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SMR/1238-8

ADRIATICO RESEARCH CONFERENCE on

LASERS IN SURFACE SCIENCE

11-15 September 2000

Miramare - Trieste, Italy

Time-resolved Valence Level Photoemission Spectroscopy: Studying Surface Reactions with sub-picosecond time resolution

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Time-resolved Valence Level Photoemission Spectroscopy: Studying Surface Reactions with sub-picosecond time resolution

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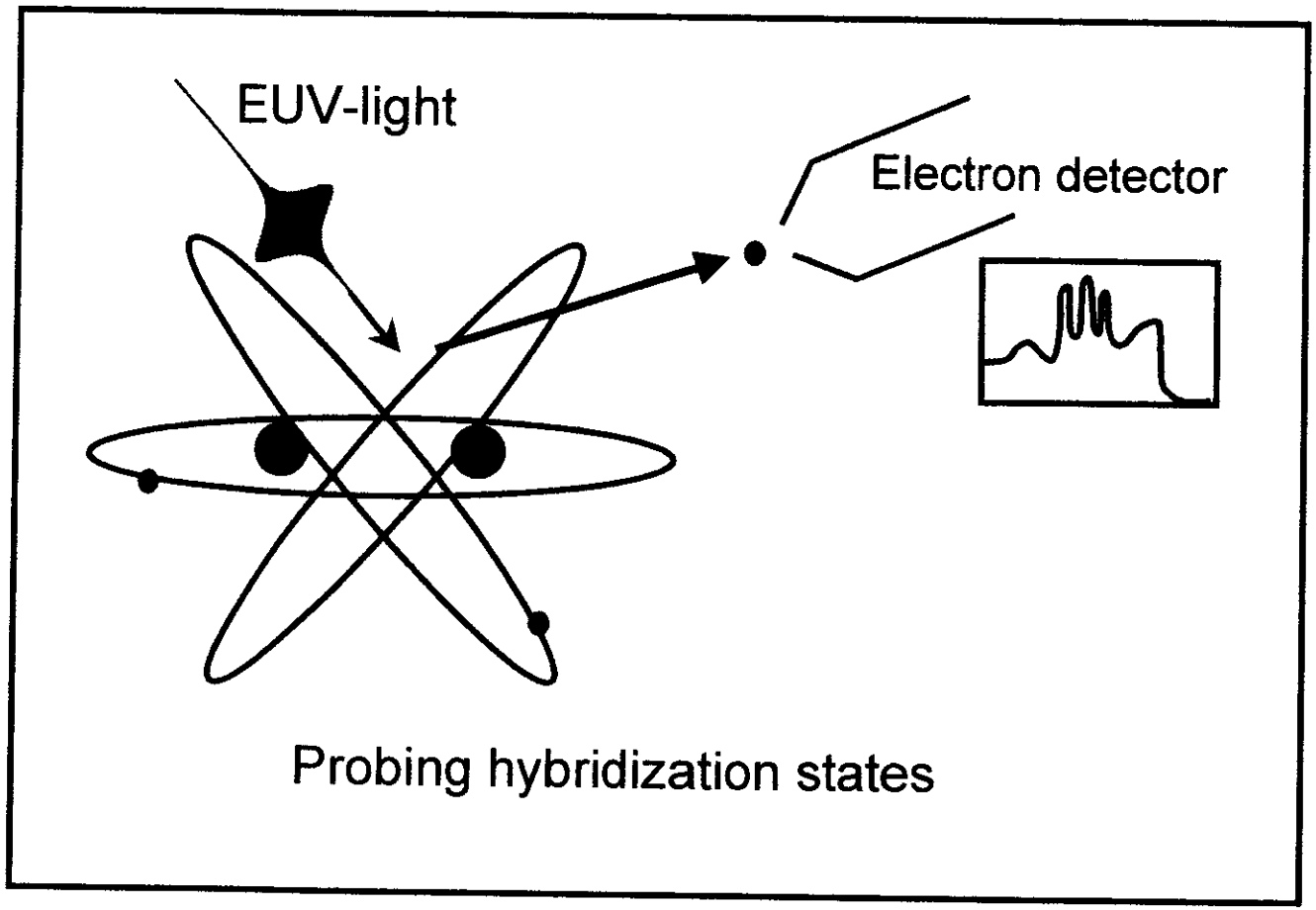
- short-pulse XUV generation: phase matched high harmonic generation
- Time-resolved Photoemission spectroscopy: experimental realization
- Experiment: O_2/Pt(111)

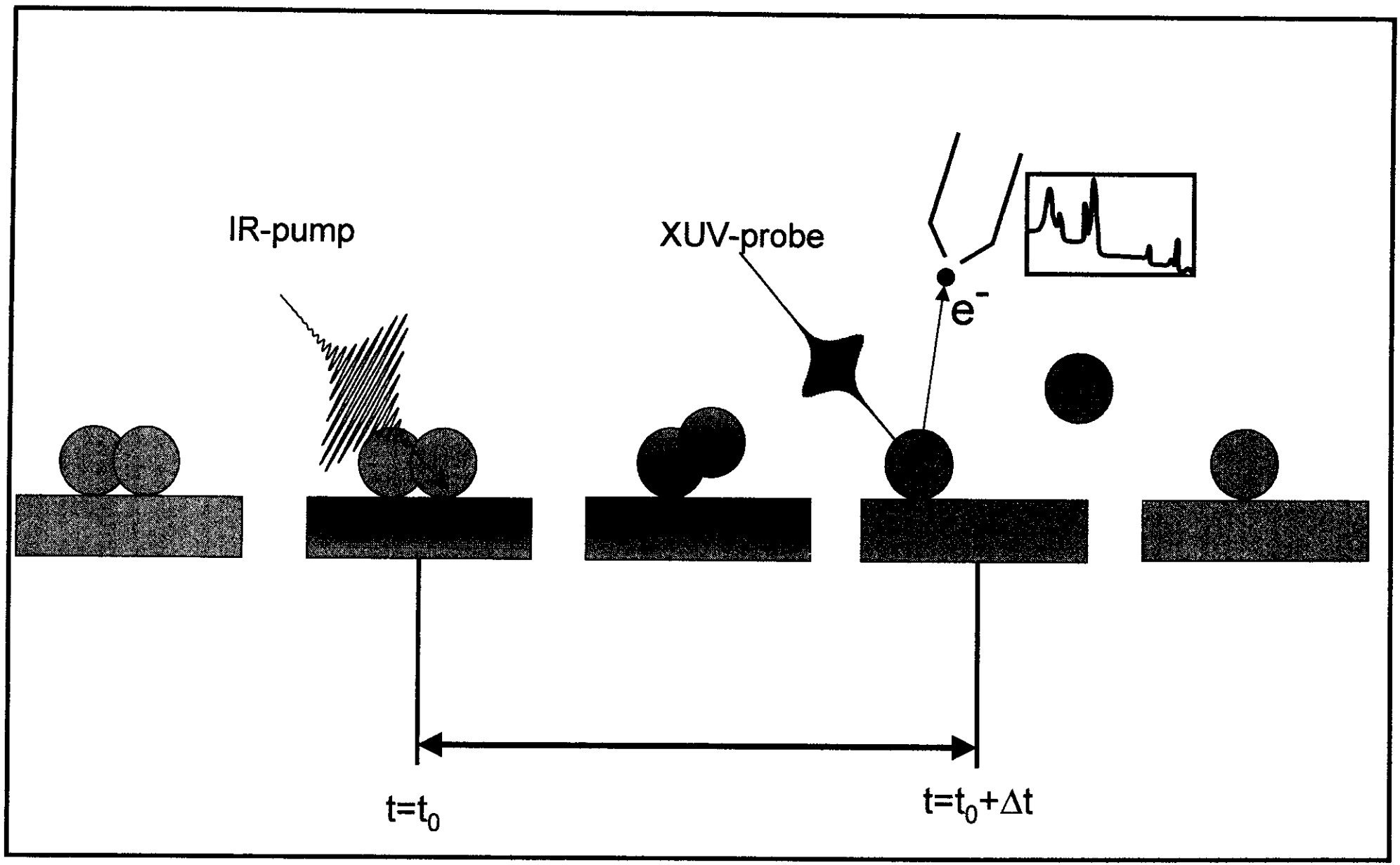
Valence level Photoemission spectroscopy - UPS



