A time-resolved x-ray view of molecular dissociation in the gas phase and in solution

Philippe Wernet

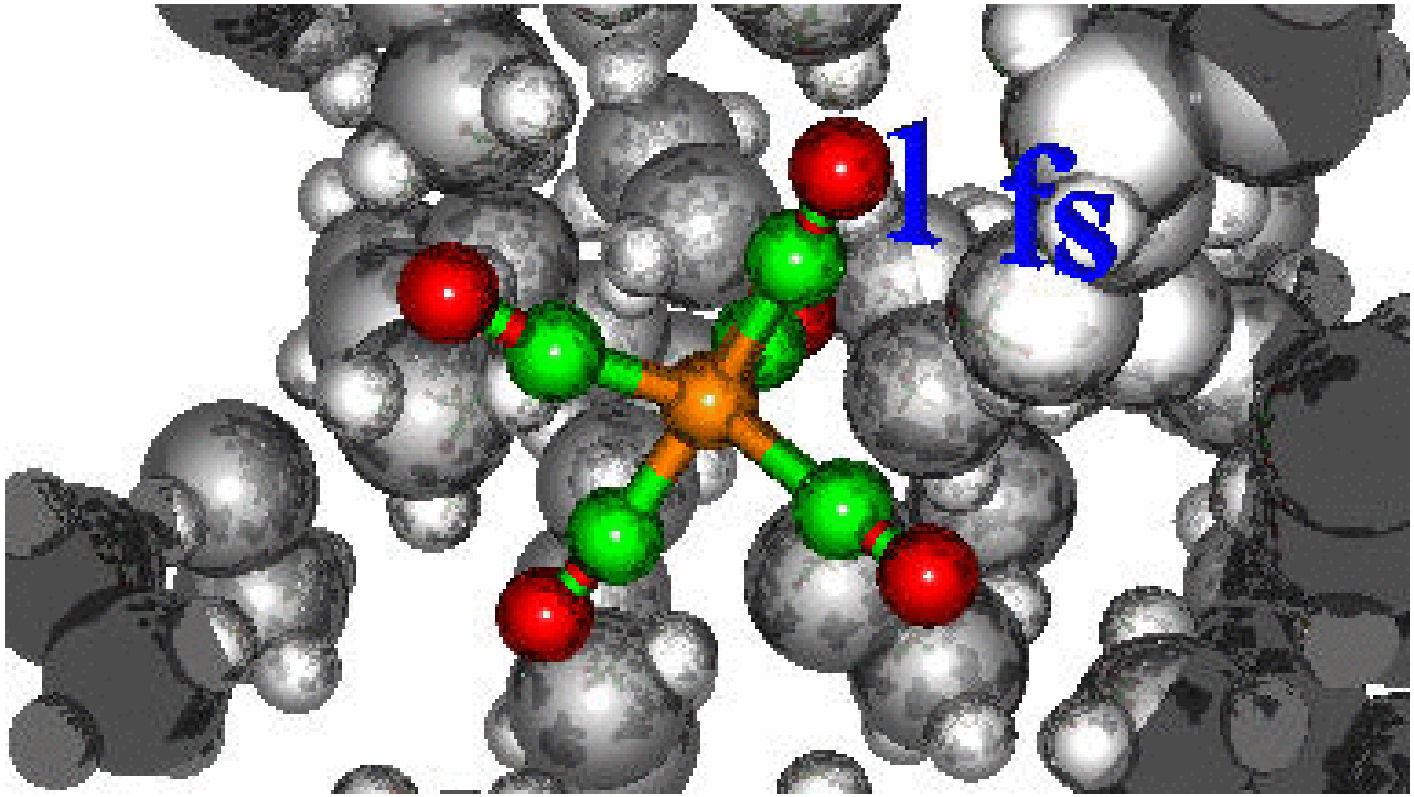
Institute for Methods and Instrumentation for Synchrotron Radiation Research

Helmholtz-Zentrum Berlin für Materialien und Energie

New Science Opportunities at FLASH
DESY (Hamburg), October 12-14, 2011

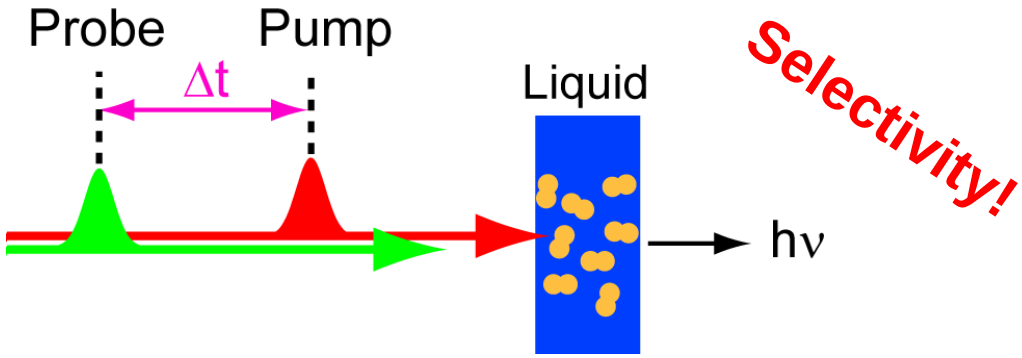
Where are the electrons?

