron spectroscopy into the ultrafast regime

Charlotte Sanders  
UK Central Laser Facility, Artemis Program

IMPACT 2024

# Overview

X-ray photoelectron spectroscopy (XPS)



X-ray photoelectron diffraction (XPD)

- Key questions
- Fundamentals of techniques
- Analysis & interpretation
- **Moving to the ultrafast regime**



# Acknowledgements

VILLUM FONDEN



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  - K. Bühlmann, R. Gort, Y. Acremann



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- Technische Universität Chemnitz, Germany
  - F. Speck, T. Seyller

- Kiel University, Kiel, Germany
  - F. Diekmann, K. Rossnagel



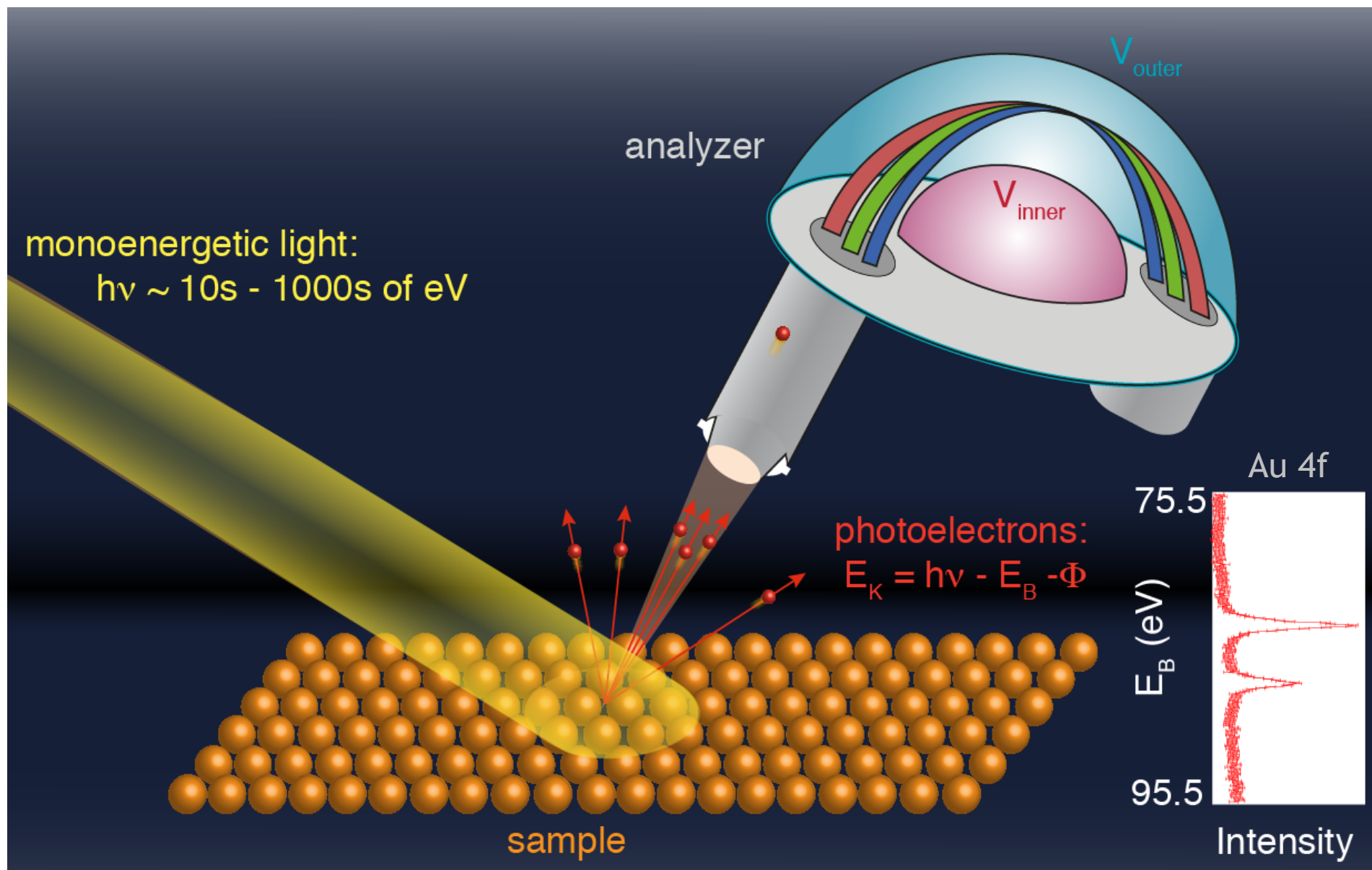
JOHANNES GUTENBERG  
UNIVERSITÄT MAINZ



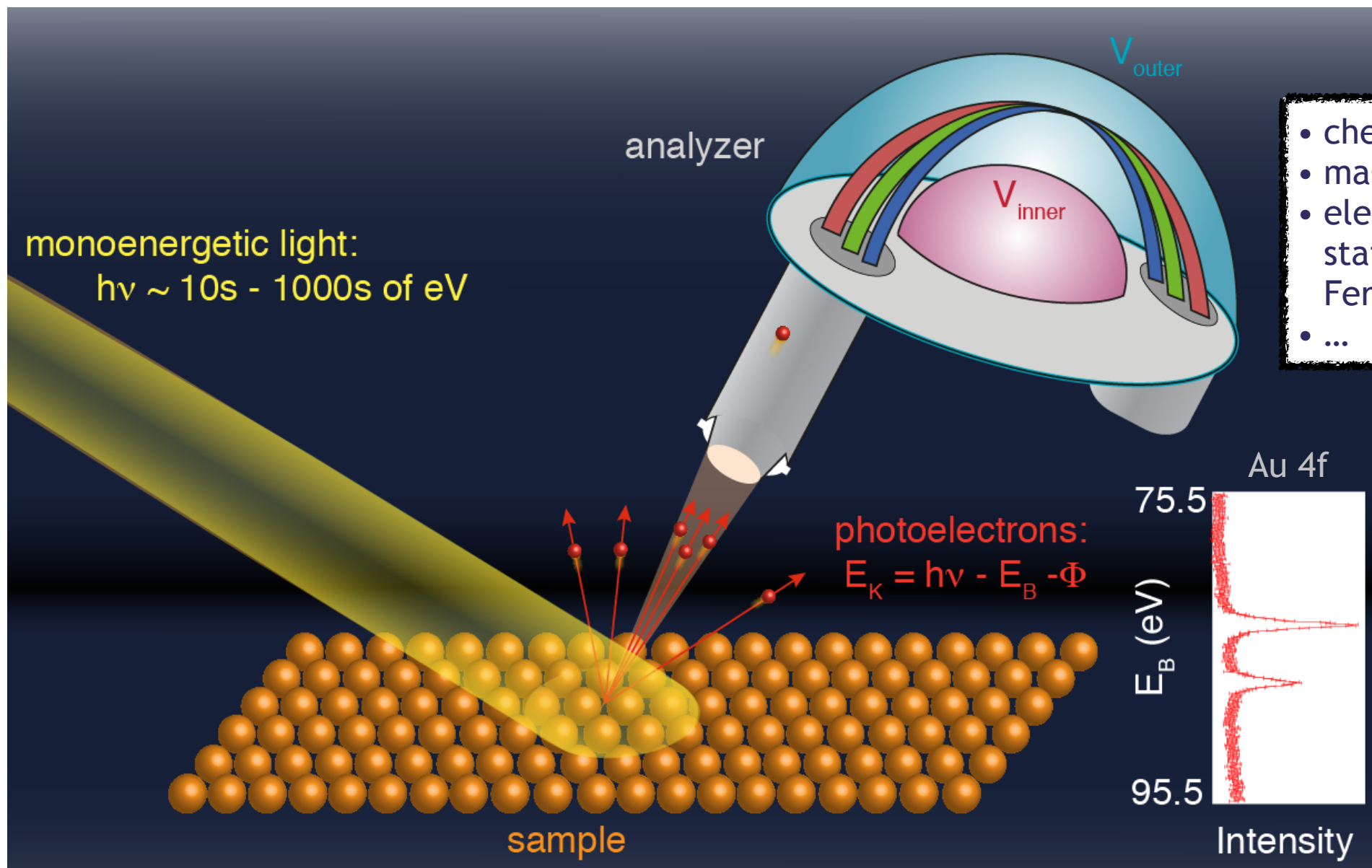
Elettra Sincrotrone Trieste



# X-ray photoelectron spectroscopy (XPS)

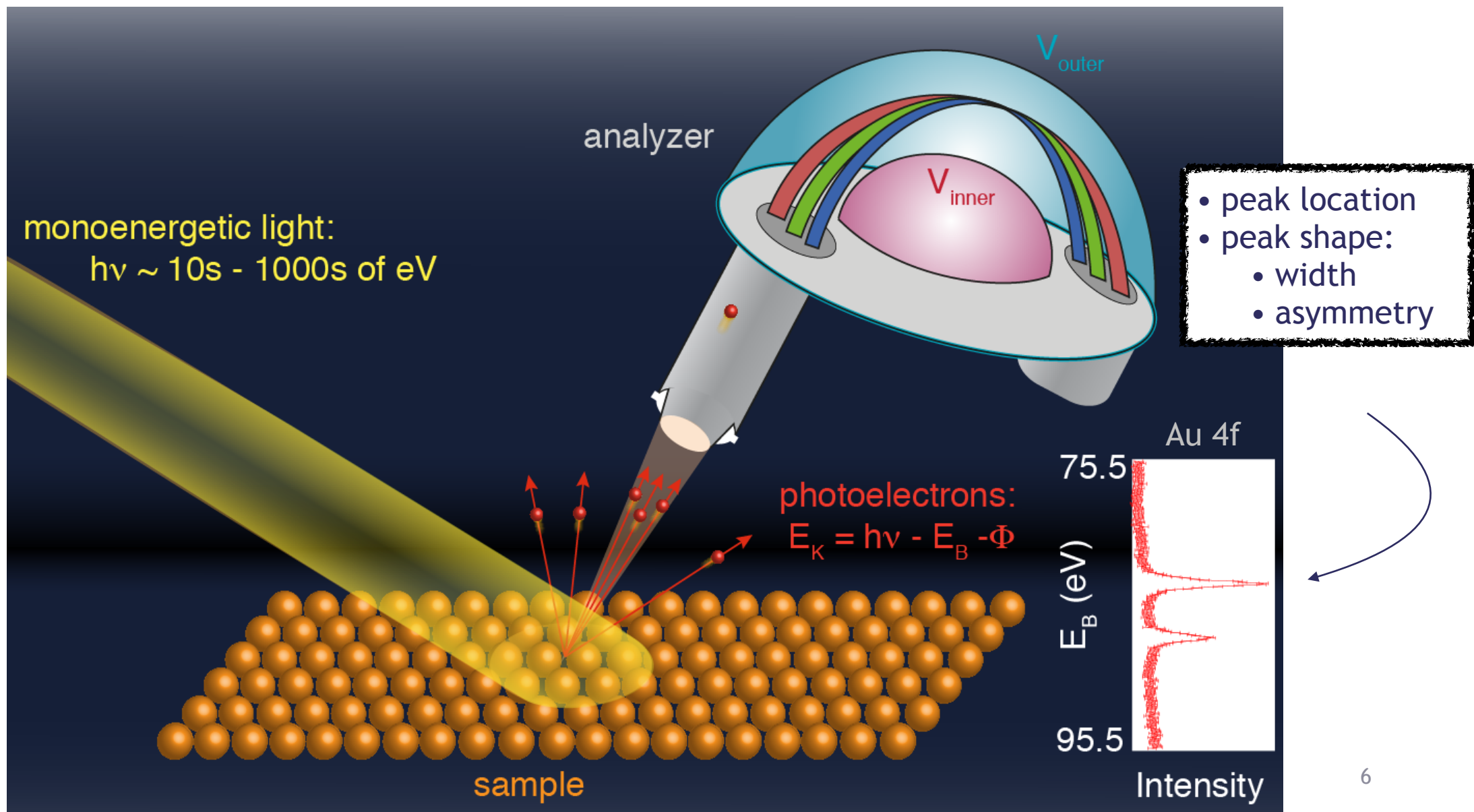


# X-ray photoelectron spectroscopy (XPS)



- chemistry
- magnetism/spin
- electronic states close to Fermi level
- ...

# X-ray photoelectron spectroscopy (XPS)



# Photoemission lineshape

$$I(E) \propto \int_{-\infty}^{+\infty} \left[ e^{-iEt} e^{-iE_0t} e^{-\lambda|t|} e^{-\frac{\sigma^2 t^2}{2}} \times \exp\left( \int_0^{+\infty} J(E') \frac{e^{iE't} - 1}{E'^2} dE' \right) \right] dt$$

$\lambda$  = Lorentzian width  
(photohole lifetime)

$\sigma$  = Gaussian width  
(phononic excitations, experimental energy resolution)

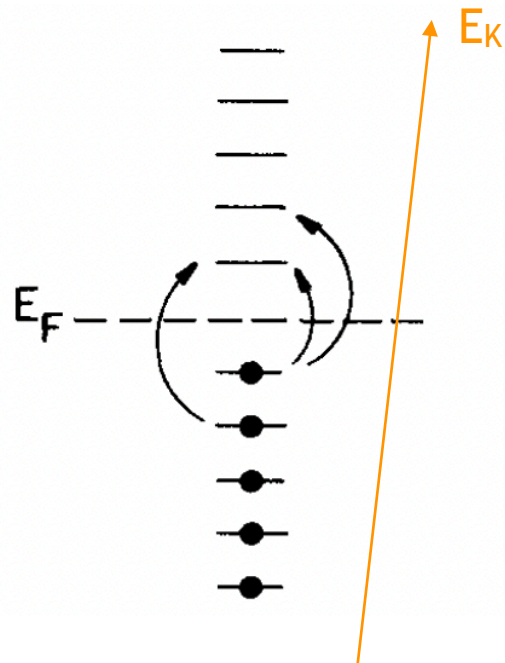
Hughes & Scarfe—*J. Phys.: Cond. Matt.* 8 (1996) 1421

# Photoemission lineshape

$$I(E) \propto \int_{-\infty}^{+\infty} \left[ e^{-iEt} e^{-iE_0t} e^{-\lambda|t|} e^{-\frac{\sigma^2 t^2}{2}} \times \exp\left( \int_0^{+\infty} J(E') \frac{e^{iE't} - 1}{E'^2} dE' \right) \right] dt$$

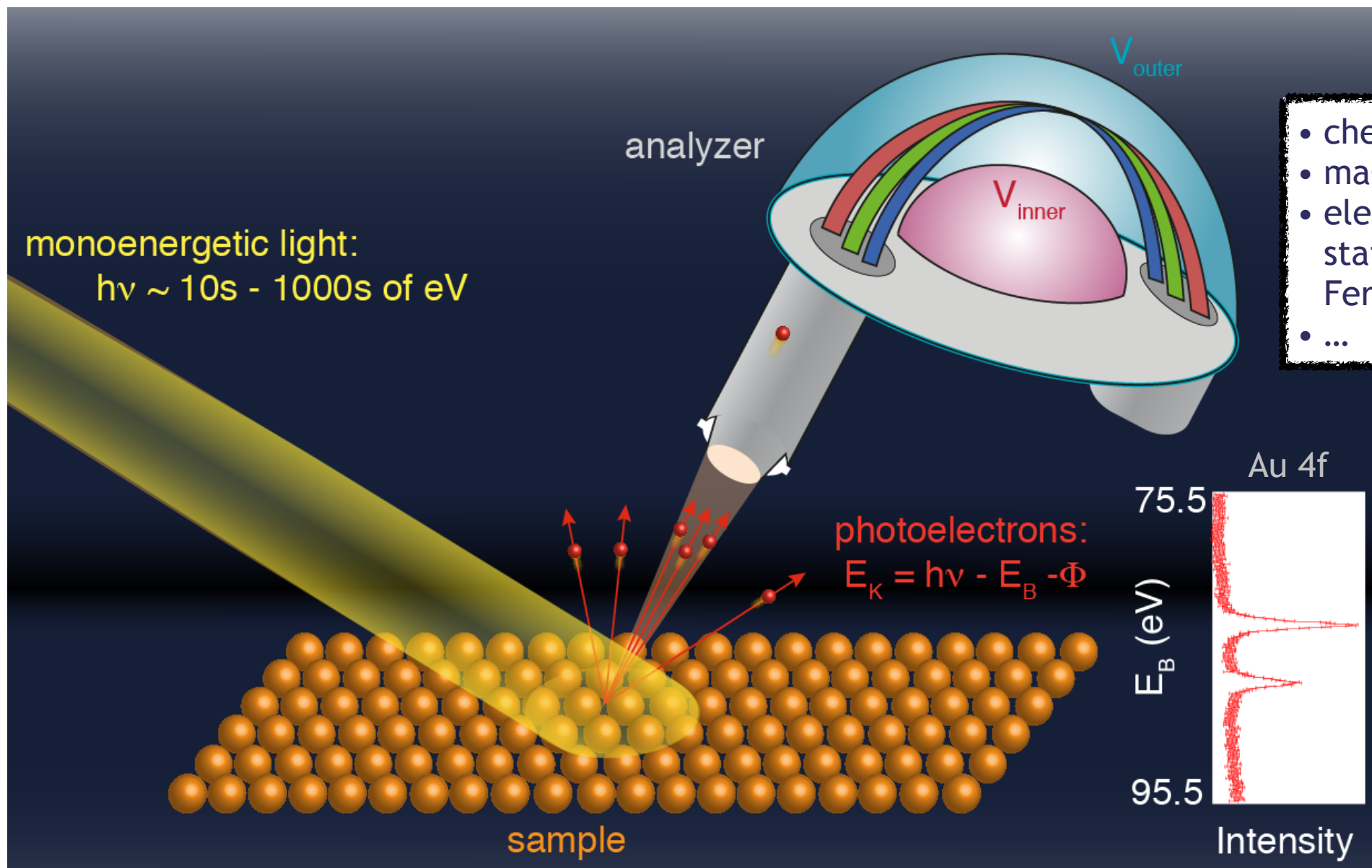
low-energy losses during photoemission

$J(E')$ : density of excitations (T=0K)



Hughes & Scarfe—*J. Phys.:*  
*Cond. Matt.* 8 (1996) 1421

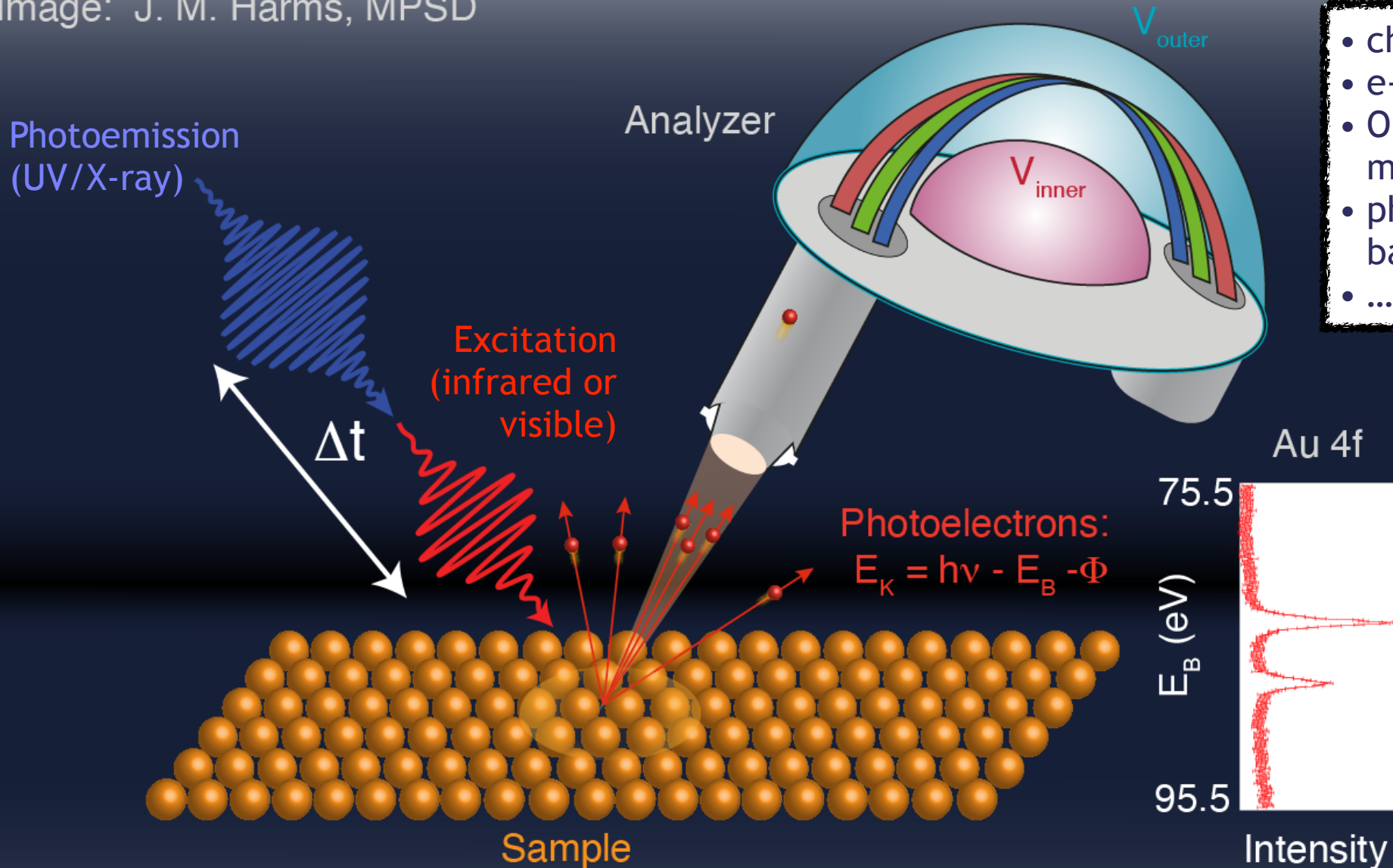
# X-ray photoelectron spectroscopy (XPS)



- chemistry
- magnetism/spin
- electronic states close to Fermi level
- ...

