Time resolved x-ray spectroscopy with free-electron lasers

Following electron dynamics on surfaces and in solids in real-time

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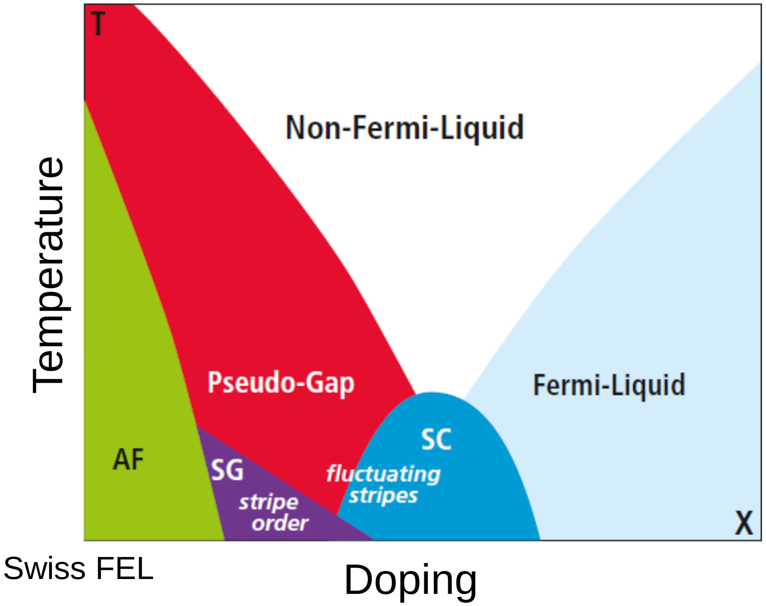
FLASH team
FERMI team
LCLS team

Some questions we might want to address



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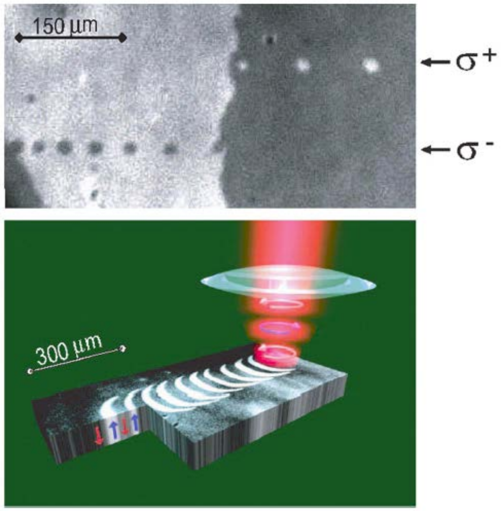
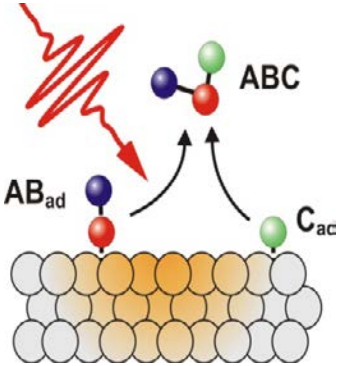


C. D. Stanciu, et al., PRL **99,** 047601 (2007)

Can we understand and control complex phases?

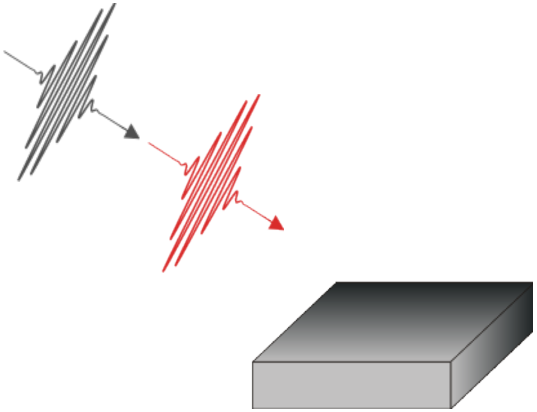
Dynamic control with light fields
e.g. how fast can one switch magnetisation ?

© Martin Wolf

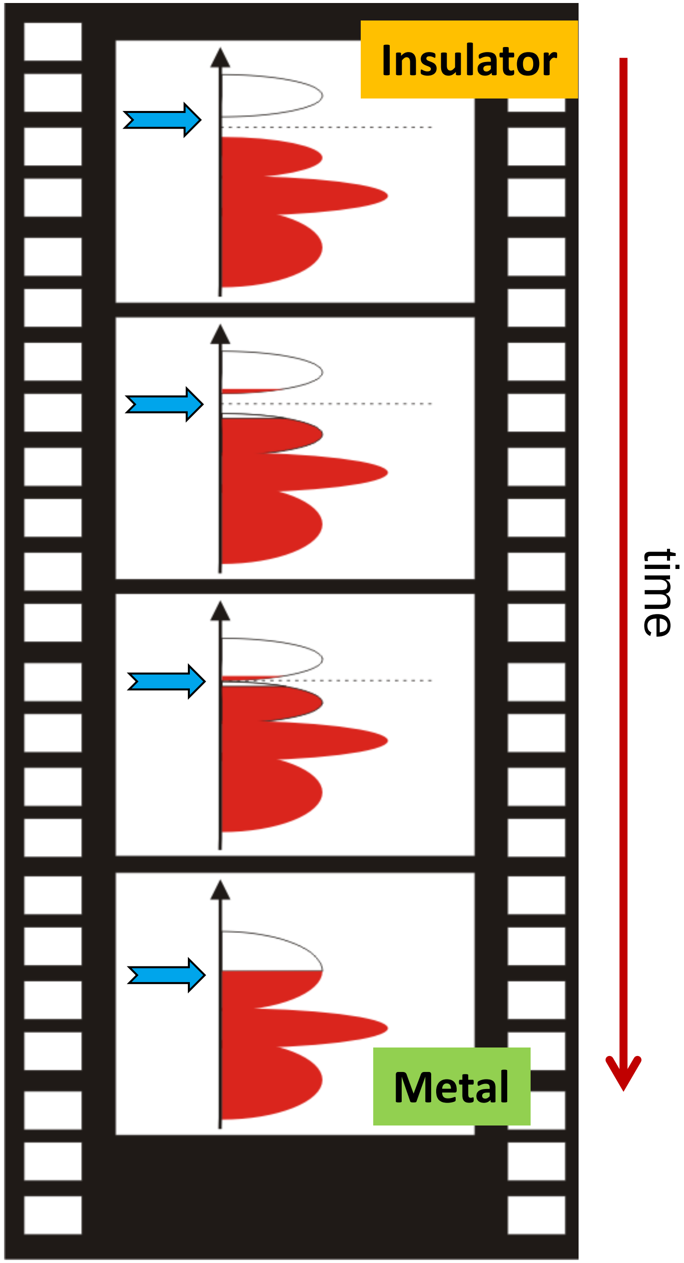


Surface catalysis
Can we observe transition states in reactions?

Finding an answer ? – Electronic structure movies



- Start a process by a controlled excitation (May be „Stay away from light“)
- Monitor the time-evolution of the electronic structure with x-ray spectroscopy



X-ray spectroscopy – the electronic structure toolbox

momentum

$E(k, R_{nuc}, \sigma)$ → spin

atomic position

ARPES

ESCA

photoemission

NEXAFS

x-ray absorption

XMCD

XMLD

x-ray emission

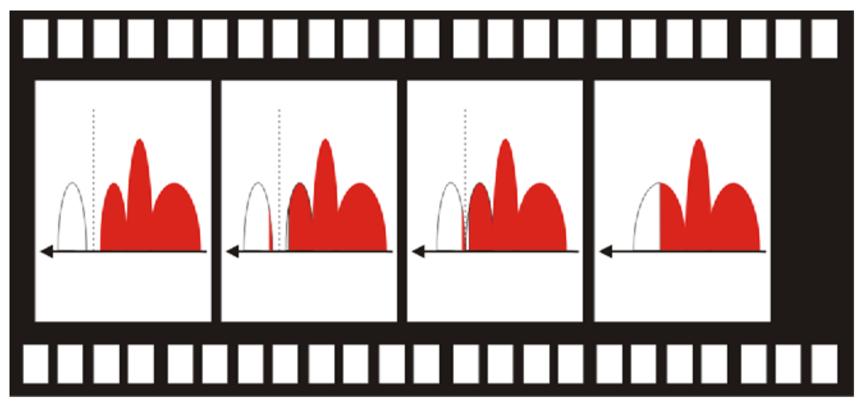
XES

RSXS

RIXS

Add time as a variable – pump-probe spectroscopy

$E(k, R_{nuc}, \sigma, \mathbf{t})$



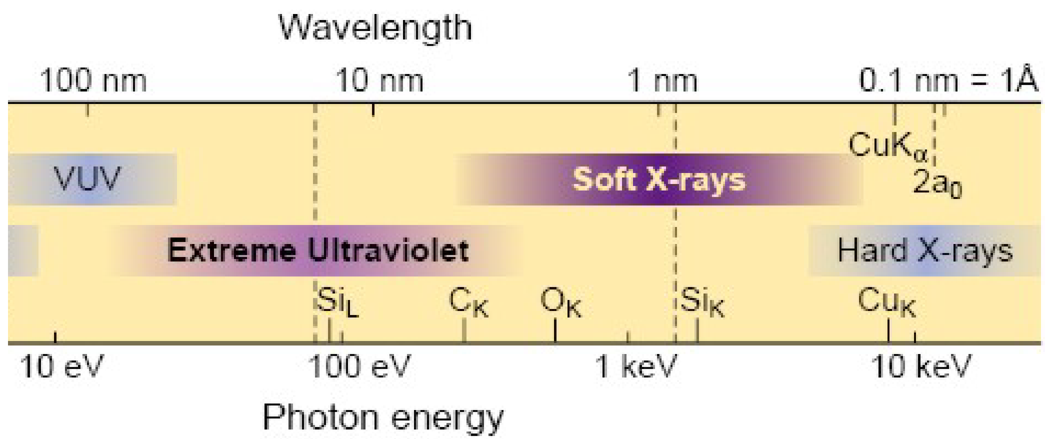
Need short pulse x-ray sources → Free-Electron Lasers

Free-electron lasers worldwide

	Start	Photon energy range [eV]	Pulse energies [mJ]	Pulse duration [fs]	No. of pulses [1/s]	Average brightness
FLASH	2005	30-310	-0.5	few fs-200	8000	1E+23
LCLS	2009	250-10k	-6	1-500	120	3E+21
SACLA	2011	6k-20k	-0.5	<20	10-60	
FERMI (seeded)	2012	20-60 (60-300)	0.1	(30)-100	10-50	
PAL FEL	~2016	12-120 1.8k-20k			60	
Swiss FEL	~2016	(180-1.8k) 1.8k-12k	0.005-0.2	1-200	100	2E+21
XFEL	~2016	250-25k	4	1-200	27000	3E+24
„LCLS II“ (cw)	~2020	250-5k	0.002-0.1	1-200	100k-1M	1E+25

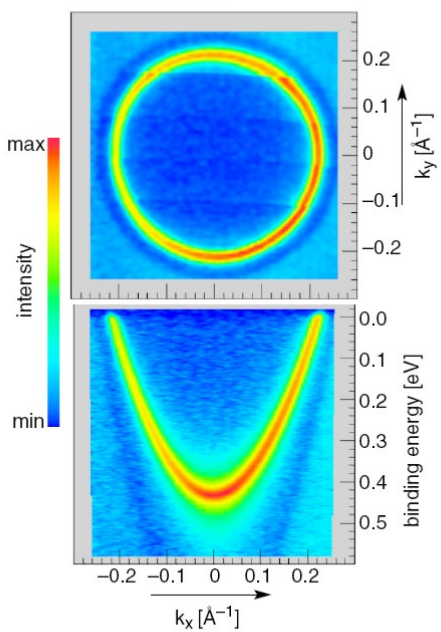
High repetition rate FEL‘s

From Extreme Ultraviolet to Hard X-Rays

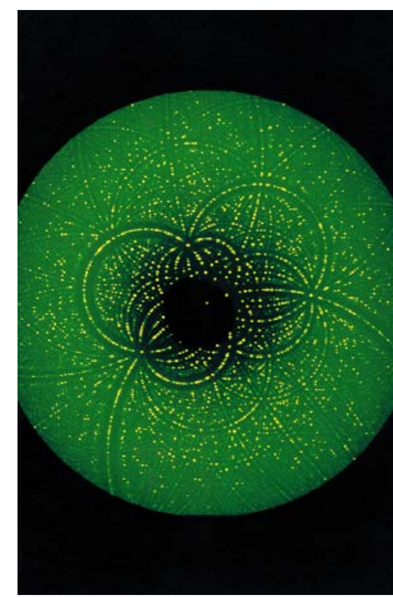


After D. Attwood

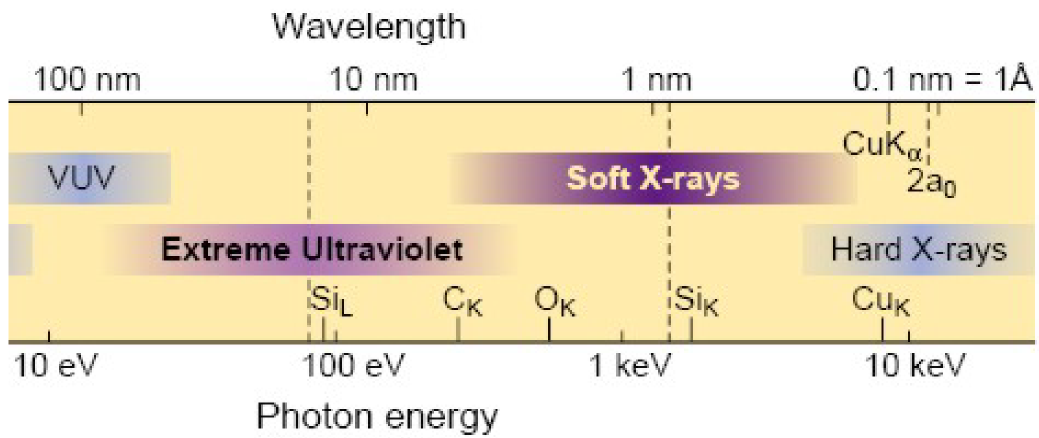
From electrons, spins and nanostructures



To images of atoms in motion



From Extreme Ultraviolet to Hard X-Rays



After D. Attwood

FERMI Sincrotrone Trieste

LCLS

FLASH
Free-electron laser FLASH

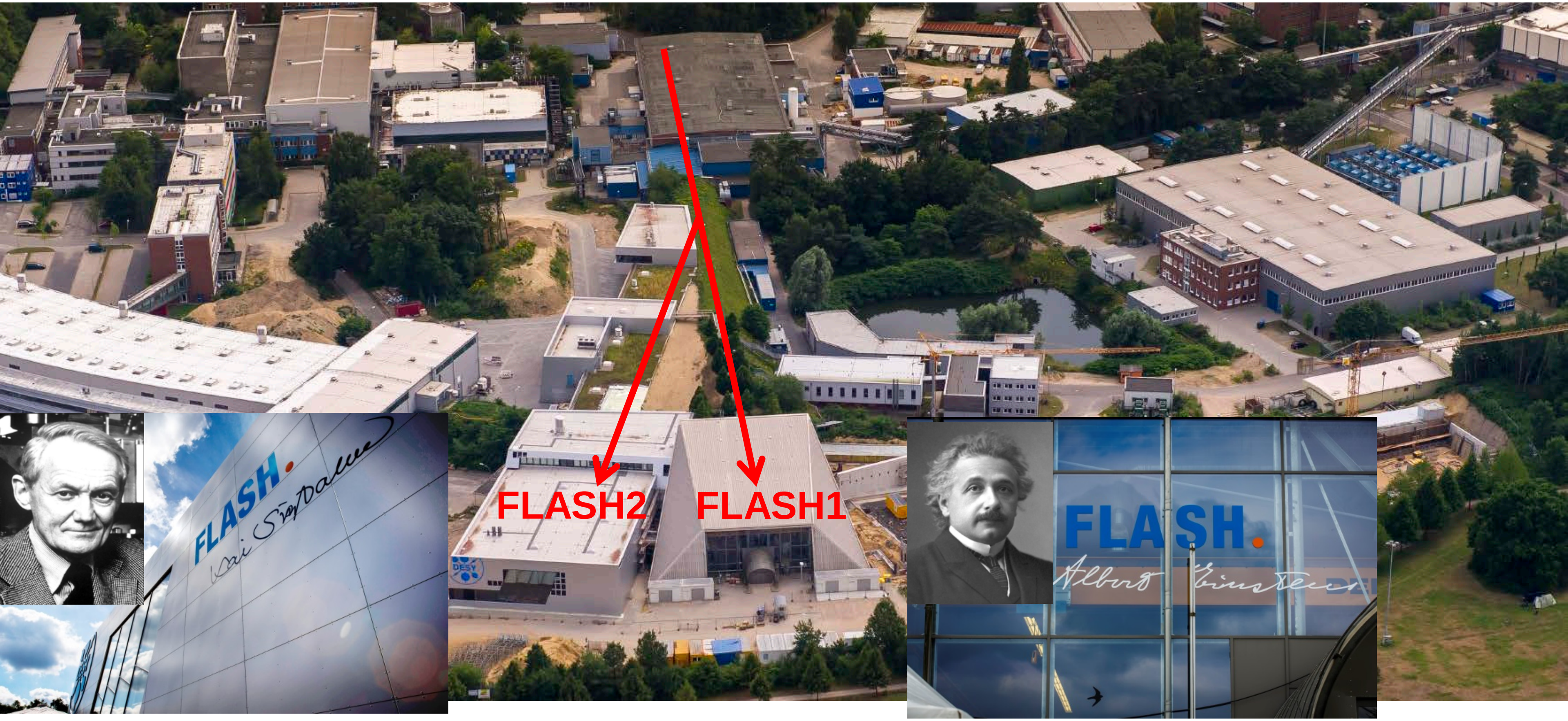
SACLA

European XFEL

PAUL SCHERRER INSTITUT
PSI
SwissFEL

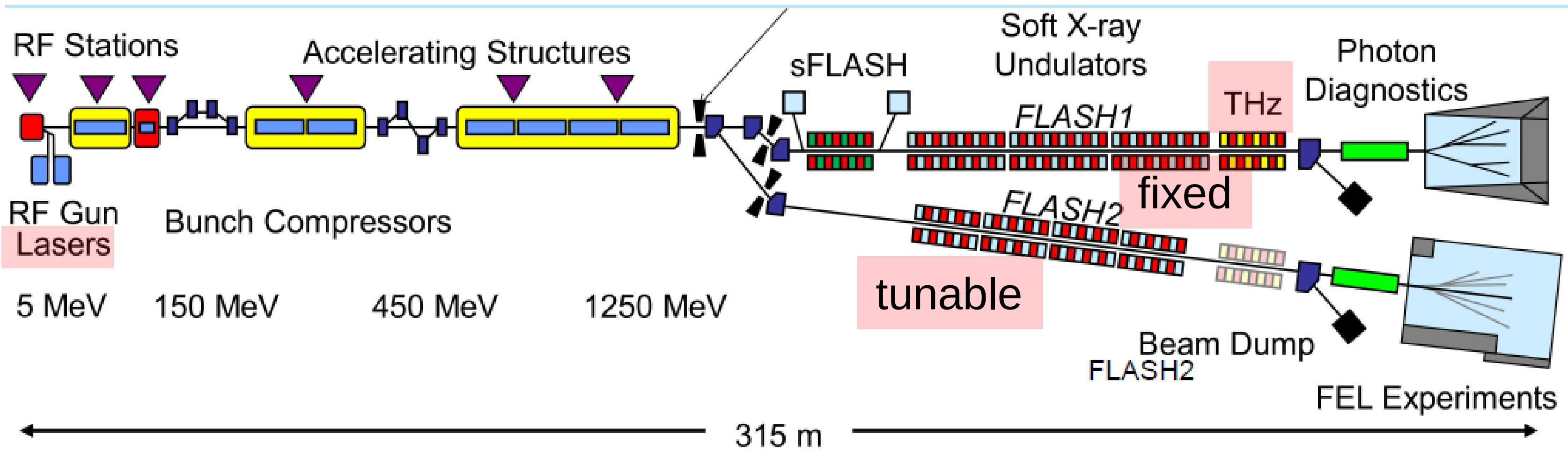
PAL

FLASH



“If I have seen further it is by standing on the shoulders of giants.”   Isaac Newton