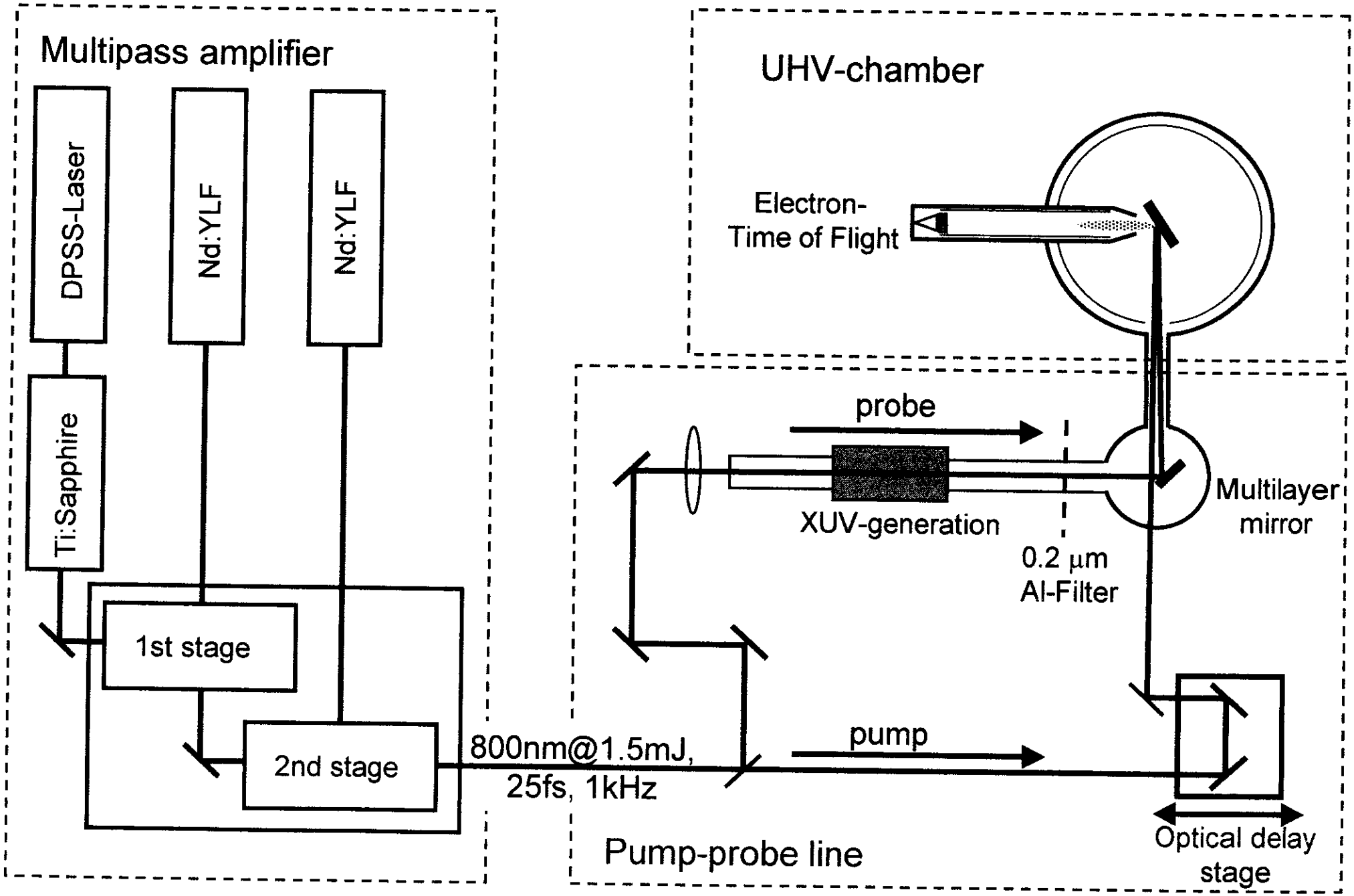
⇒Gain information about the chemical state of a sample

Goal: study dynamics of chemical processes on surfaces on their fundamental timescales

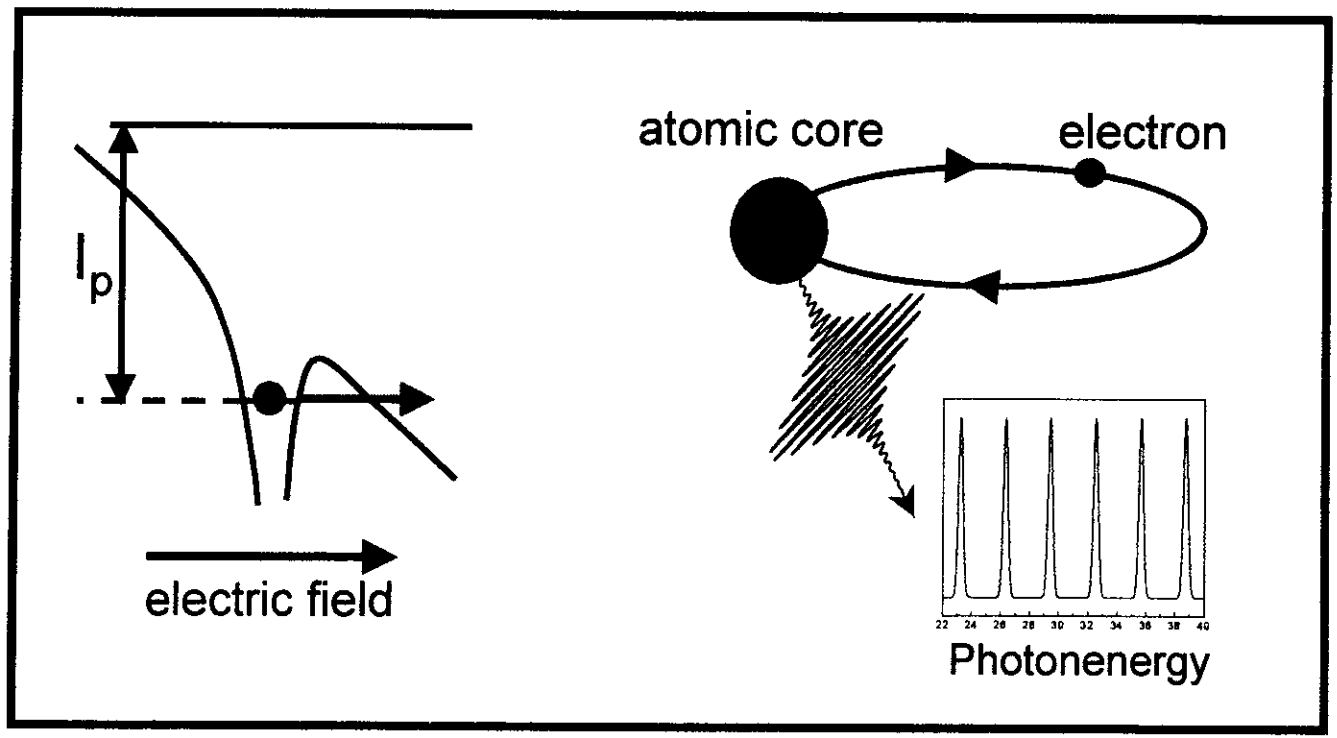
Time-resolved photoemission spectroscopy