# Extending our model to dynamical systems

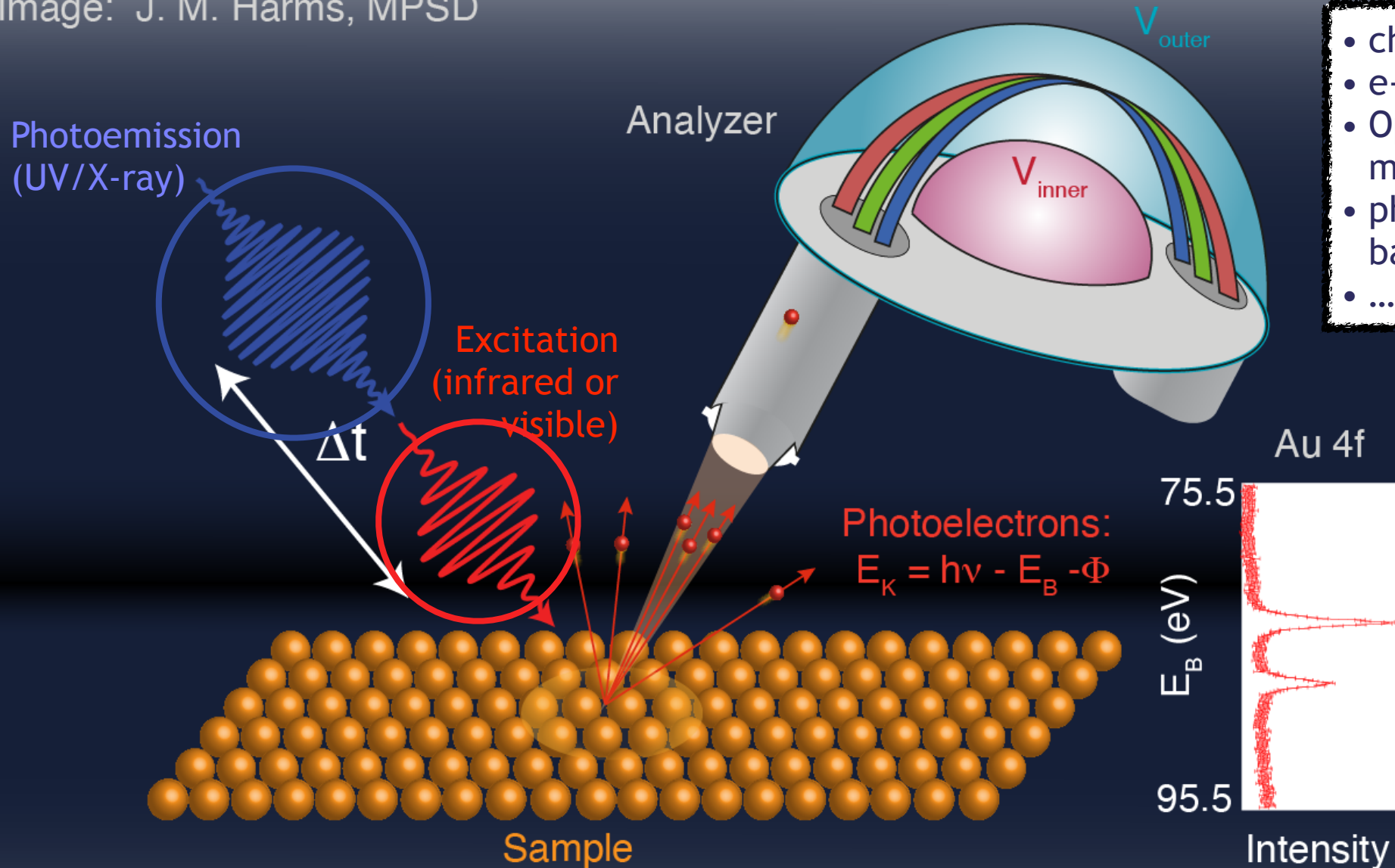
Image: J. M. Harms, MPSD



- chemical processes
- e-ph coupling
- Optical excitations of magnetic/spin states
- physics in conduction band
- ...

# Extending our model to dynamical systems

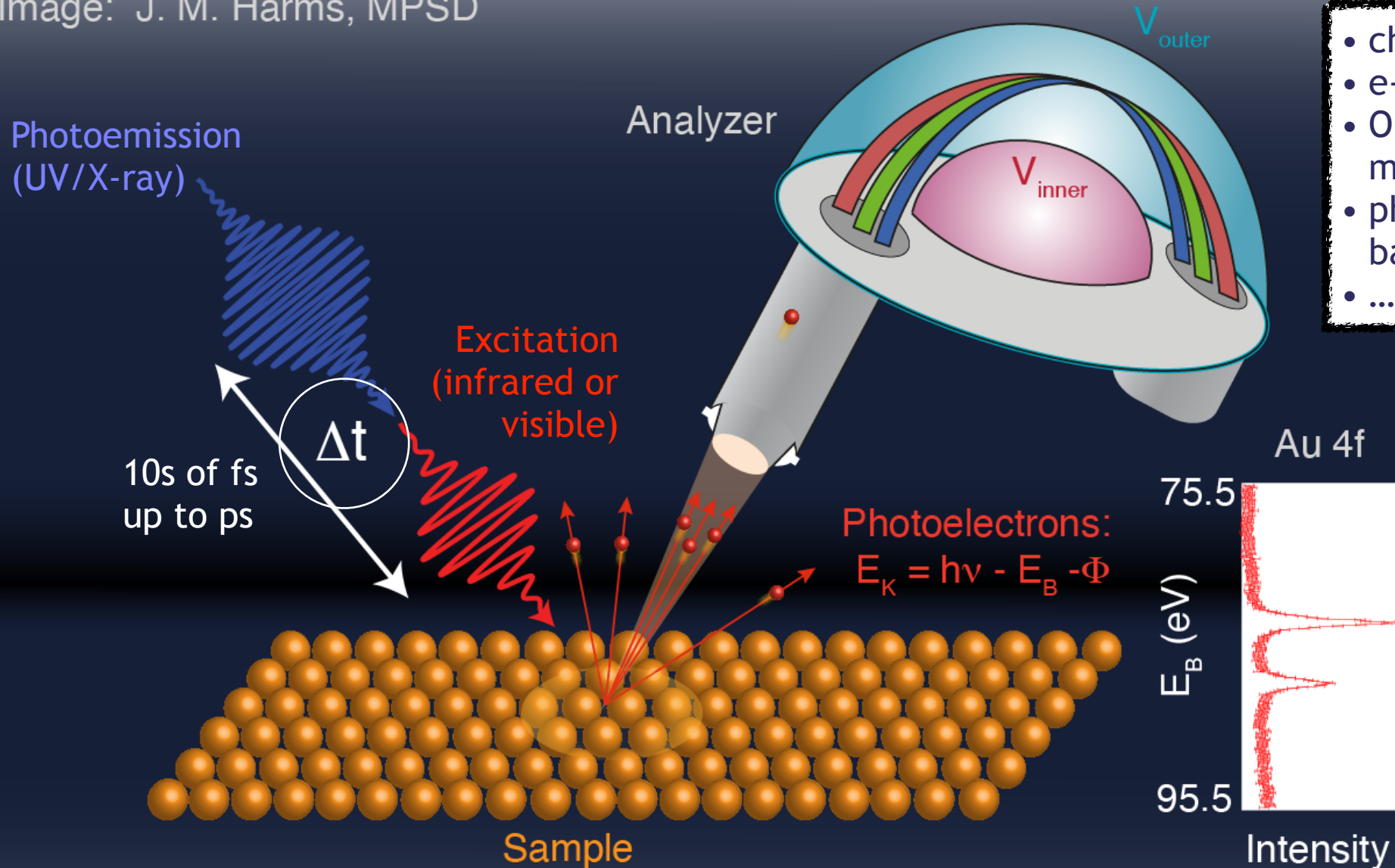
Image: J. M. Harms, MPSD



- chemical processes
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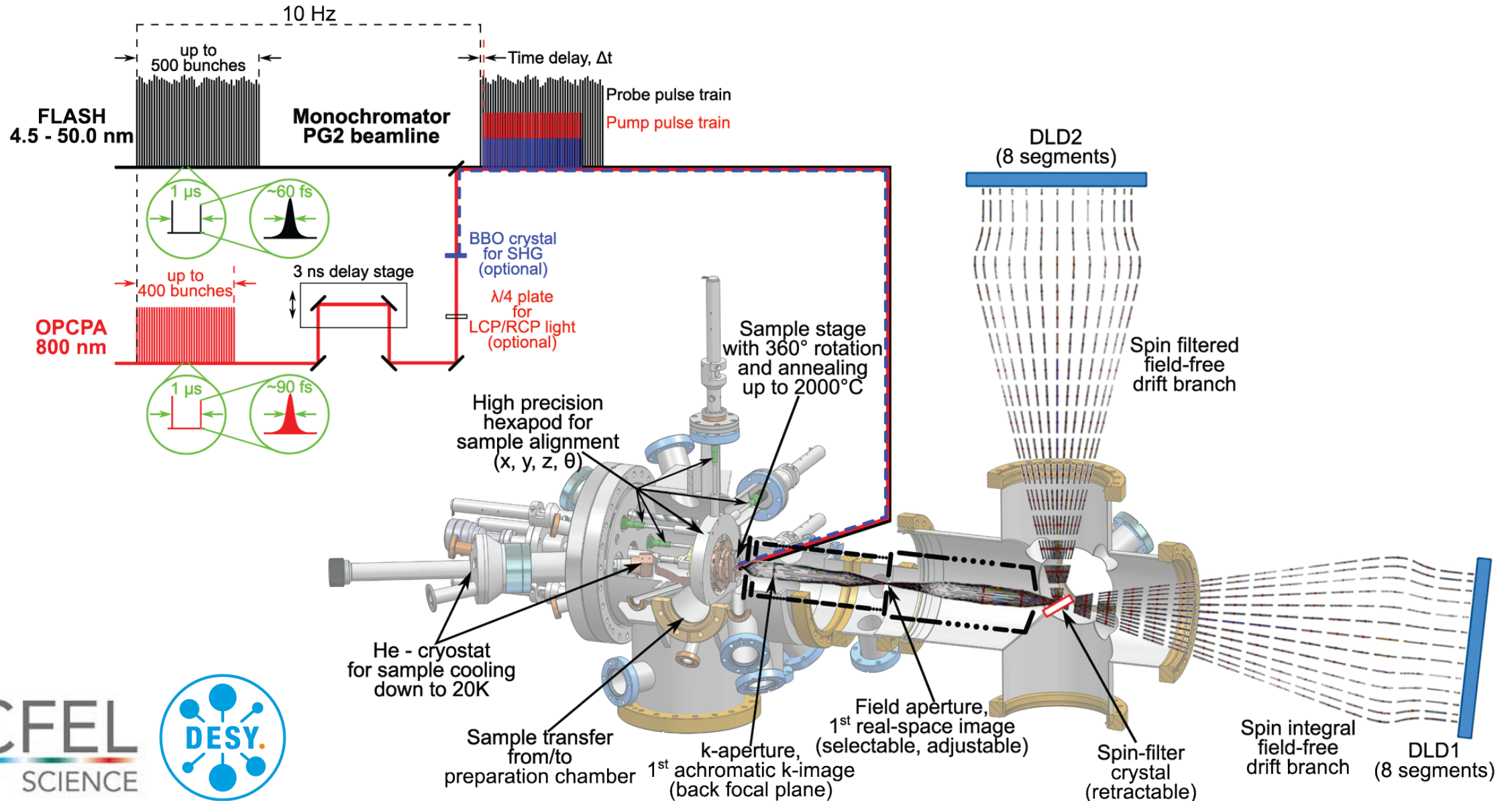
# Extending our model to dynamical systems

Image: J. M. Harms, MPSD

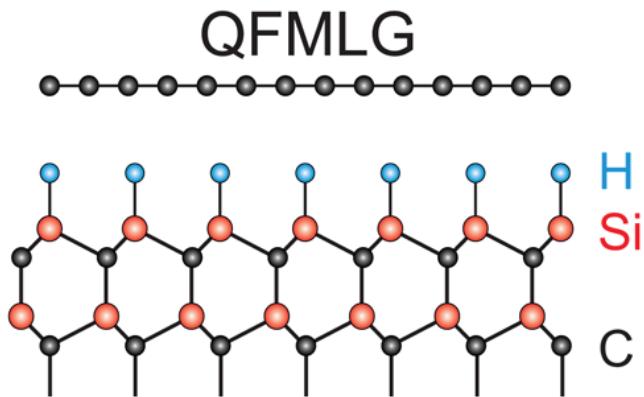


- chemical processes
- e-ph coupling
- Optical excitations of magnetic/spin states
- physics in conduction band
- ...

# Free-Electron Laser (FEL) FLASH PG2 Beamline

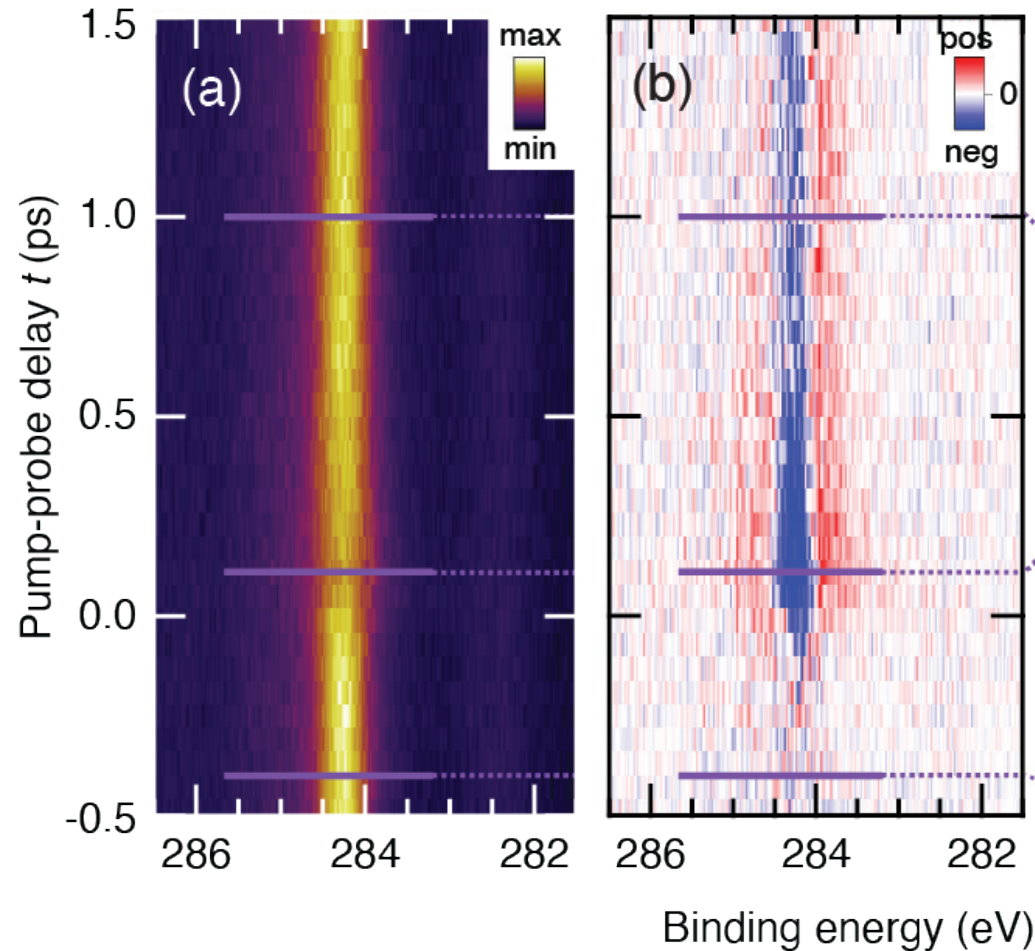


# XPS: quasifreestanding monolayer graphene



*Appl. Phys. Lett.* **99** (2011)  
122106

$h\nu = 337.5$  eV, C 1s



pump fluence:  
 $0.5$  mJ/cm<sup>2</sup>

$t$  resolution: 210 fs  
 $E$  resolution: 190 meV

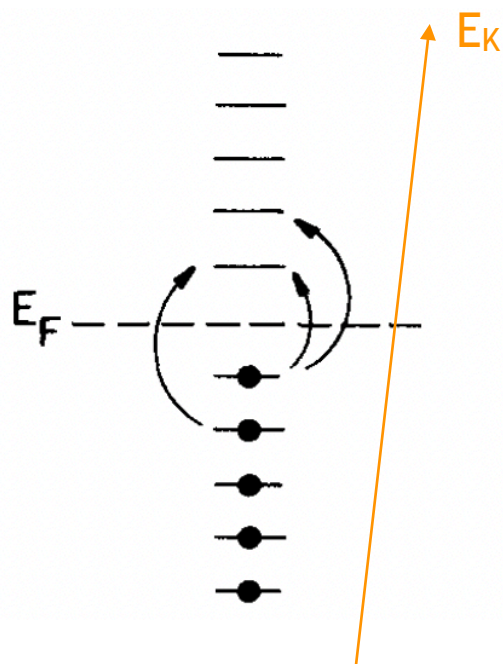
*Phys. Rev. B* **103** (2021)  
L161104

# Photoemission lineshape: pump-induced changes, high electronic temps

$$I(E) \propto \int_{-\infty}^{+\infty} [e^{-iEt} e^{-iE_0t} e^{-\lambda|t|} e^{-\frac{\sigma^2 t^2}{2}} \times \exp(\int_0^{+\infty} J(E') \frac{e^{iE't} - 1}{E'^2} dE')] dt$$

low-energy losses during photoemission

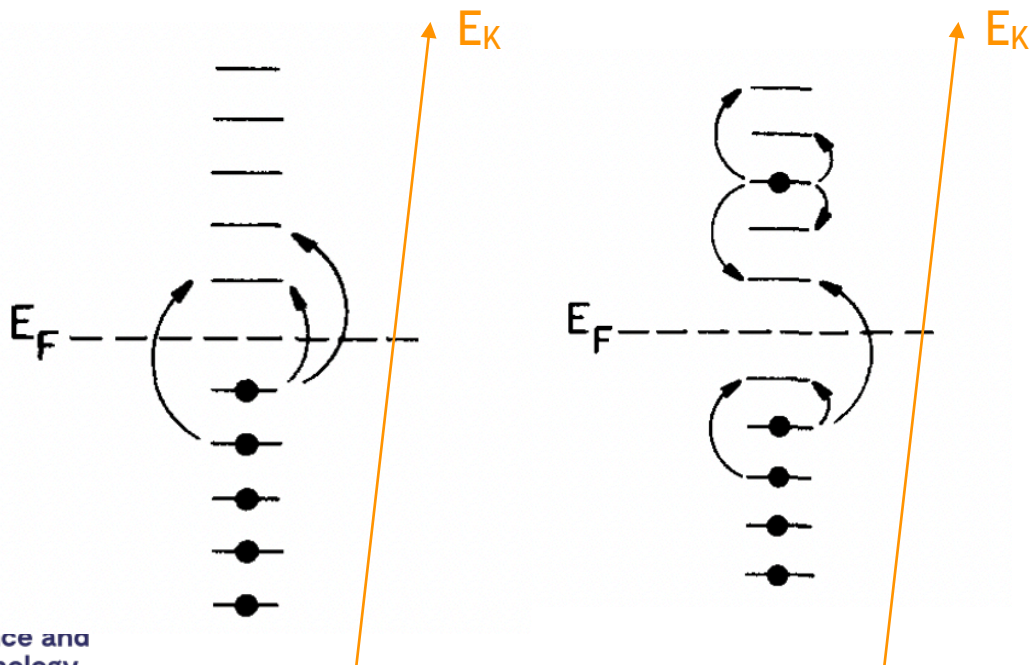
$J(E')$ : density of excitations (T=0K)