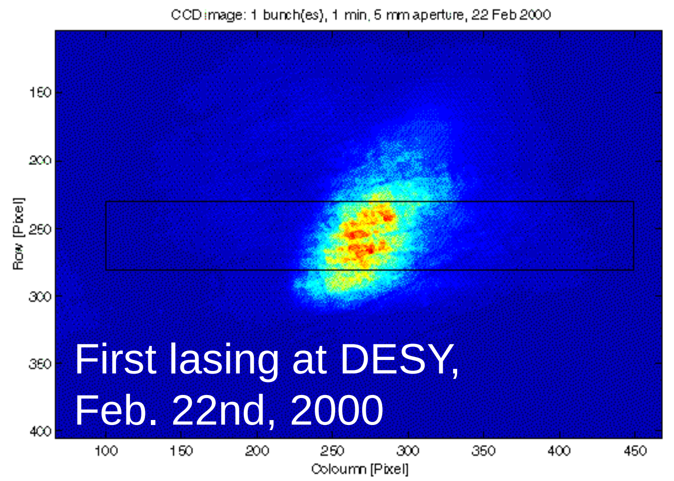
FLASH – FLASH1 and FLASH2

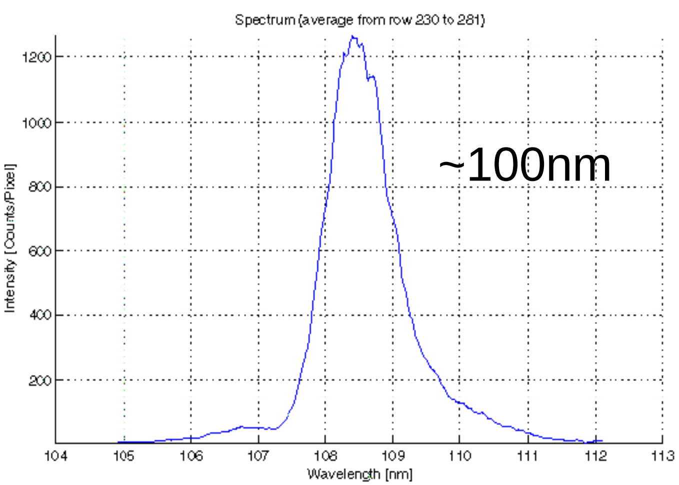


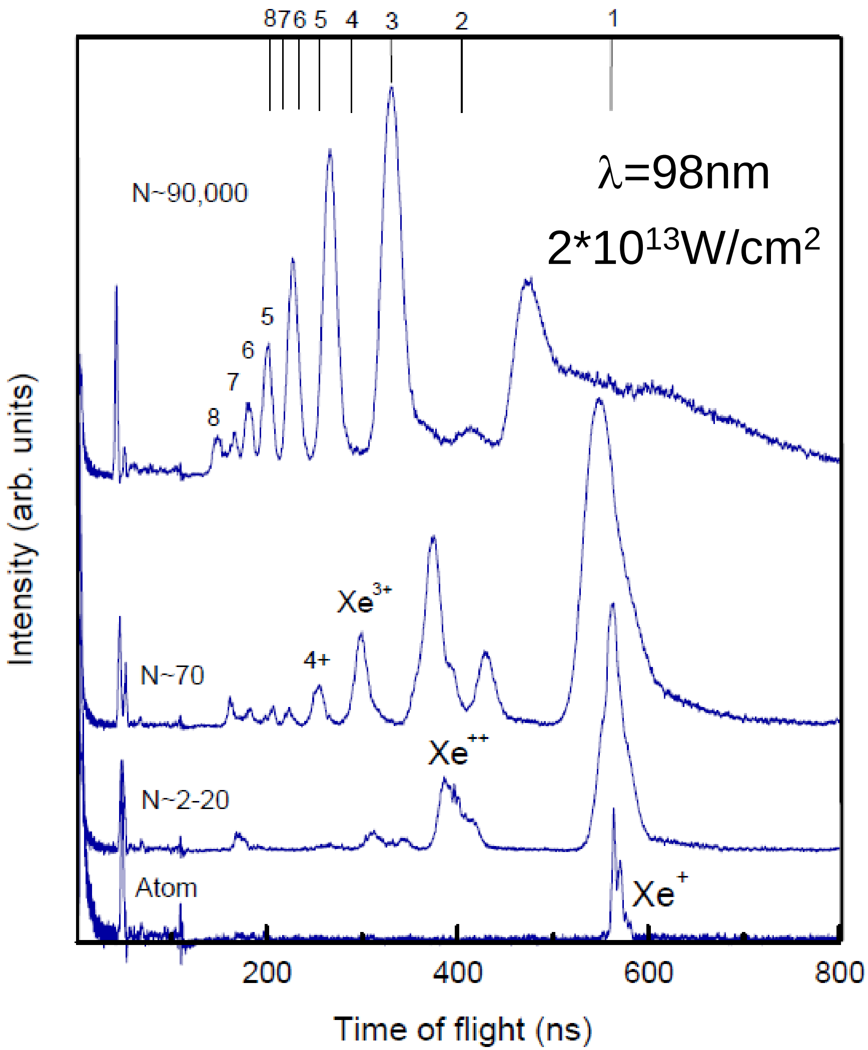
Photon energy range: 30-300eV tunable, up to 8000 pulses/s, pulse energy up to 500µJ

- **Only high repetition rate XUV and soft x-ray FEL world-wide**
- **Since 2014 two independent FEL lines**
- **Very short FEL pulses (3fs-200fs)**
- **Fully optically synchronised**
- **Integrated THz sources**

TTF-1 – The first short wavelength SASE FEL

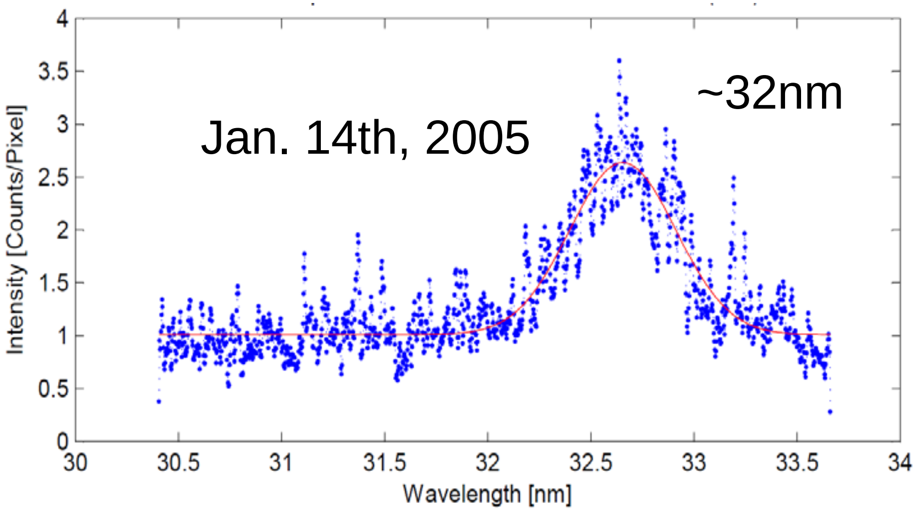


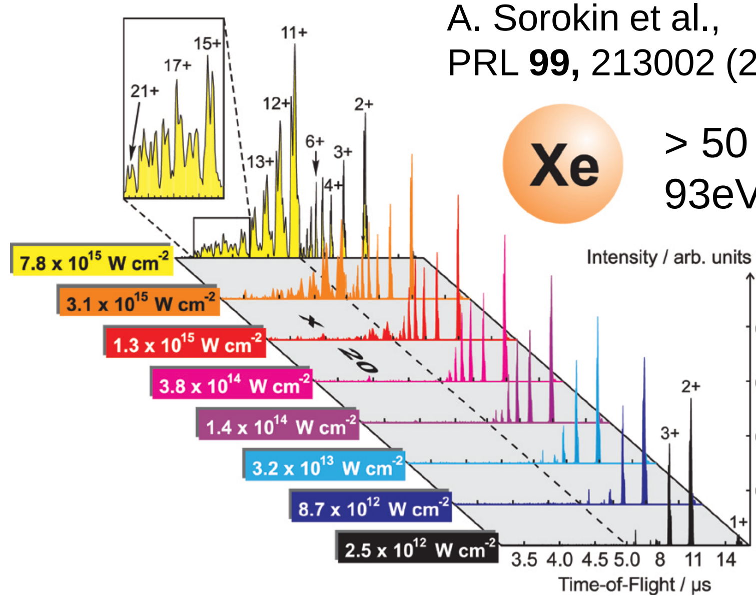




H. Wabnitz et al., Nature **420**, 482 (2002)

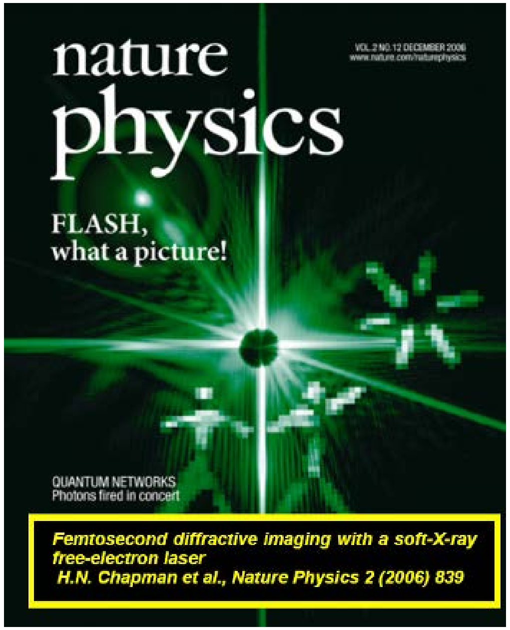
FLASH - 10 years of operation as a user facility



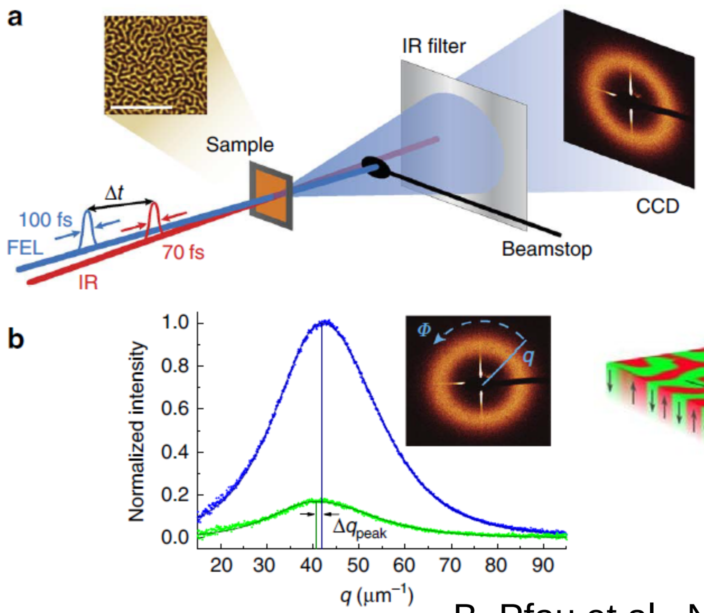


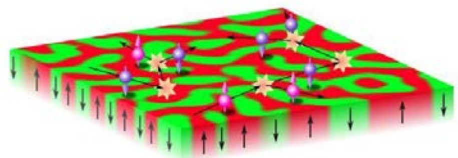
A. Sorokin et al.,
PRL **99,** 213002 (2007)

> 50 photons
93eV



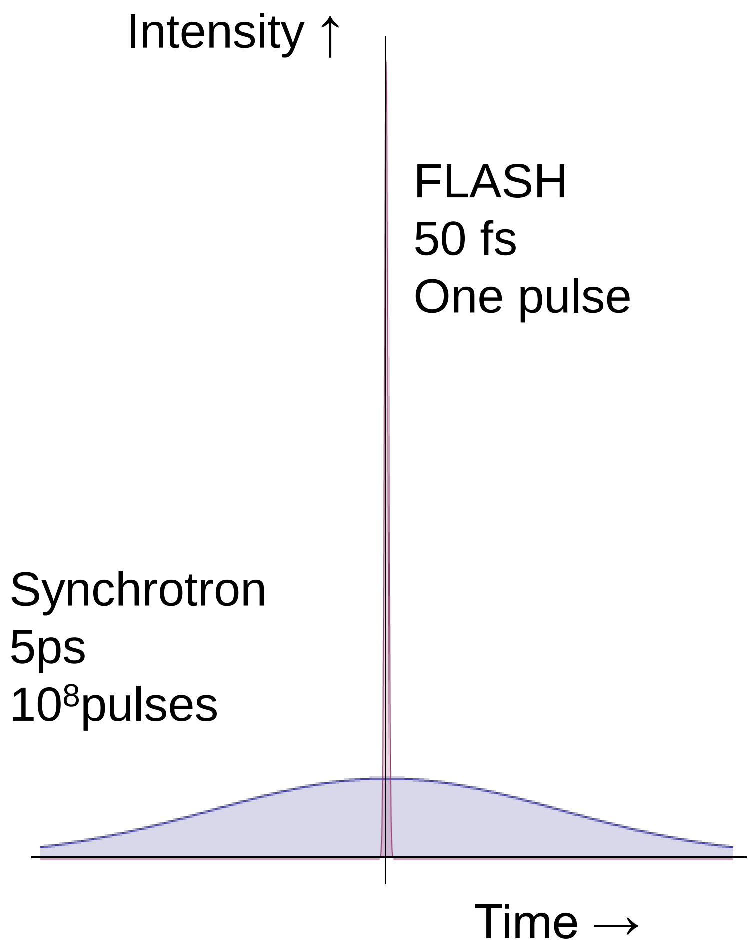
Femtosecond diffractive imaging with a soft-X-ray free-electron laser
H.N. Chapman et al., Nature Physics 2 (2006) 839





B. Pfau et al., Nature Commun. 2012

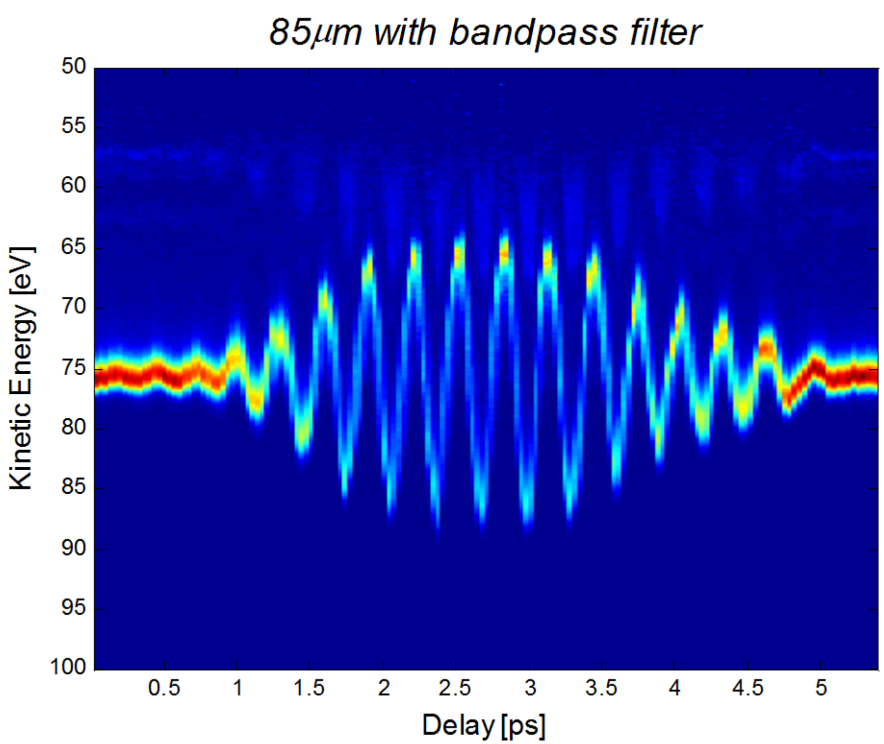
Extreme brillance – ultrashort pulses



Photon energy range: 30-300eV

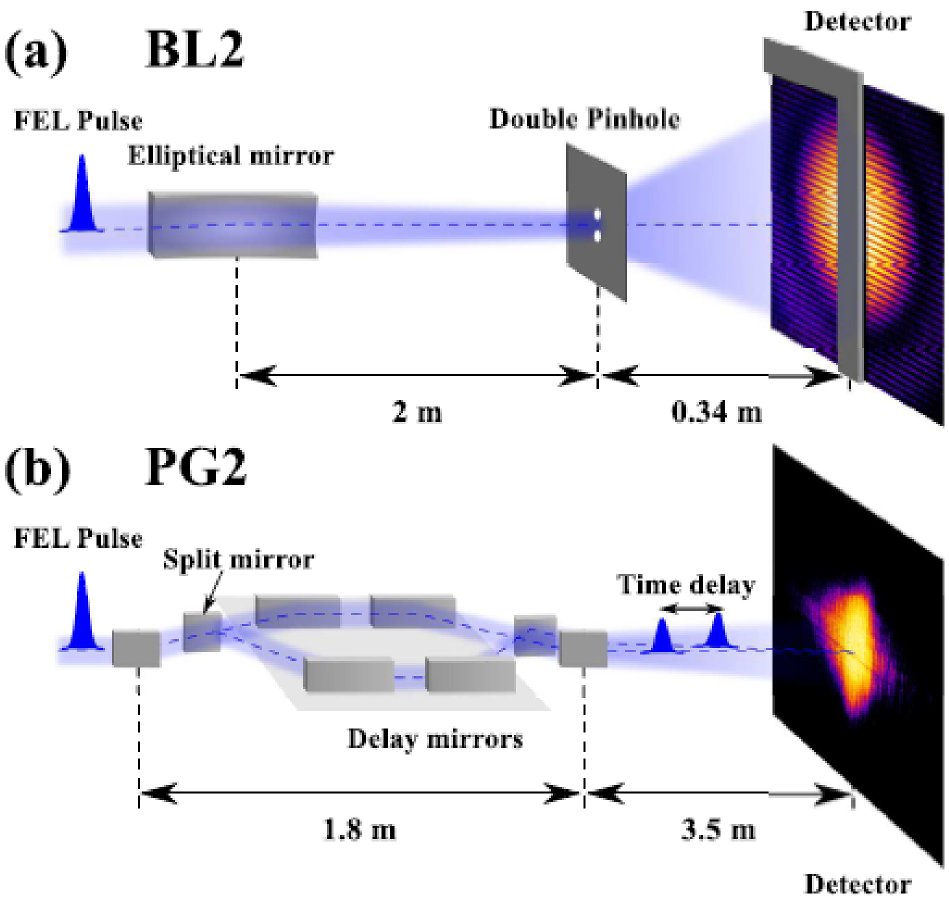
Photoelectron pulses image light fields

Krypton 4p photoelectrons emitted with 13.5nm FLASH pulses in a THz field

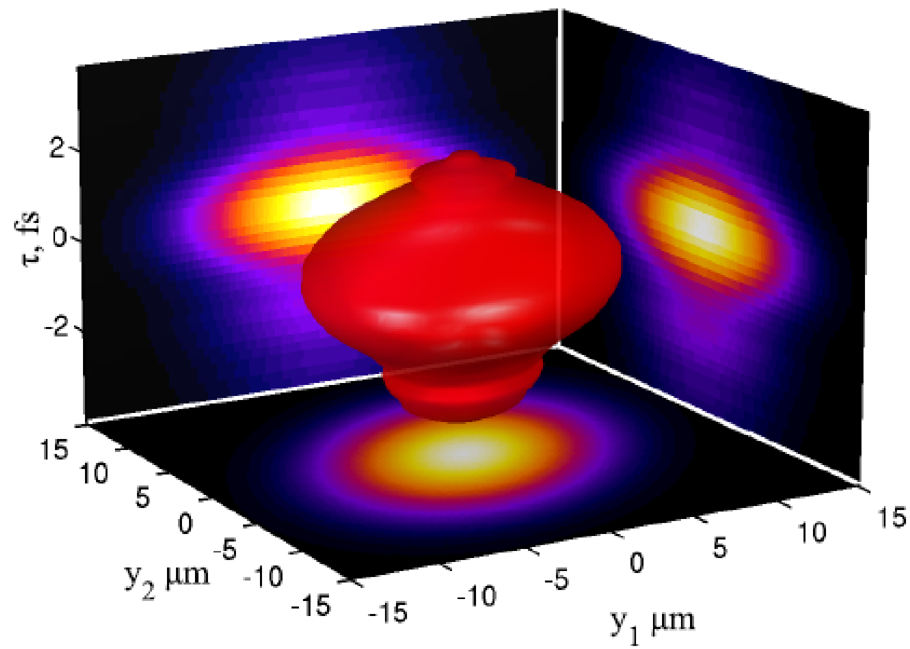


Ulrike Frühling et al.
Nat. Photonics 3, 523, (2009)

Coherence properties of FLASH



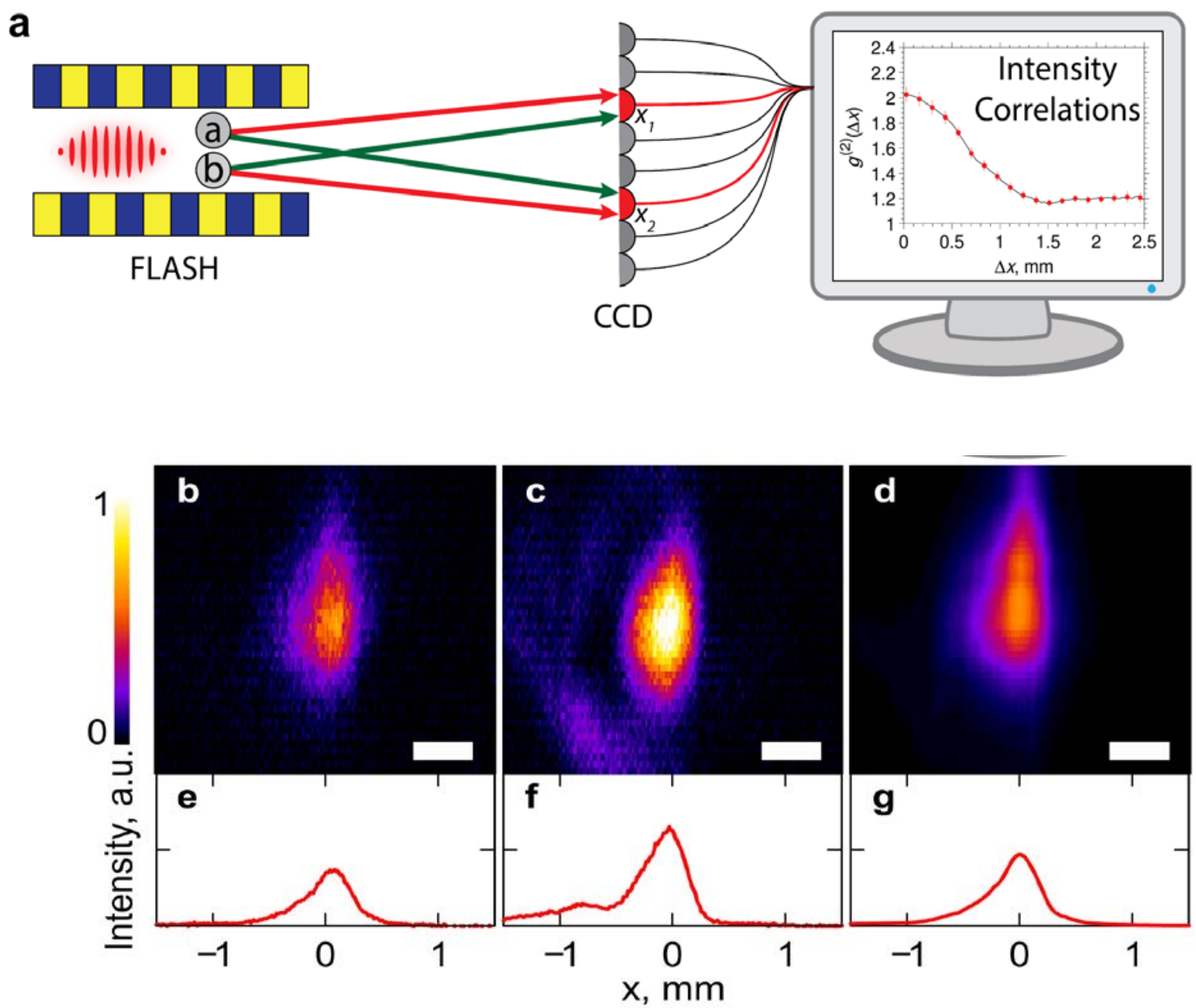
Mutual coherence function



About 1% of total power in a single mode
~10^{10} photons

collaboration with the group of I.A. Vartanyants
A. Singer et al., Optics Express 16, 17480 (2012)