Experimental setup



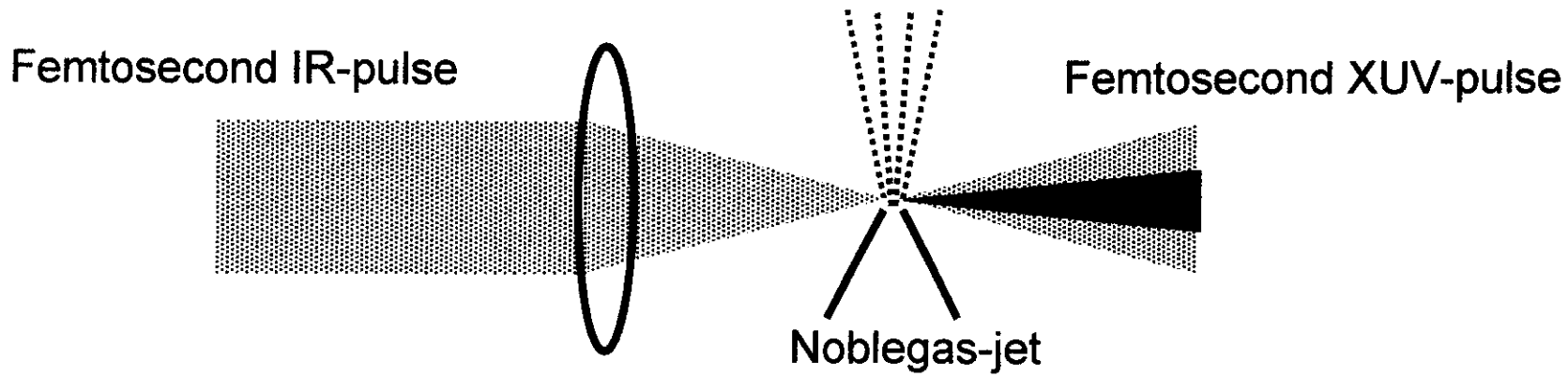
XUV-Source: High Harmonic Generation



maximum Photonenergy

$$h\upsilon_c = I_p + 3.17 \cdot U_p$$

$$U_p \propto I_S \cdot \lambda^2$$



Phasematched high harmonic generation

Condition for phasematching: $\boxed{\Delta k = qk_{laser} - k_{XUV} = 0}$

XUV-High Harmonic

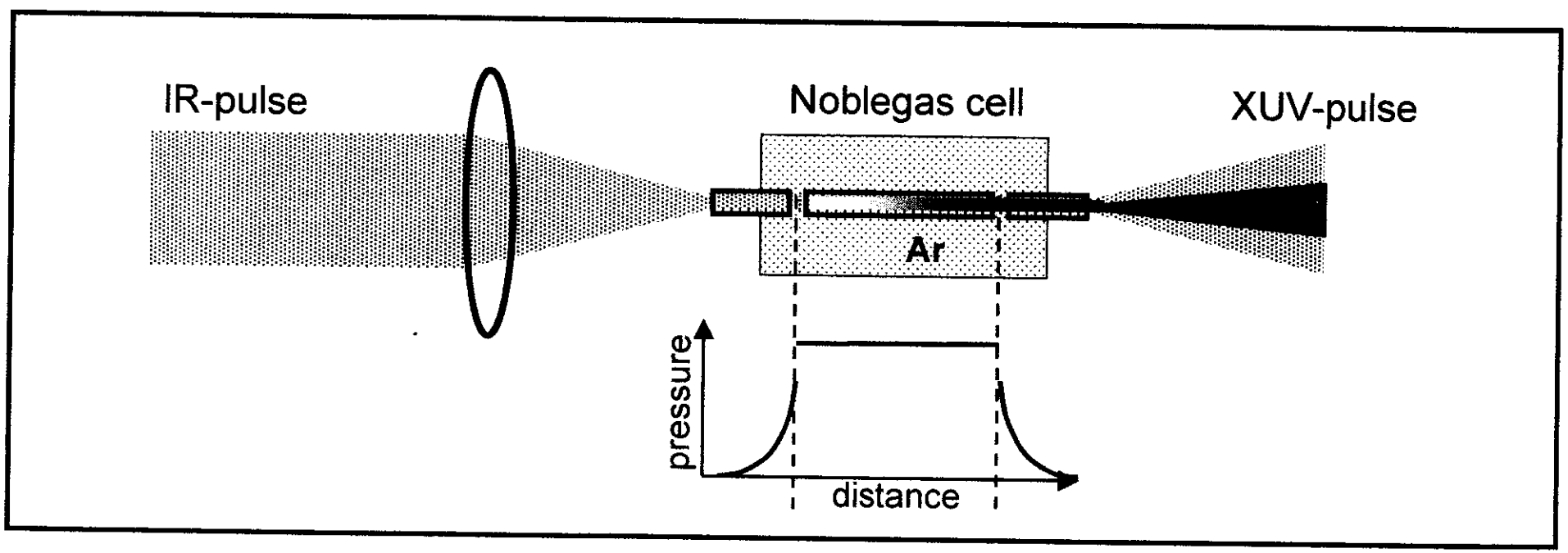
$$k_{XUV} \approx \frac{2\pi}{\lambda_{XUV}}$$

Fundamental Laser

$$k_{laser} \approx \frac{2\pi}{\lambda_{laser}} + \frac{2\pi N_a \delta(\lambda)}{\lambda_{laser}} - N_e r_e \lambda_{laser}$$