Hughes & Scarfe—*J. Phys.:*  
*Cond. Matt.* 8 (1996) 1421

# Photoemission lineshape: pump-induced changes, high electronic temps

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$$\int_0^{+\infty} J(E') \frac{e^{iE't} - 1}{E'^2} dE'$$

low-energy losses/gains during photoemission

$J(E')$ : density of excitations (finite temp)

# Photoemission lineshape: pump-induced changes, high electronic temps

$$I(E) \propto \int_{-\infty}^{+\infty} \left[ e^{-iEt} e^{-iE_0 t} e^{-\lambda|t|} e^{-\frac{\sigma^2 t^2}{2}} \times \exp\left( \int_{+\infty}^{+\infty} J(E') \frac{e^{iE't} - 1}{E'^2} dE' \right) \right] dt$$

low-energy losses/  
gains during  
photoemission

$$J(E') = a^2 \int_{-\infty}^{+\infty} [D(\epsilon) f(\epsilon, T_e) D(\epsilon + E') \times [1 - f(\epsilon + E', T_e)]] d\epsilon$$

$D(\epsilon)$  = density of states

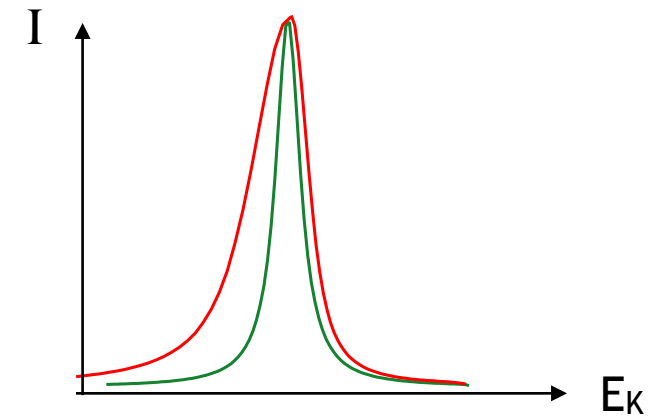
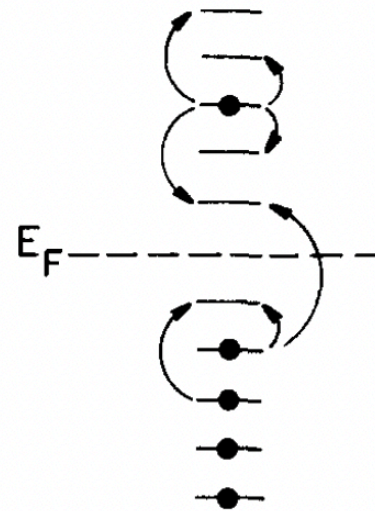
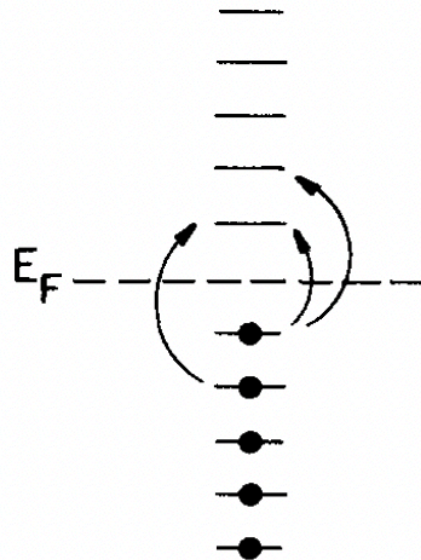
$f(\epsilon, T_e)$  = Fermi-Dirac dist.

$T_e$  = electronic temp

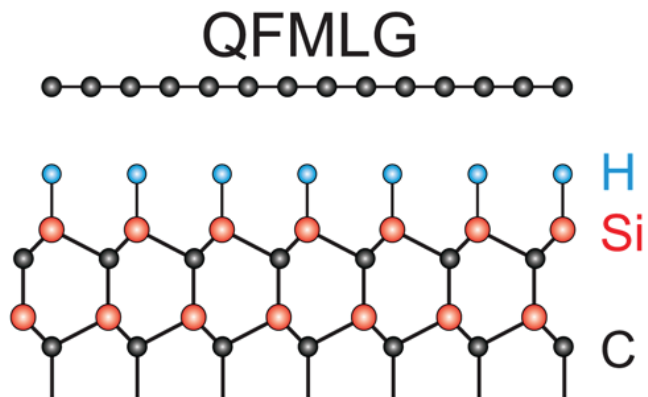
# Photoemission lineshape: pump-induced changes, high electronic temps

$$I(E) \propto \int_{-\infty}^{+\infty} [e^{-iEt} e^{-iE_0 t} e^{-\lambda|t|} e^{-\frac{\sigma^2 t^2}{2}} \times \exp(\int_{+\infty}^{+\infty} J(E') \frac{e^{iE't} - 1}{E'^2} dE')] dt$$

Fourier transform gives *asymmetry kernel*



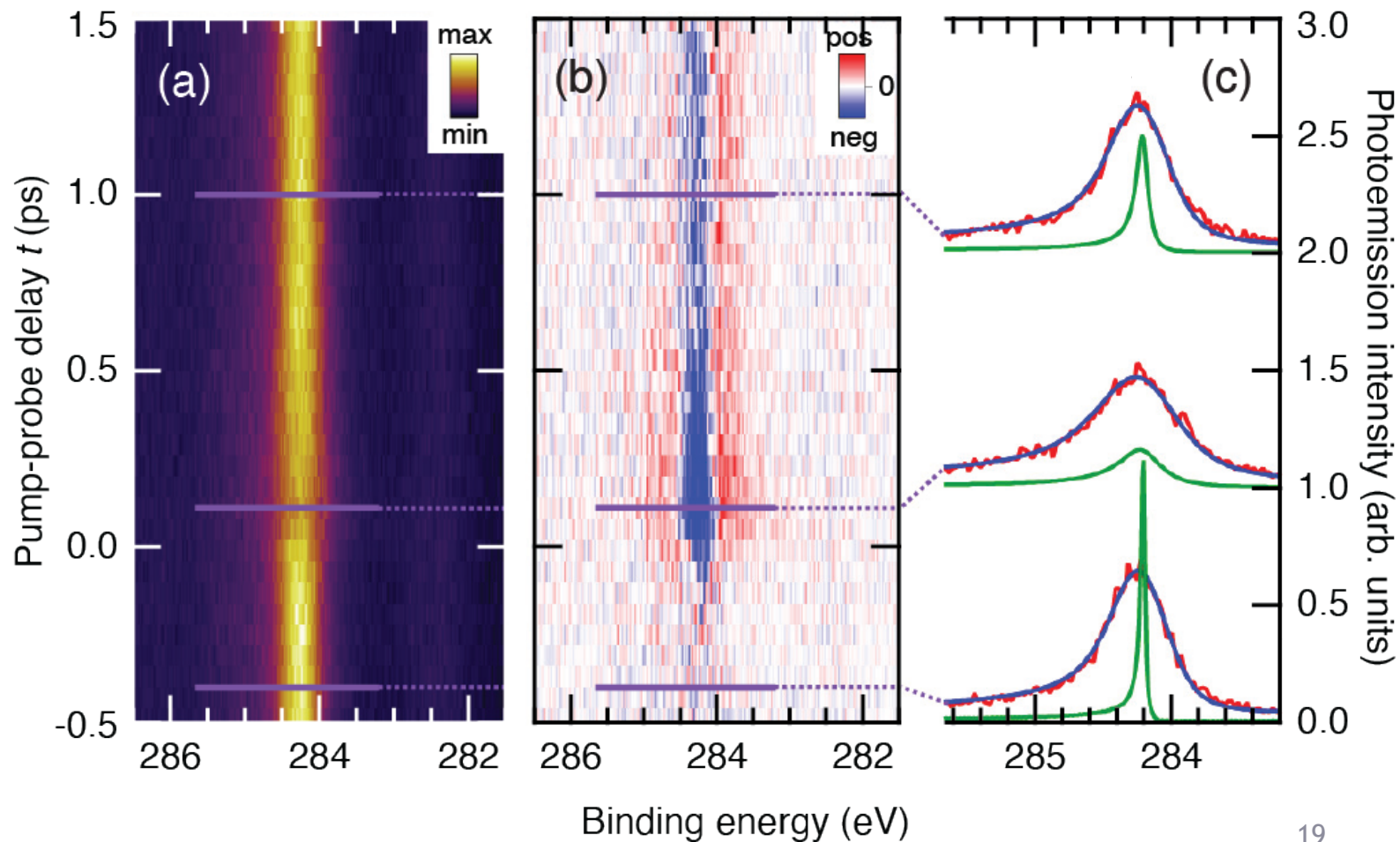
# Fitting the pumped lineshape



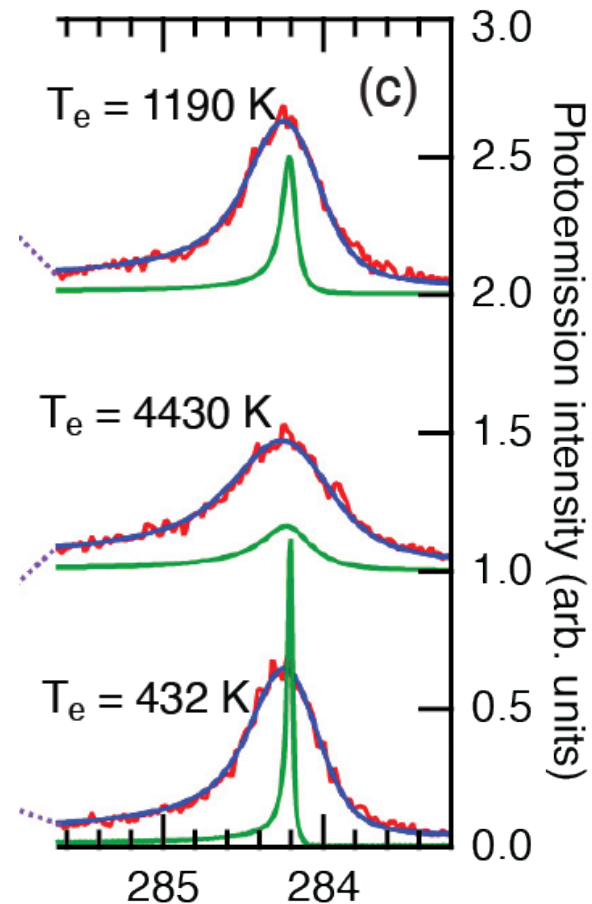
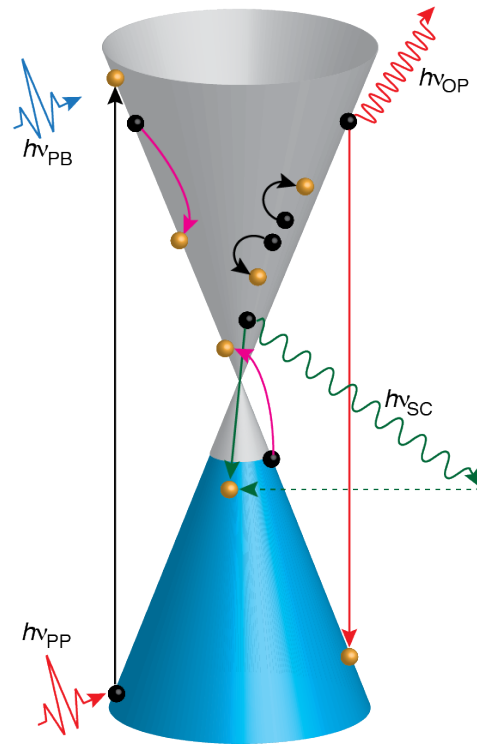
*Appl. Phys. Lett.* **99** (2011)  
122106

$h\nu = 337.5$  eV, C 1s

red: data  
blue: fit  
green: asymmetry kernel



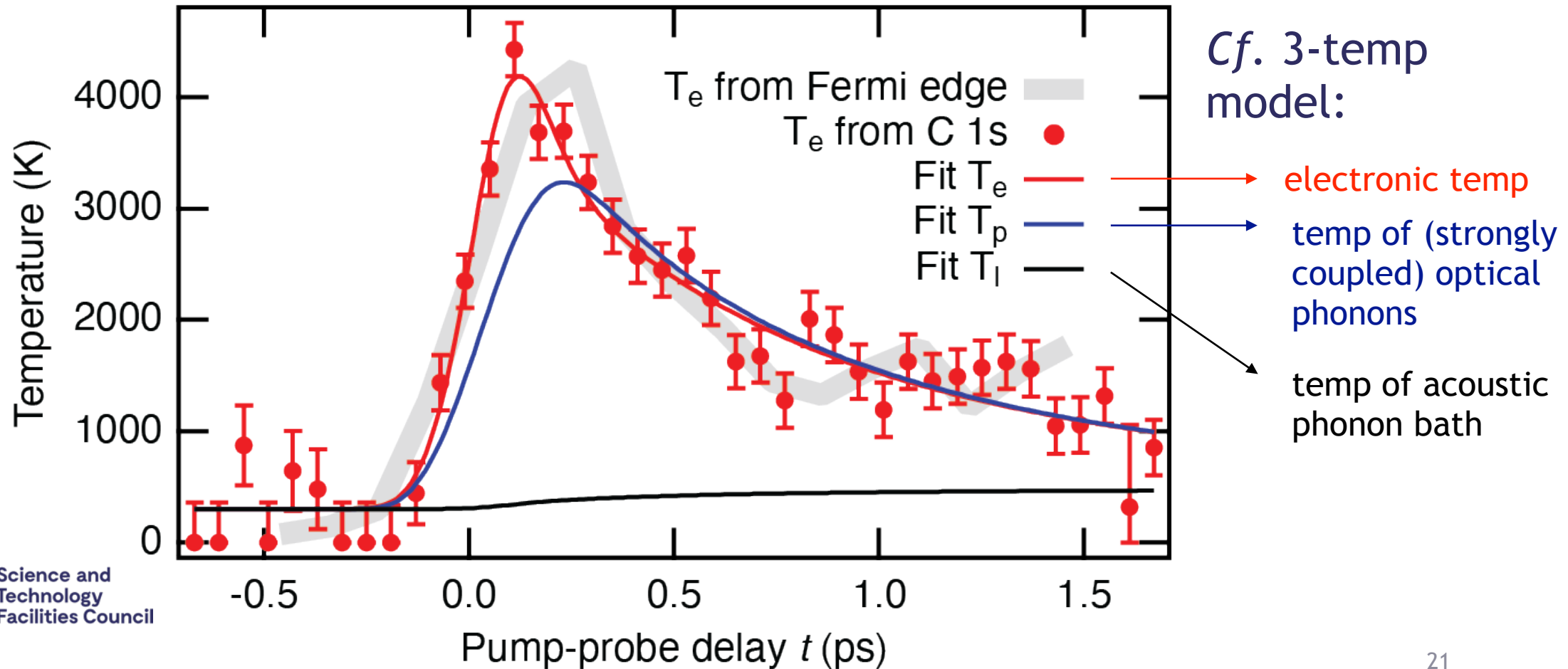
# Fitting the pumped lineshape



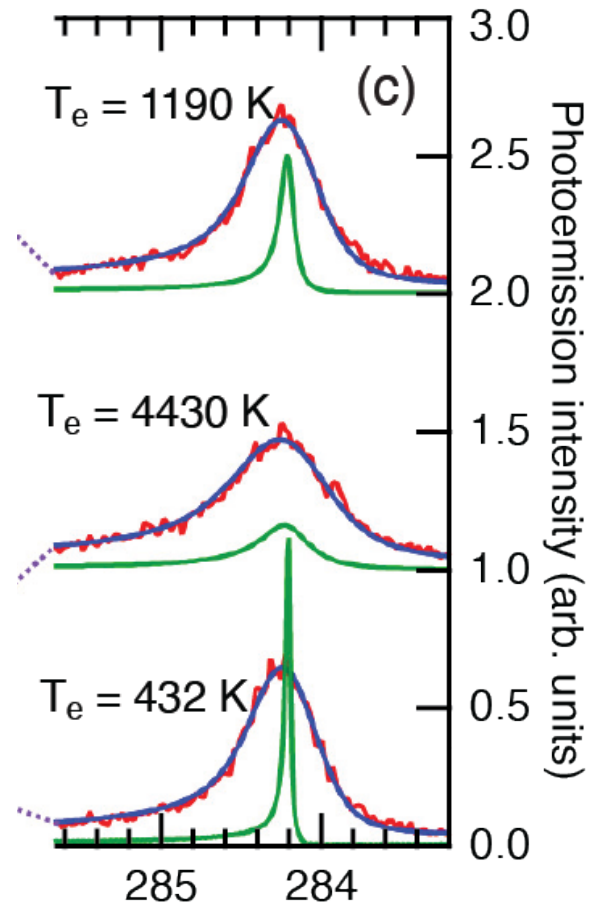
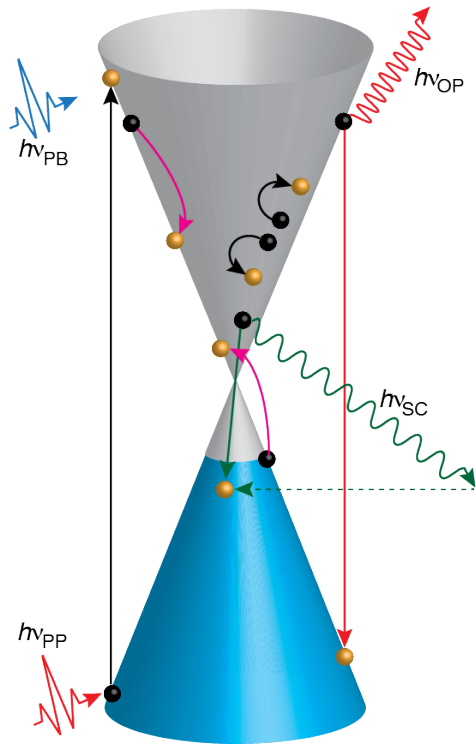
- Electronic temps extracted from fitting, using model
- Consistent with earlier work based on angle-resolved measurements: *Phys. Rev. Lett.* 111 (2013) 027403

# Electronic temperature fitting

Phys. Rev. Lett. 111 (2013) 027403



# Fitting the pumped lineshape



Fit to 3-temp model yields e-ph coupling constants:

$$\lambda_{\text{opt}} = 0.06$$

$$\lambda_{\text{acous}} = 0.0029$$

*Phys. Rev. Lett.* 111 (2013) 027403

*Phys. Rev. B* 86 (2012) 161402(R)