$Fe(CO)_5$ dissociation in ethanol

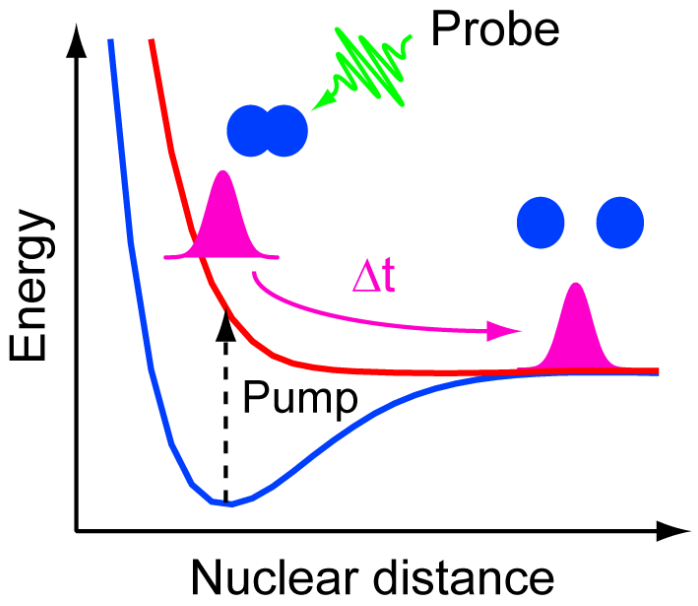


Molecular dynamics simulation
Michael Odelius (Stockholm University)

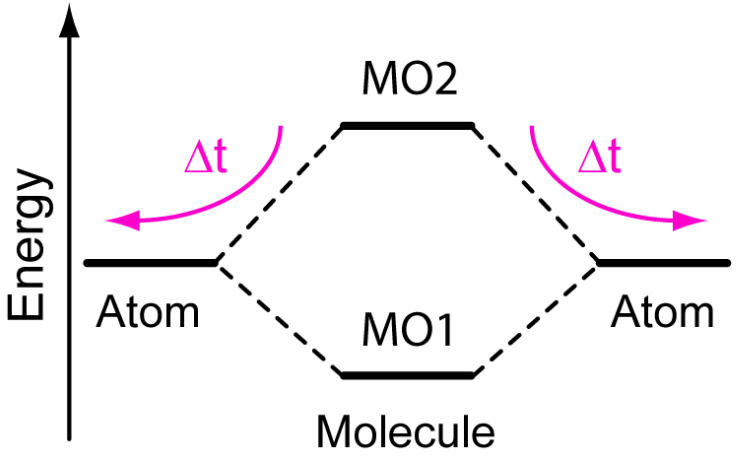
Probing electronic structure during chemical reactions



Nuclear dynamics



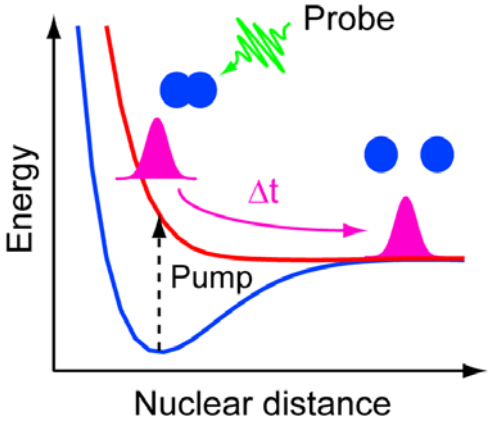
Chemical bonding

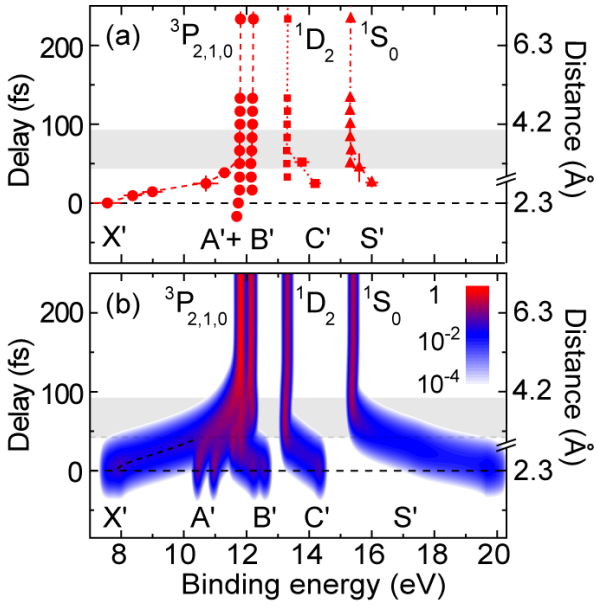


Ph. Wernet, *Electronic structure in real time: Mapping valence electron rearrangements during chemical reactions*, Phys. Chem. Chem. Phys. **13**, 16941 (2011).

Probing electronic structure during chemical reactions

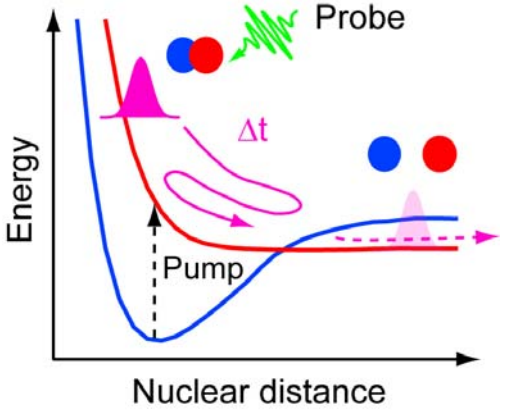
Br_2

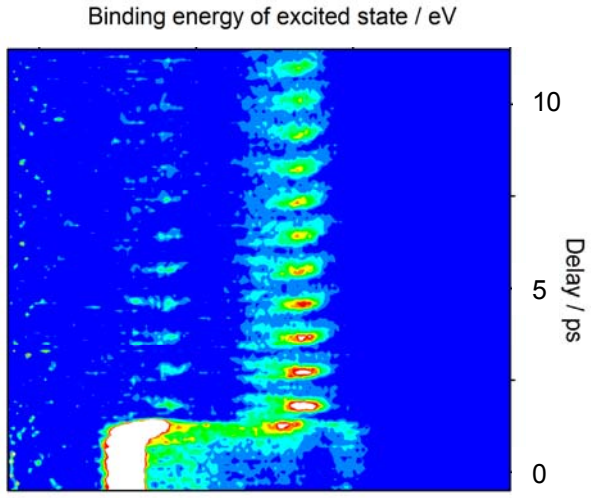




Wernet et al., PRL **103**, 013001 (2009).