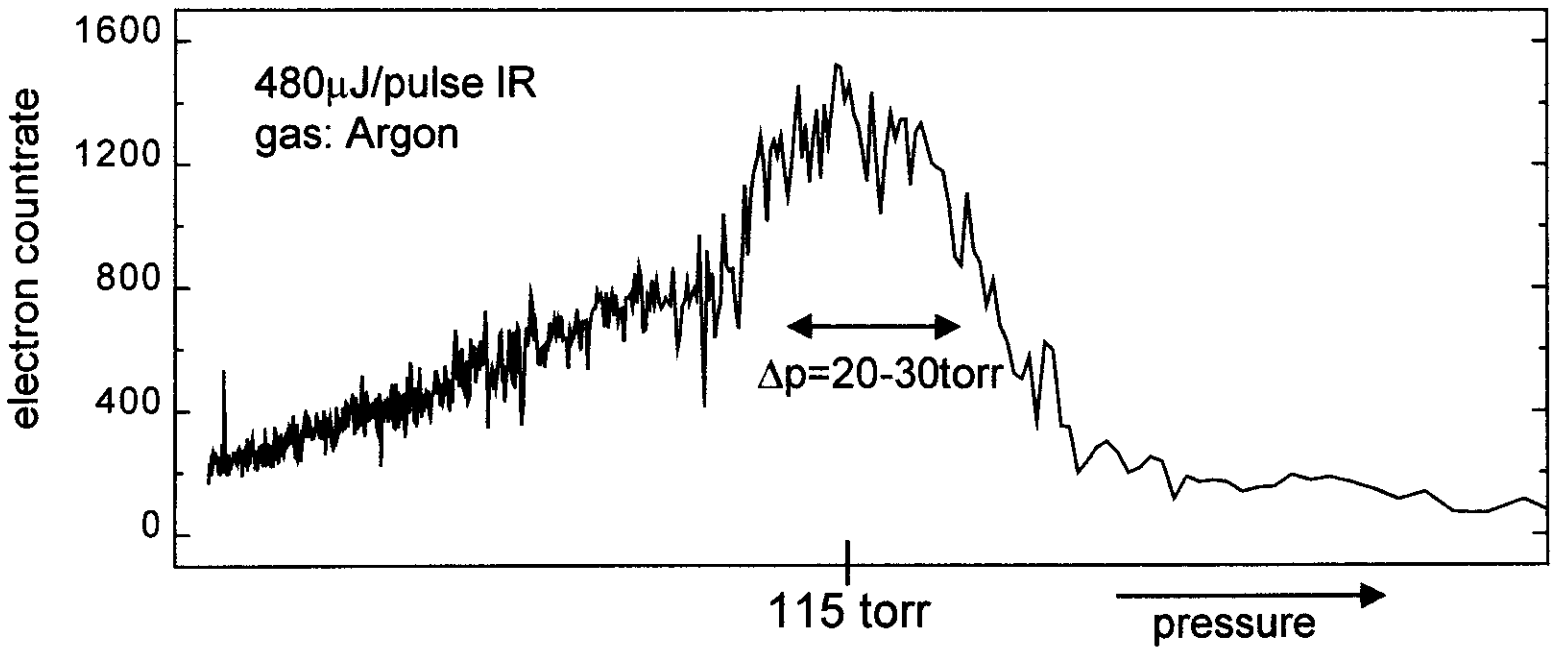
Noblegas pressure

Ionisation

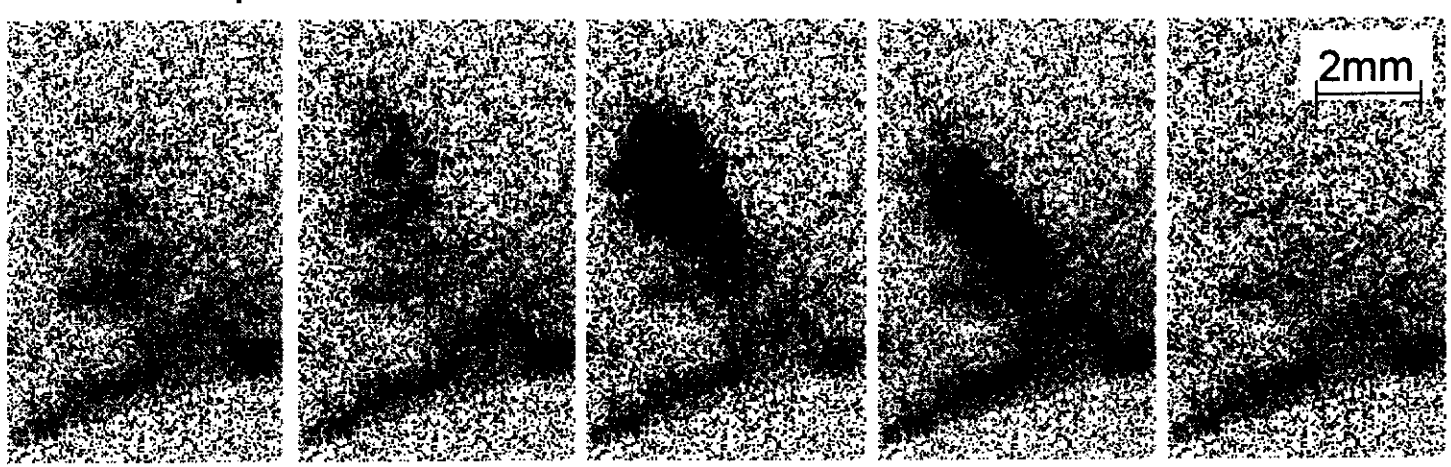


Phasematched generation of high harmonics

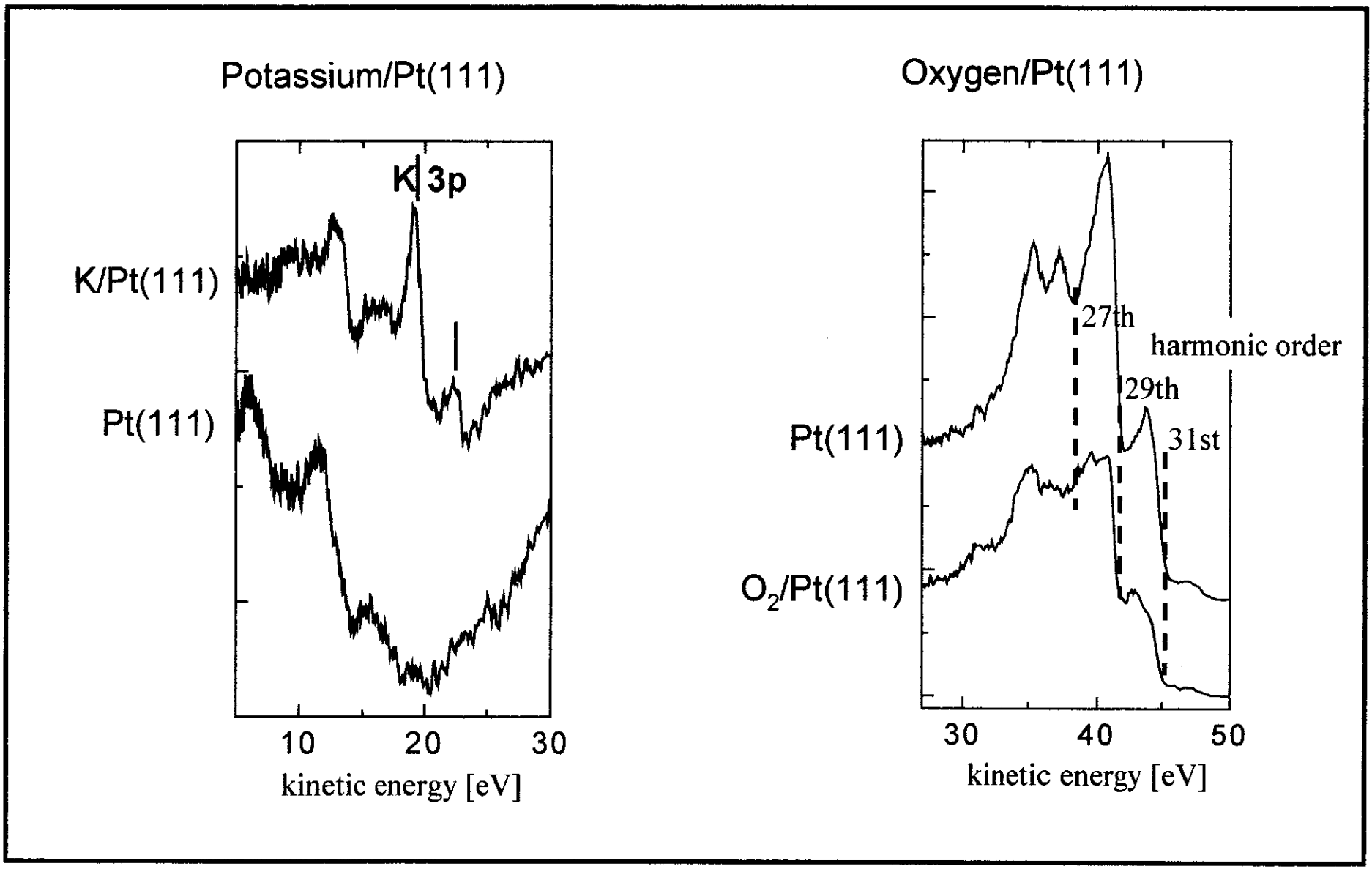
1) photoemission yield vs. cell pressure