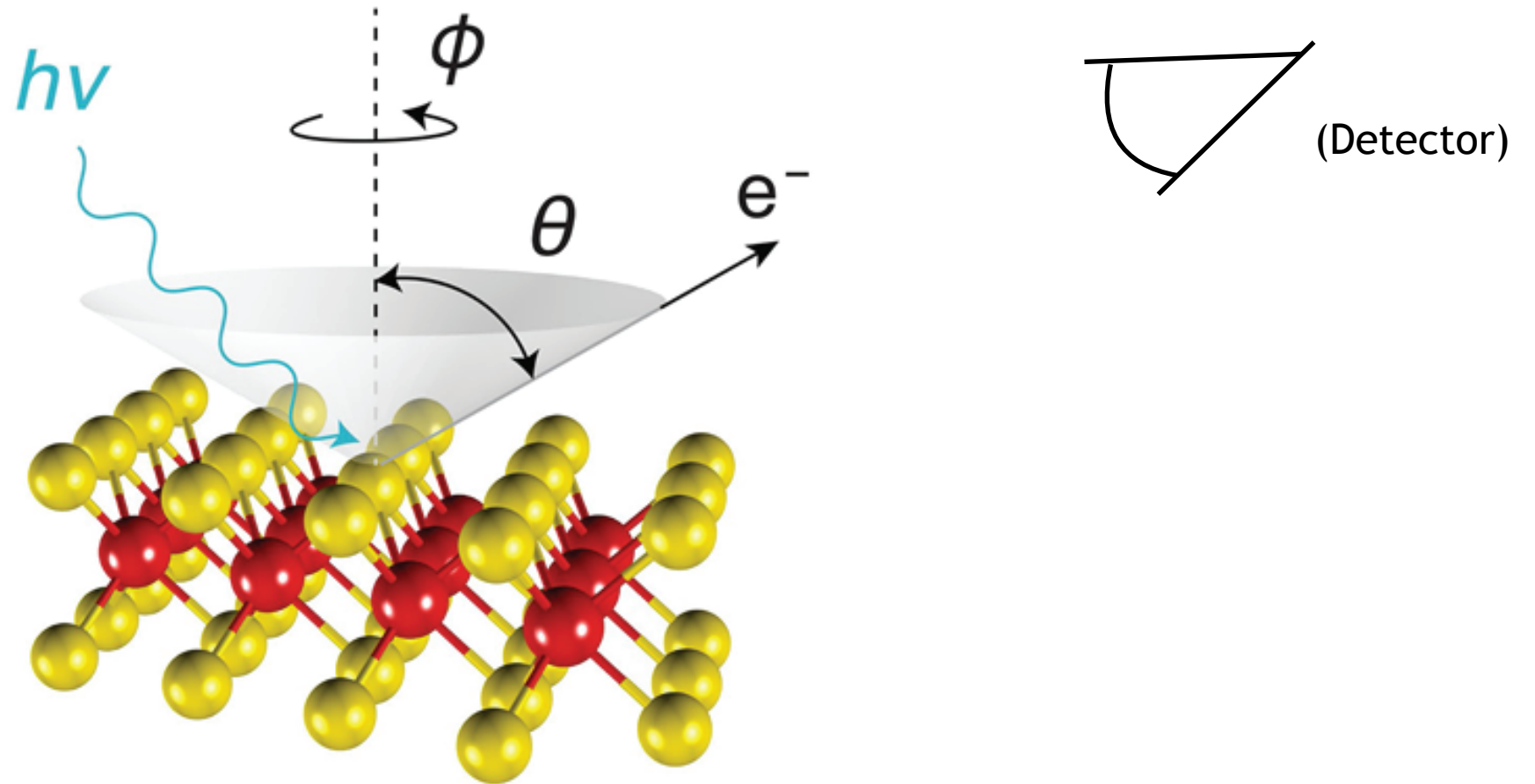
*Phys. Rev. B* 76 (2007) 205411

(Electronic temps extracted from fitting)

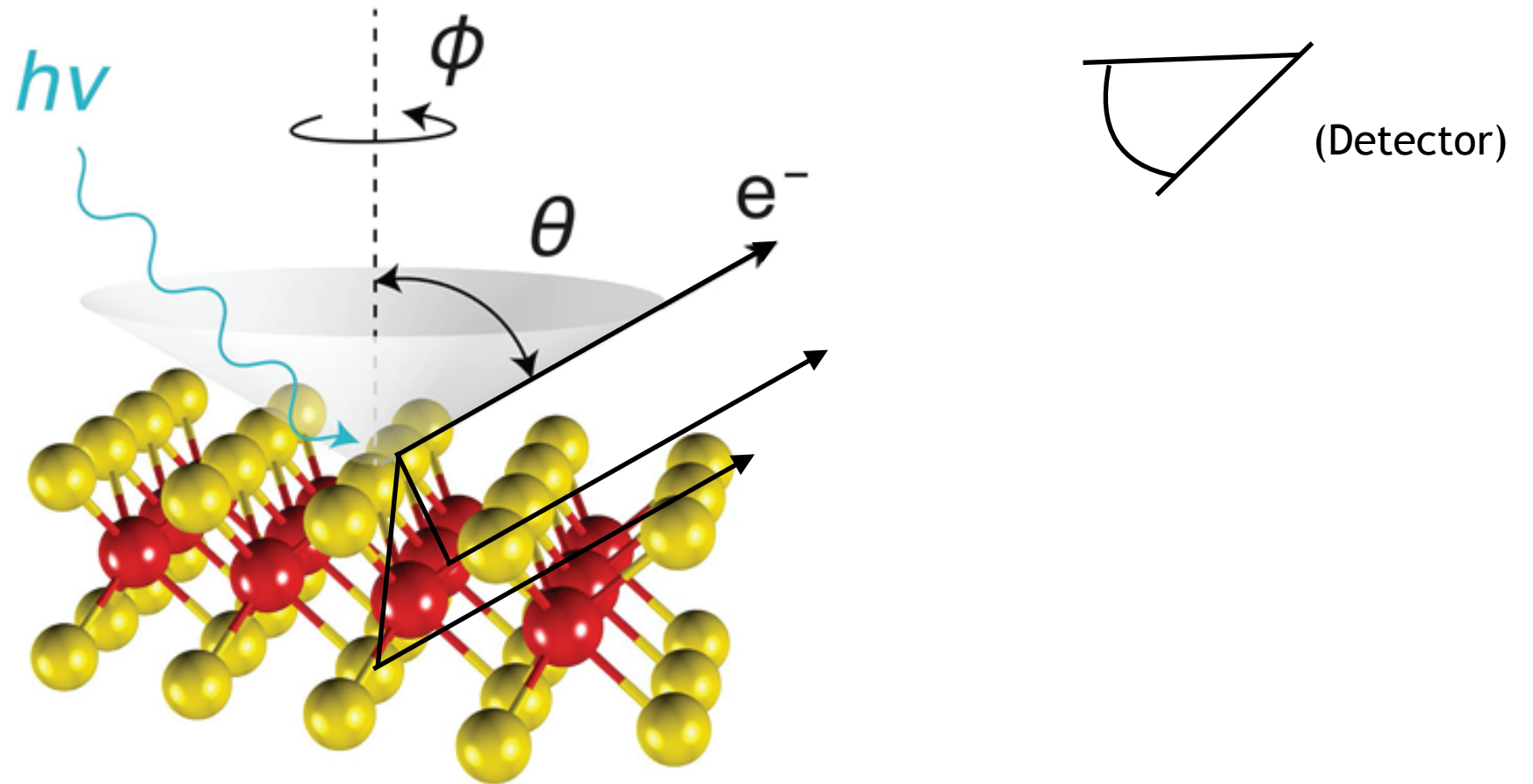
# Recap so far...

- Through detailed lineshape fitting, we can extract detailed information about surfaces:
  - Chemistry, electronic properties, ...
- With pump-probe, we can further investigate:
  - Evolution & decay of excitations in electrons and lattice, at short time scales and in strongly-out-of-equilibrium systems
  - Time-dependent changes in chemistry, electronic properties, ...
- Can we use these techniques to gain information about structure?

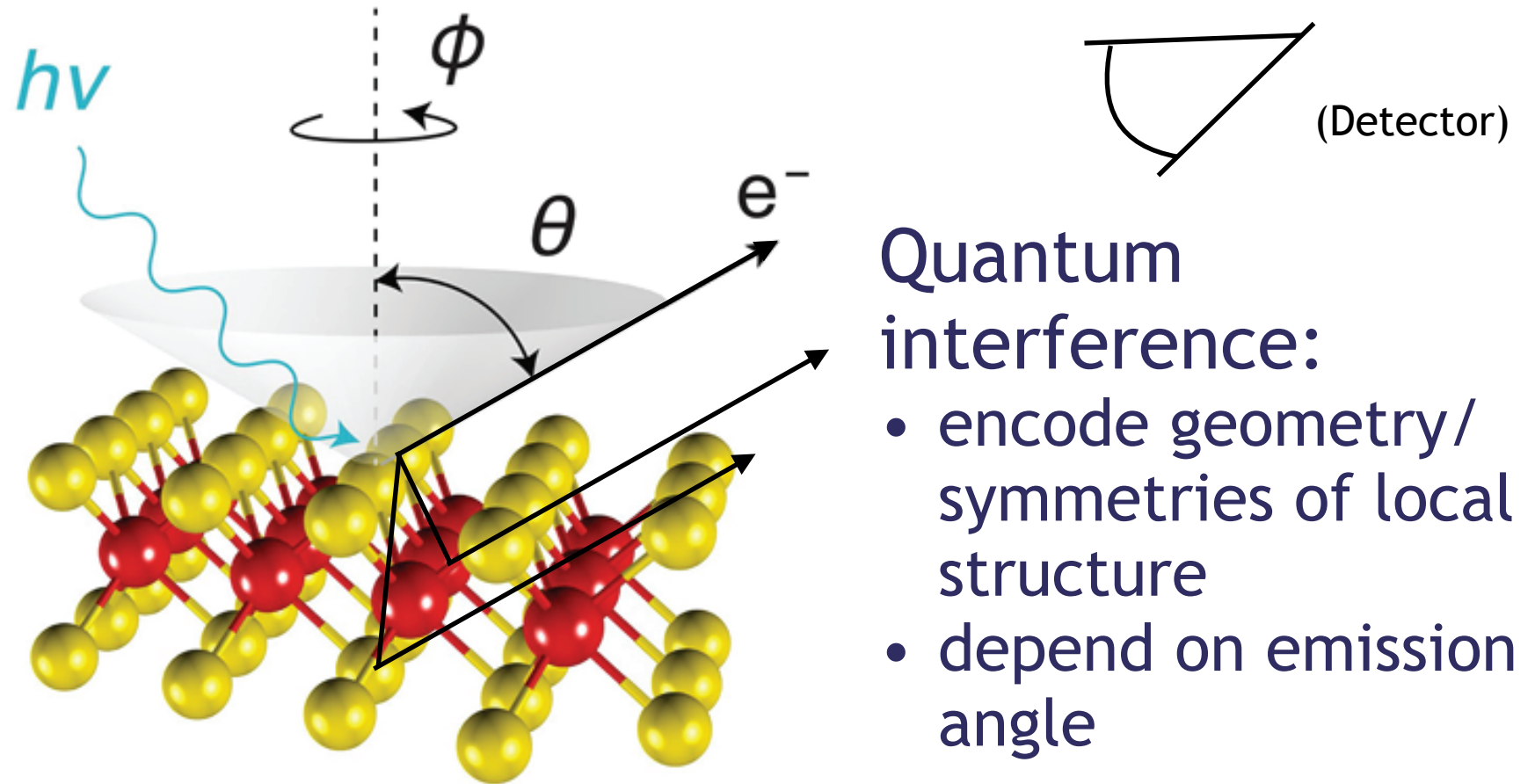
# X-ray photoelectron diffraction (XPD)



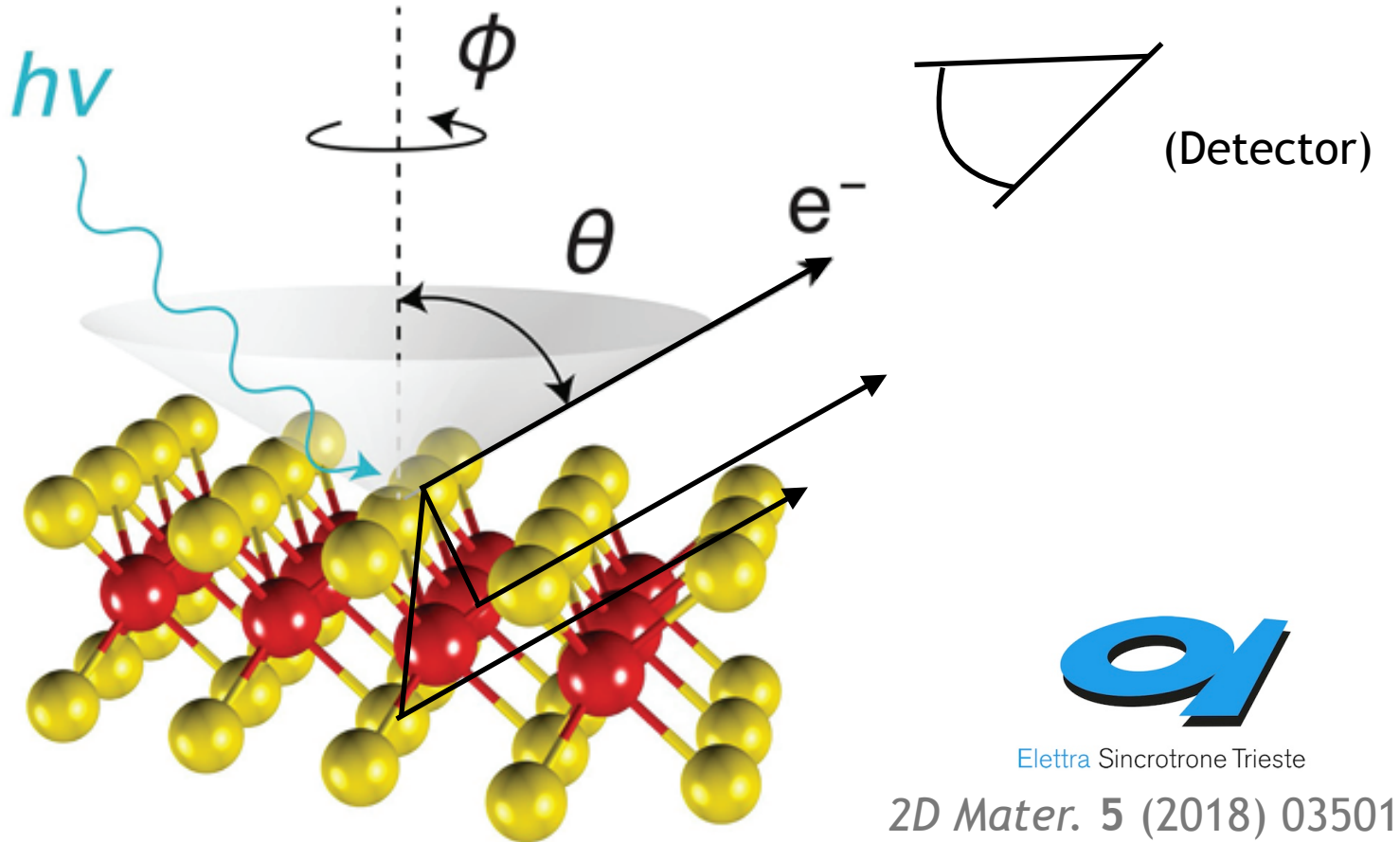
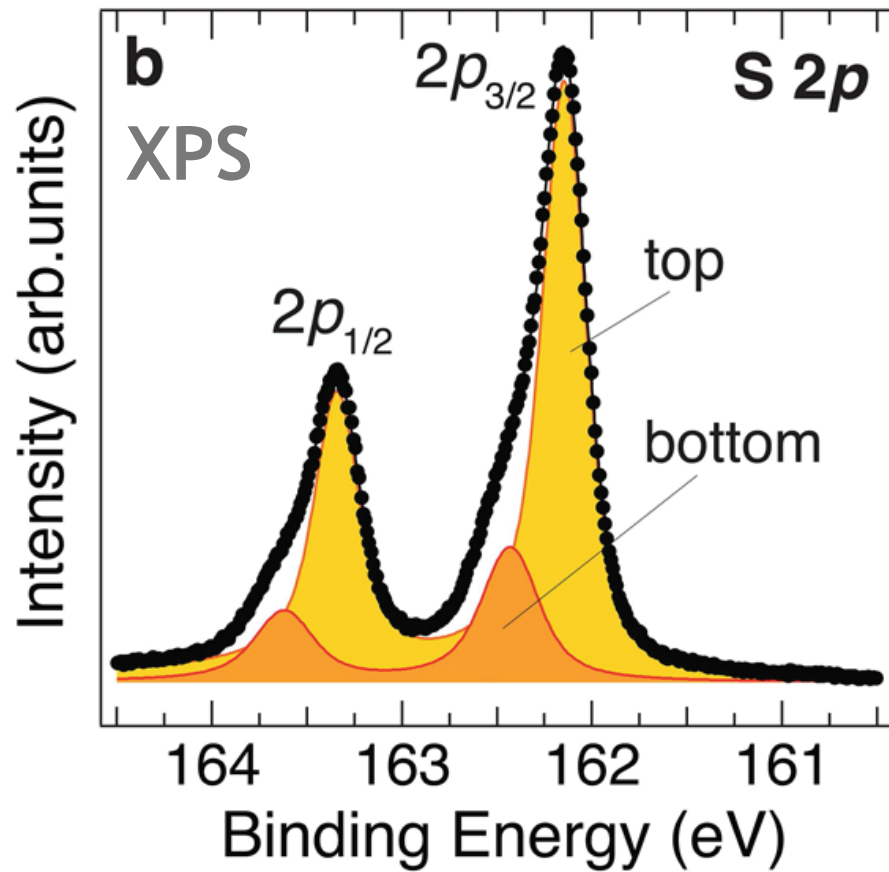
# X-ray photoelectron diffraction (XPD)