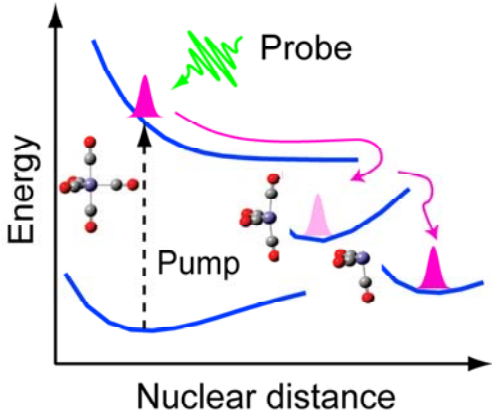
NaI

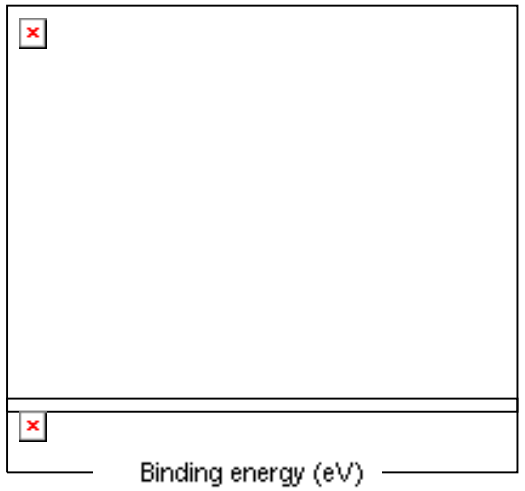




In collaboration with A. Lübcke, A. Rouzée, P. Johnsson, M. Vrakking et al.

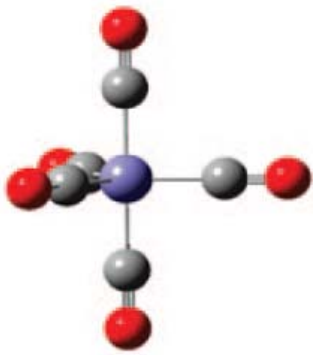
$Fe(CO)_5$



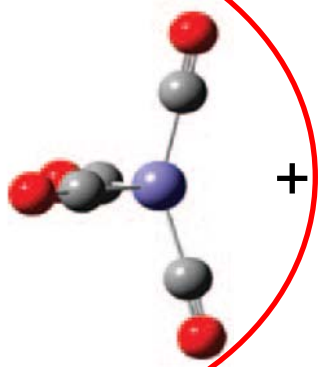


In collaboration with S. Düsterer, M. Meyer et al.