2) beam mode vs. cell pressure



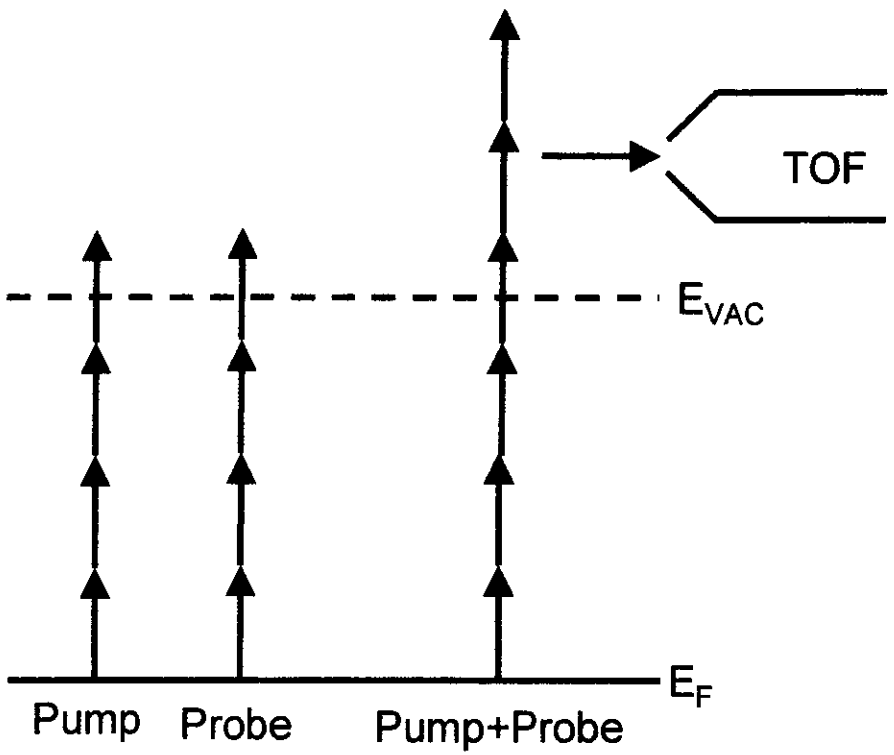
Experiment: Photoemission with XUV

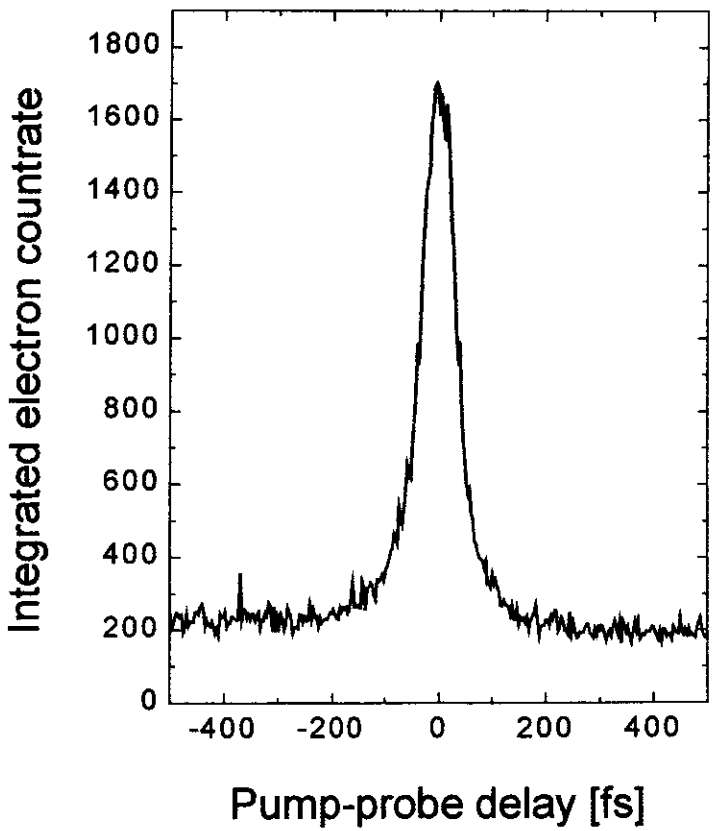


Pump-Probe time-zero

Crosscorrelation between pump and *fundamental* of probe at sample:

IR induced Multiphoton process:





Pulsewidth at sample:	IR -pump	70 fs
	XUV -probe	<20 fs

Oxygen adsorbed on Pt(111)