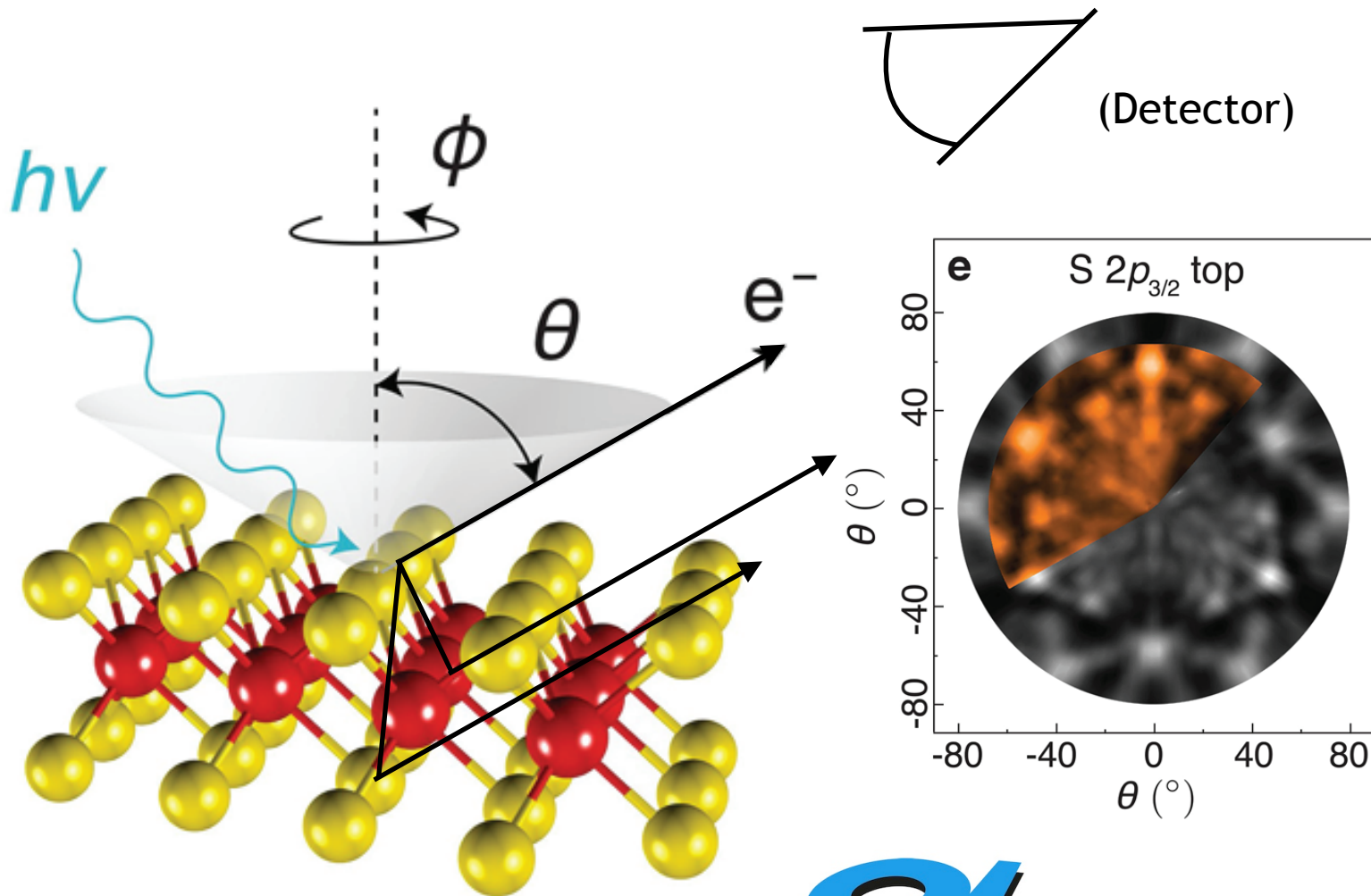
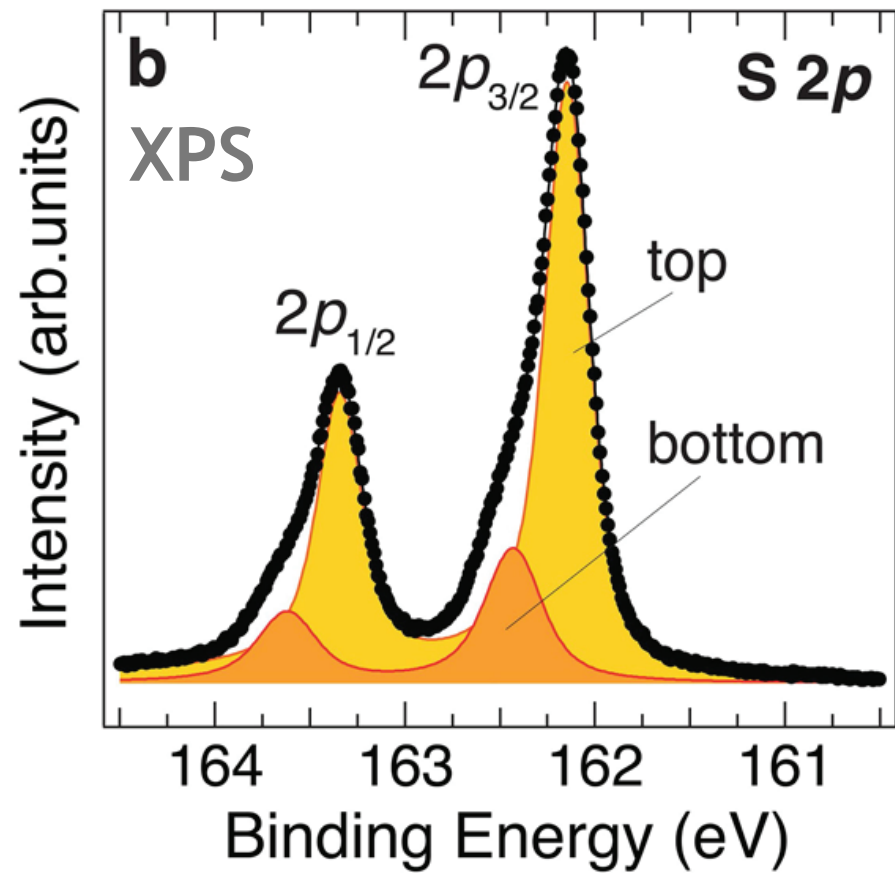
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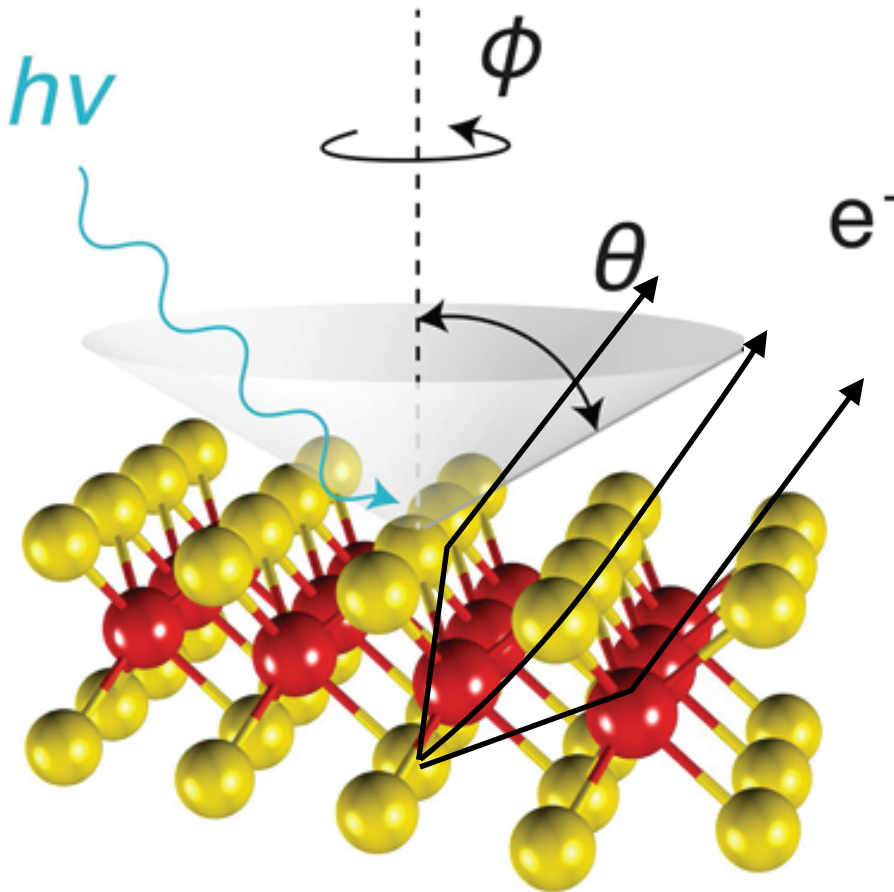
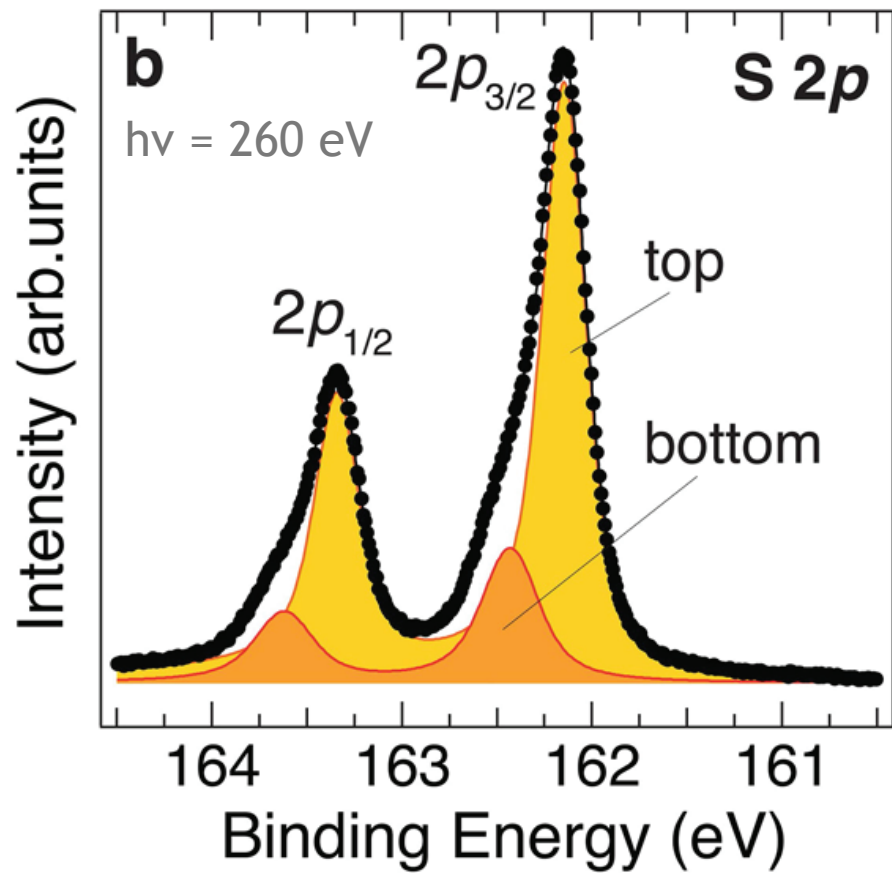
# X-ray photoelectron diffraction (XPD)



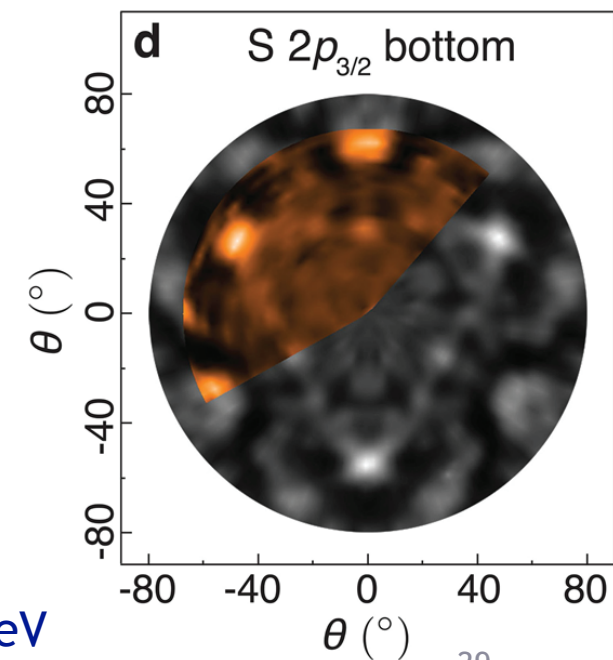
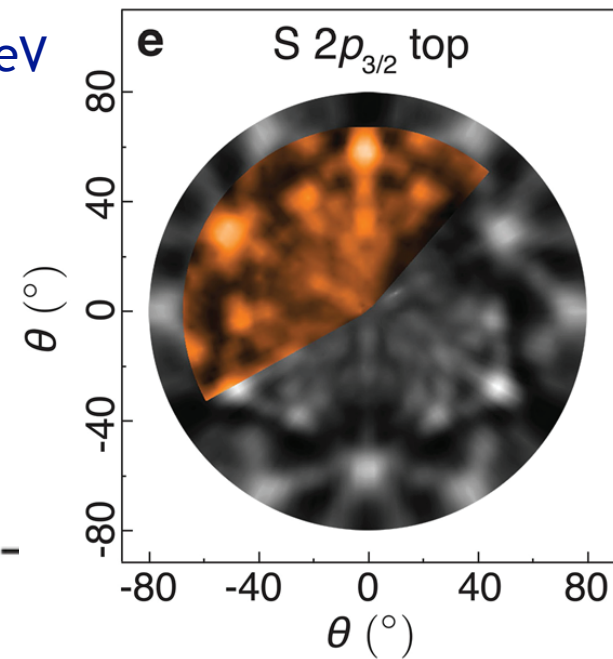
# XPD



# XPD



$h\nu = 270$  eV



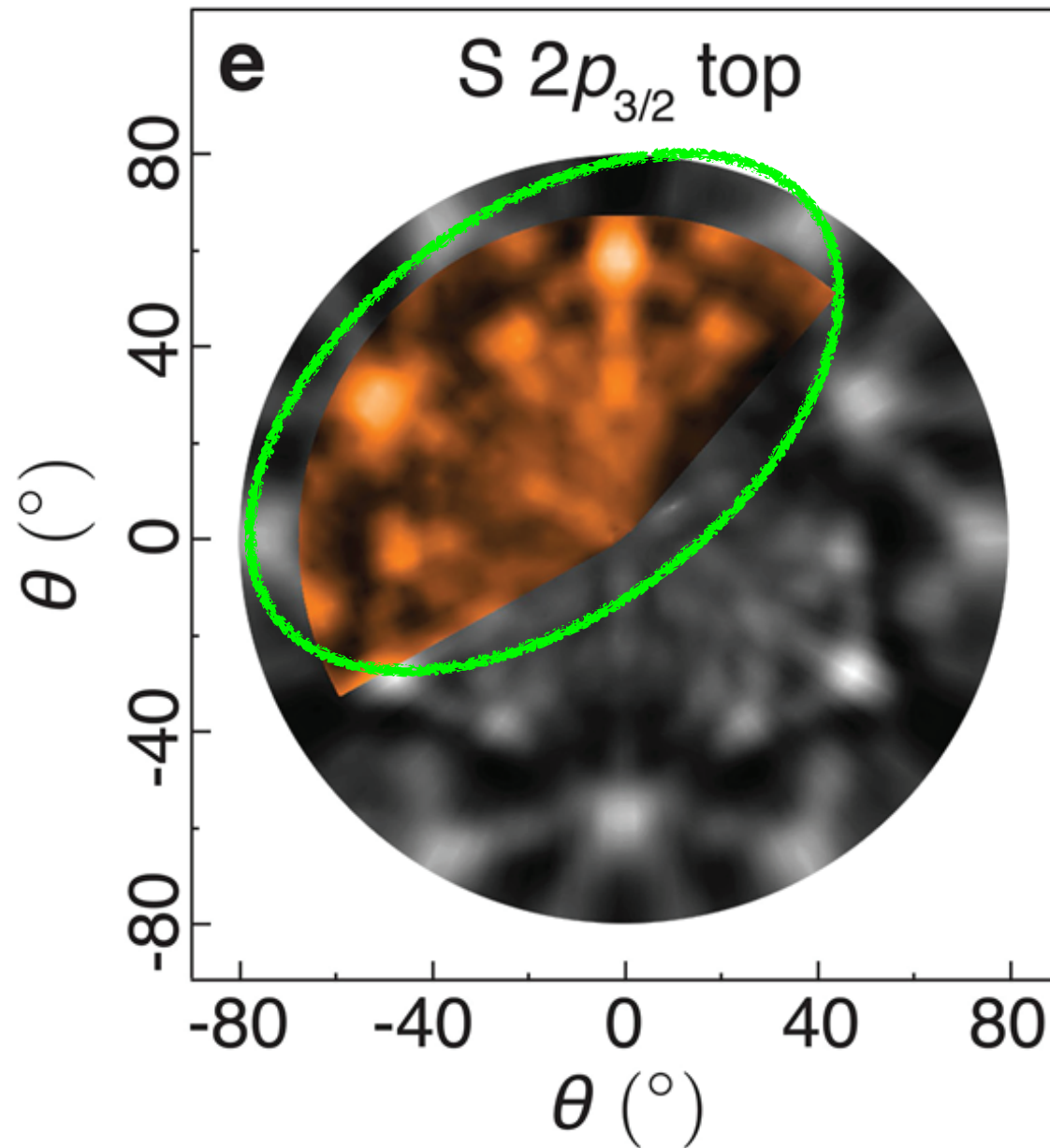
$h\nu = 560$  eV

# XPD analysis

$$\chi = \frac{I(\theta, \phi) - I_0(\theta)}{I_0(\theta)}$$

modulation  
function

intensity averaged across  
all azimuths at polar angle  $\theta$



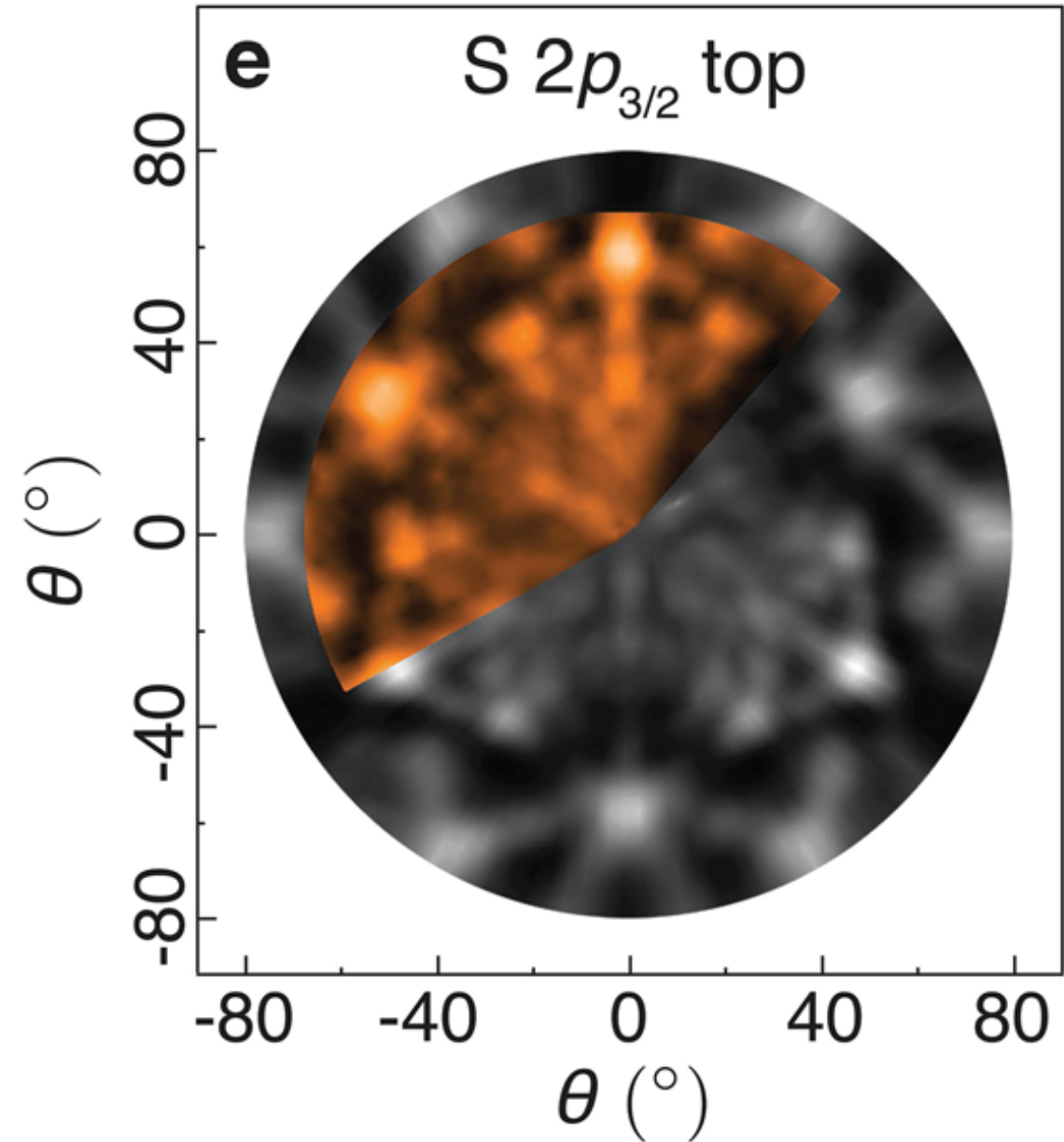
# XPD analysis

$$\chi = \frac{I(\theta, \phi) - I_0(\theta)}{I_0(\theta)}$$

modulation  
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“Electron Diffraction in Atomic Clusters”  
(EDAC)