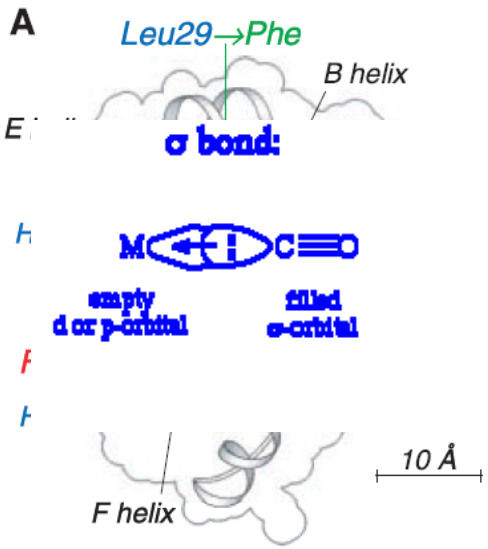
The photo-dissociation of $Fe(CO)_5$

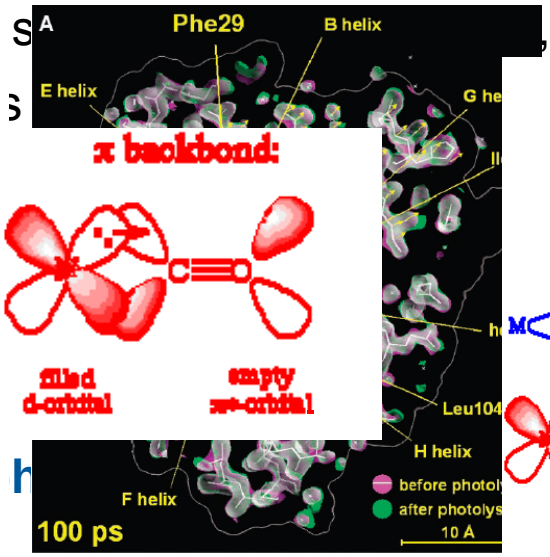


$Fe(CO)_5 + hv \rightarrow Fe(CO)_4 + \ldots$

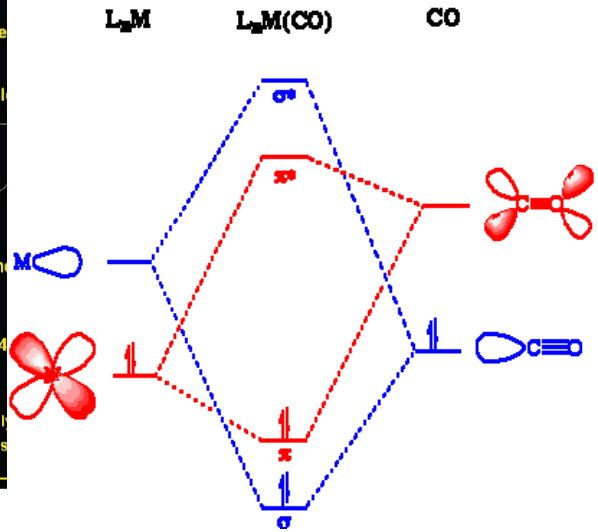


- Coordinatively unsaturated carbonyl intermediates catalyze chemical reactions
- Fe-CO bonding and dissociation is important in nature

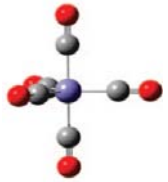




F. Schotte. M. Lim. T. A. Jackson, J. S. M. Wulff, 00, 1944



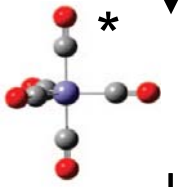
Proposed UV photo-dissociation of $Fe(CO)_5$



$^1Fe(CO)_5$

UV pump = MLCT

Fe 3d  → CO π* 



$^1Fe(CO)_5$*

Gas phase Singlet pathway

Solution Triplet pathway

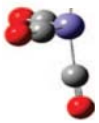
$^1Fe(CO)_4$

„Vibrationally hot“

$^3Fe(CO)_4$ 

Thermal before | *(slow) CO elimination ISC can occur*

Diffusion (slow) | *Solvation*

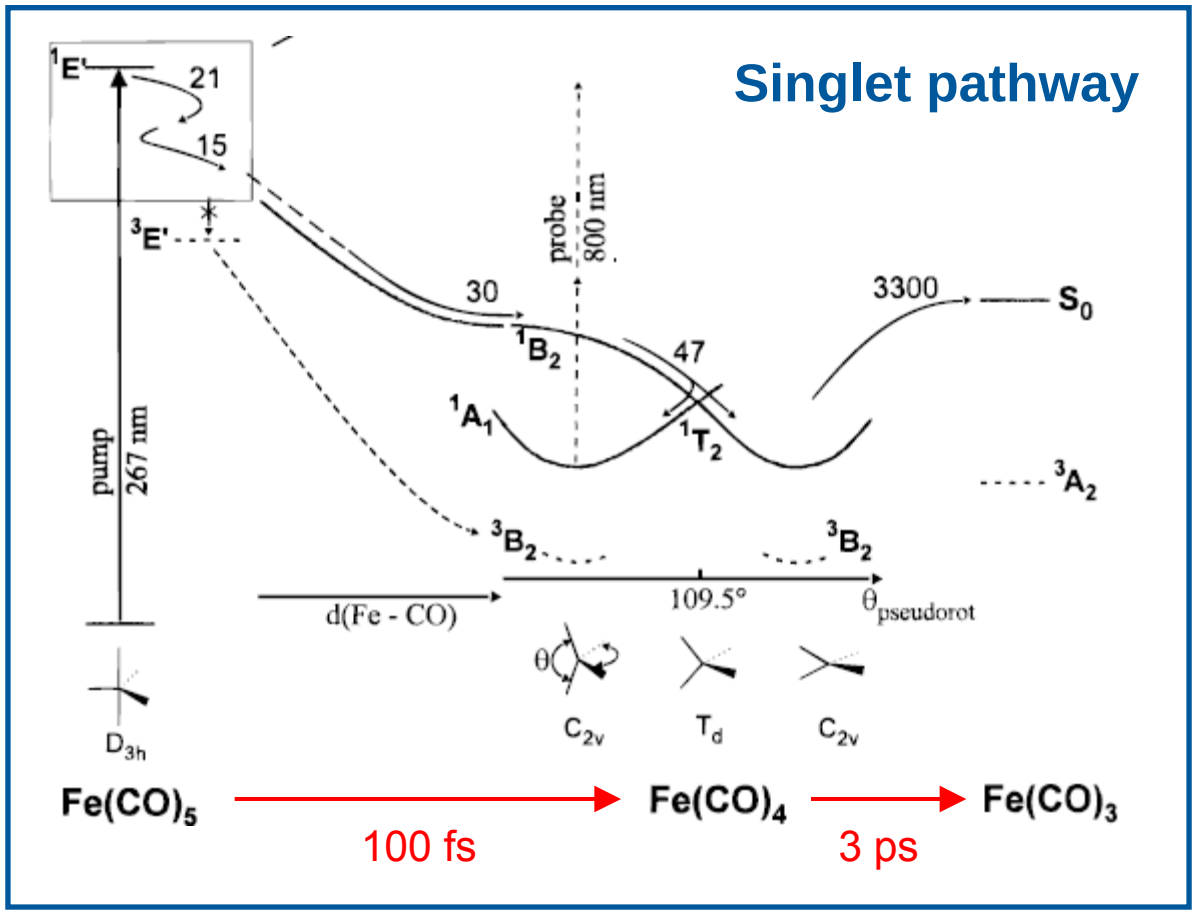


$^1Fe(CO)_3$

$^1Fe(CO)_4$ 

Poliakoff, Turner, Angew. Chem. Int. Ed. **40**, 2809 (2001).