Molecular Oxygen

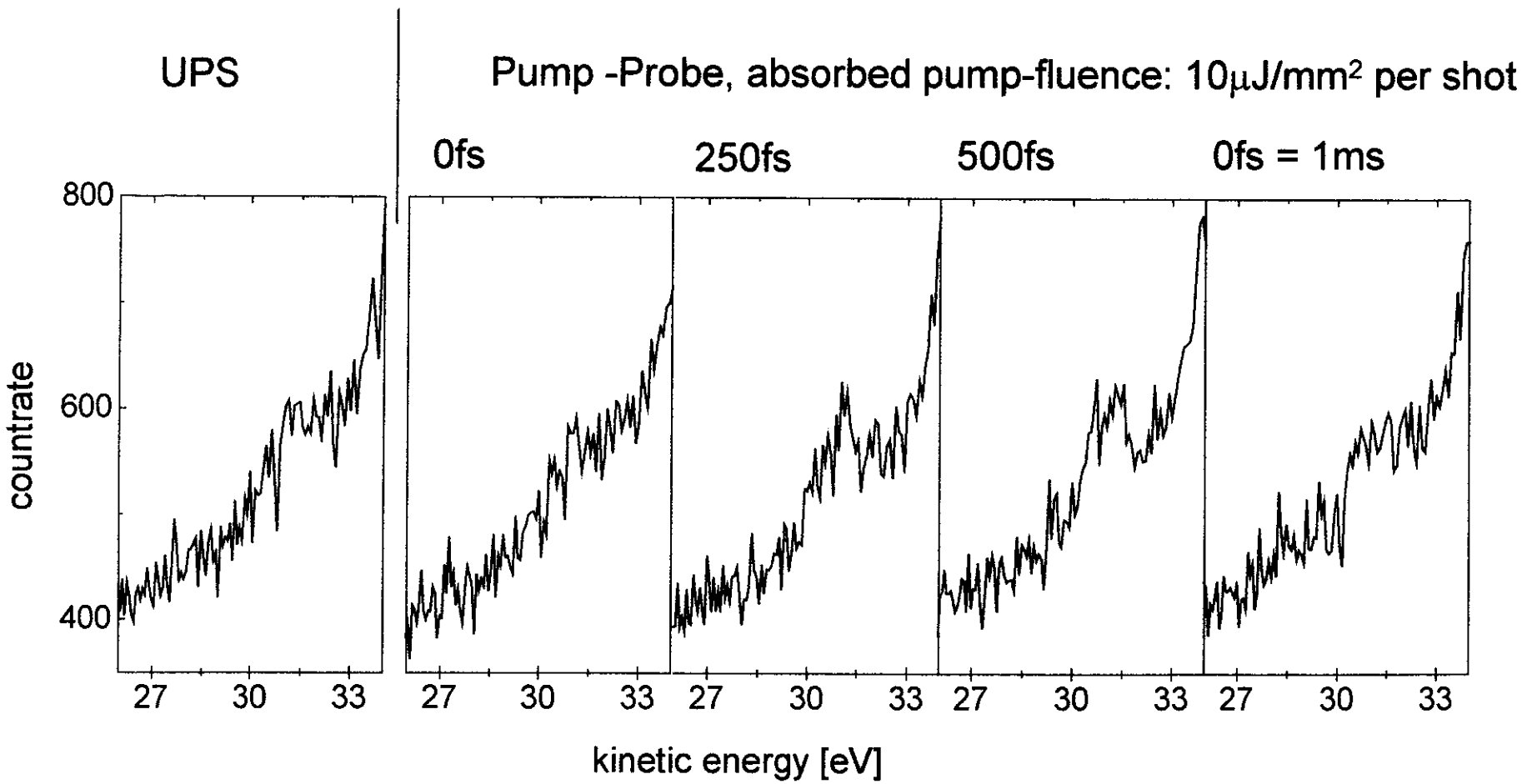
Physisorbed	T<40K	
Chemisorbed	T<150K	2 phases