Hanbury Brown-Twiss experiment



Single shots

Average

$$g^{(2)}(\mathbf{r}_1, \mathbf{r}_2) = \frac{\langle I(\mathbf{r}_1) \cdot I(\mathbf{r}_2) \rangle}{\langle I(\mathbf{r}_1) \rangle \langle I(\mathbf{r}_2) \rangle}$$

$$g^{(n)}(\mathbf{r}_1, \ldots, \mathbf{r}_n) = \frac{\langle \prod_{i=1}^{n} I(\mathbf{r}_i) \rangle}{\prod_{i=1}^{n} \langle I(\mathbf{r}_i) \rangle}$$

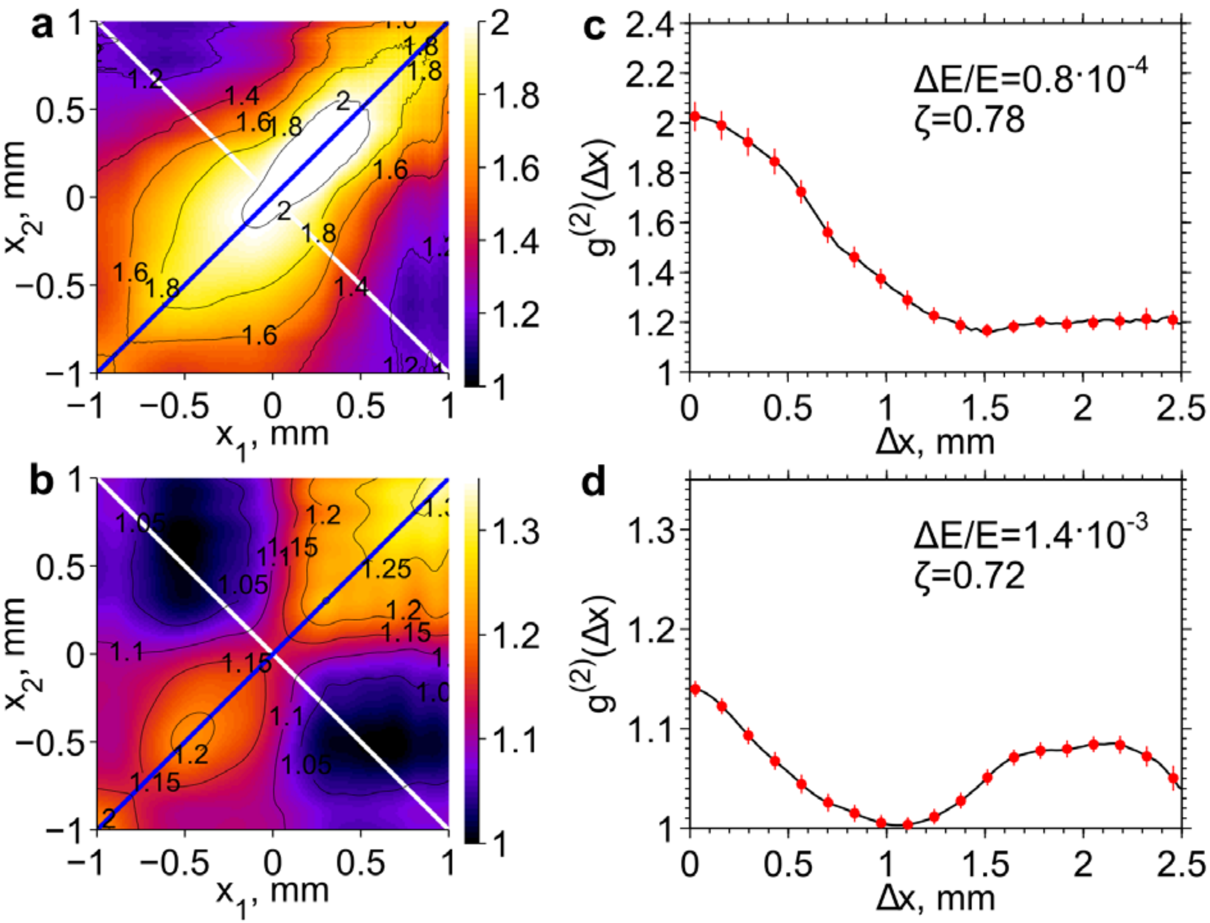
λ=5.5nm

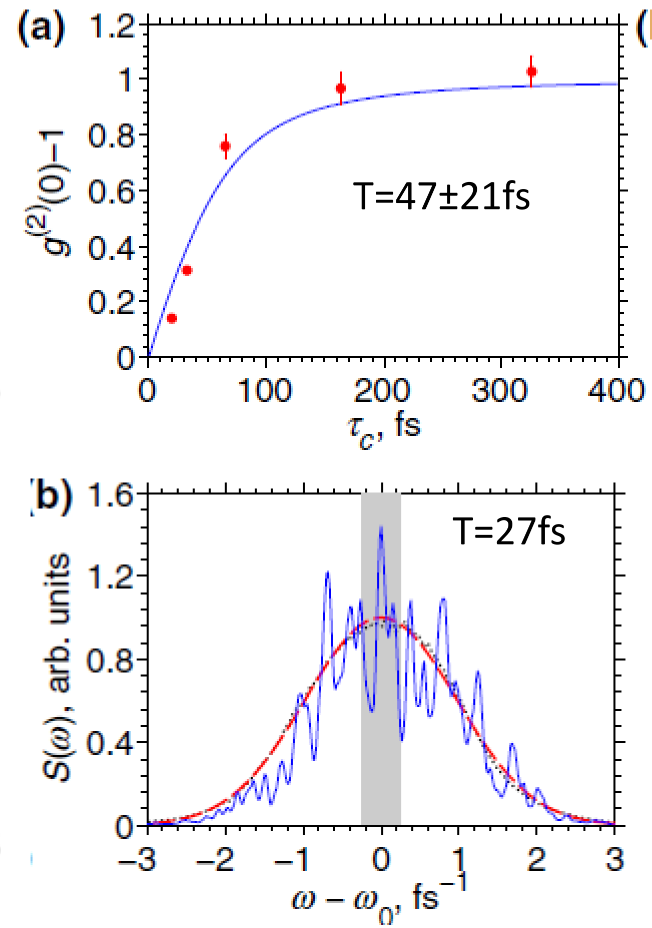
A. Singer et al., PRL 111, 034802 (2013)

Gaussian statistics – chaotic source

Averaged over $2x10^4$ shots

$g^{(2)}$ depends on $\frac{\tau_c}{T}$





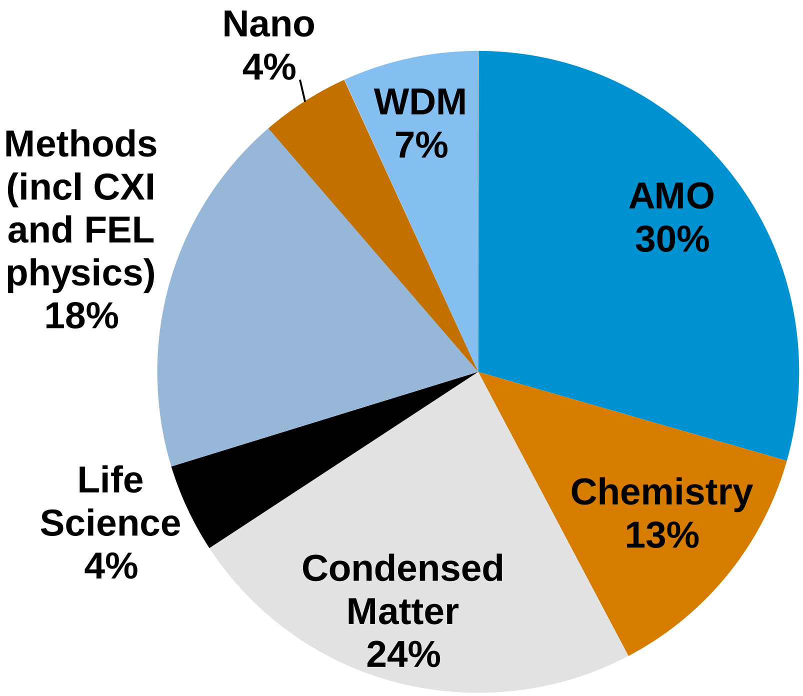
transverse coherence 80%, average pulse duration <50fs, degeneracy parameter 10^9

A. Singer et al., PRL 111, 034802 (2013)

High repetition rate free-electron lasers – perfect for time-resolved spectroscopy

Ultra bright

- High **average** brightness (8000 pulses/s (FLASH) – 27000 pulses/s (XFEL) -100kHz-1MHz (LCLS II)



Ultra short

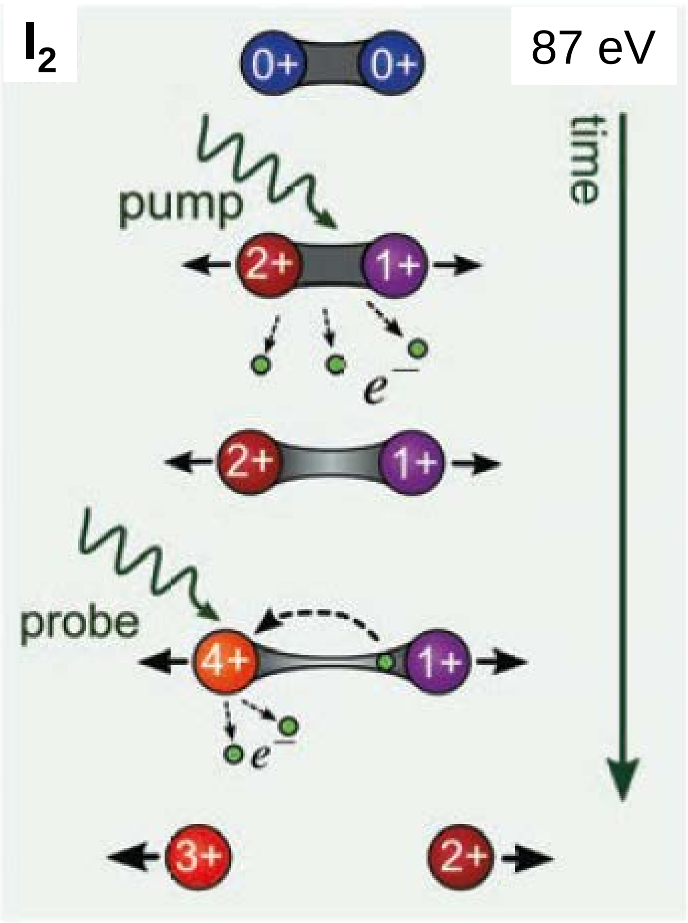
Pulse length down to a few fs – single spike SASE

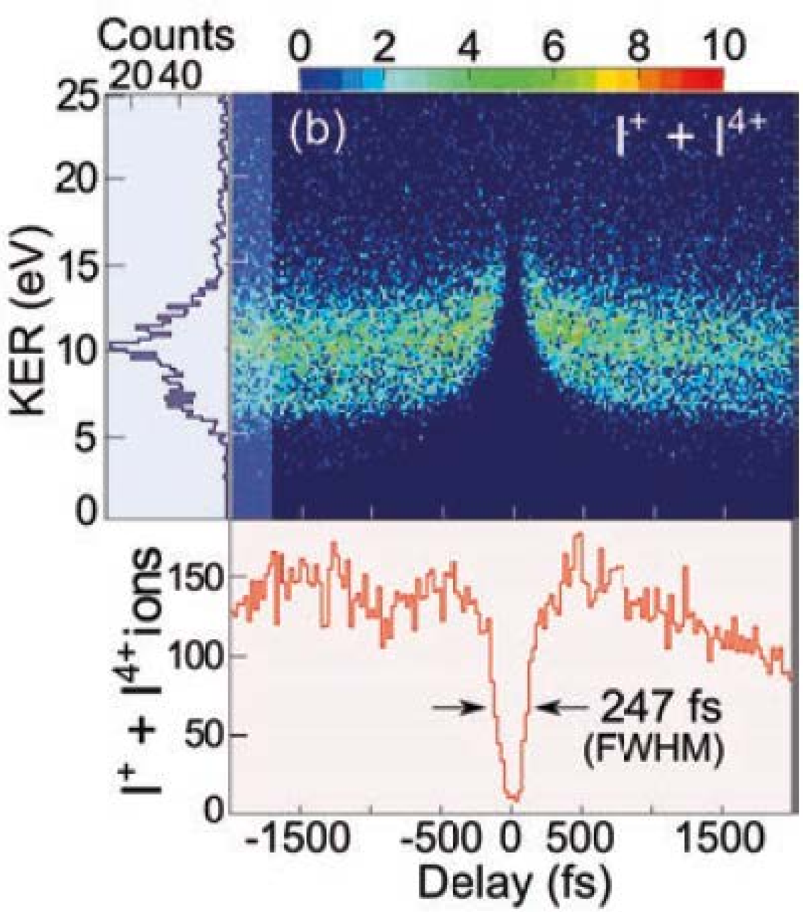
80-90% pump-probe exp.

- 50% optical/XUV
- 30% XUV/XUV
- 20% THz/XUV

AMO physics – XUV Pump – XUV probe

Electron rearrangement in dissociating molecules





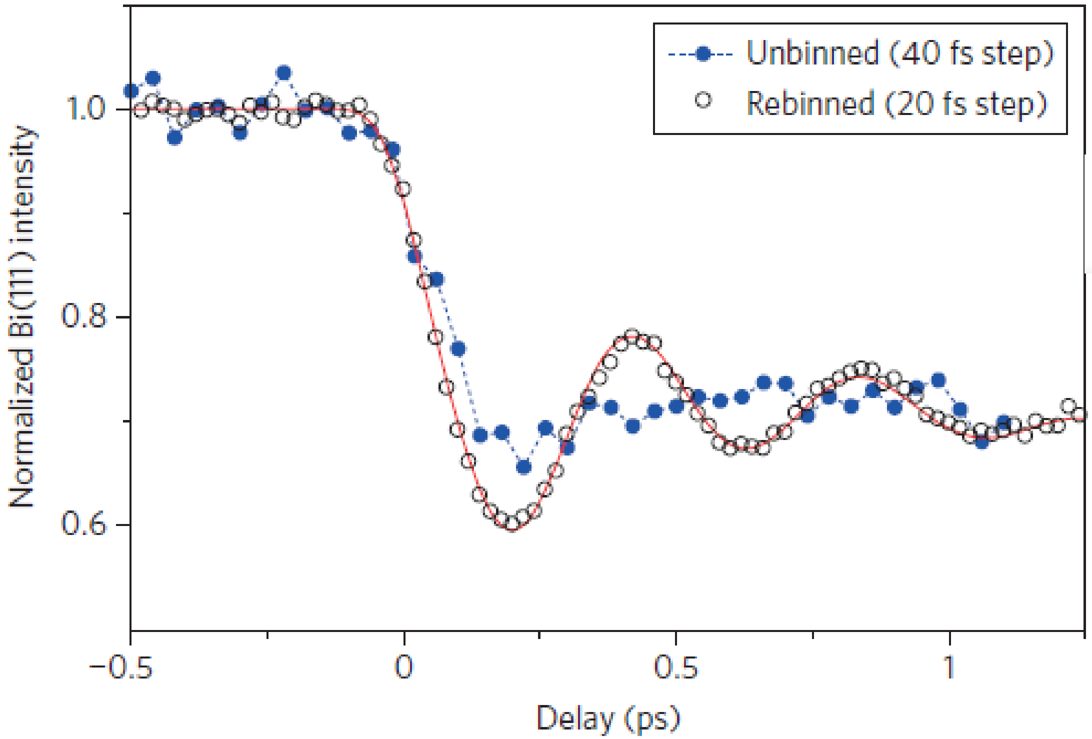
K. Schnorr et al. PRL 113, 073001 (2014)

Challenges for TR-studies: Synchronisation and timing

Problem: Timing jitter between external lasers and FEL's

Solution:

a) perfect synchronisation (eg. Seeding – FERMI 7fs rms)
or b) shot-to-shot timing diagnostics

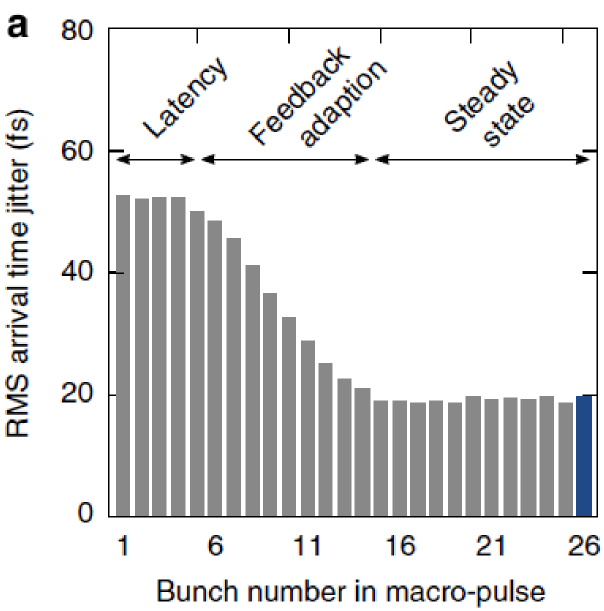


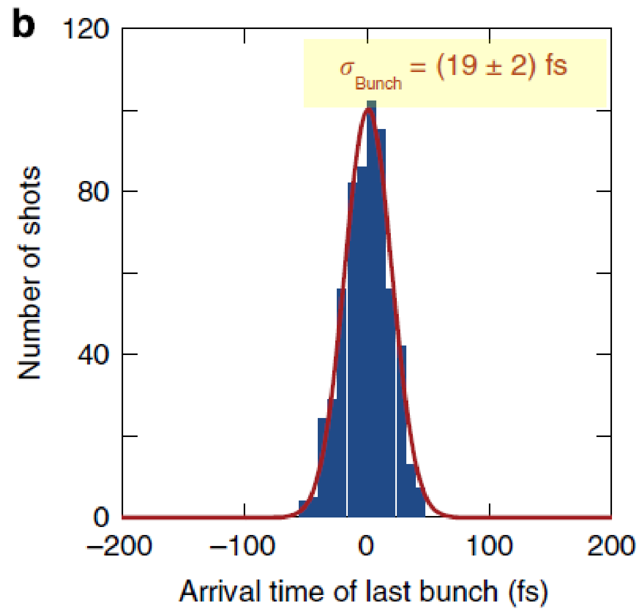
LCLS

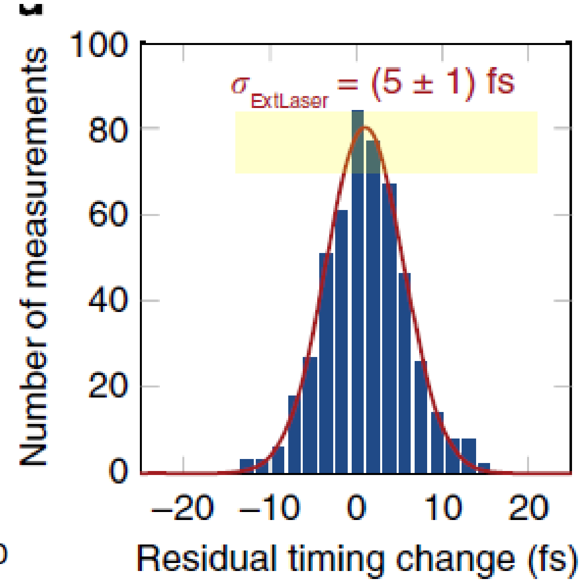
M. Harmand et al.,
Nat. Phot. 7, 215 (2013)

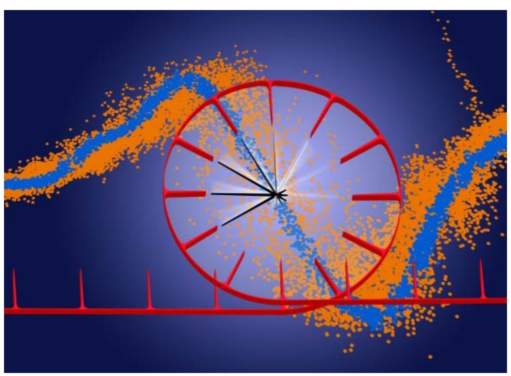
→ b) has to be combined with single-shot detection capabilities

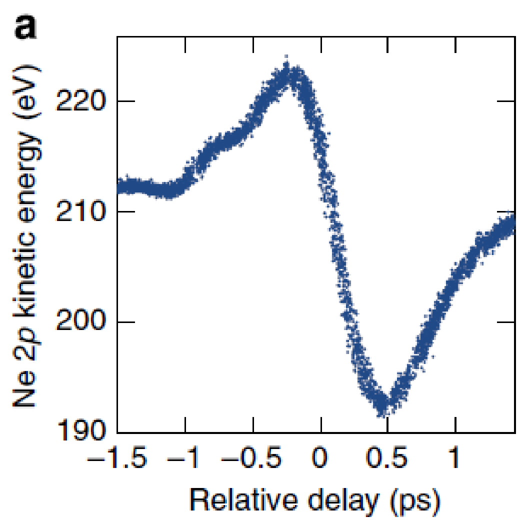
Stability of FLASH: All-optical synchronization