*Phys. Rev. B* 63 (2001) 075404



# XPD analysis

$$\chi = \frac{I(\theta, \phi) - I_0(\theta)}{I_0(\theta)}$$

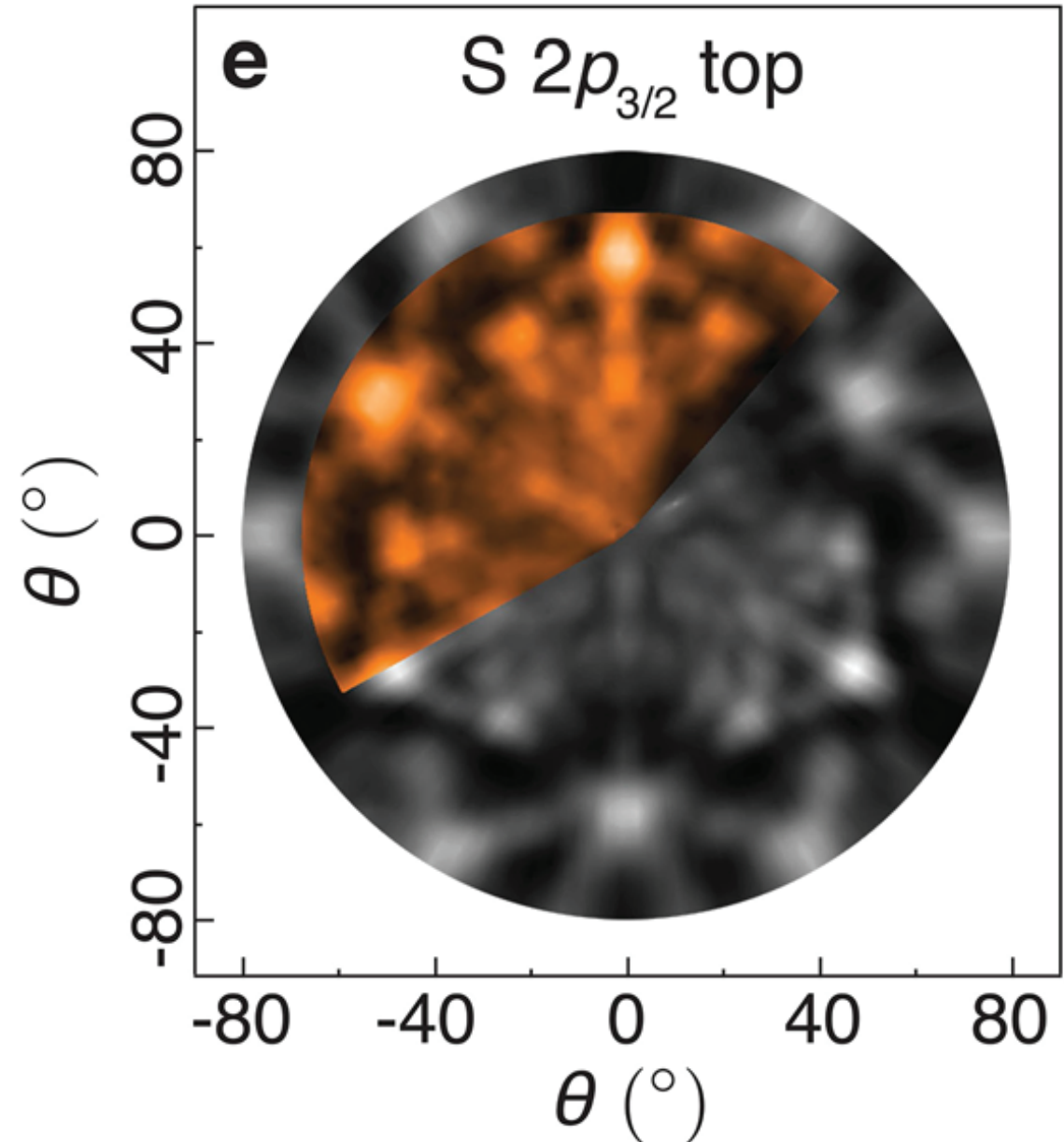
modulation  
function

“Electron Diffraction in Atomic Clusters”  
(EDAC)

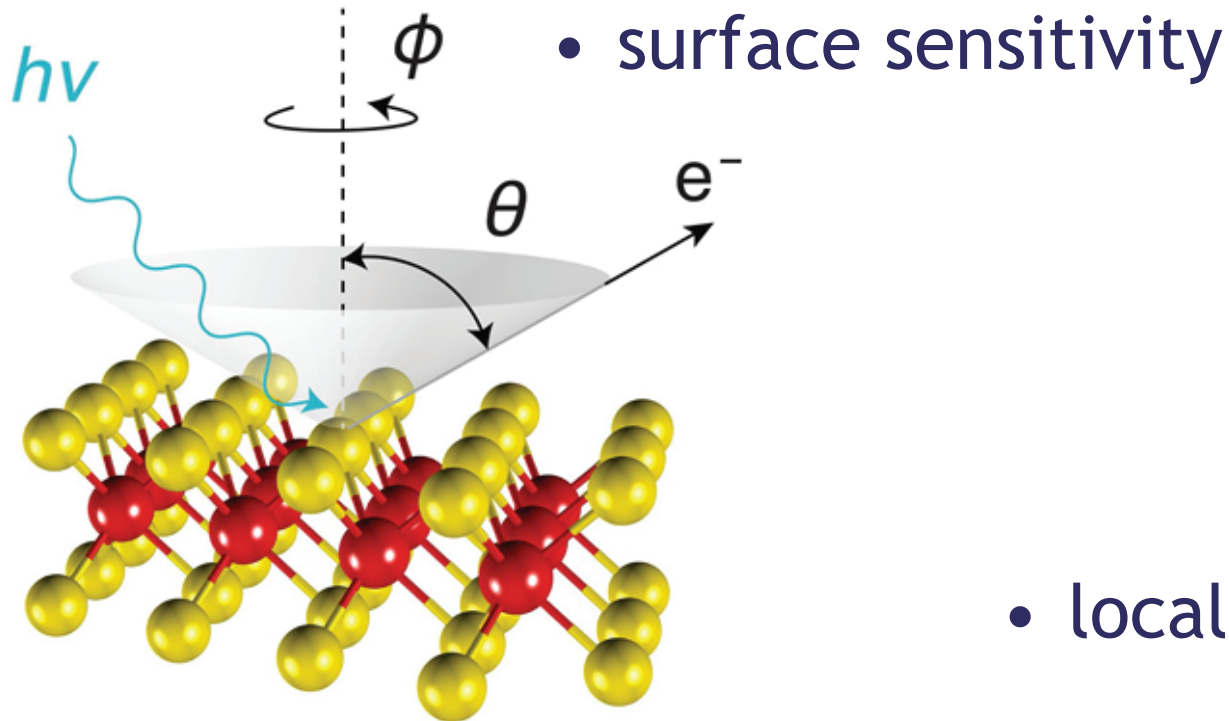
*Phys. Rev. B* **63** (2001) 075404

$$R = \frac{\sum_i (\chi_{exp,i} - \chi_{sim,i})^2}{\sum_i (\chi_{exp,i}^2 + \chi_{sim,i}^2)}$$

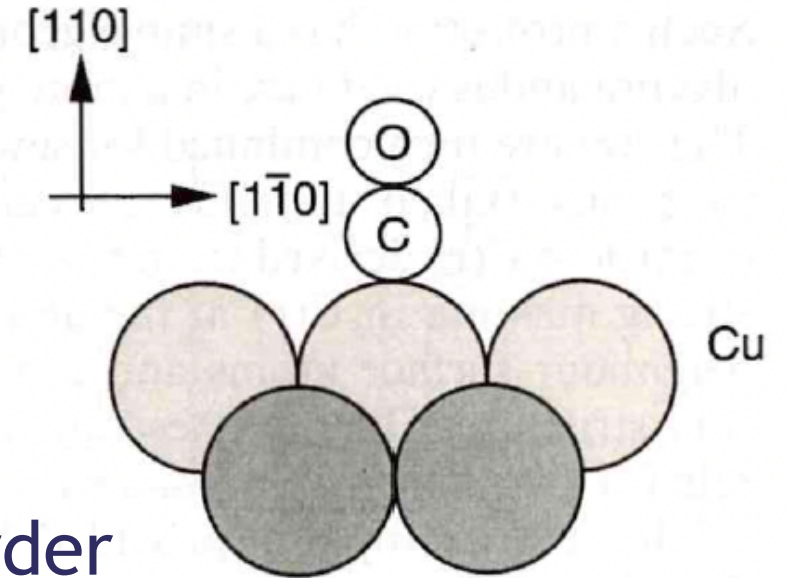
reliability  
factor



# Range of applicability



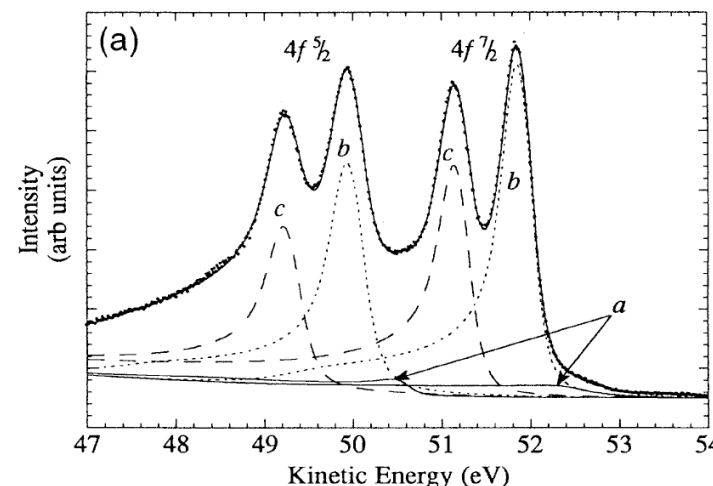
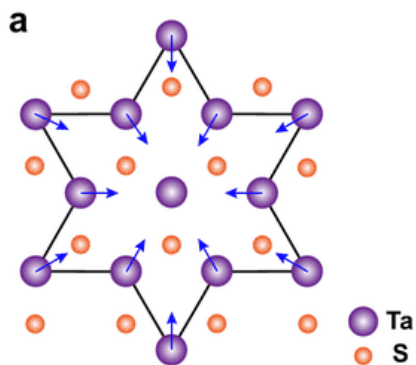
- local order



# Can we take this to the time domain?

- Dynamical studies of
  - Structural changes
  - Phonon modes
- Combine chemical/electronic info from XPS with structural information from XPD:
  - Correlated states: charge density waves, etc.

*New J. Phys.* 14  
(2012) 013062

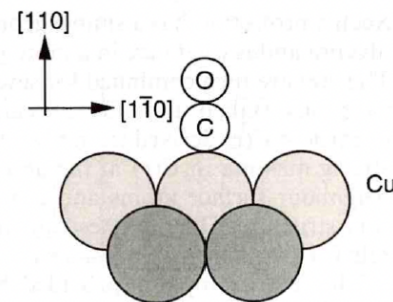


*Phys. Rev. Lett.*  
74 (1995) 3069

*Nat. Comm.* 146 (2019) 146

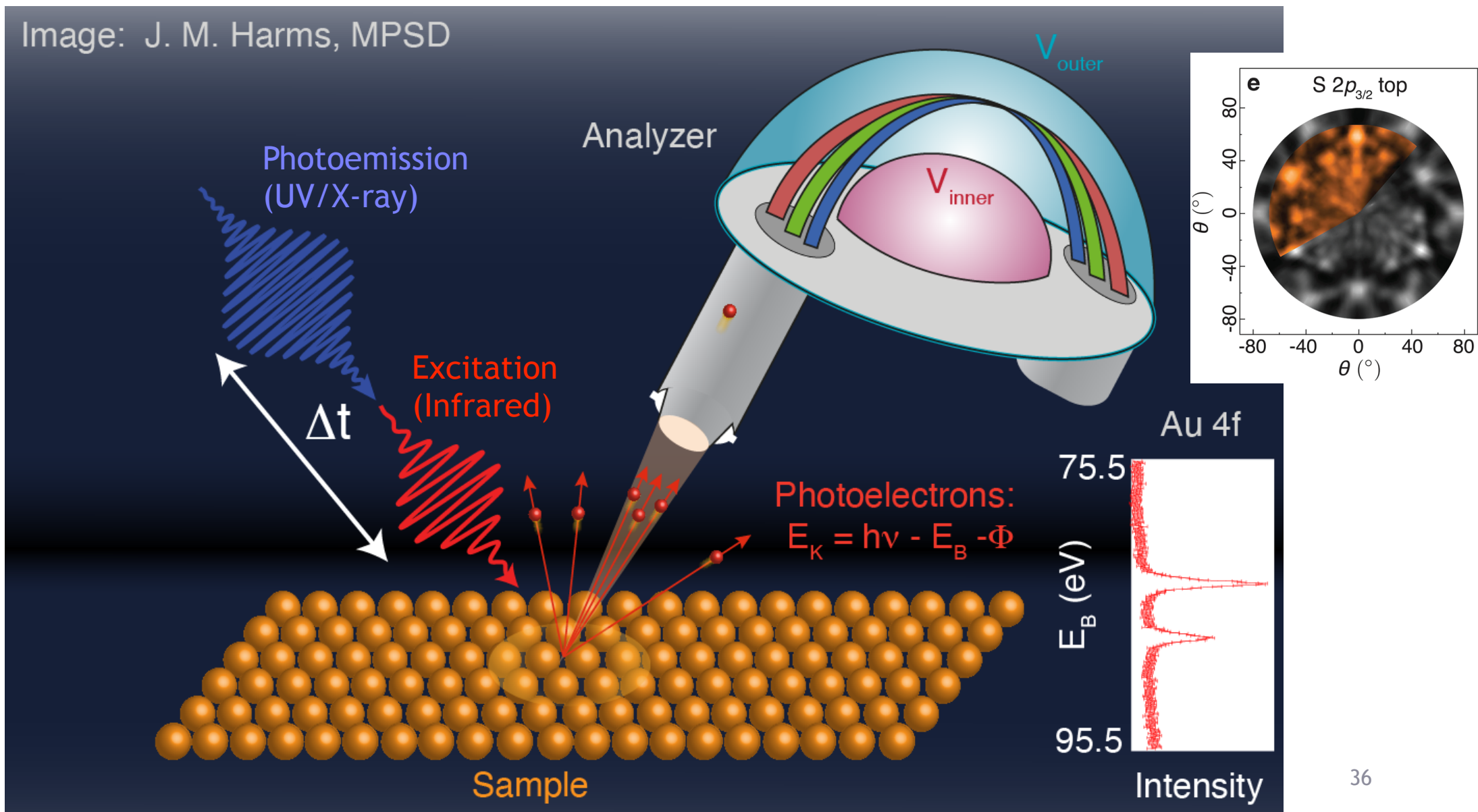
# Can we take this to the time domain?

- Dynamical studies of
  - Structural changes
  - Phonon modes
- Combine chemical/electronic info from XPS with structural information from XPD:
  - Correlated states: charge density waves, etc.
  - “Movies” of surface catalytic processes, photocatalysis
    - Local geometric information about adsorption sites from XPD