$Fe(CO)_5$ dissociation in the gas phase



TR mass spectrometry:

Trushin, Fuss, Kompa, Schmid, J. Phys. Chem. A **104**, 1997 (2000).

Indirect

TR electron diffraction:

Ihee, Cao, Zewail, Angew. Chem. Int. Ed. **40**, 1532 (2001).

Geometric structure

Time window of 100 fs to 3 ps after pumping for characterizing $Fe(CO)_4$

$Fe(CO)_5$ dissociation in the gas-phase with TR-PES at FLASH

HZB: Torsten Leitner, Martin Beye, Kristjan Kunnus, Simon Schreck, Alexander Föhlisch, Philippe Wernet

European XFEL: Paul Radcliffe, Tommaso Mazza, Michael Meyer

DESY: Stefan Düsterer

PG 2, April and June 2011
12 (4+8) Shifts scheduled

Theory: Ida Josefsson, Michael Odelius

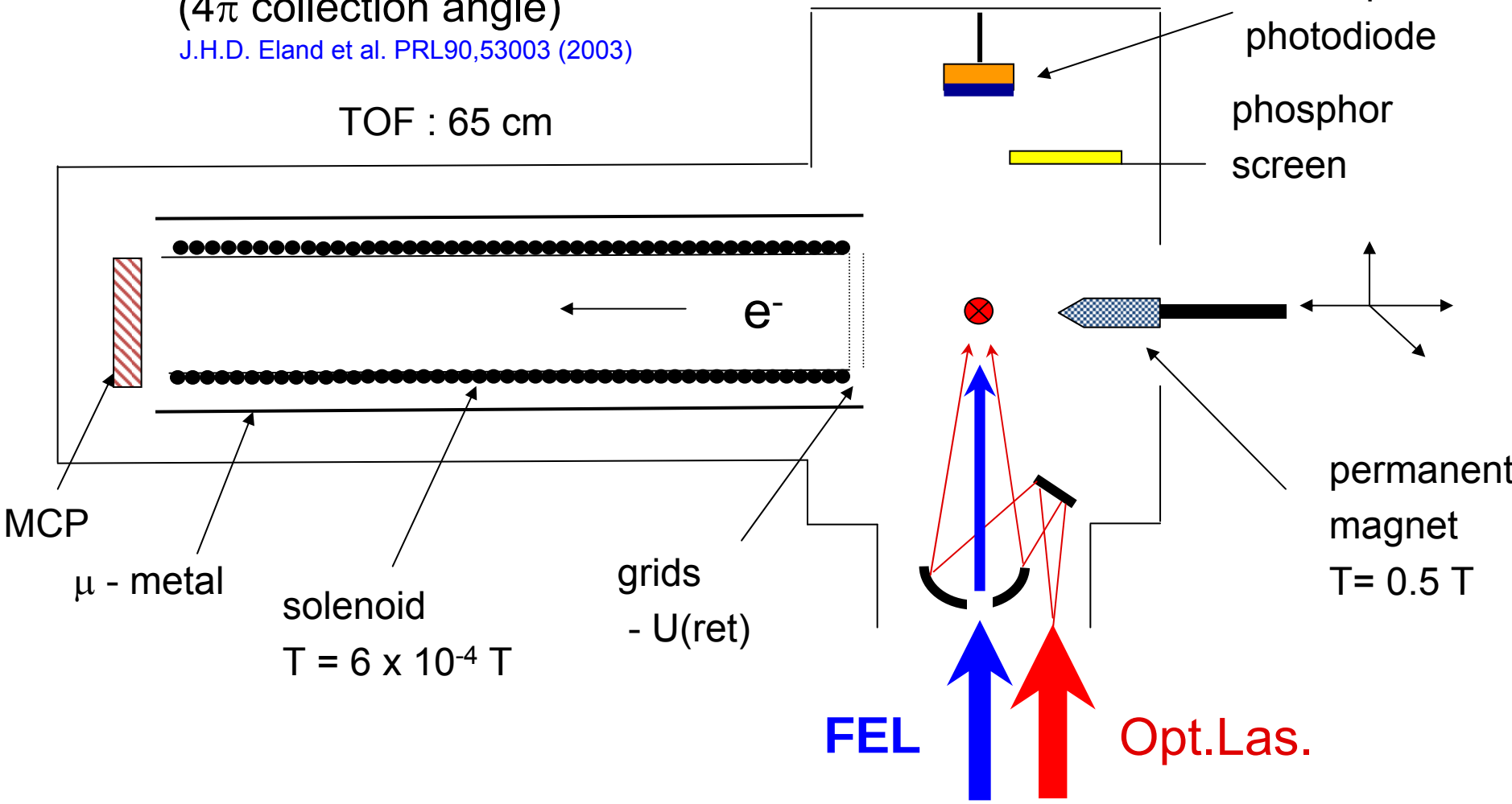
Thank you: Maschine operators, run coordinators, Harald Redlin

Set up for TR-PES at FLASH

MBES: Magnetic Bottle Electron Spectrometer

(4π collection angle)

J.H.D. Eland et al. PRL90,53003 (2003)