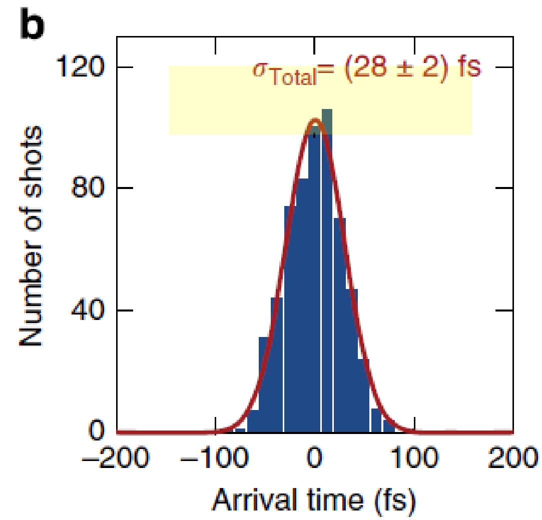






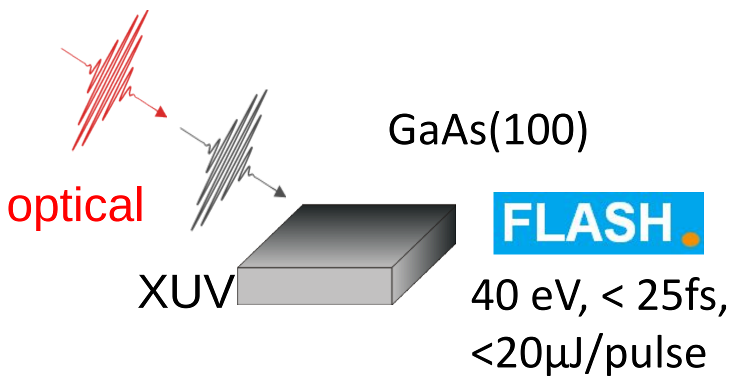




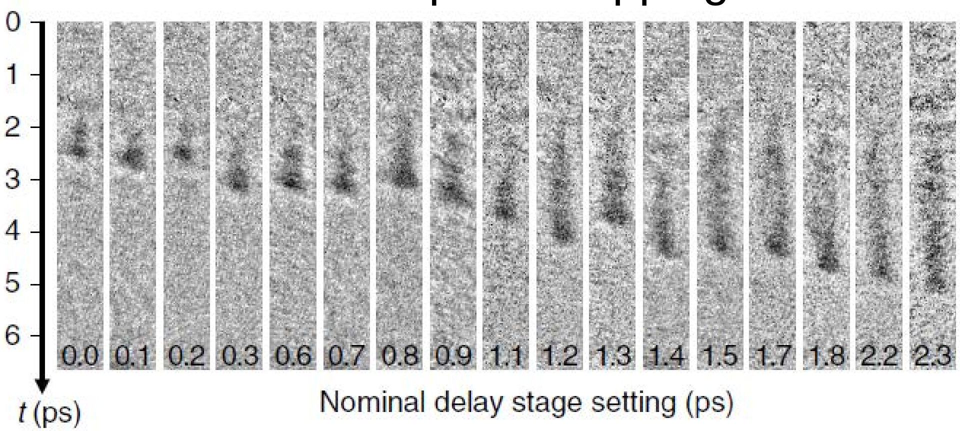


S. Schulz et al, Nature Comm. DOI: 10.1038/ncomms6938

Timing diagnostics - Cross correlation

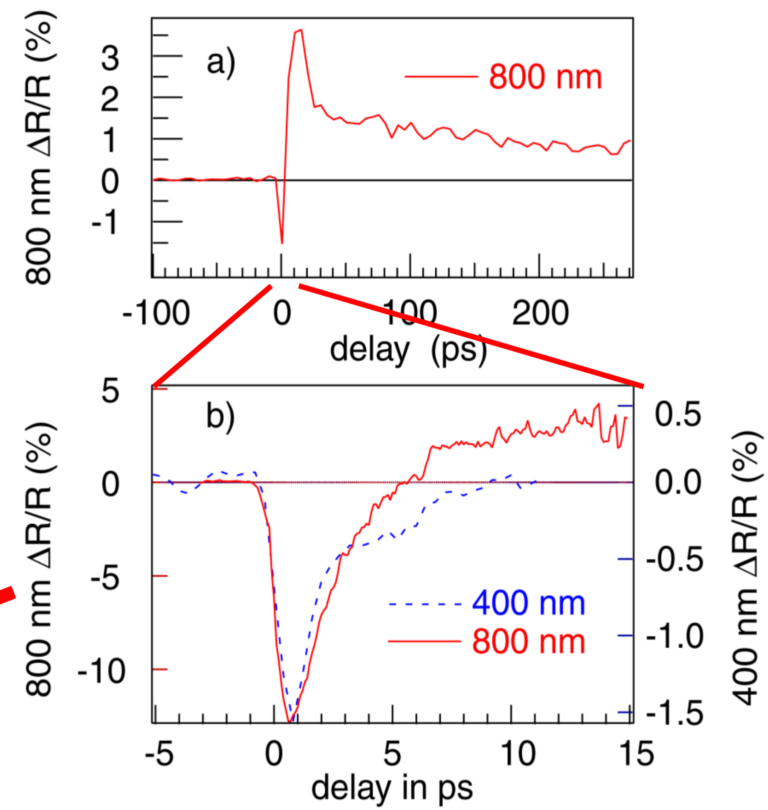


Time-to-space mapping



T. Maltezopoulos et al., NJP 10 (2008) 033026

Transient Optical Reflectivity

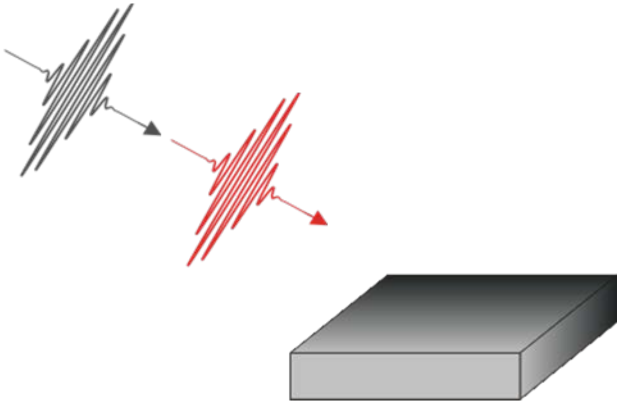


C. Gahl et al., Nature Photonics 2, 165 (2008)

Standard tool nowadays at all sources

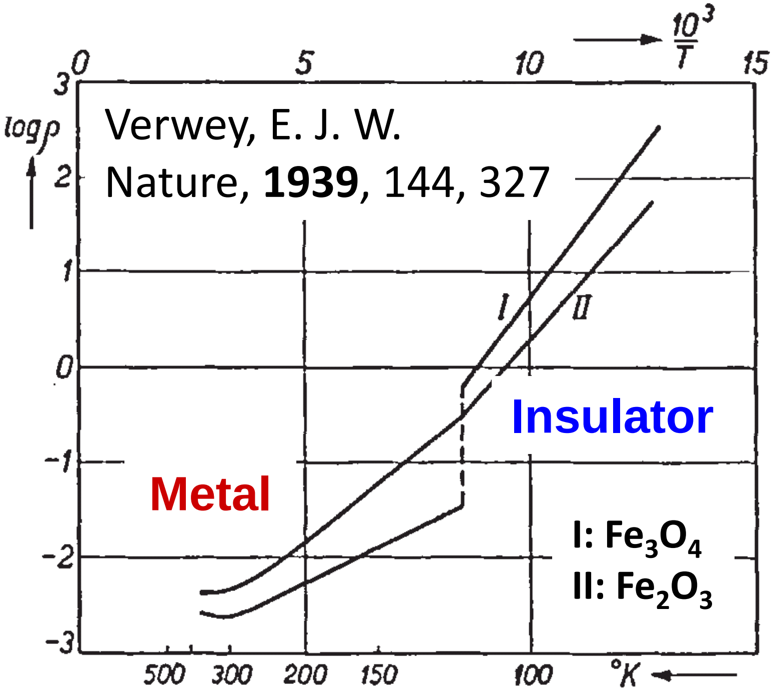
Time-resolved spectroscopy with FEL's

Some examples from FLASH and LCLS



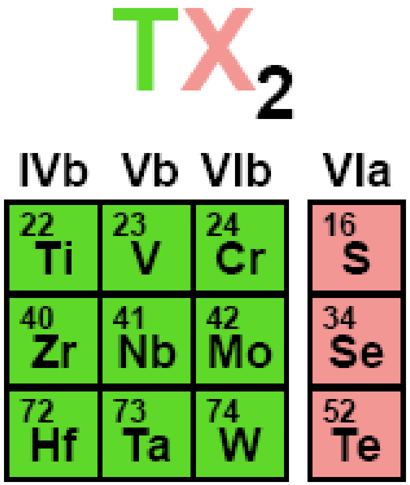
Chicken or Egg

©http://www.guardian.co.uk/science/2006/may/26/uknews

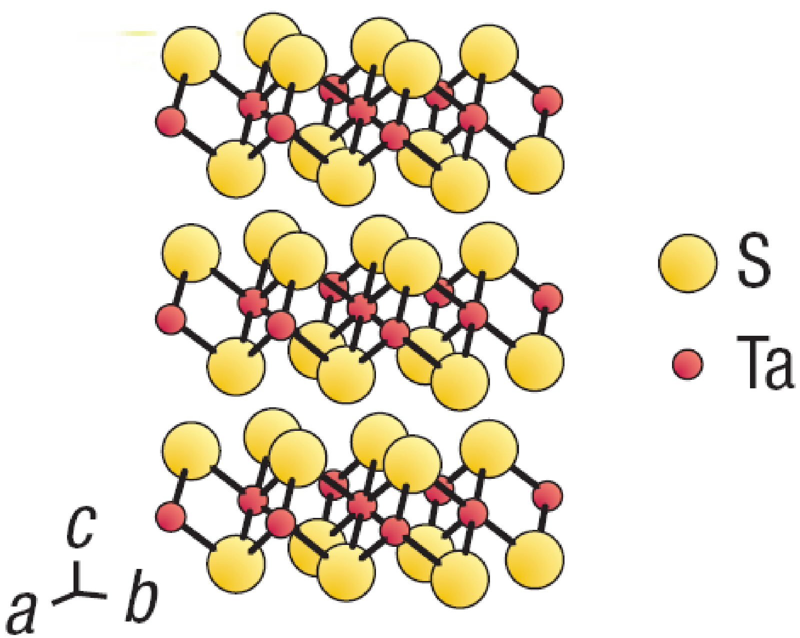


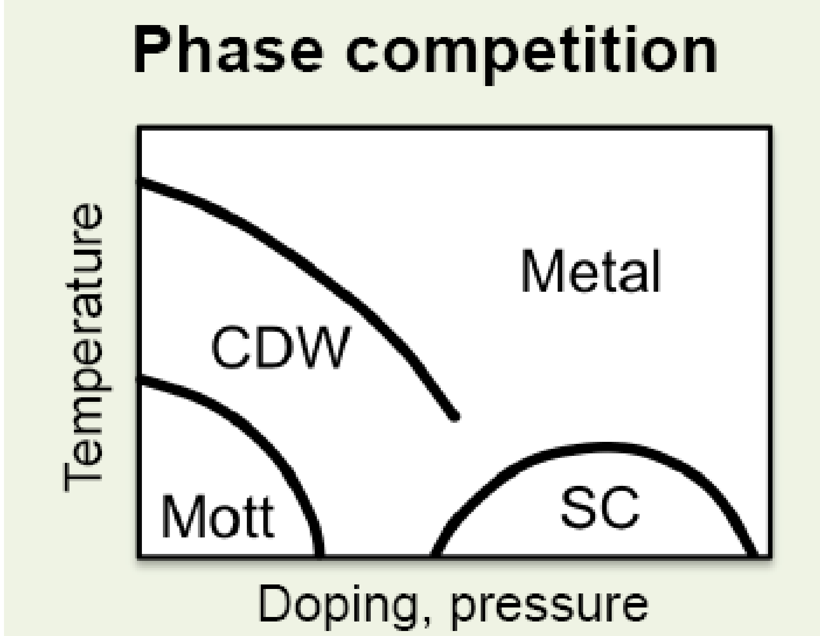
Lattice driven or electron driven metal-insulator transitions ?

Transition metal dichalcogonides



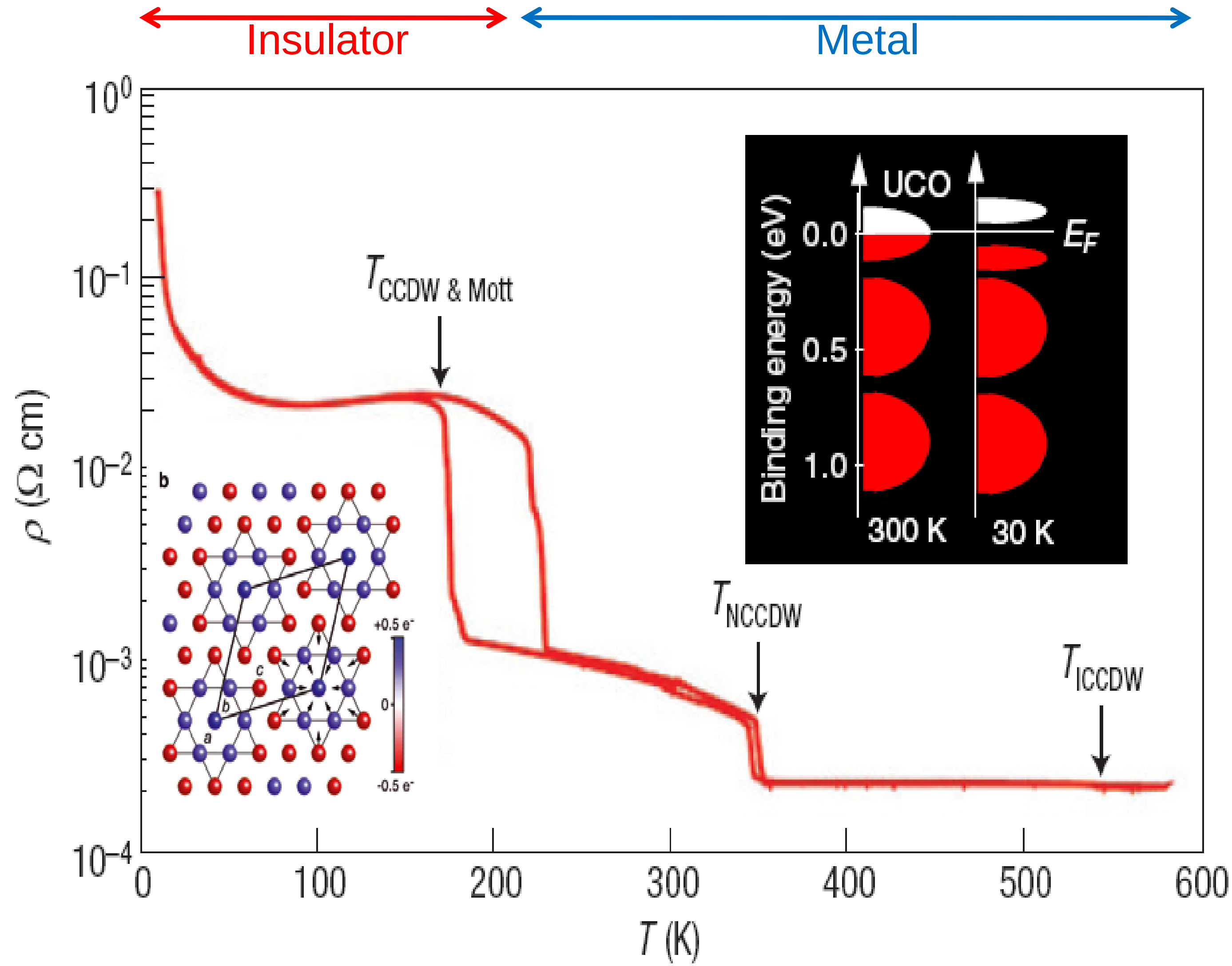
Layered 2-dim-systems





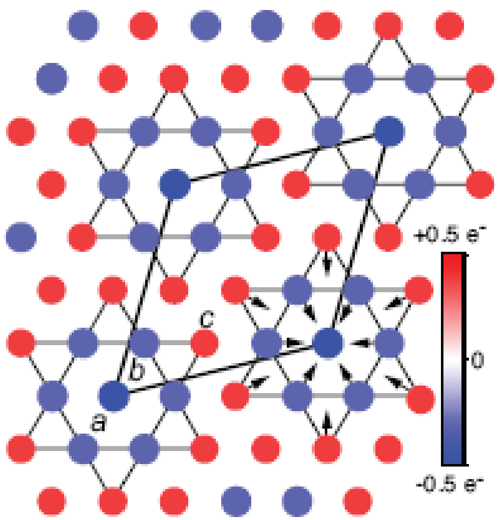
Morosan *et al*., NPHYS **2**, 544 (2006)
Sipos *et al*., NMAT **7**, 960 (2008)