Atomic Oxygen

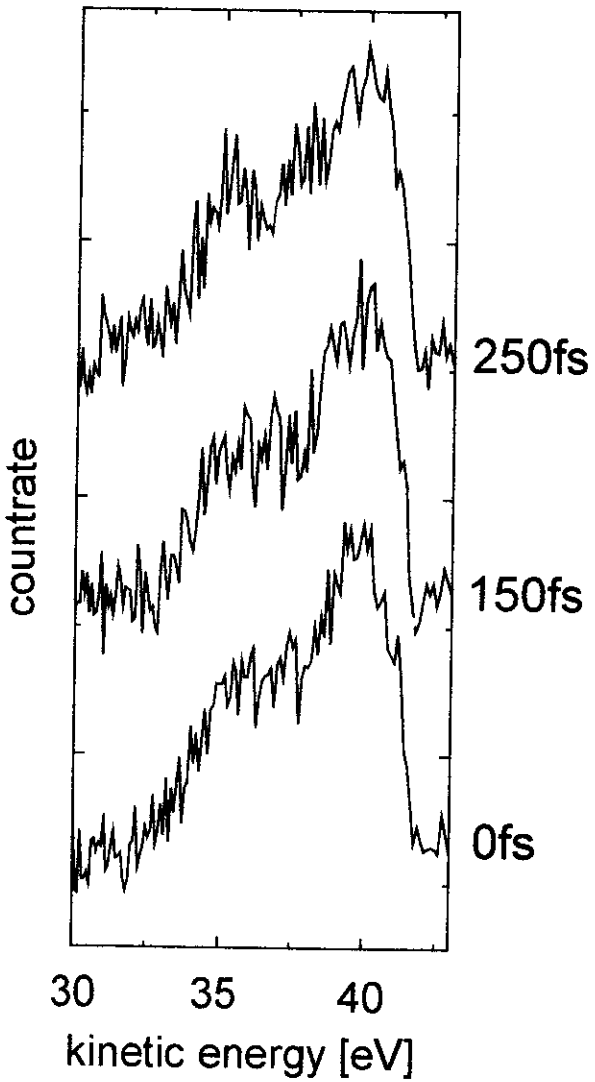
Chemisorbed	T<800K

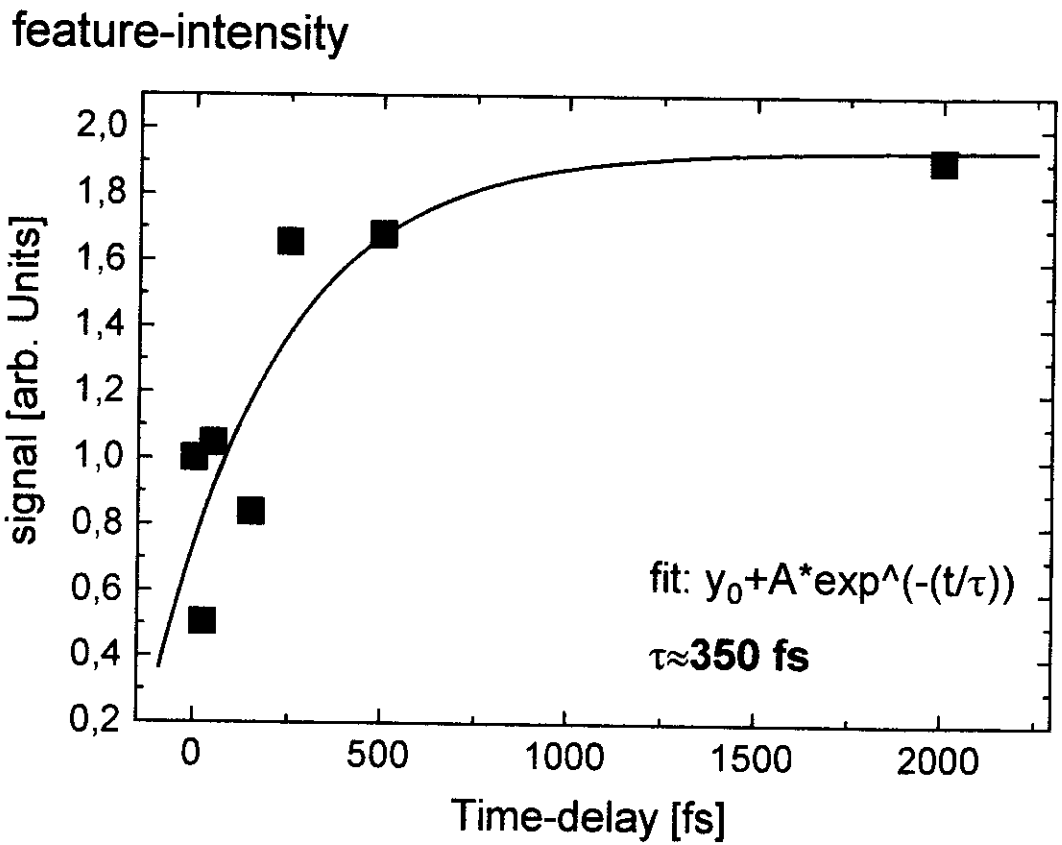
Pump-Probe experiment

sample: 1 saturation layer of O_2@77K - chemisorbed O_2



Pump-Probe experiment

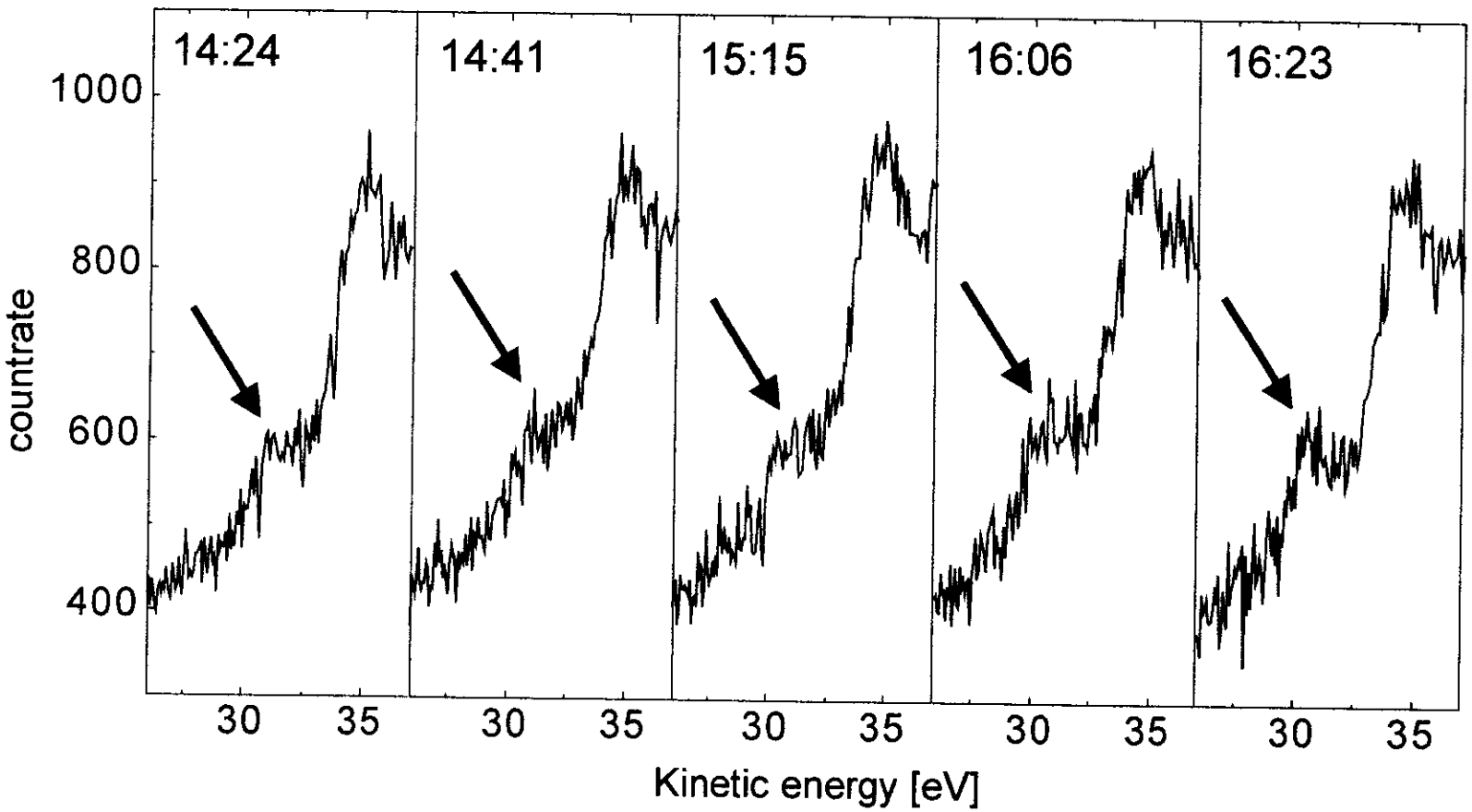




- distinct change in the valence-spectrum as function of time-delay
- binding energy: ~6eV
- rise-time: ~350 fs
- lifetime τ of excited state: 4.5 ps < τ < 1 ms
- excitation out of molecular oxygen state
- laser-induced desorption at higher fluence

Long-term changes of sample due to IR-irradiation

Absorbed fluence: 10μJ/mm² per shot



⇒Stabilization of transient state over timescale of hours

What do we observe?

Three possible mechanism

- depletion of surface due to Oxygen-desorption

  ⇒long term: present, but no directly indicated

- transition between the molecular chemisorption state

  ⇒transient: non-equilibrium (metastable) distribution

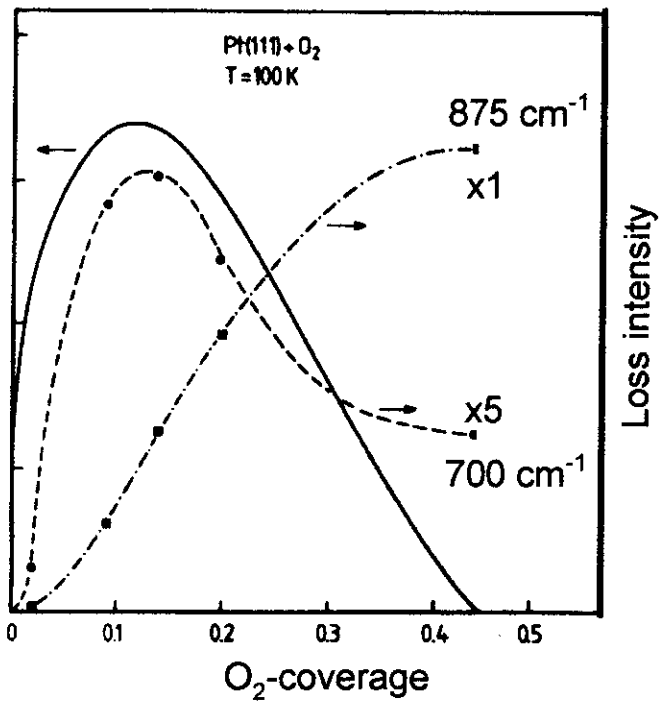
  ⇒long-term: stabilization due to depletion of surface