Slide courtesy of Michael Meyer

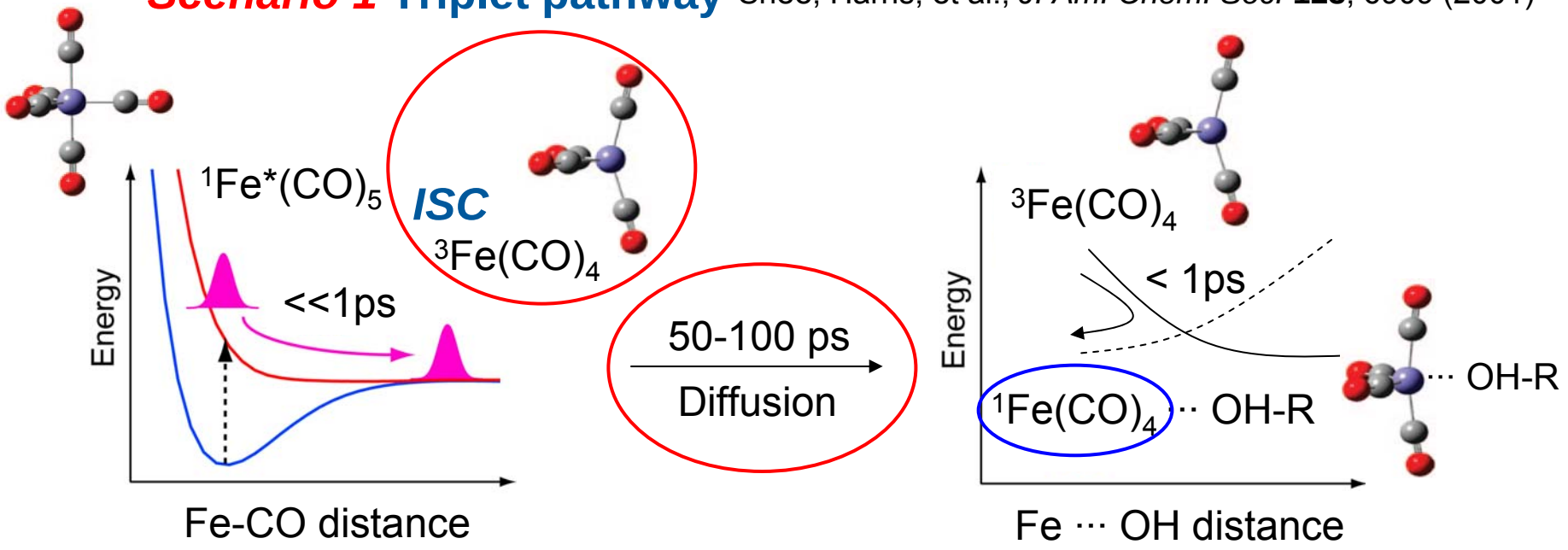
Outlook

- New challenges for theory
  - **“Ab initio” electronic structure spectroscopy (including core hole)**
  - **Coupled with molecular dynamics simulations (trajectories)**
  - **Excited state dynamics, many electrons**
- Very fast time scales (various excited singlet states in the gas phase at < 100 fs) remain unsolved
- Needed temporal resolution << 100 fs
- Reliable jitter correction needed
- Higher photon energies to reach 3d TM 2p levels
- Probing coordination in reaction intermediates with angularly resolved core-level PES?
- Electron-Ion coincidence for higher selectivity to certain intermediates?

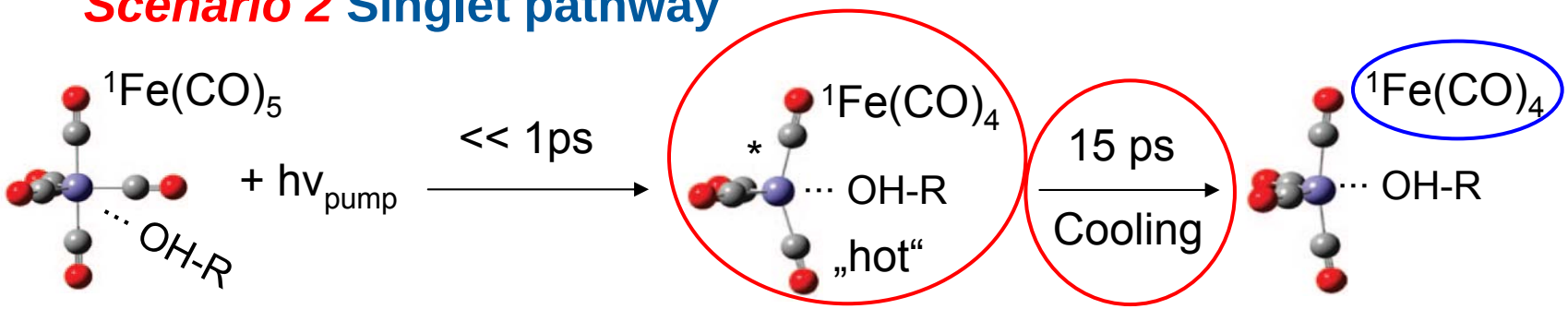
$Fe(CO)_5$ dissociation in solution

Scenario 1 Triplet pathway

Snee, Harris, et al., *J. Am. Chem. Soc.* **123**, 6909 (2001)