Metal - Insulator –Transition



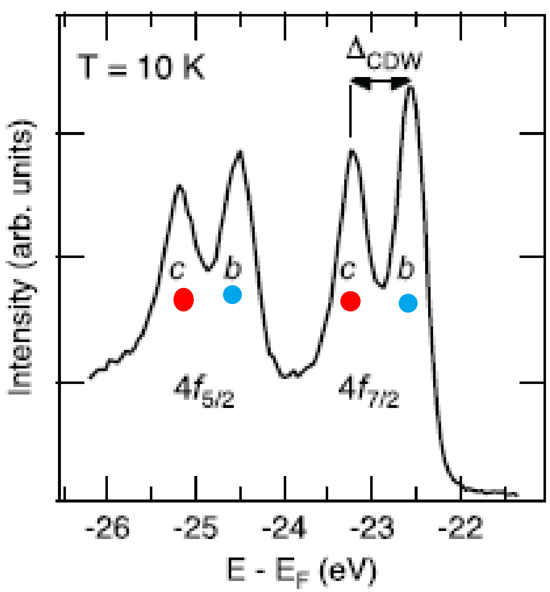
Kai Rossnagel

Ta 4f photoemission – a local probe for charge order in TaS_2

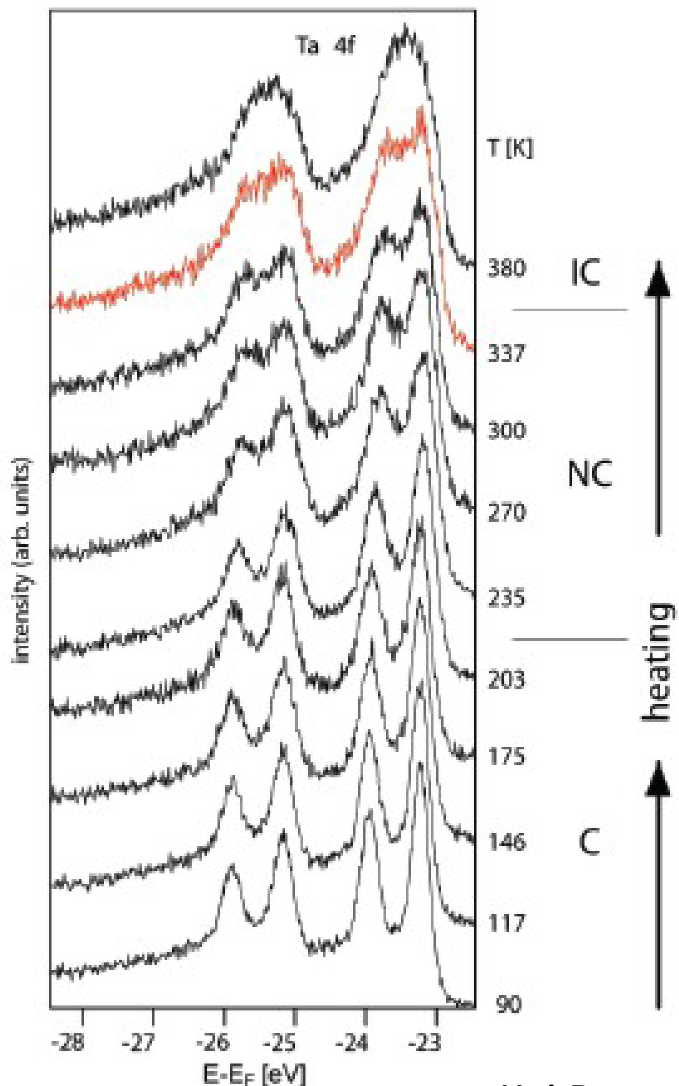


Low T state

- Charge ordered
- Periodic lattice distortion

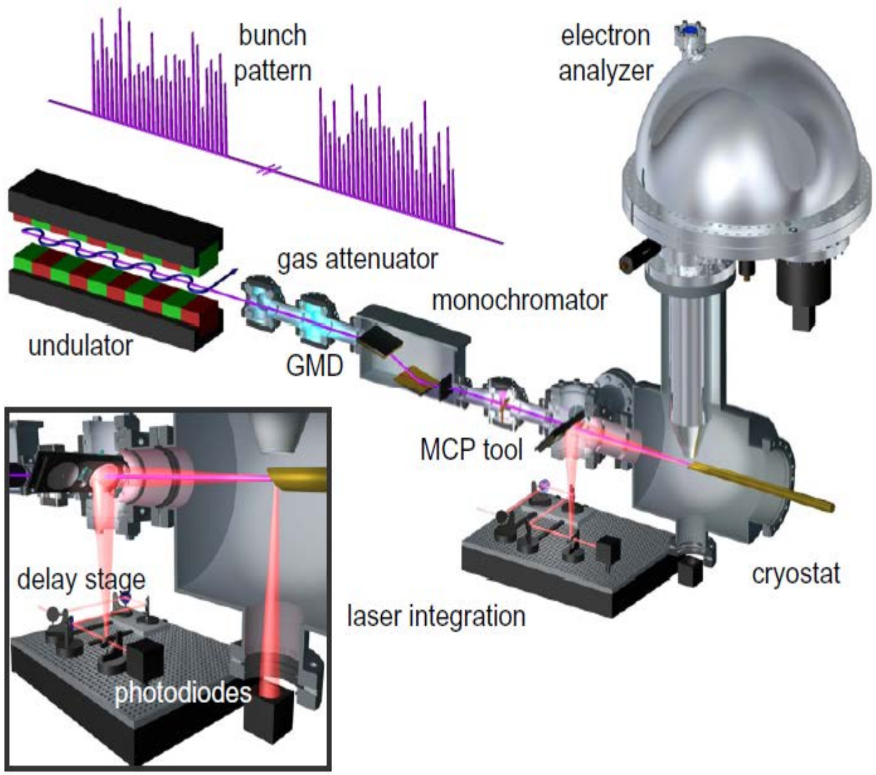


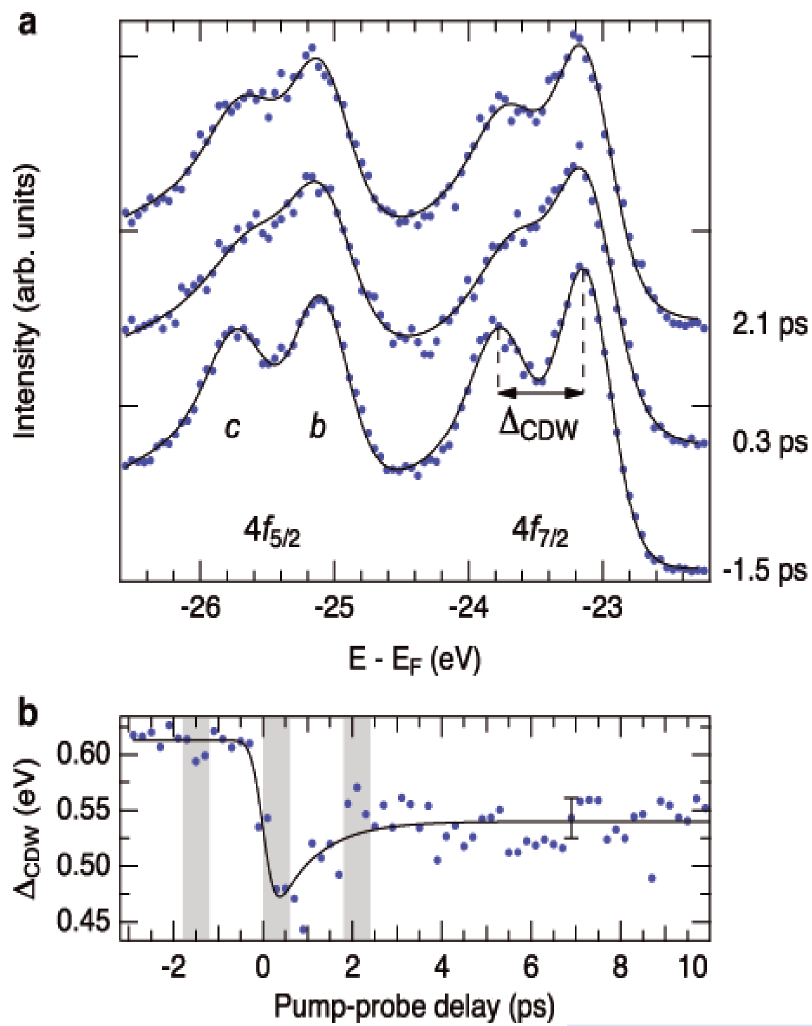
Equilibrium dynamics



Kai Rossnagel

Photo-induced melting of charge order





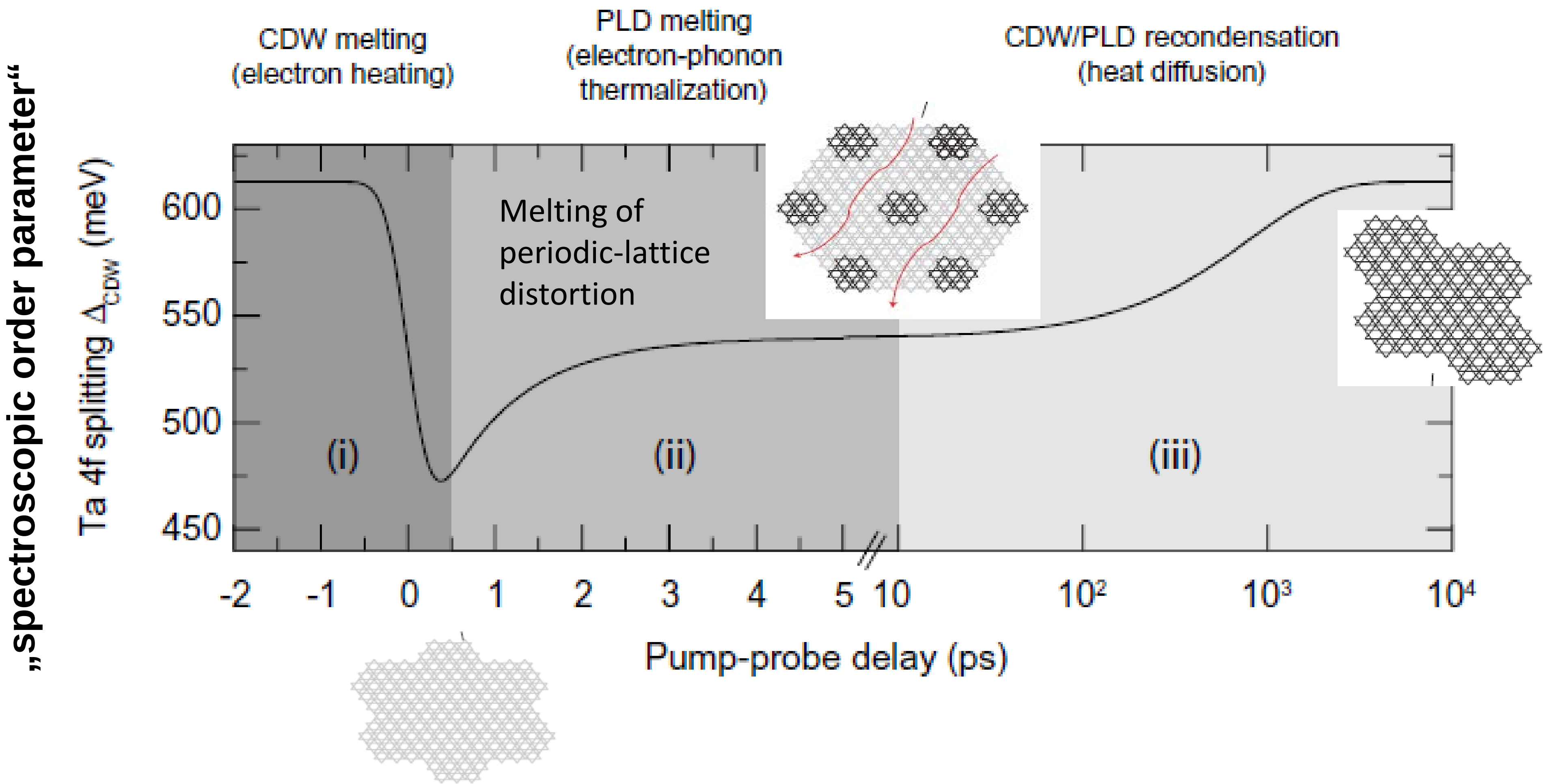
Photoexcitation
800nm, 120fs,
1.8mJ/cm^2, 2.5mJ/cm^2

XPS probe (30 pulses/train) FLASH
156eV, 100fs

S. Hellmann et al., PRL 105, 187401 (2010)

Kai Rossnagel

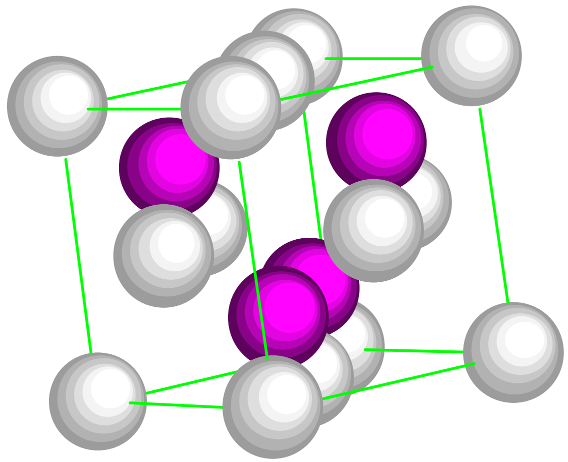
The picture - Non-thermal melting of charge order and subsequent thermalization

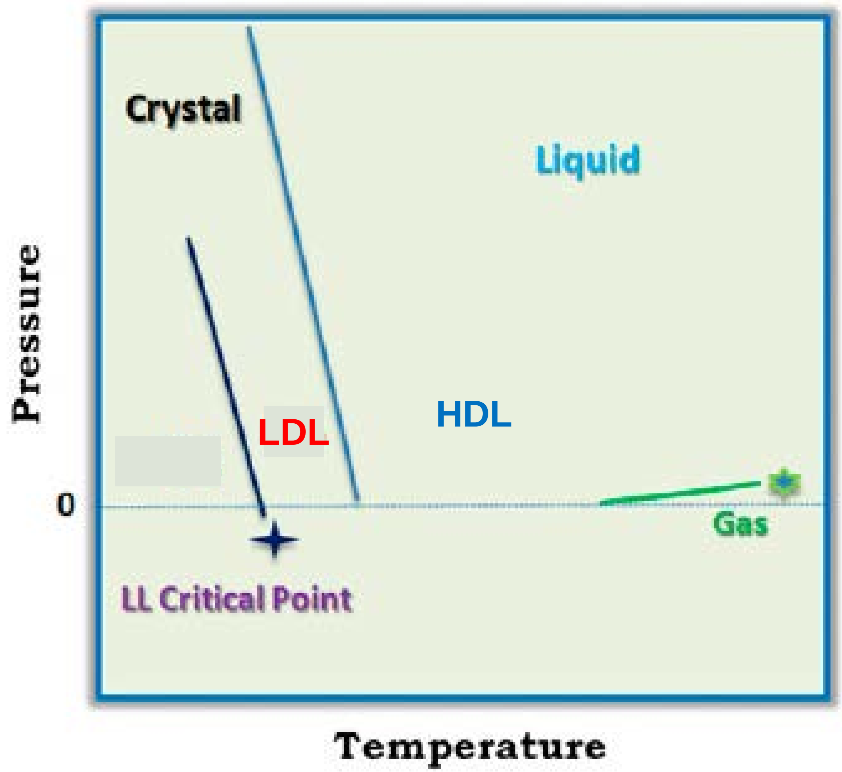


S. Hellmann et al., New Journal of Physics **14** (2012) 013062

Kai Rossnagel

Liquid polymorphism in silicon

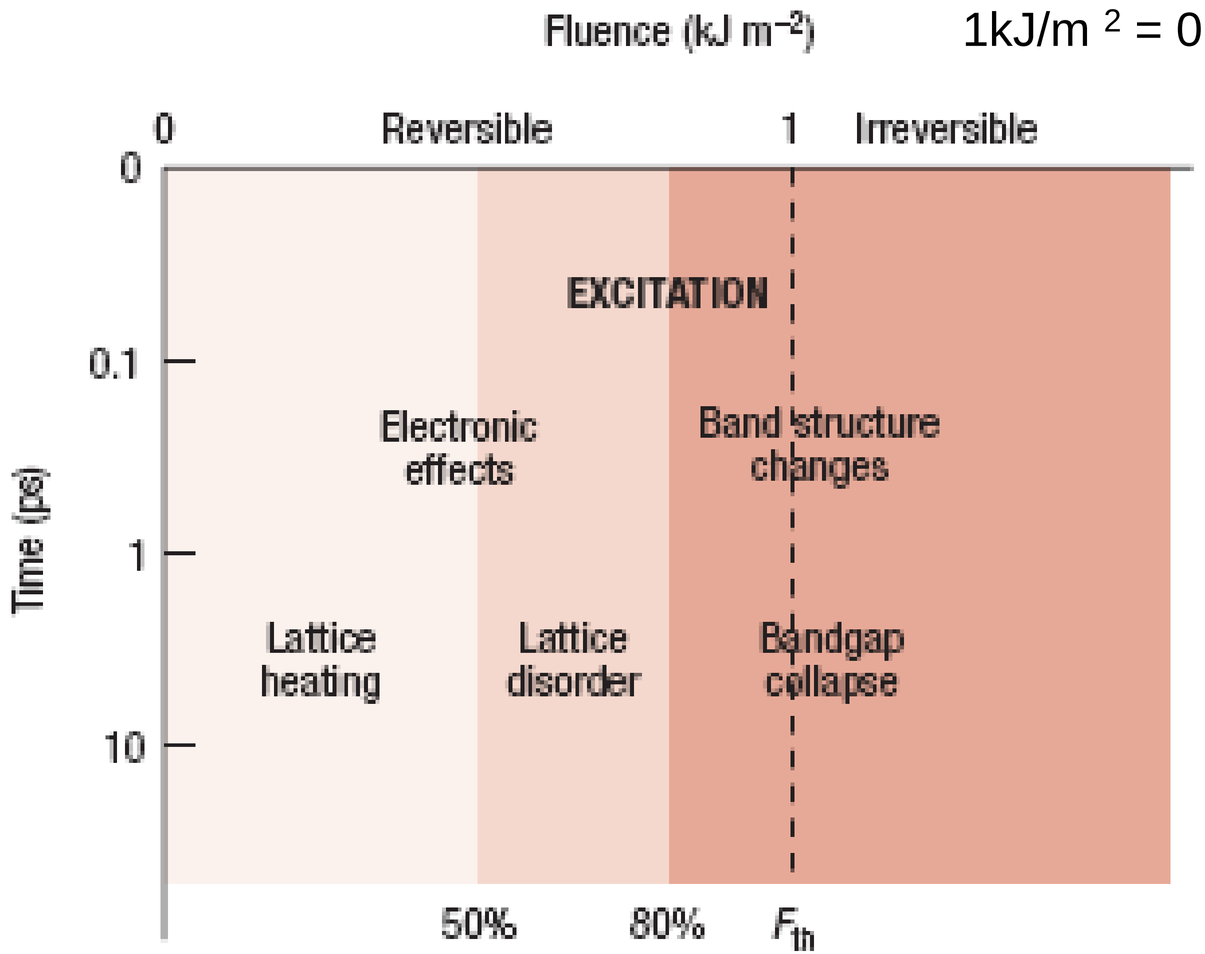




- Existence of „transient“ low density liquid phase ?
- Identification through **time-resolved electronic structure maps ?**

Fluence dependence of induced effects by femtosecond laser pulses in semiconductors

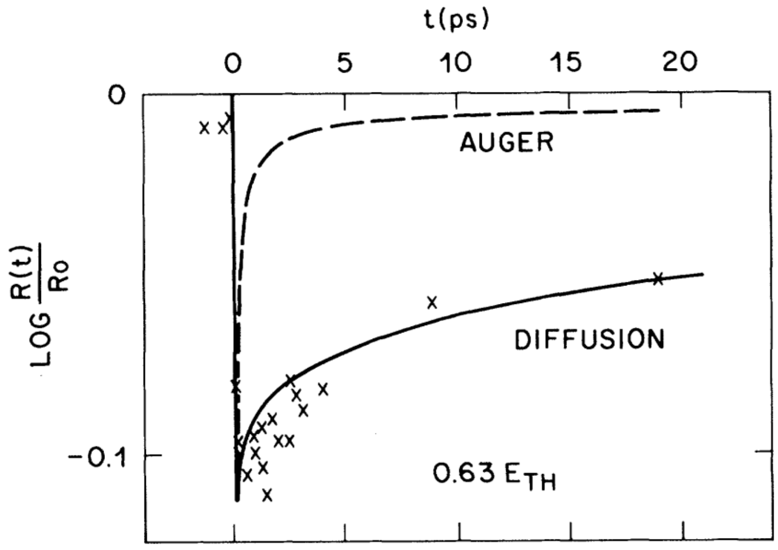
$1 kJ/m^2 = 0.1 J/cm^2$



Sundaram, S.K. and Mazur, E. Nature Materials, 1, 217, 2002

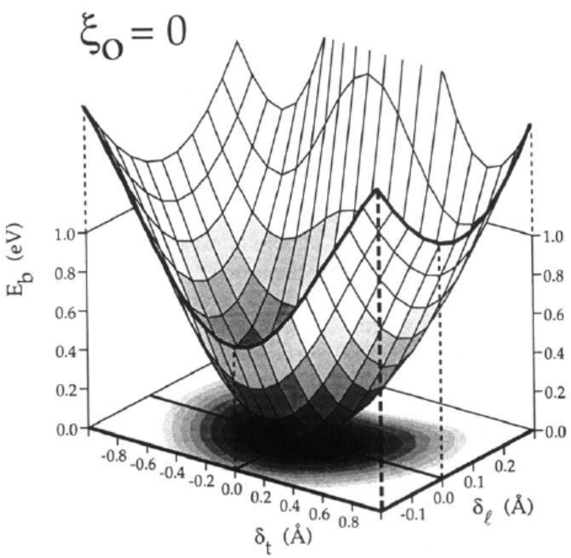
Effects of strong photodoping in silicon

Transient reflectivity change



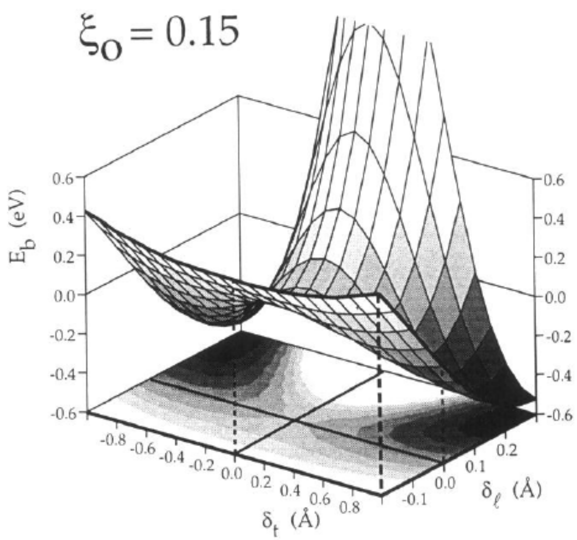
e-h-plasma formation

C.V. Shank, R. Yen and C. Hirlimann, PRL 50, 454 (1983)



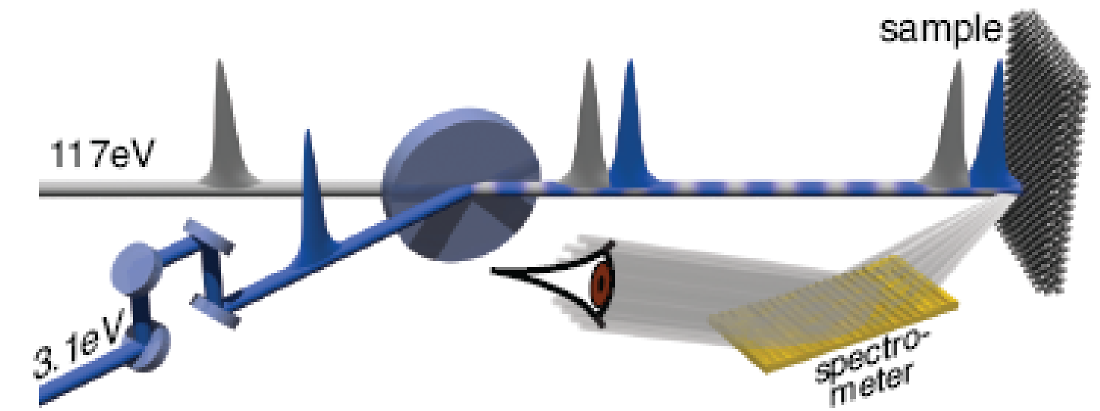
Excitation of ~10% of valence electrons leads to drastic changes of potential energy surface of atoms

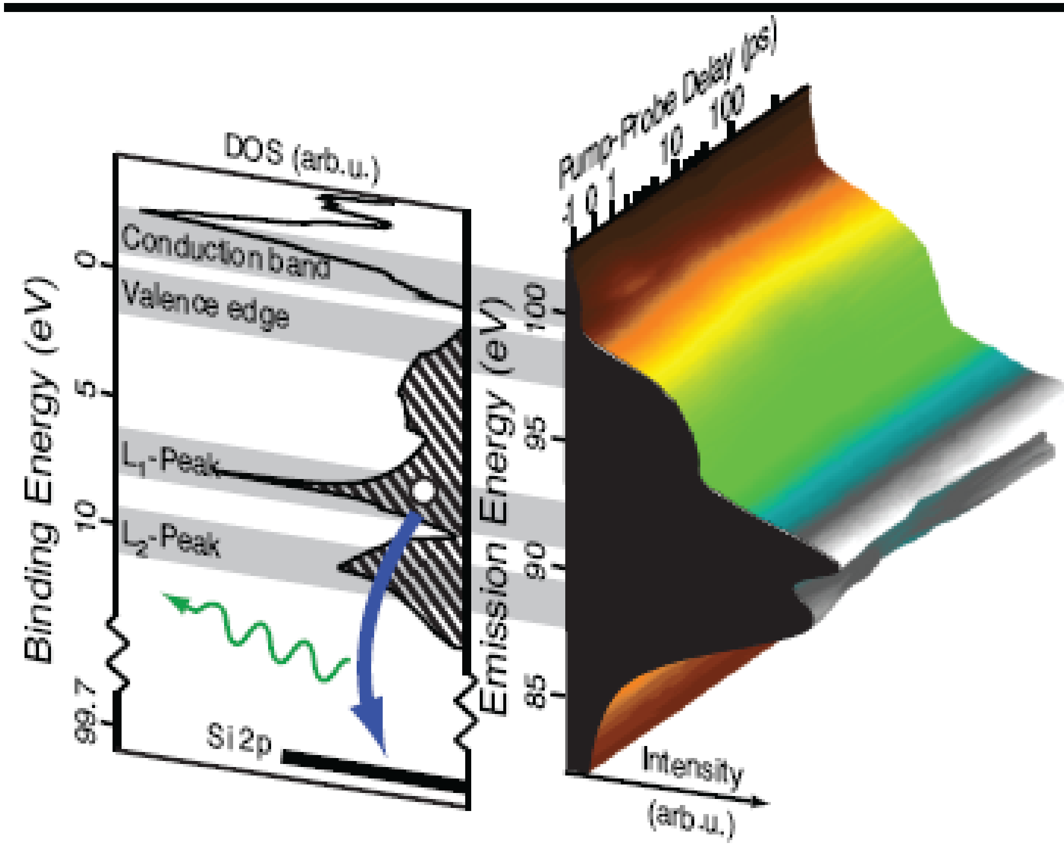
→ Nonthermal melting



P. Stampfli and K.H. Bennemann, PRB 49, 7299 (1994)

Dynamics of highly photoexcited silicon-TR-XES





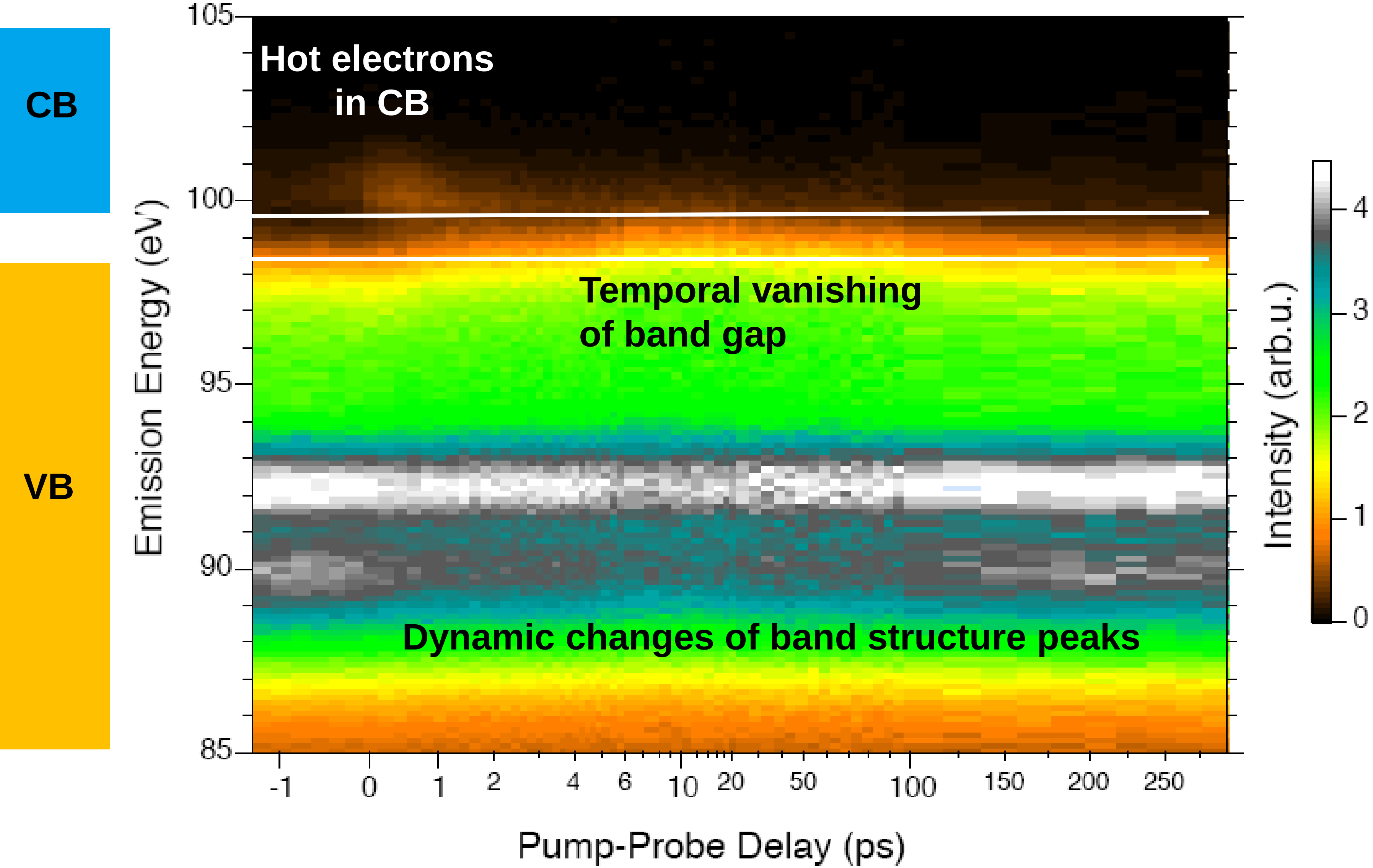
Ti:Sa LASER:

- 400nm
- time structure synchronized to FLASH
- 260mJ/cm^2 on sample
- 120fs pulse length
- **10^{22}/cm^3 excitation density**

FLASH:

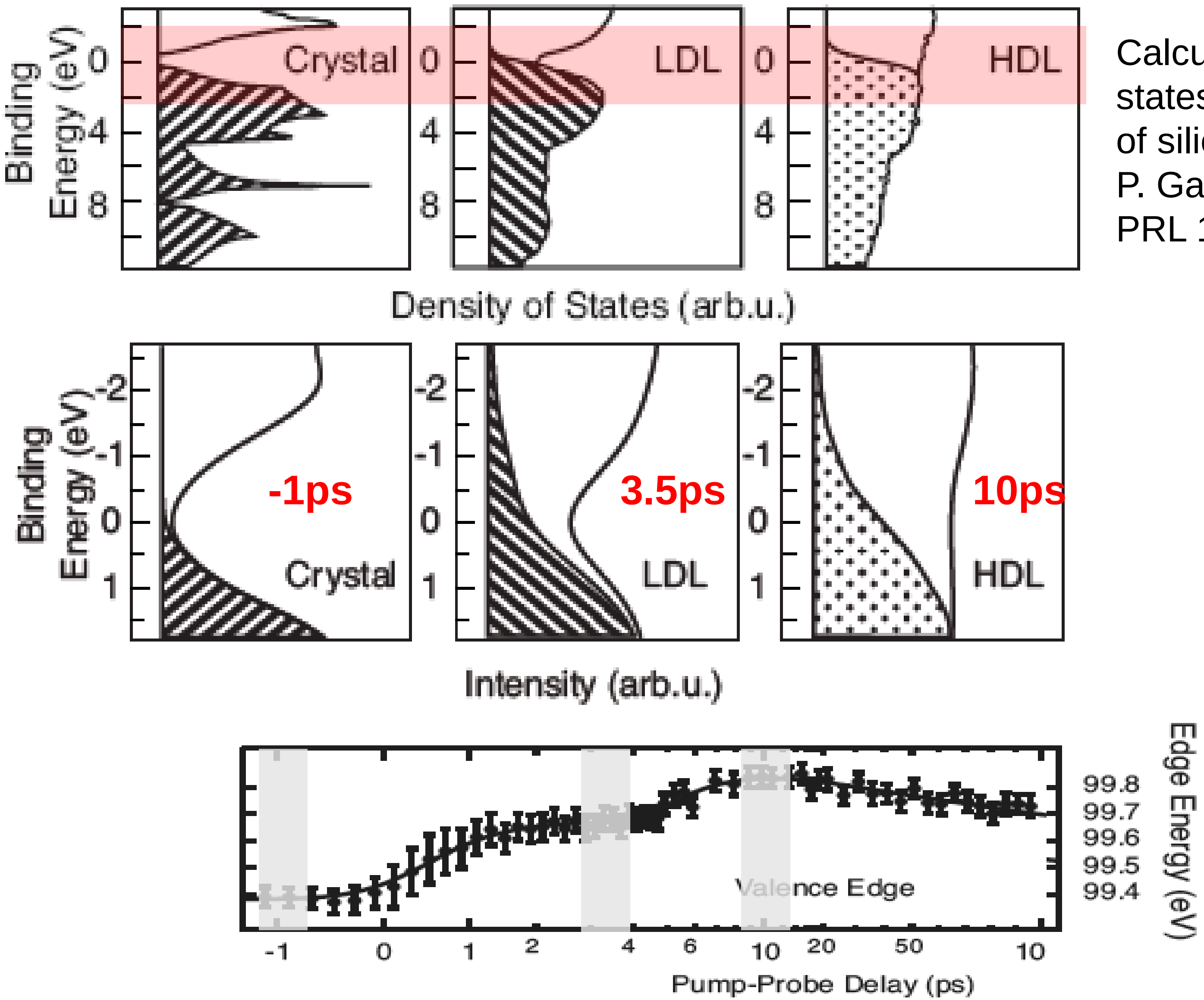
- Si 2p ionisation 117eV Photons
- 30 bunches@250kHz
- every 200ms
- around 40µJ per pulse
- 30fs pulse length
- attenuated
- ~80mJ/cm^2

Evolution of electronic structure after strong photoexcitation



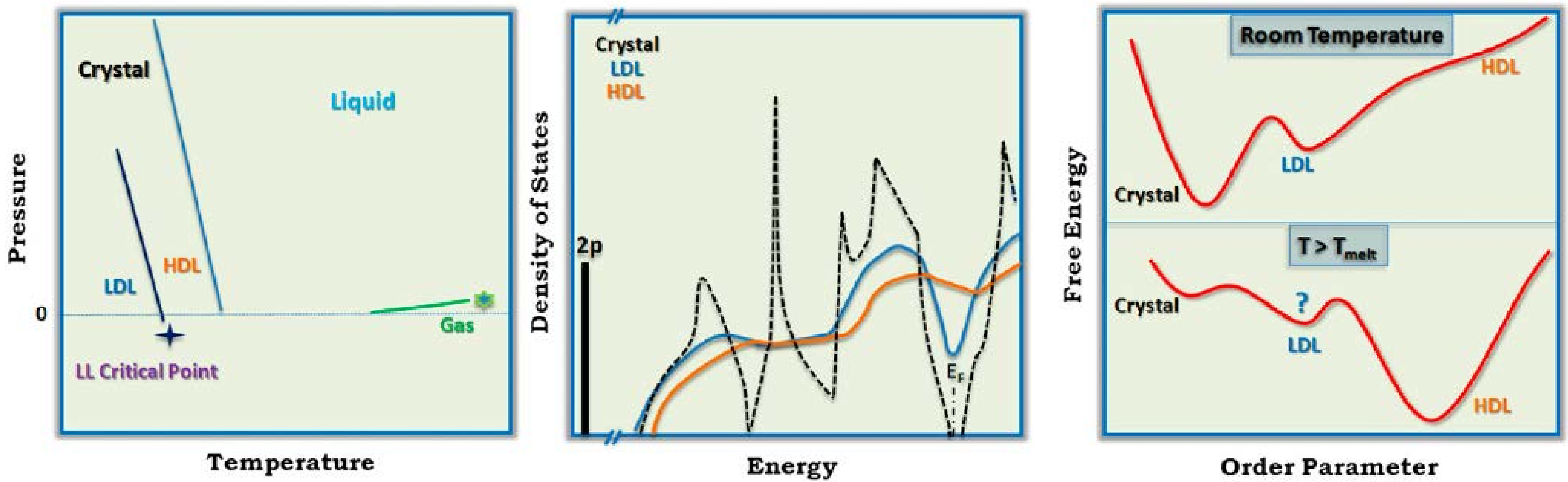
M. Beye et al., 16772 | PNAS | 2010 | vol. 107

Liquid-liquid transition in silicon



Calculated density of states for different phases of silicon
P. Ganesh and M. Widom, PRL 102, 075701 (2009)

Liquid polymorphism in silicon



Commentary by S. Sastry in PNAS | 2010 | vol. 107 | no. 40 | 17063

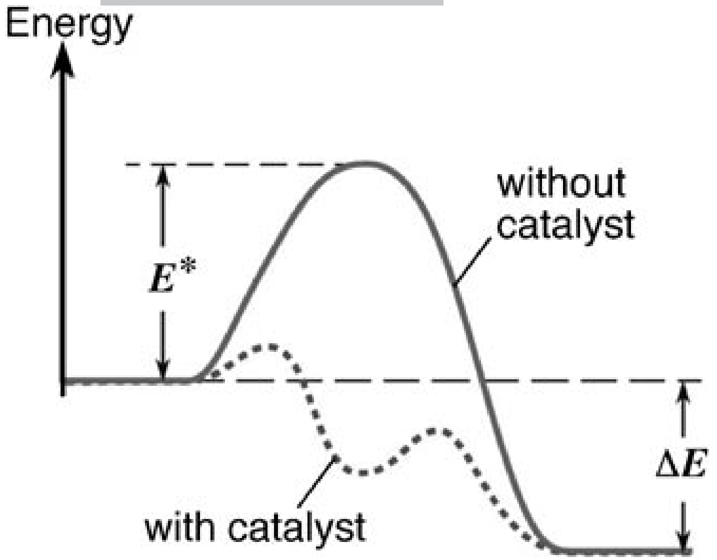
„Transient“ low density liquid phase accessible on short time scales ☑

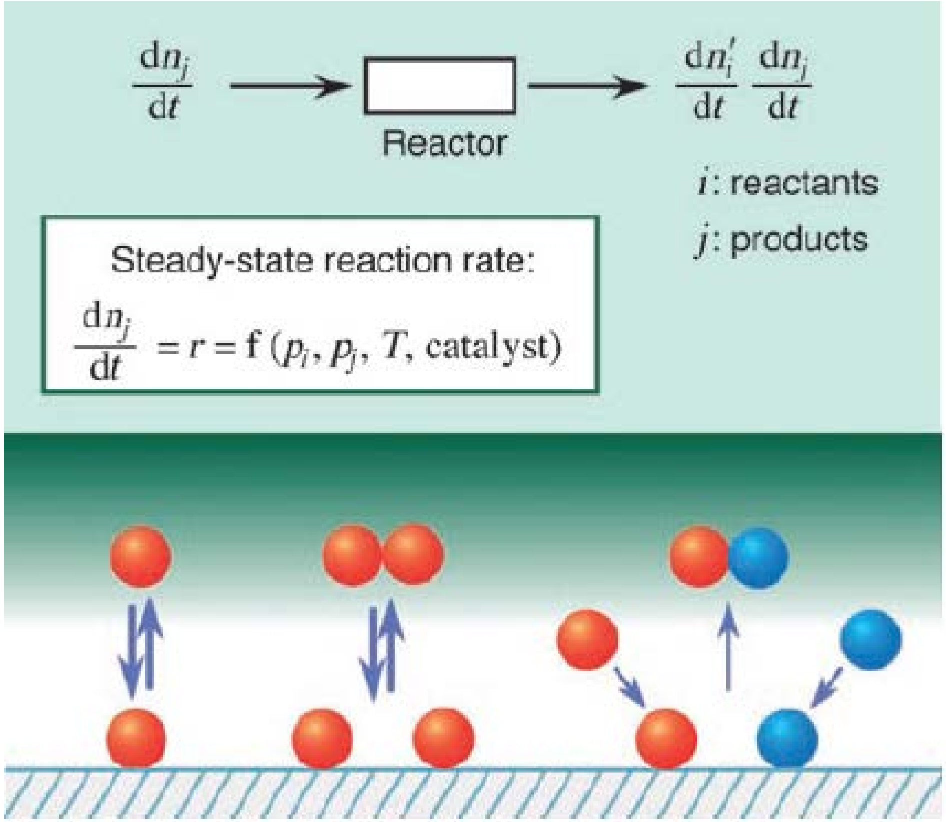
Identification through time-resolved electronic structure maps ☑

Evidence for first-order transition

Heterogeneous catalysis

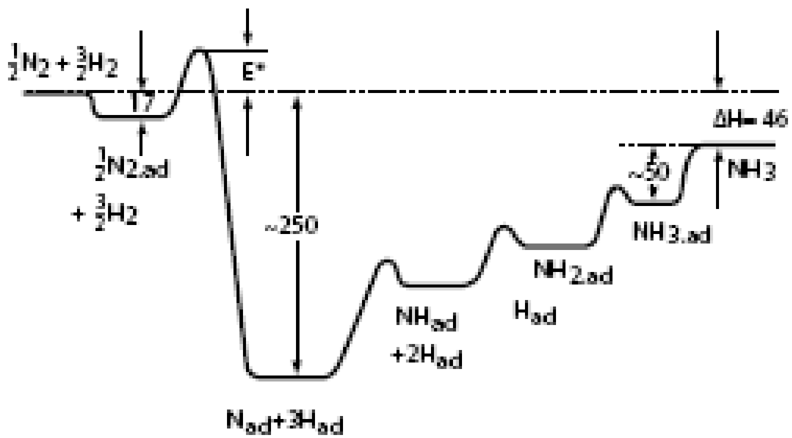
Nobel Prize in Chemistry Gerhard Ertl 2007





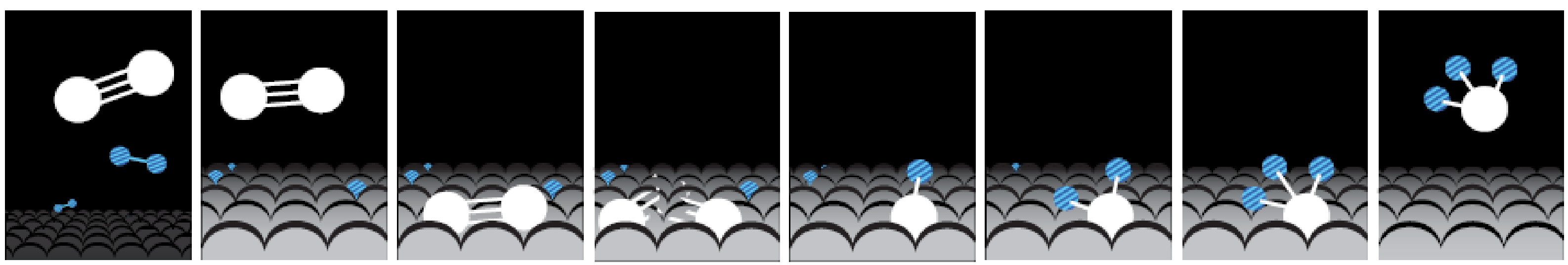
Angew. Chem. Int. Ed. 2008, 47, 3524

Real catalysts on the nanoscale - Understanding transition states

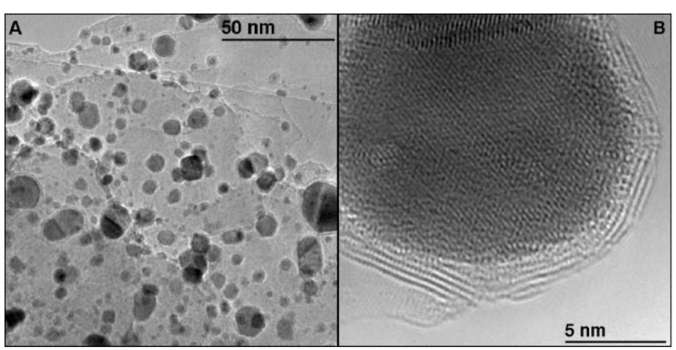


Haber-Bosch Process

$$1/2N_2+3/2H_2 \leftrightarrows NH_3$$



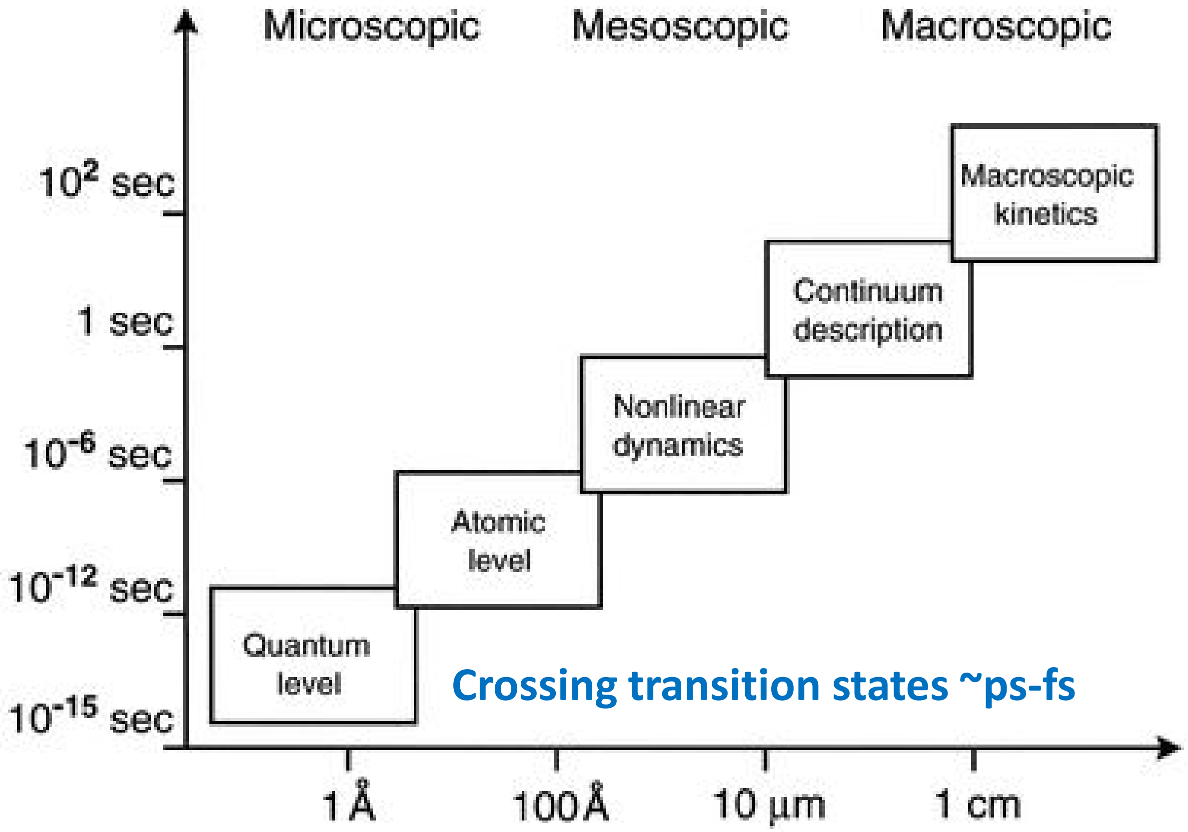
Nobel lecture by G. Ertl



Ba-promoted Ru-catalyst on BN for ammonia synthesis

Hansen et.al. Science 294, 1508 (2001)

Dynamics of surface reactions



Turnover rates ~s

Crossing transition states ~ps-fs

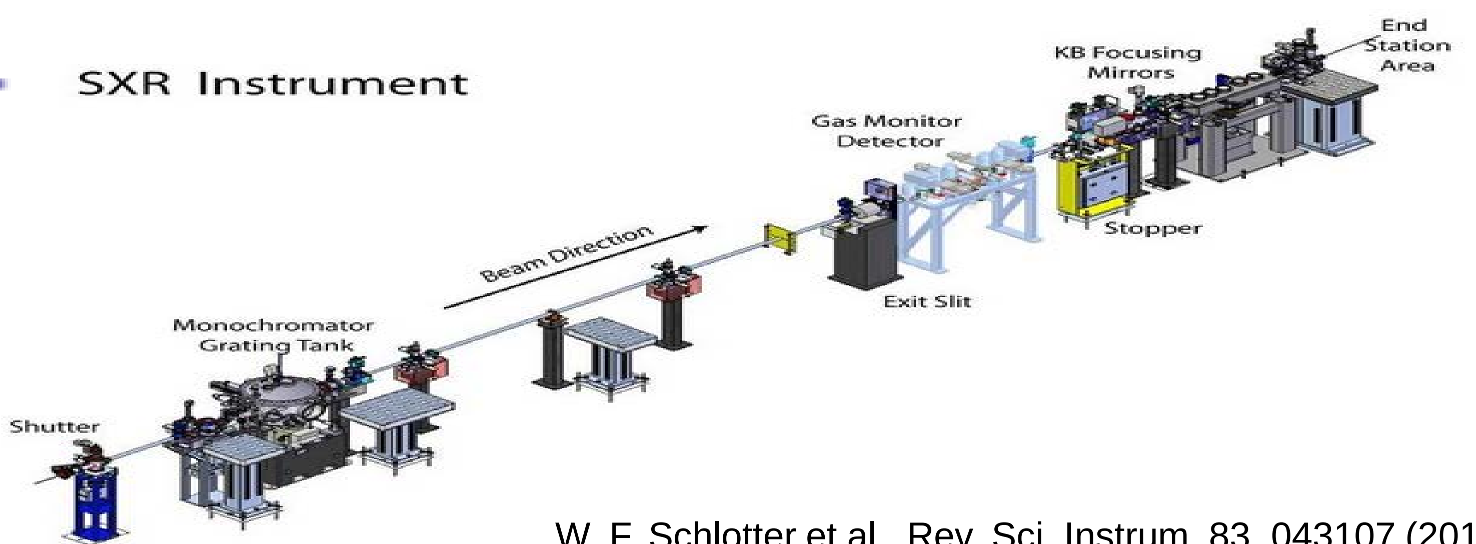
FIG. 1. Schematic classification of the various aspects of the dynamics of surface reactions.