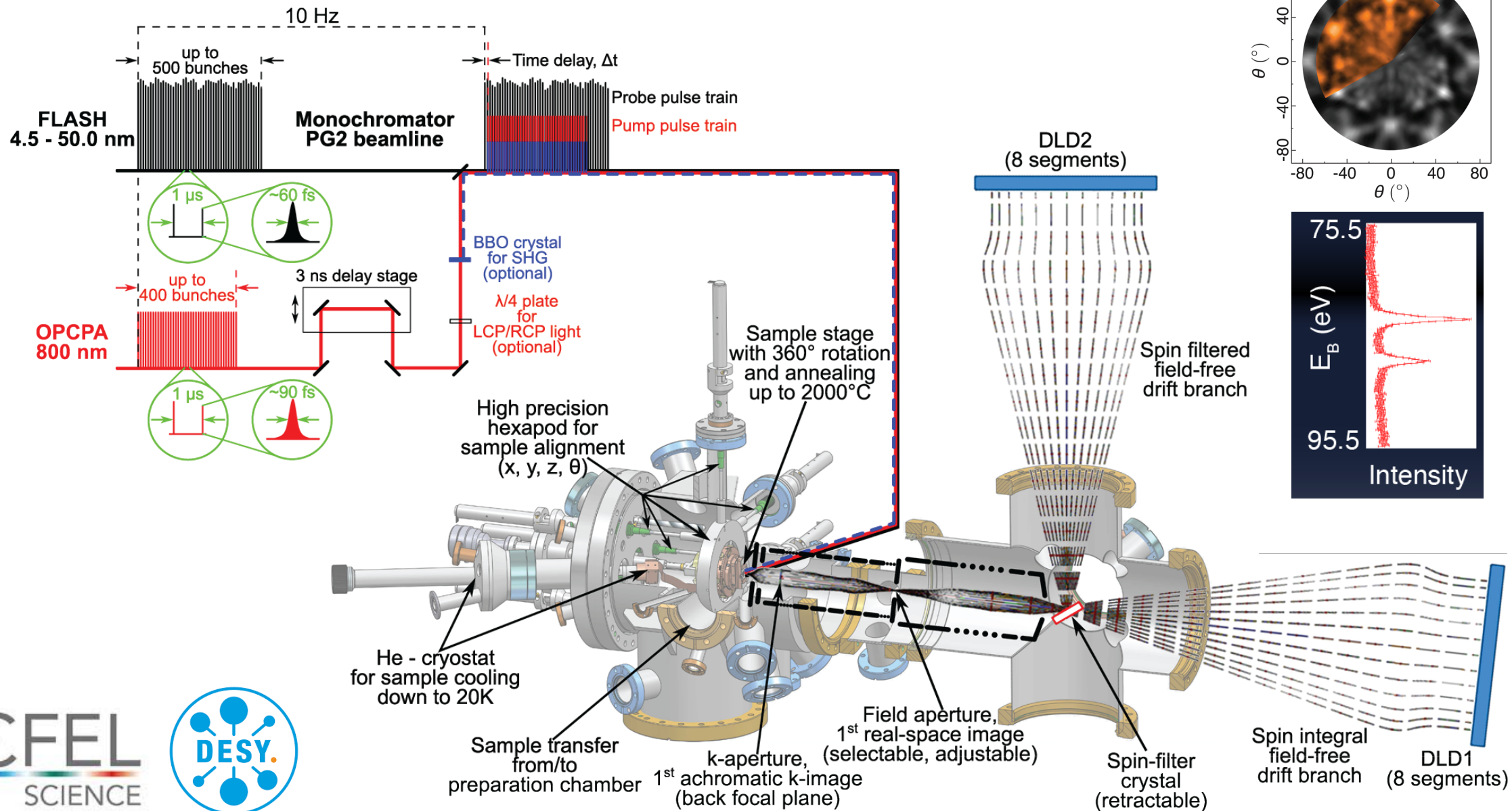


*Nature* 368 (1994) 131

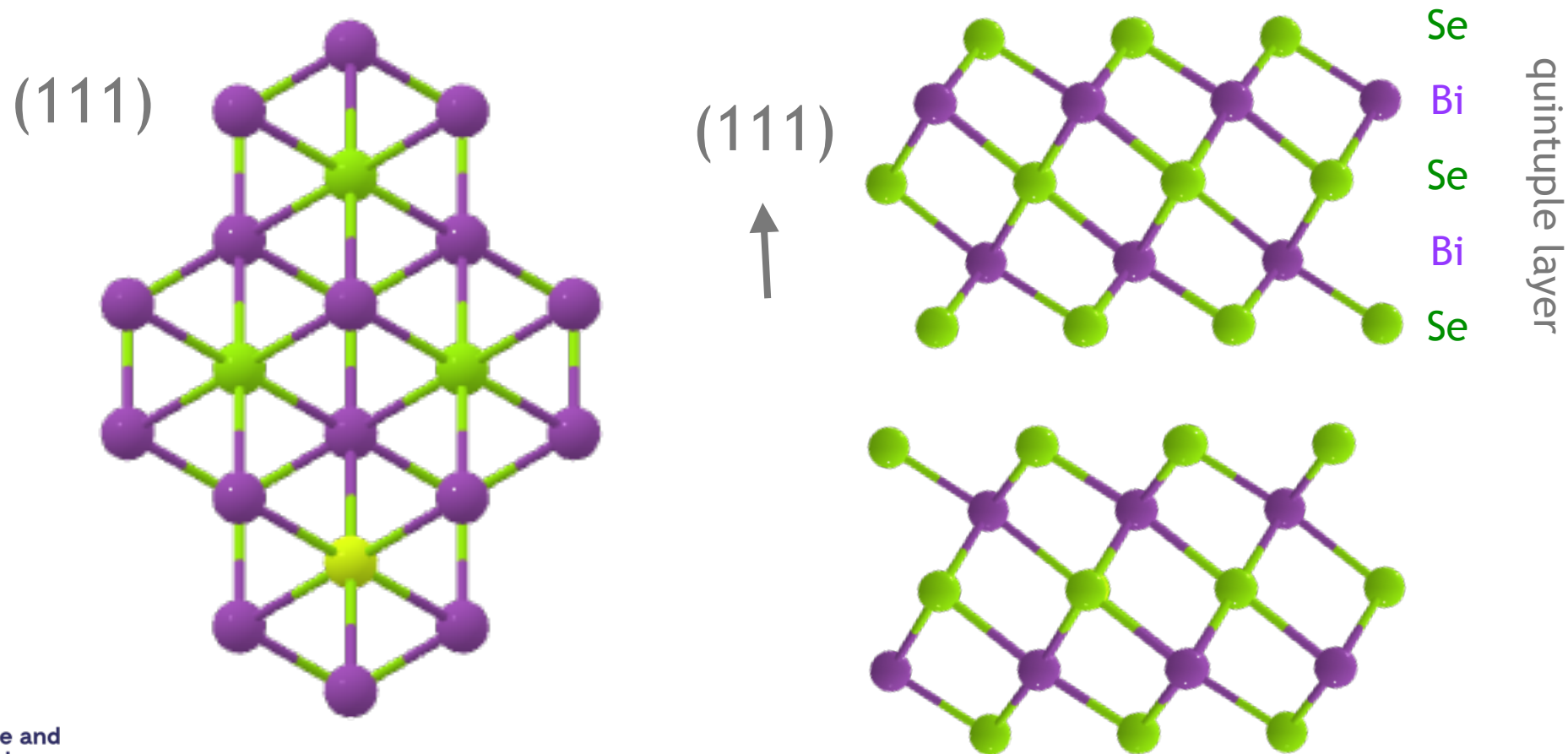
# Pump-Probe XPD



# Time-of-flight momentum microscope

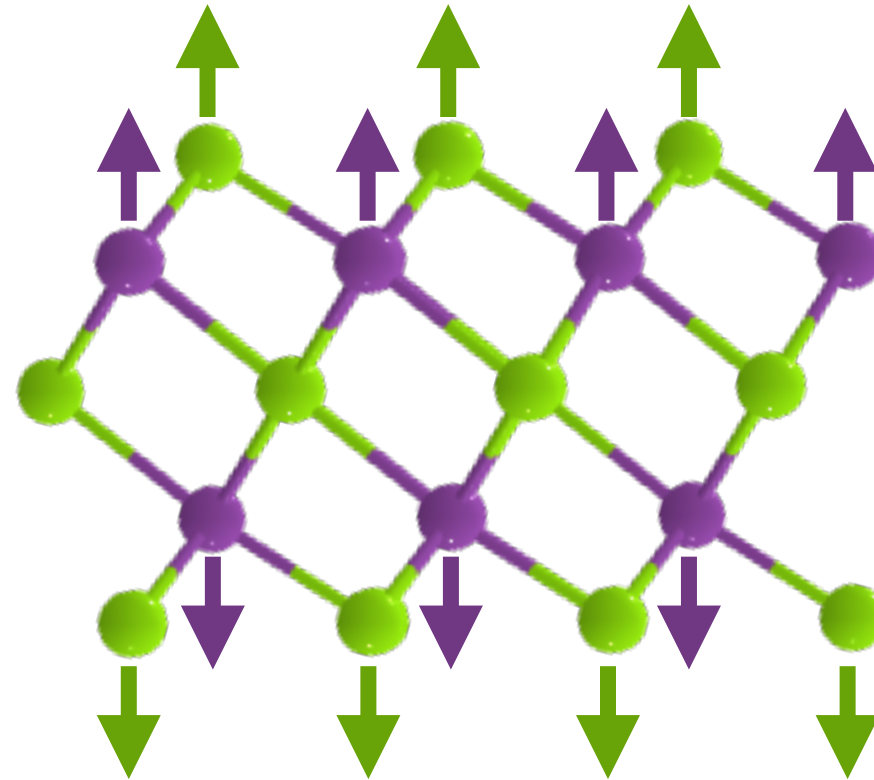


# XPD: $\text{Bi}_2\text{Se}_3$



# $A_{1g}^1$ phonon mode

- Coherent mode
- 2 THz / 500-fs oscillation
  - 140-fs time resolution in measurement
- 3-ps decay time
- Easy to pump



Se

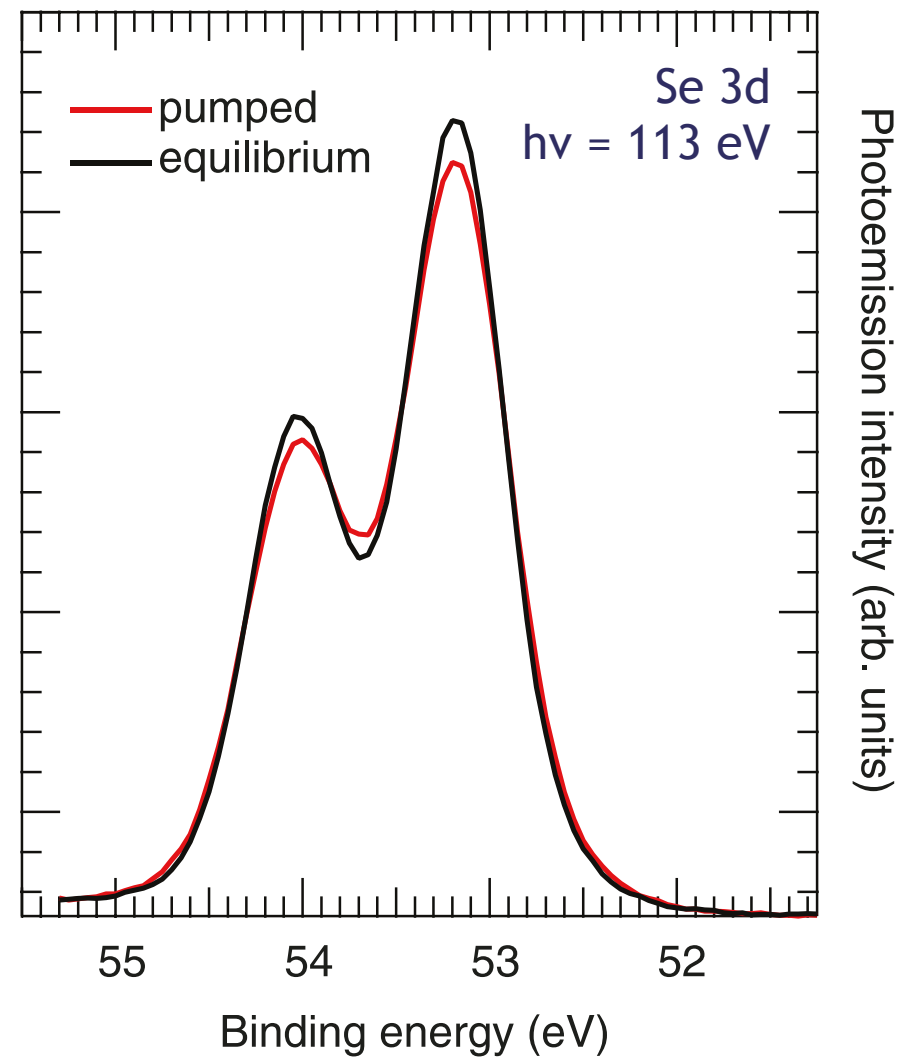
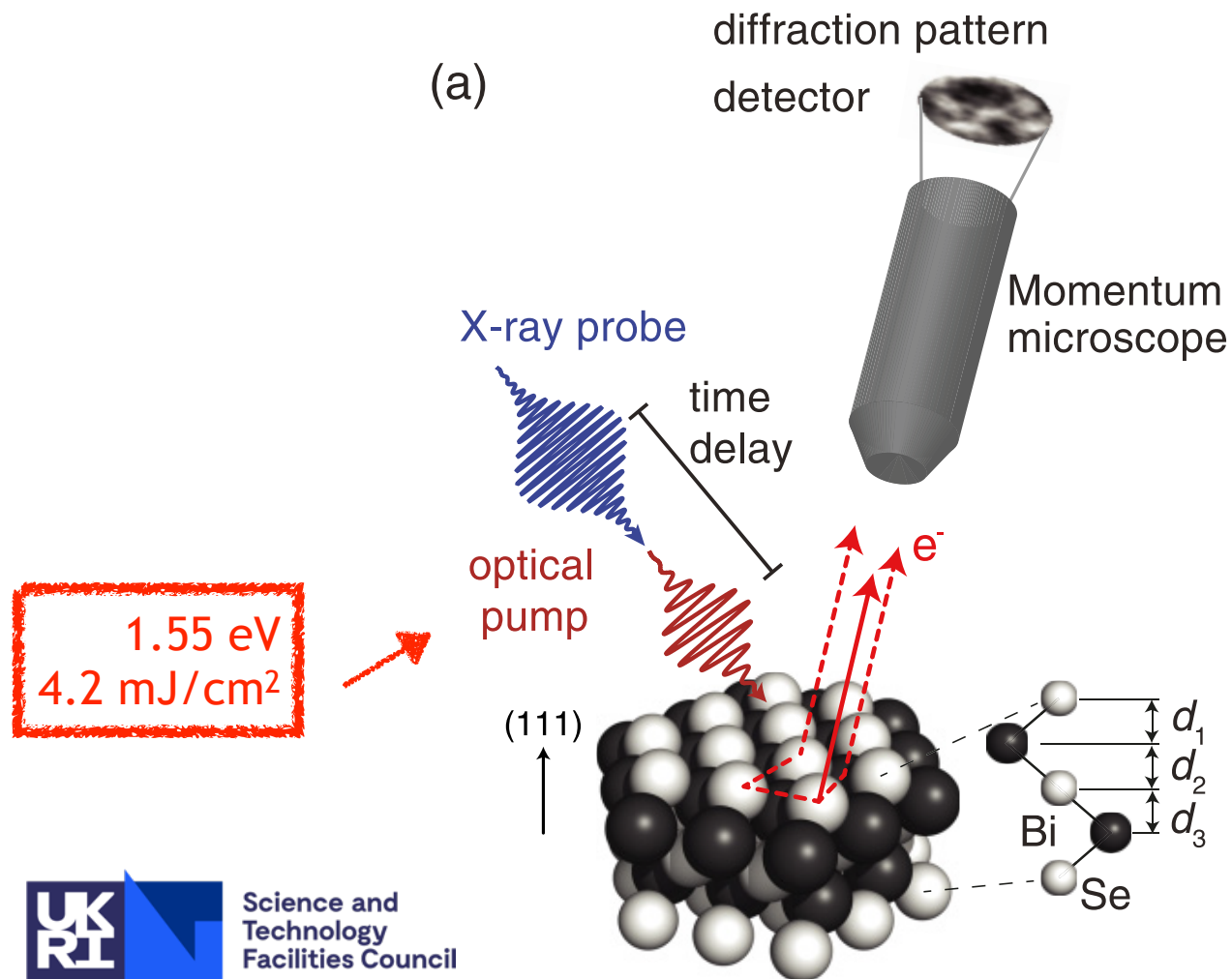
Bi

Se

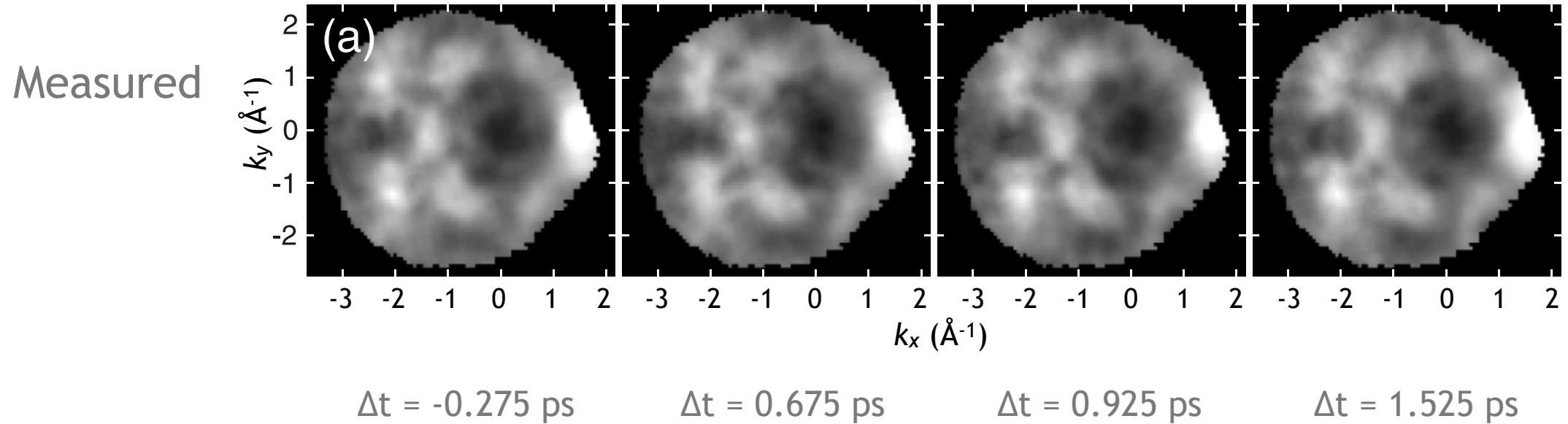
Bi

Se

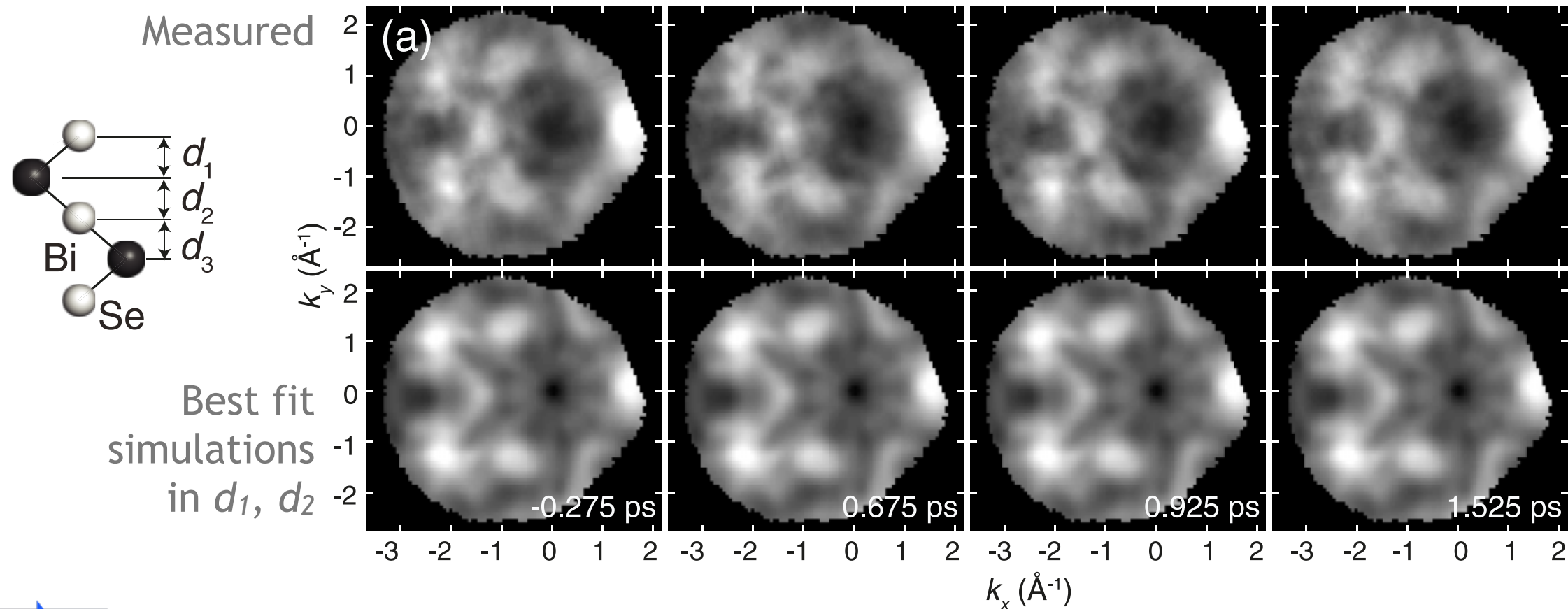
# Time-dependent measurements



# Time-dependent measurements

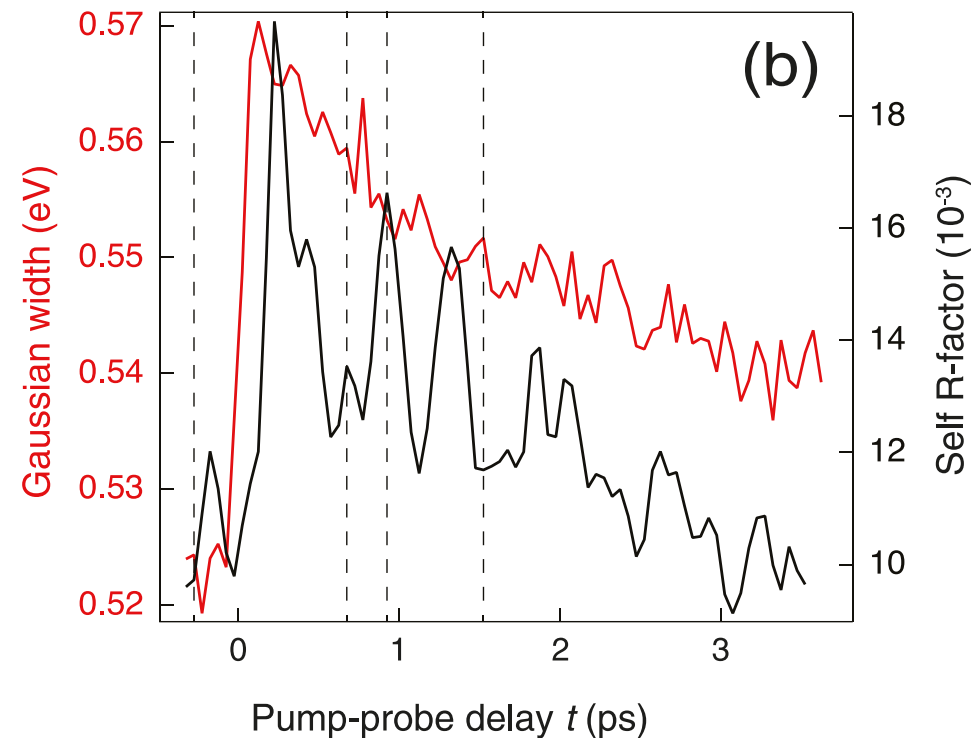
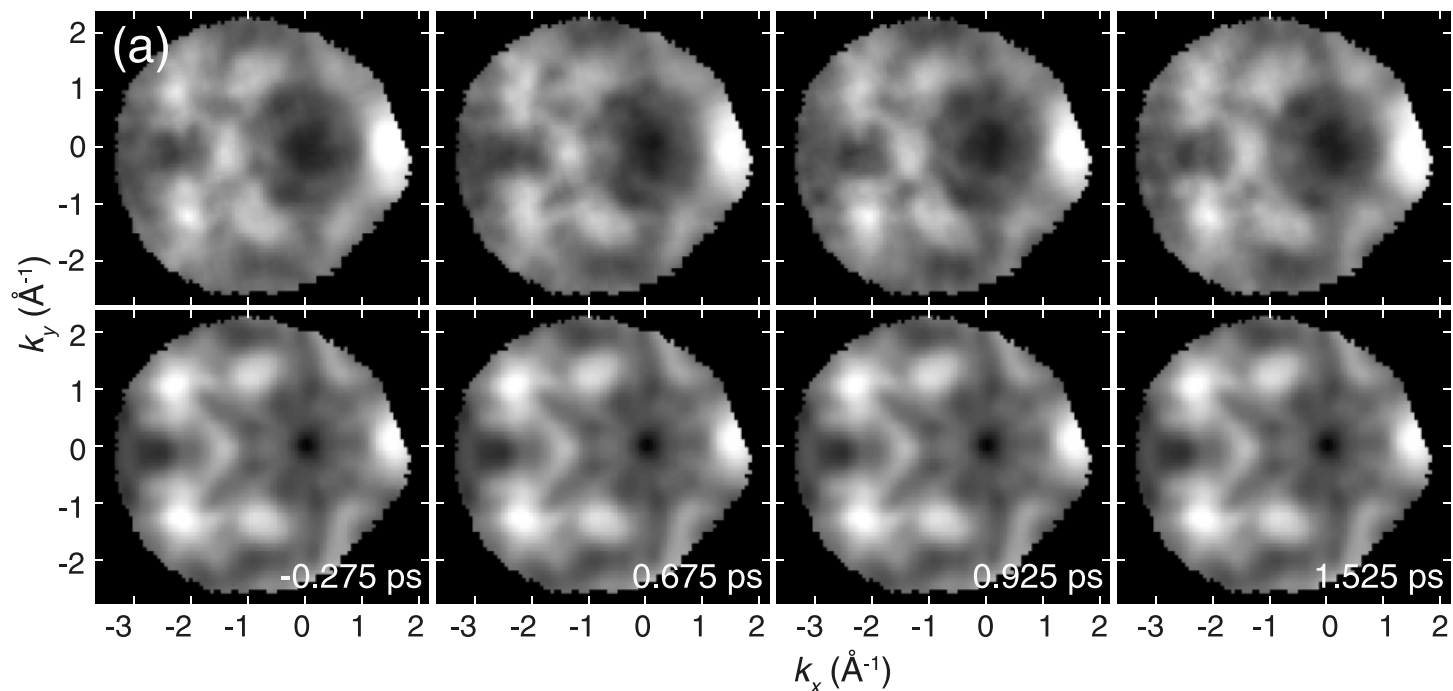