Scenario 2 Singlet pathway

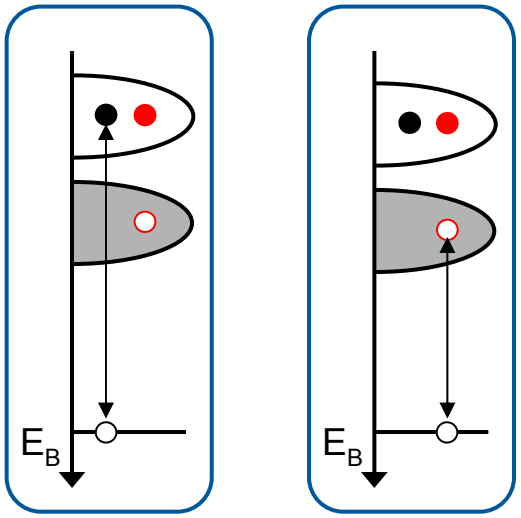


B. Ahr, M. Cholle, B. Adams, E. M. Lunny, C. M. Laperle, C. Rose-Petruck, *PCCP* **13**, 5590 (2011)

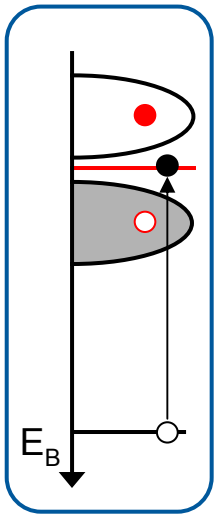
Time-resolved RIXS

Pump: **Optical excitation**
Probe: **RIXS**

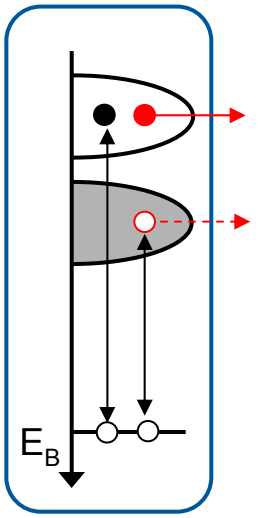
„Electronic dynamics“ (orbital population e.g.)?



Selecting species?



Charge transfer?



Liquid Jet Experiment (LJE) for LCLS

Contact: Philippe Wernet (HZB), Simone Techert (MPI-BPC), Alexander Föhlisch (HZB)

HZB: Martin Beye, Kristjan Kunnus, Simon Schreck, Edlira Suljoti, Christian Weniger

MPI-BPC: Sebastian Grübel, Wilson Quevedo, Ivan Rajkovic, Mirko Scholz

MAX-lab: Brian Kennedy, Franz Hennies

SSRL/SLAC: Dennis Nordlund

PULSE/SLAC: Kelly Gaffney, Robert Hartsock, Wenkai Zhang

LCLS/SLAC: Bill Schlotter, Josh Turner

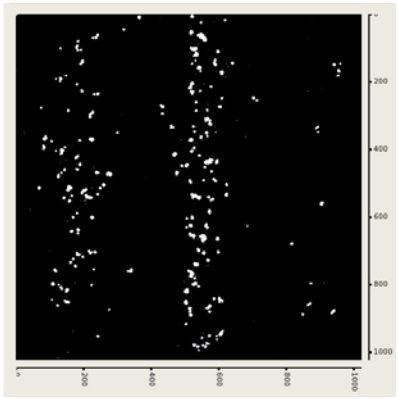
Stockholm University: Ida Josefsson, Michael Odelius (Theory)

Utrecht University: Frank de Groot (Theory)

Liquid Jet Experiment (LJE)

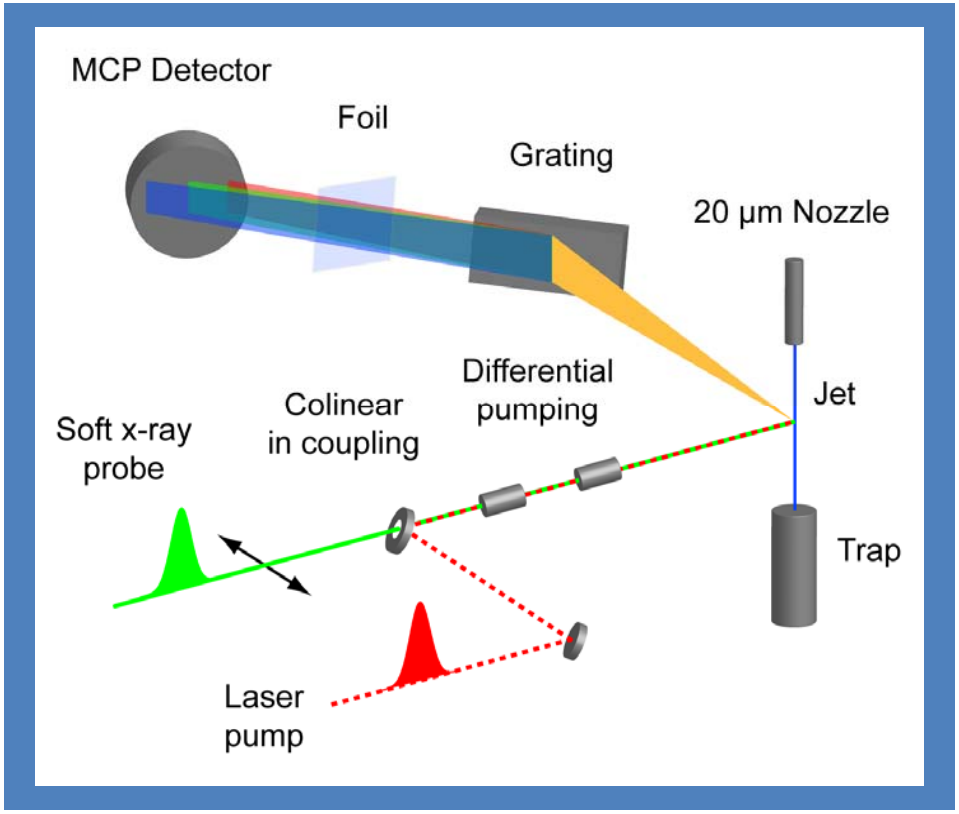
Time-resolved XES/RIXS on liquid jets in vacuum