G. Ertl, in Advances in Catalysis

Ultrafast Surface Chemistry and Catalysis Collaboration

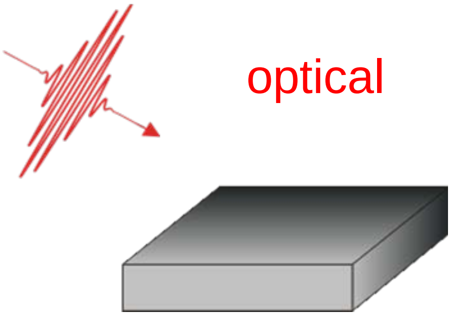
F. Abild-Petersen, T. Anniyev, Martin Beye, R. Coffee, G.L. Dakowski, Martina Dell'Angela, A. Föhlisch, J. Gladh, M. Hantschmann, F. Hieke, T. Katayama, S. Kaya, O. Krupin, D. Kühn, J. LaRue, G. Mercurio, M.P. Minitti, A. Mitra, S. P. Möller, Andreas Moegelhoej, M.L. Ng, A. Nilsson, J. K. Norskov, D. Nordlund, Henrik Öberg, Hirohito Ogasawara, Henrik Öström, L. G.M. Pettersson, M. Persson, W. F. Schlotter, J. A. Sellberg, F. Sorgenfrei, J. J. Turner, M. Wolf, W. Wurth, Hongliang Xin

Stockholm University, Helmholtz-Zentrum Berlin, Fritz Haber Institute, University of Liverpool, SLAC (LCLS, SIMES, SSRL, SUNCAT), University of Hamburg and CFEL

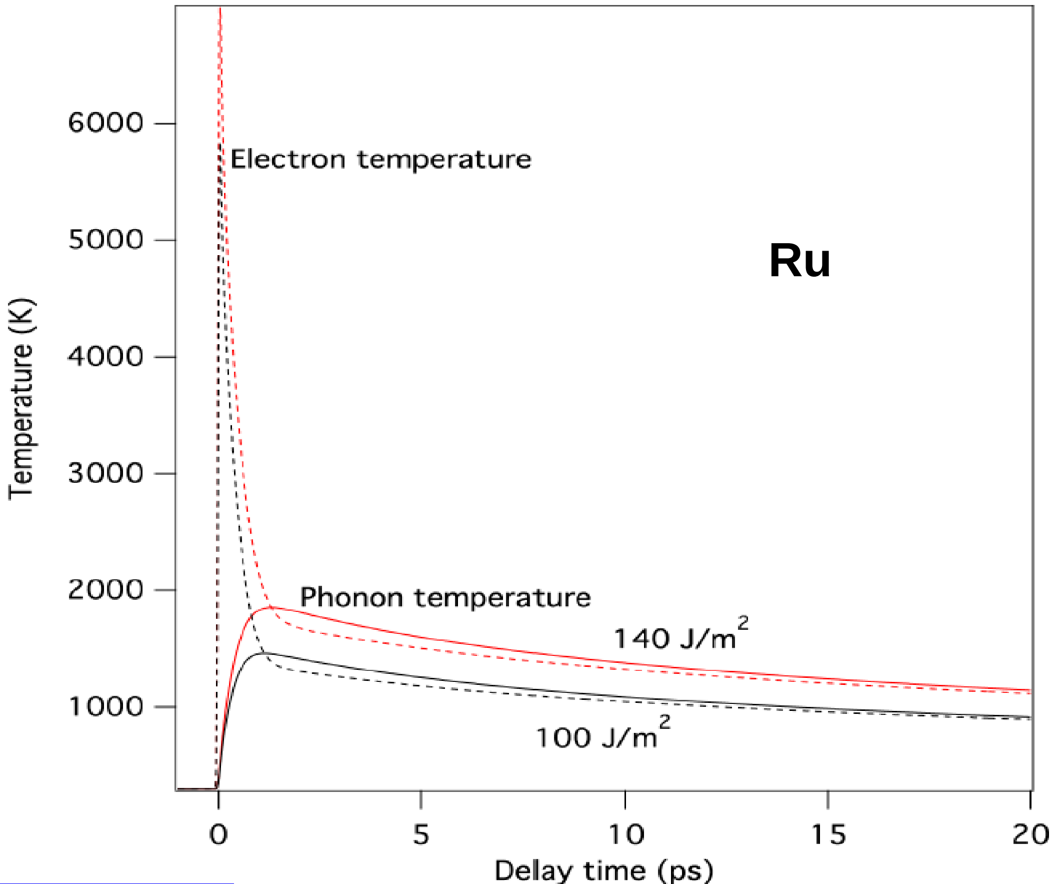


W. F. Schlotter et al., Rev. Sci. Instrum. 83, 043107 (2012)
P. A. Heimann et al., Rev. Sci. Instrum. 82, 093104 (2011)

„Trigger“ surface femtochemistry – the pump step



Non-equilibrium electron distribution which rapidly (<100fs) thermalizes



Two-temperature model

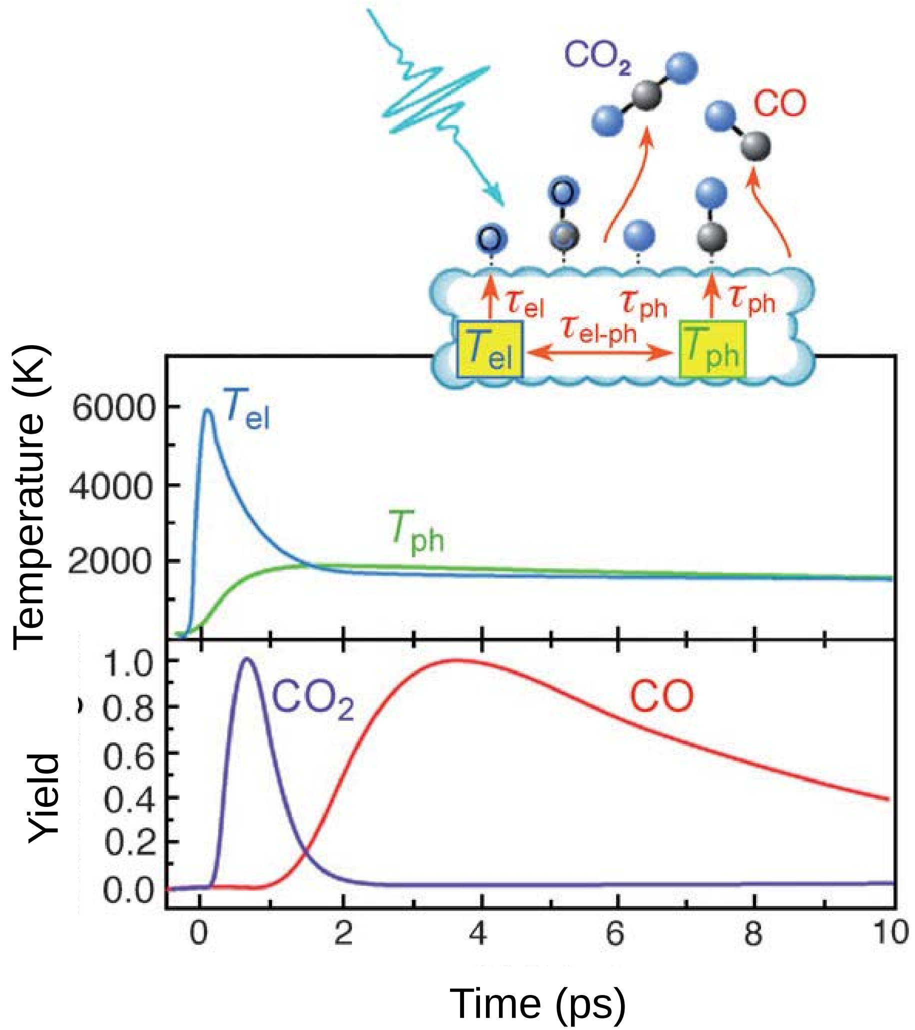
$$C_{\mathrm{el}} \frac{\partial}{\partial t} T_{\mathrm{el}} = \overbrace{\nabla_z (\kappa \nabla_z T_{\mathrm{el}})}^{\text{therm.diffusion}} - \overbrace{g(T_{\mathrm{el}} - T_{\mathrm{ph}})}^{\text{el-ph.coupling}} + \overbrace{S(z,t)}^{\text{opt.excitation}} \quad (1)$$

$$C_{\mathrm{ph}} \frac{\partial}{\partial t} T_{\mathrm{ph}} = g(T_{\mathrm{el}} - T_{\mathrm{ph}}) \quad (2)$$

Kaganov M.I. et al, Sov. Phys. JETP 4, 173 (1957)
Ansimov S.I. et al, Sov. Phys. JETP 39, 375 (1975)

A model phototriggered reaction

$O_{ad} + CO_{ad} \rightarrow CO_2/Ru(0001)$

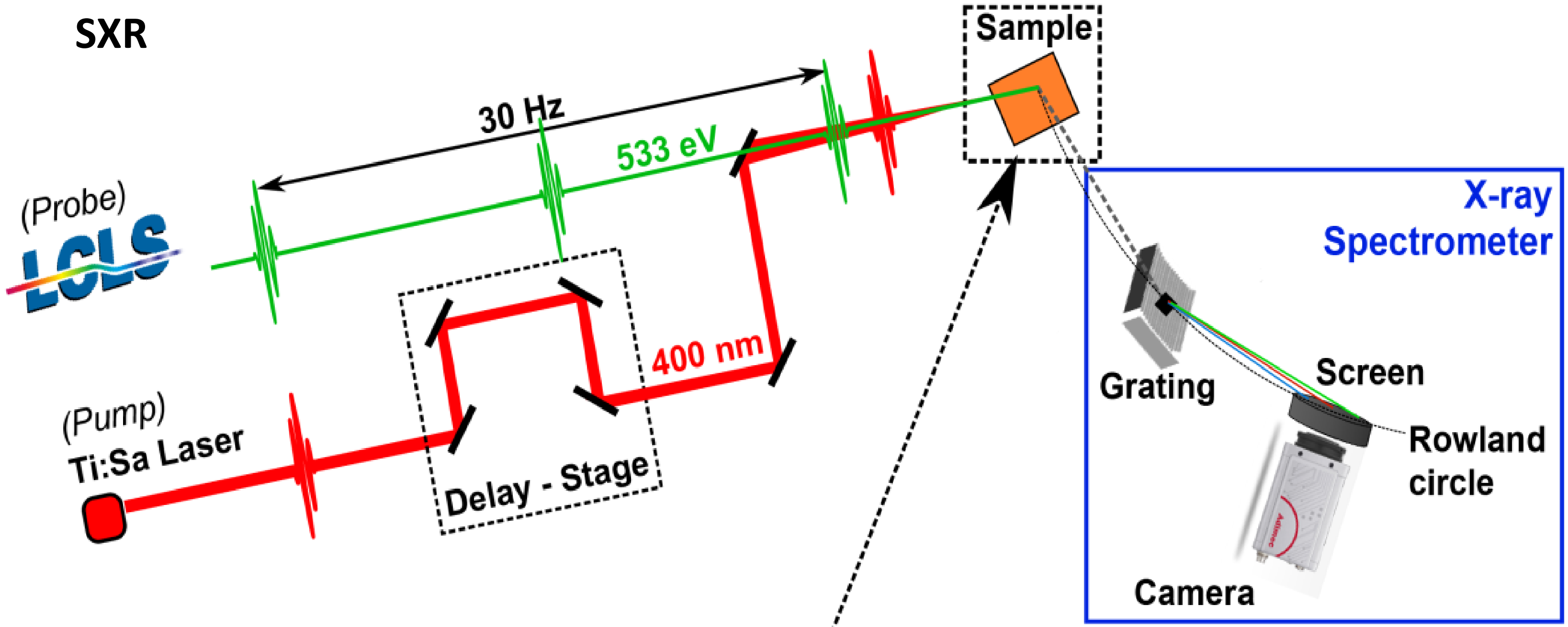


Investigate:

- CO desorption
- O activation
- CO_2 production

after M. Bonn et al., Science 285, 1042 (1999)

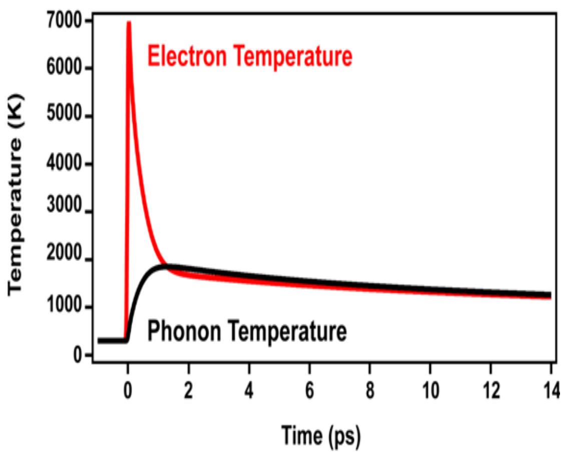
Time-resolved RIXS and surface catalysis

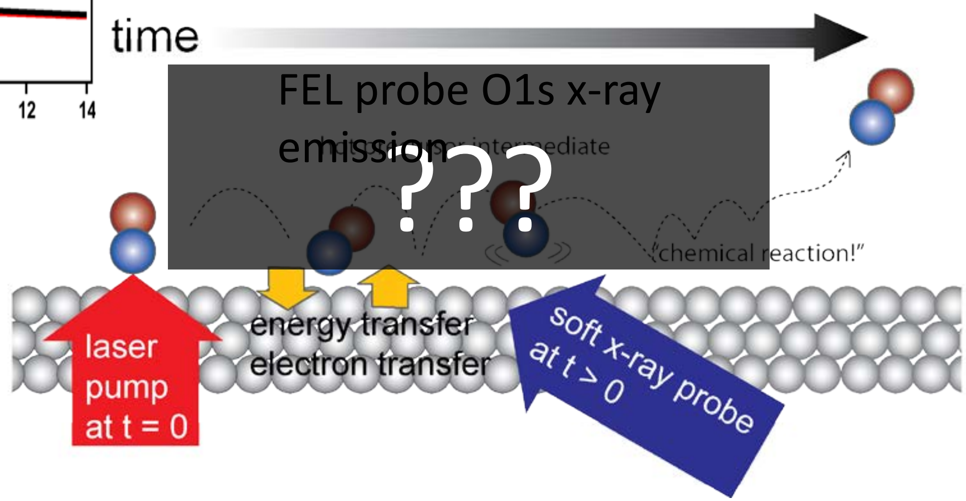


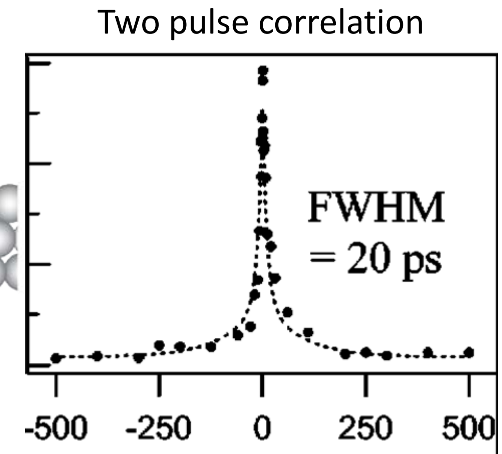
Use resonant inelastic x-ray scattering (RIXS) as electronic structure probe

Element specificity, chemical sensitivity, independent of environment

Photoinduced desorption of CO molecules







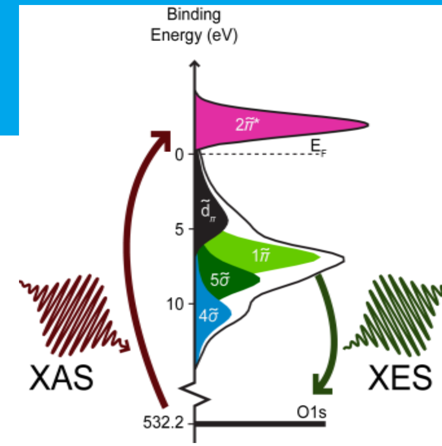
S. Funk et al, J. Chem. Phys. 112, 9888 (2000)

M. Dell'Angela et al., Science 339, 1302 (2013)

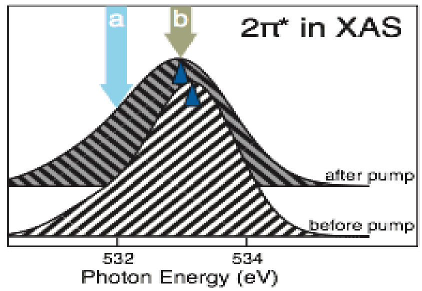
M. Beye et. al., PRL 110, 186101 (2013)