# Time-dependent measurements



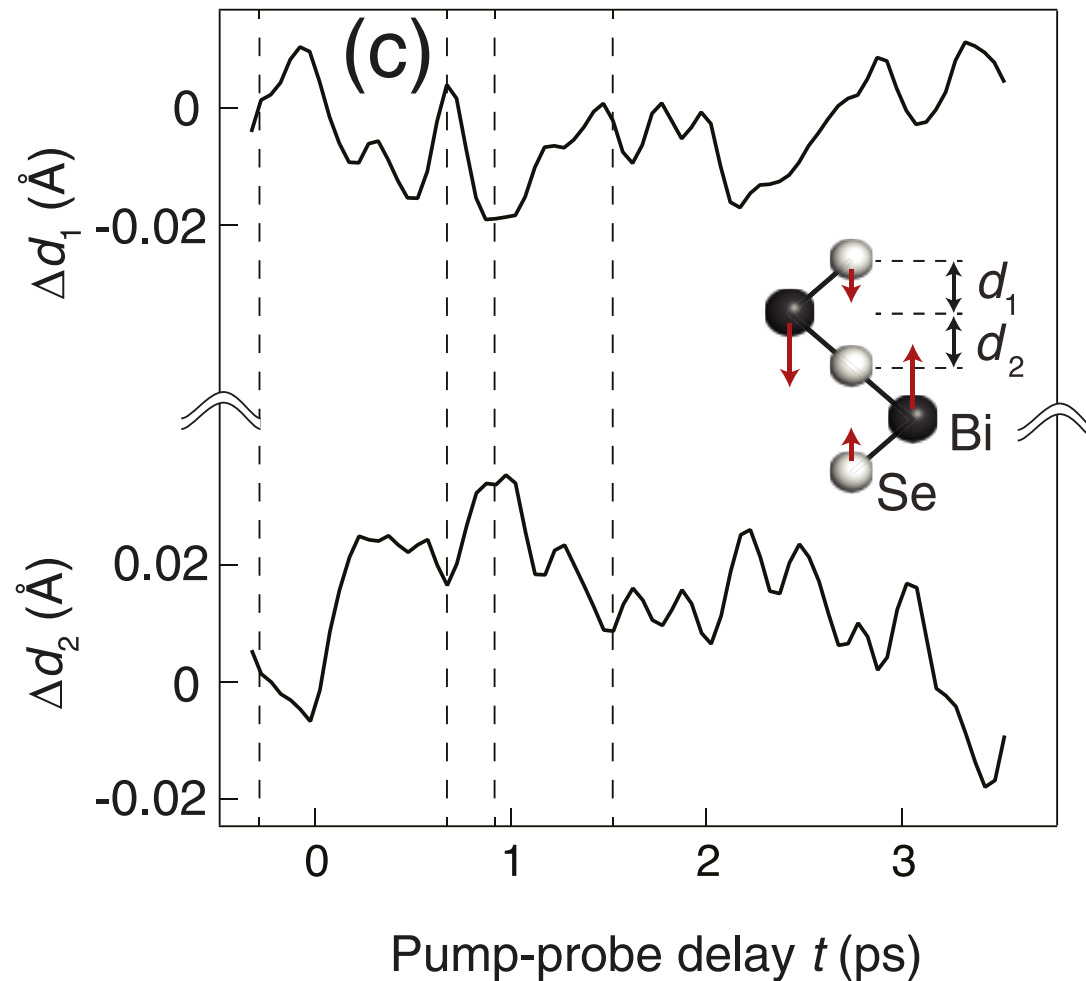
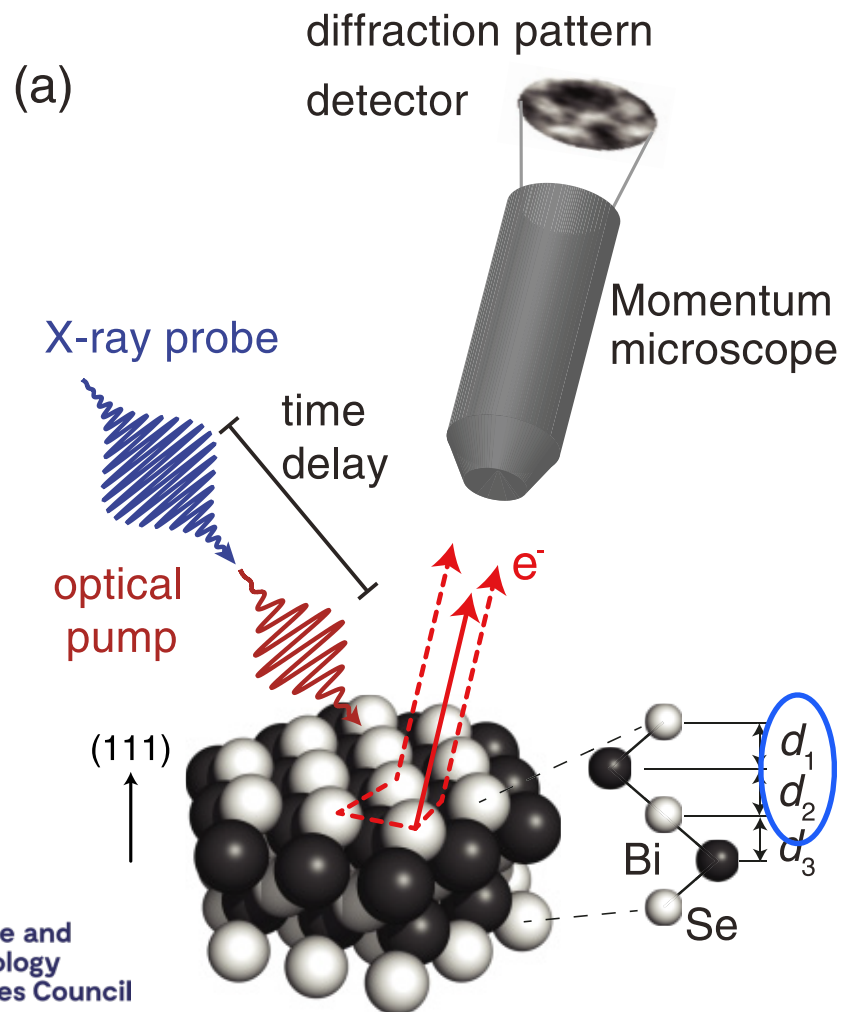
(Starting point for structural optimization: equilibrium bulk values)

# Time-dependent measurements



$$R = \frac{\sum_i (\chi_{exp,i} - \chi_{sim,i})^2}{\sum_i (\chi_{exp,i}^2 + \chi_{sim,i}^2)} \rightarrow R_{self} = \frac{\sum_i (\chi_{exp(t),i} - \chi_{exp(t_0),i})^2}{\sum_i (\chi_{exp(t),i}^2 + \chi_{exp(t_0),i}^2)}$$

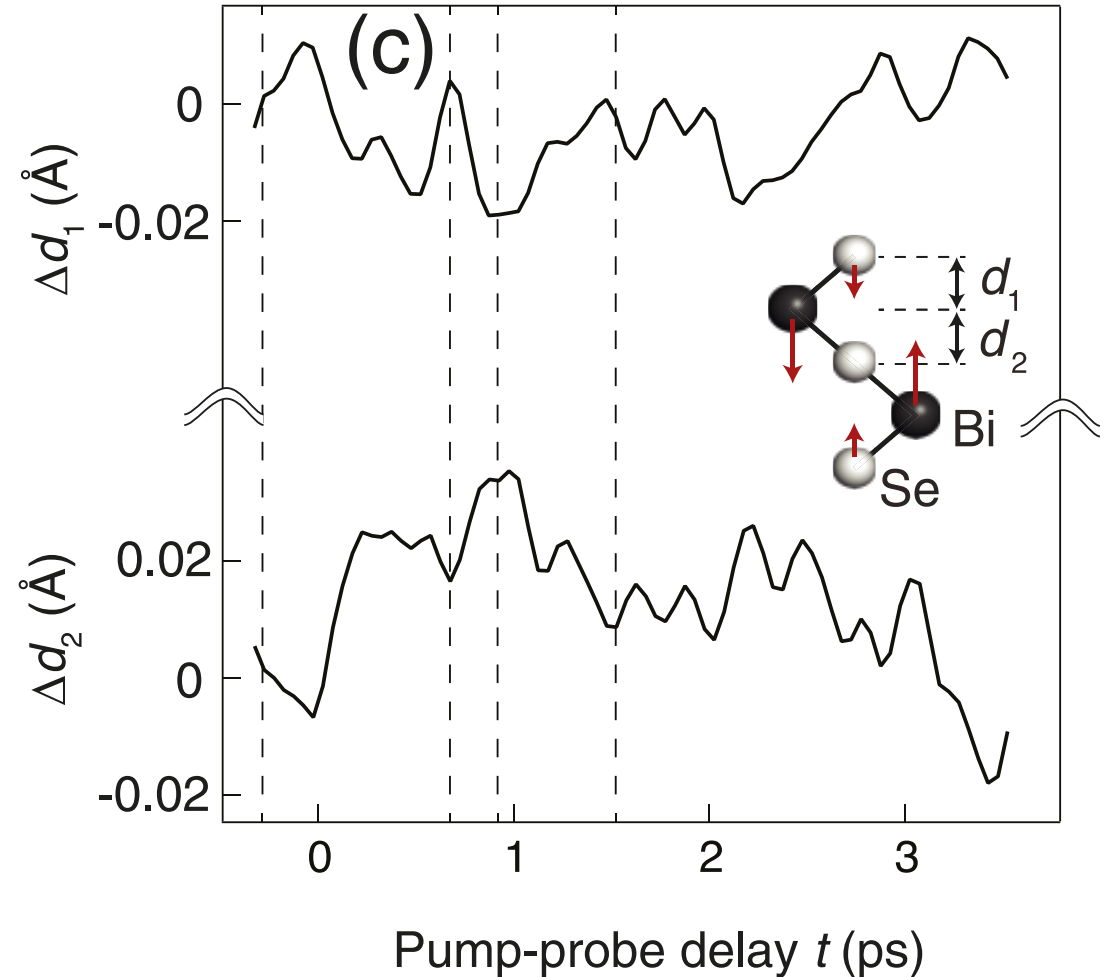
# Surface-softened phonon mode



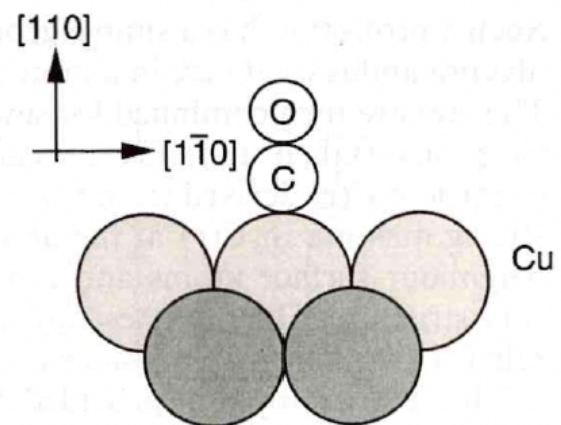
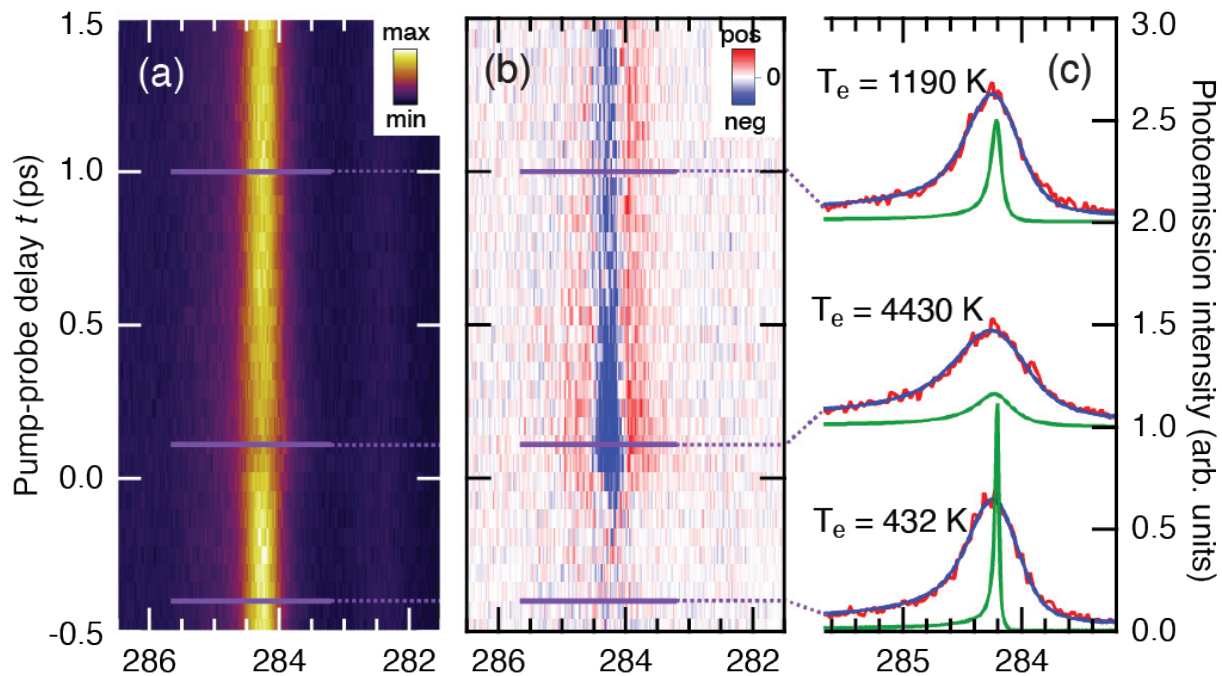
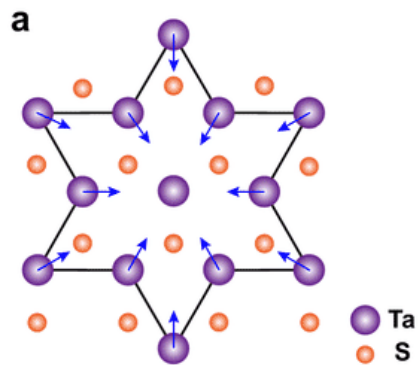
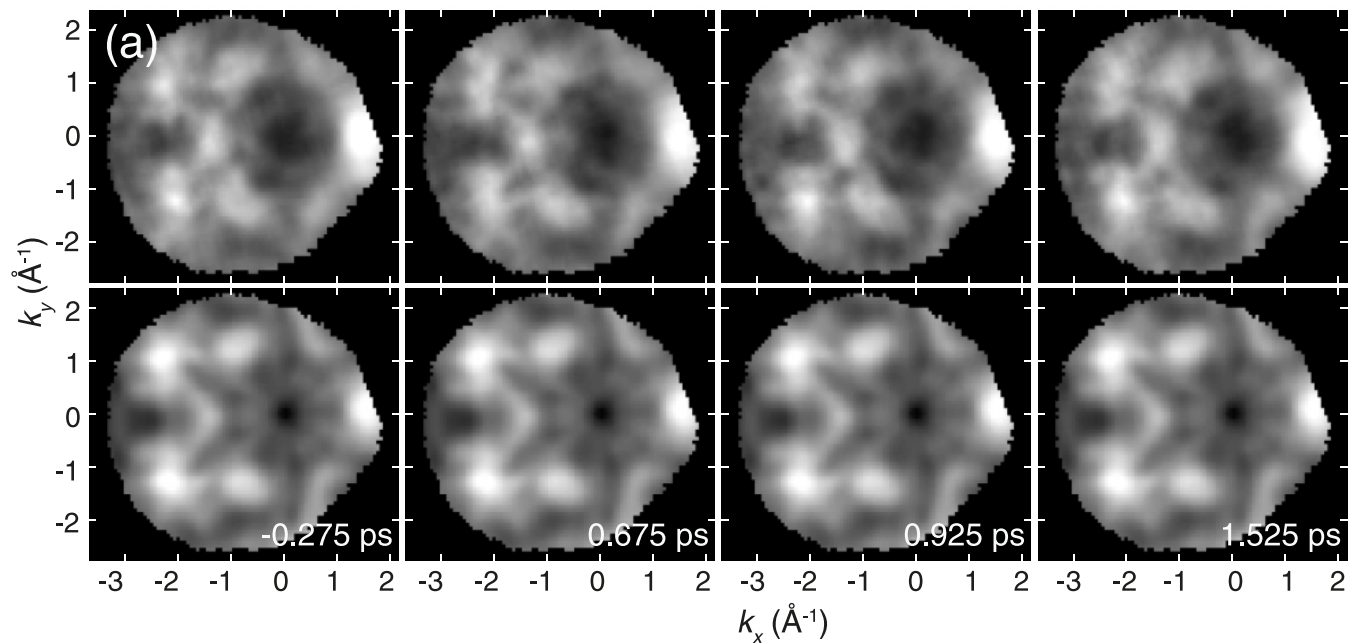
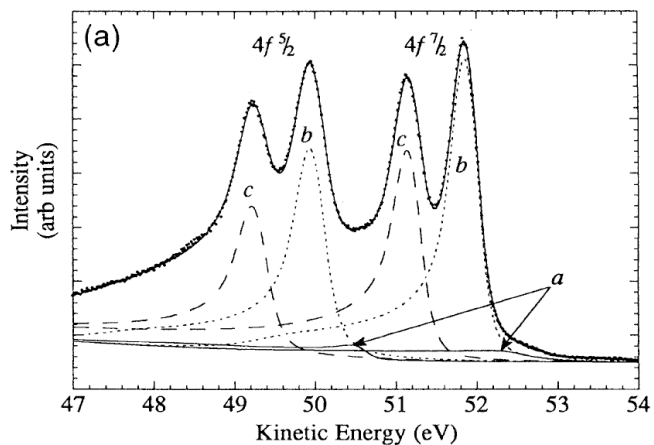
# Surface-softened phonon mode

- Approx. 500-fs period of oscillation, few-ps decay time
- Consistent with 2-THz  $A_{1g}^1$  softened mode at surface

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# Outlook





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# Thank you



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