Counts on MCP



Emission energy

Methanol O K-edge emission (**1 shot!**)

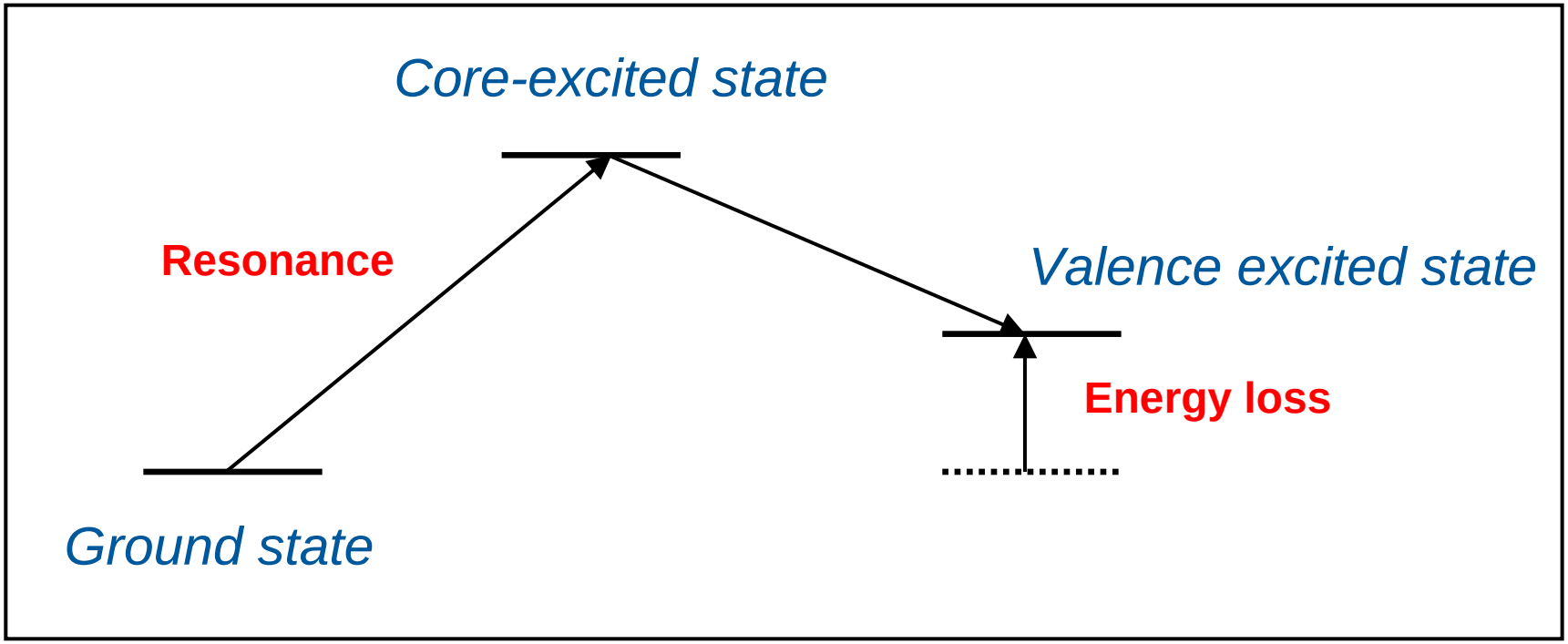


X-rays on jet

Nozzle

Available for experiments at LCLS and BESSYII

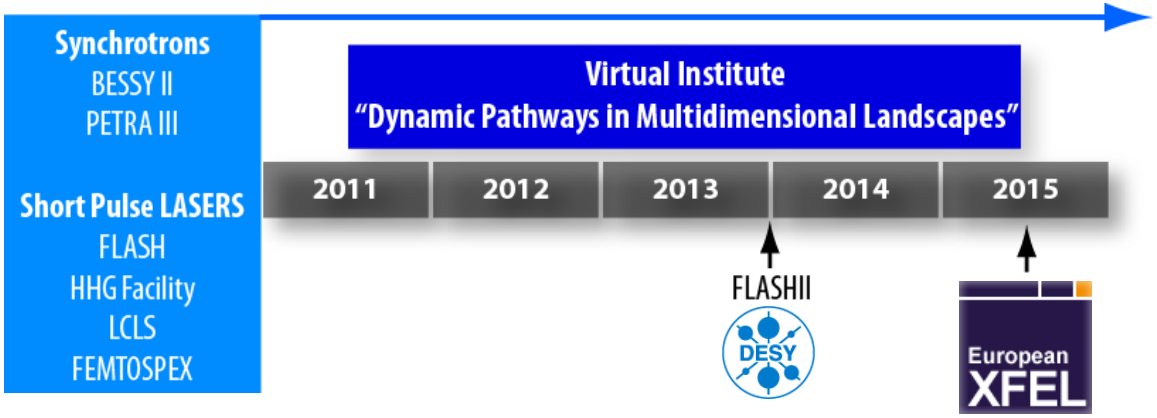
RIXS for probing valence excitations



- Element-specific
- Symmetry-selective

Helmholtz Virtual Institute

Dynamic Pathways in Multidimensional Landscapes



S. Eisebitt
TUB, HZB

A. Föhlisch
UP, HZB

M. Weinelt
FUB

H. Chapman
UHH, DESY

G. Grübel
DESY

R. Santra
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• MAX-lab	Annette Pietzsch, Nils Mårtensson
• SXR team	Michael Rowan, Tom Benson, Oleg Krupin, Michael Holmes
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