T. Katayama et al, J.of El. Spec. 187, 9 (2013)

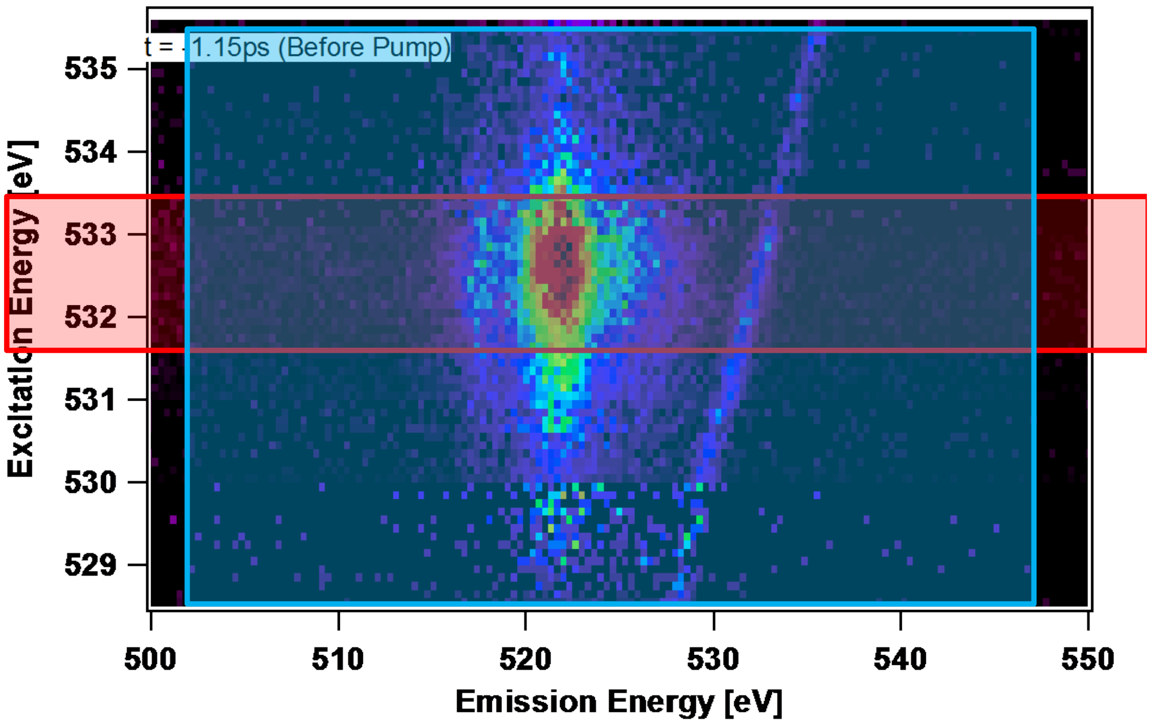
„4-Dim“-RIXS maps – the probe step

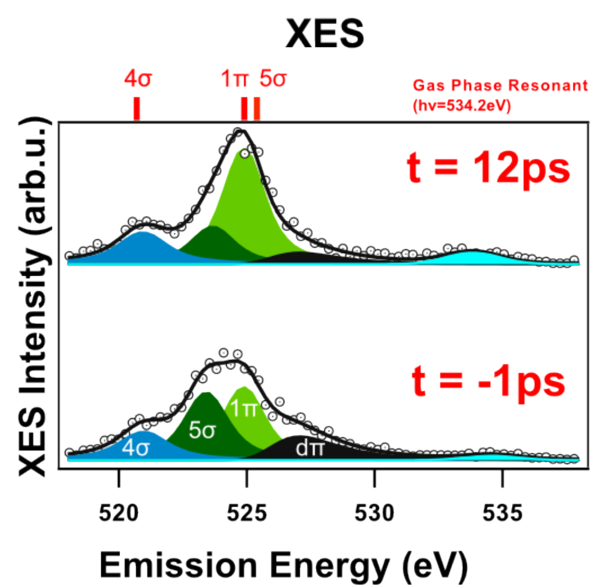


XAS

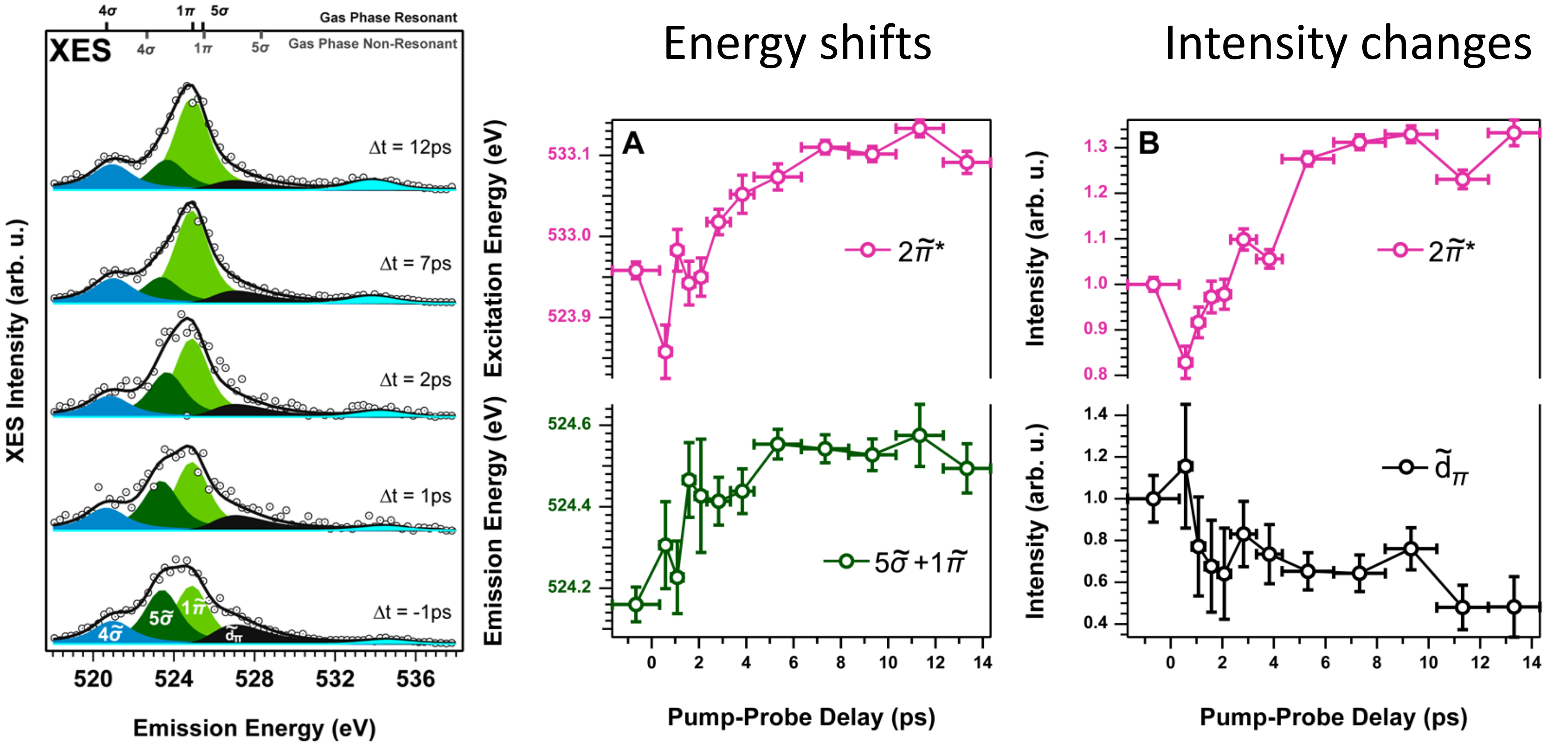


XES





Time evolution of valence states

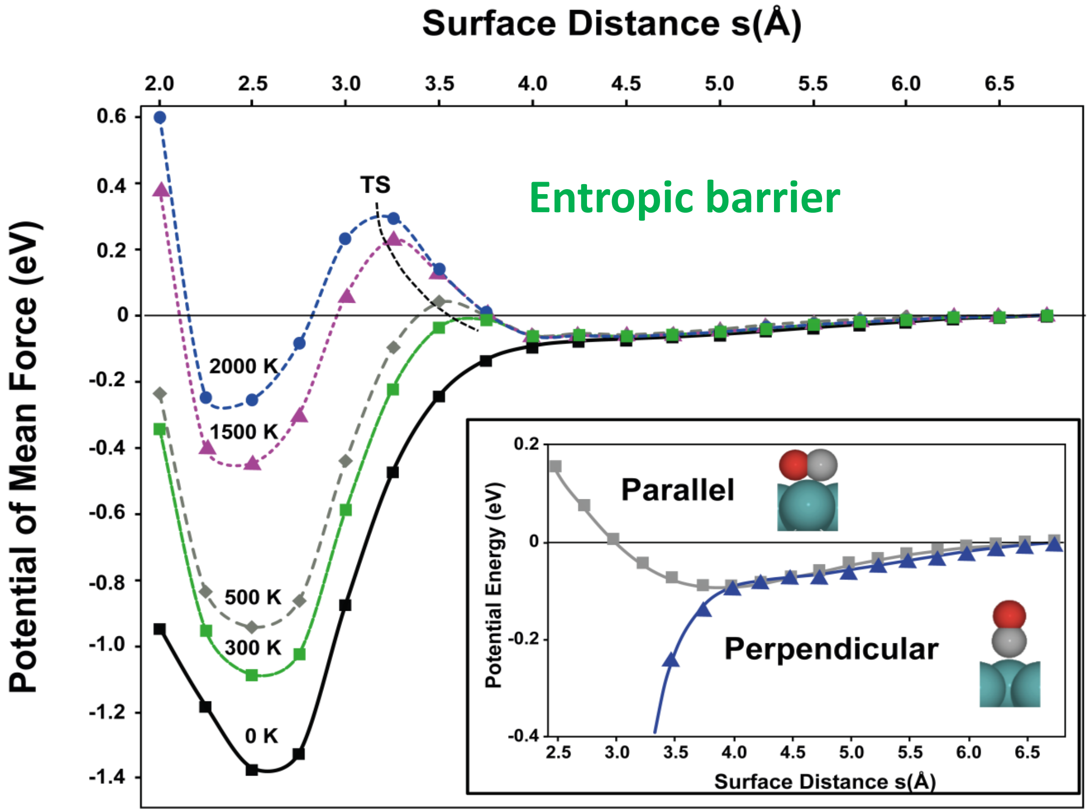


Transient changes on time scale up to 10 ps
show pronounced weakening of bond to surface

Transient precursor state of CO

Postulated from kinetic exp. – first direct observation!

The Nobel Prize in Chemistry 1932
Irving Langmuir

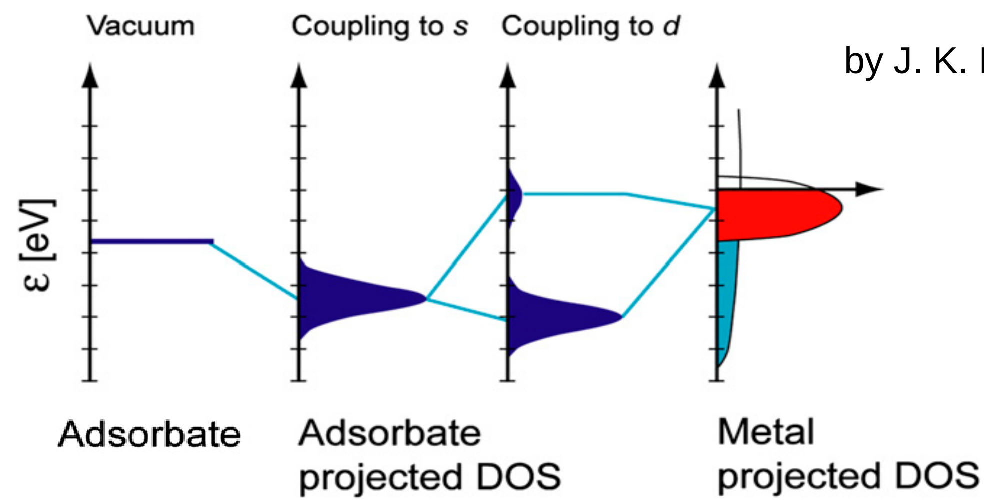


Transients cannot be explained by thermal population of ground state PES

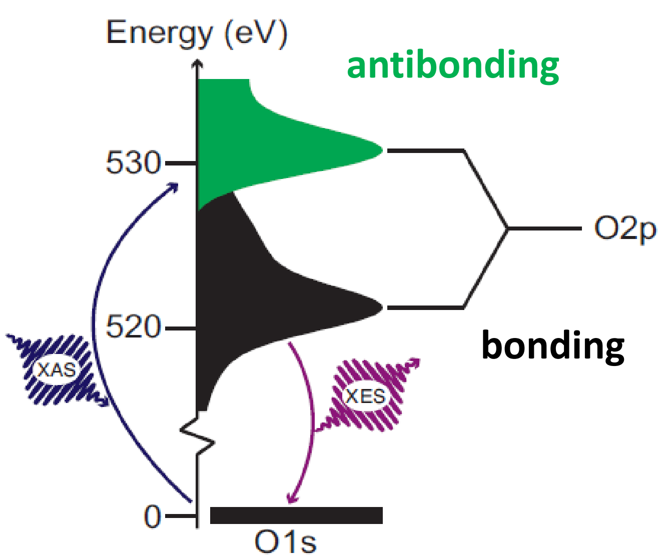
Entropic barrier – dynamic precursor state populated

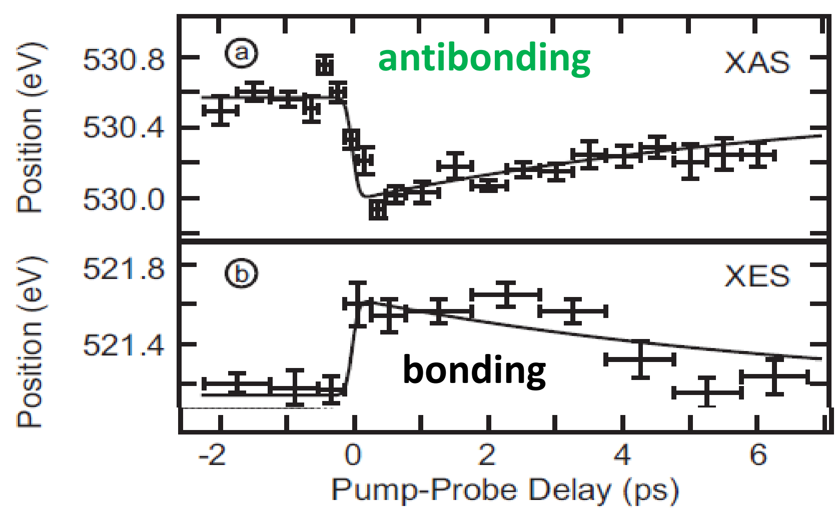
Theory by J. K. Norskov, L.G.M. Petterson and coworkers

Oxygen activation



by J. K. Norskov

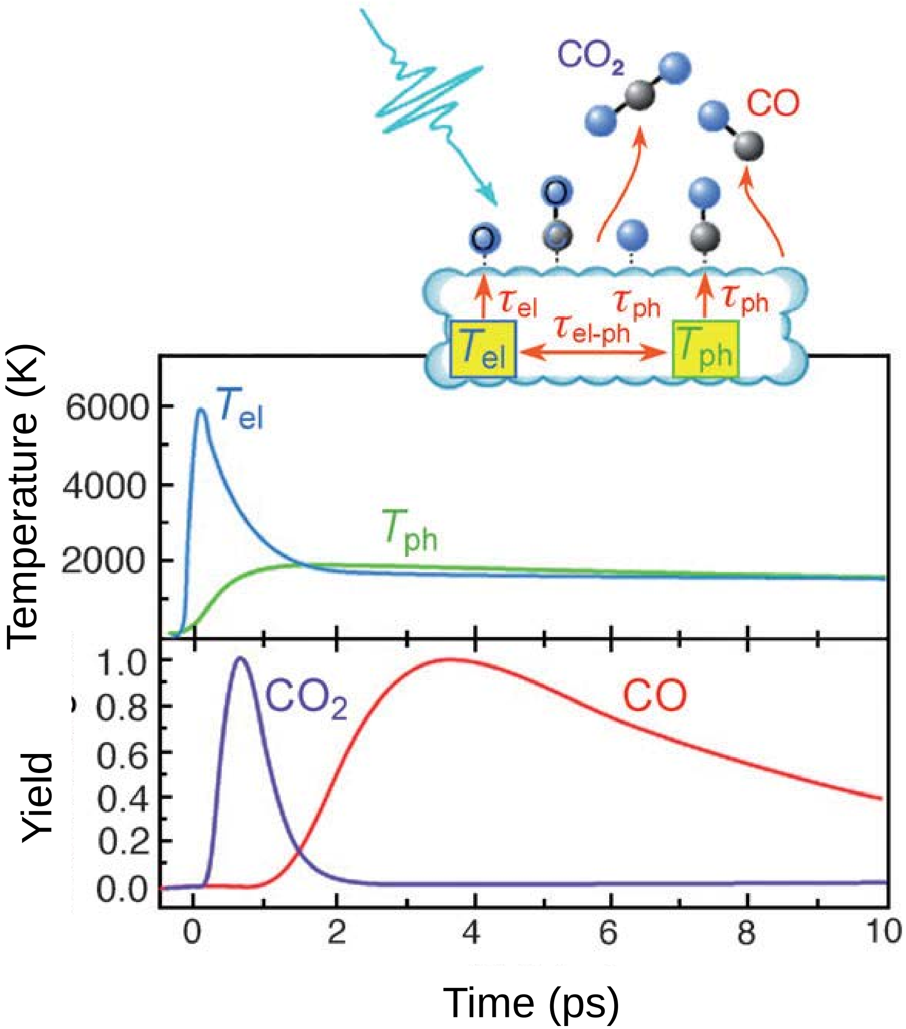


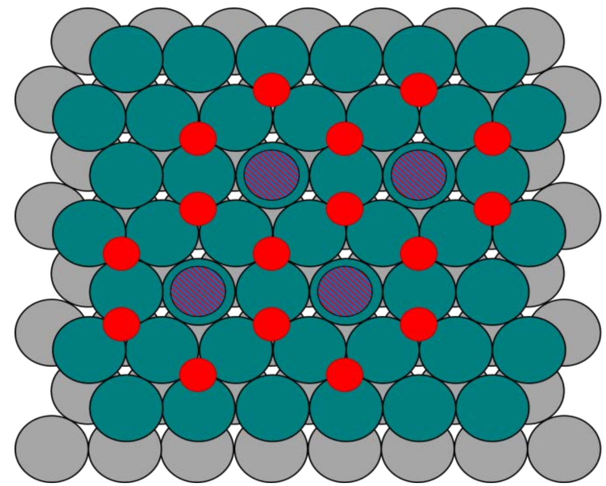


M. Beye et al. submitted

CO oxidation

$$O_{ad} + CO_{ad} \rightarrow CO_2/Ru(0001)$$

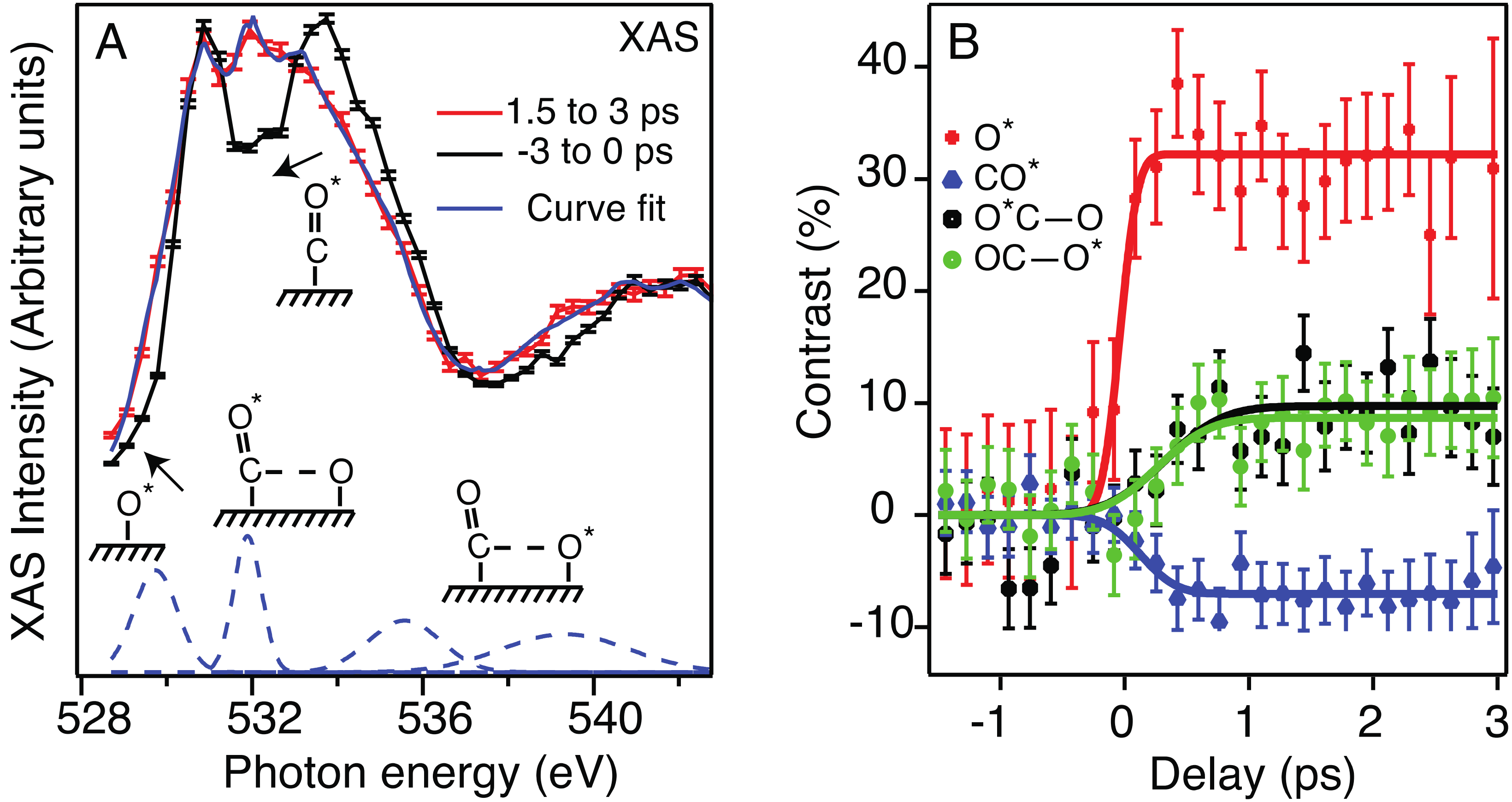




H. Öström et al. Science 347,978 (2015)

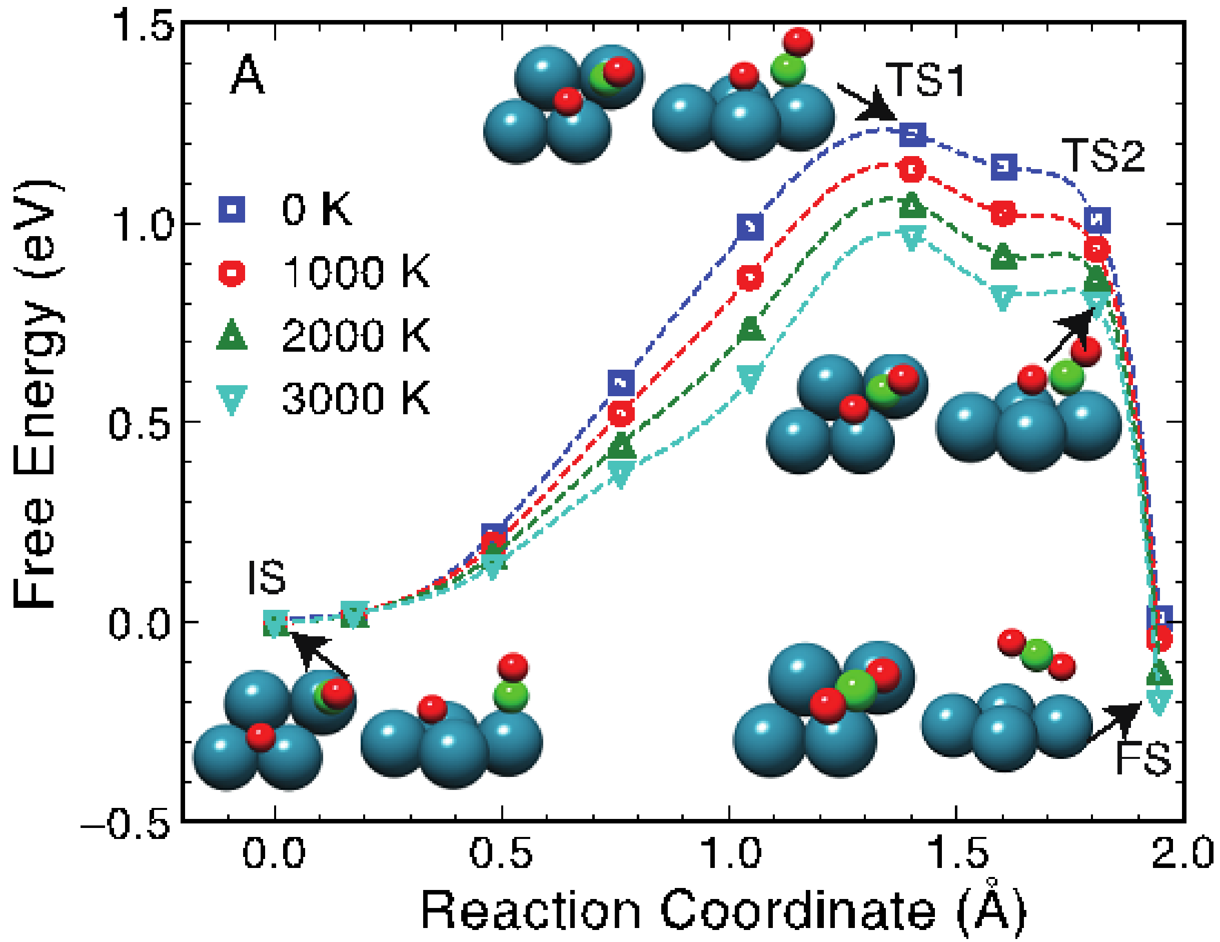
CO oxidation

Time-resolved XAS



H. Öström et al. Science 347,978 (2015)

CO oxidation



H. Öström et al. Science 347,978 (2015)

Summary: CO + O on Ru(001)

CO desorption:

- Triggered by laser-induced „temperature jump“
- Transient precursor state observed after a few ps

Oxygen activation:

- Triggered by „hot electrons“
- Activation from hcp-hollow site to bridge site in less than 200fs

CO oxidation:

- Critical step – oxygen activation
- Transient state reached on timescale of about 1ps

Towards electronic structure movies

- Time-resolved x-ray spectroscopies can provide electronic structure movies of dynamic changes in condensed matter physics, chemistry and biochemistry, and nanoscience

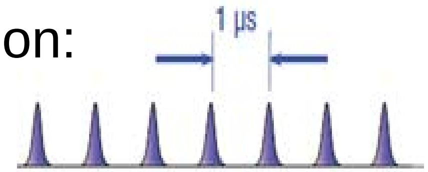
- Ideally a combination of lab-based short pulse XUV sources and (seeded) x-ray free-electron laser sources with high repetition rate is needed
  - „next generation FEL facility“

- Requires joint effort from theory and experiment

- Development of new methods (e.g. stimulated Raman) and new instrumentation (e.g. efficient spectrometers and fast detectors) is very important

FLASH 2020 – The Future

Key properties of FLASH 2020 currently under discussion:



- CW operation with up to 1MHz repetition rate
- Extended energy range ~30-550eV 1st harmonic (chemistry and biology driven: C-, N-,O-K edges, “water window”)
- up to 1keV 2nd harmonic (materials science driven: 3d transition metals)
- operation of multiple FEL lines with 100kHz
- variable polarization
- external seeding up to 100kHz

Free-electron-laser research requires a combined effort