- dissociation of oxygen → atomic oxygen

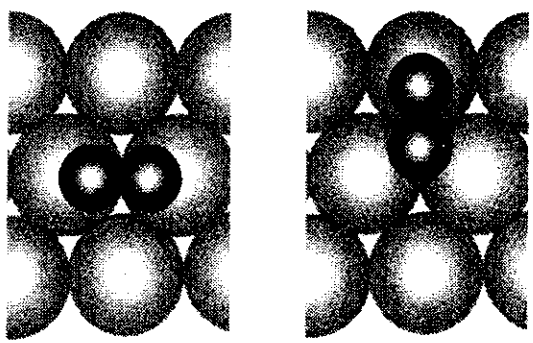
  ⇒long-term: possible

Molecular Oxygen chemisorbed on Pt(111)

EELS (H. Steininger et al., Surf. Sci. (1982))



STM (C. Stipe et al., PRL (1997))



bridge site
875 cm^{-1}

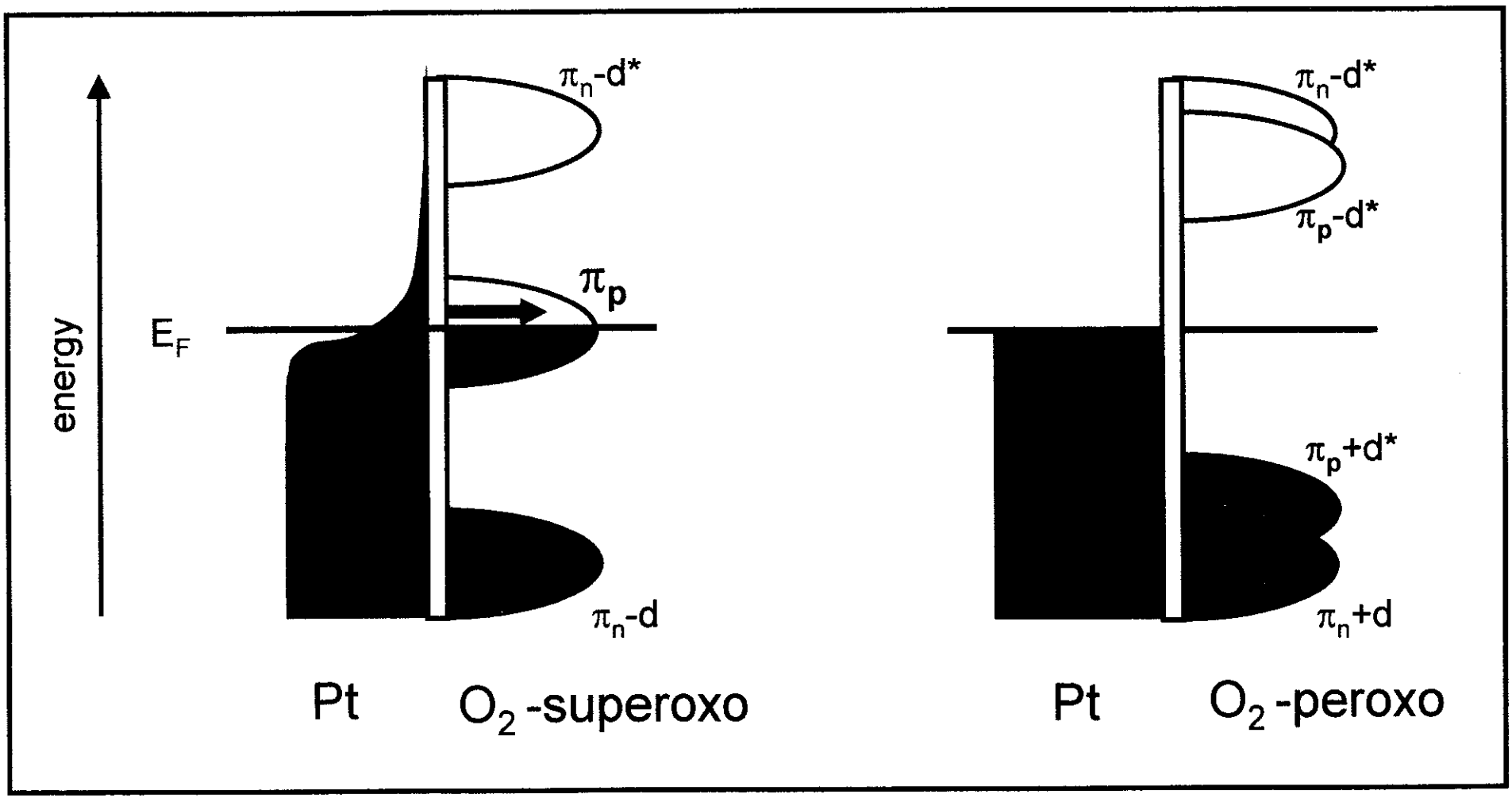
fcc site
700 cm^{-1}

Theory (A. Eichler and J. Hafner, PRL 1997):

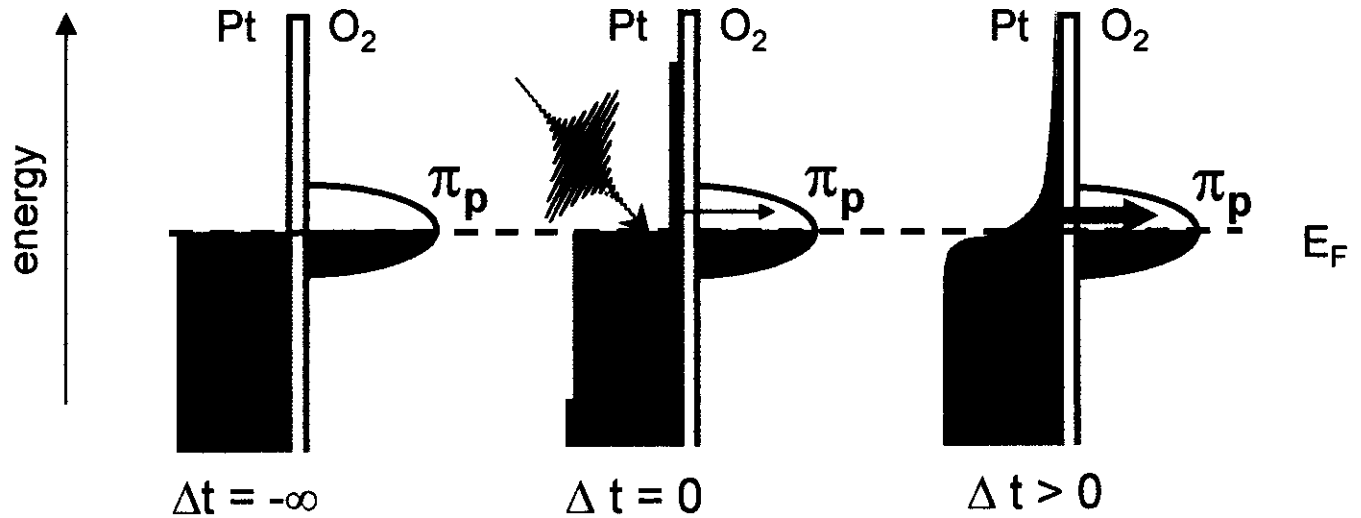
Adsorption site	O-O stretching	O-O bondlength	charge state
1) bridge site	850 cm^{-1}	1.39 Å	O_2^- (superoxo)
2) fcc site	700 cm^{-1}	1.43 Å	O_2^{2-} (peroxo)

Excitation mechanism

Substrate electron mediated excitation

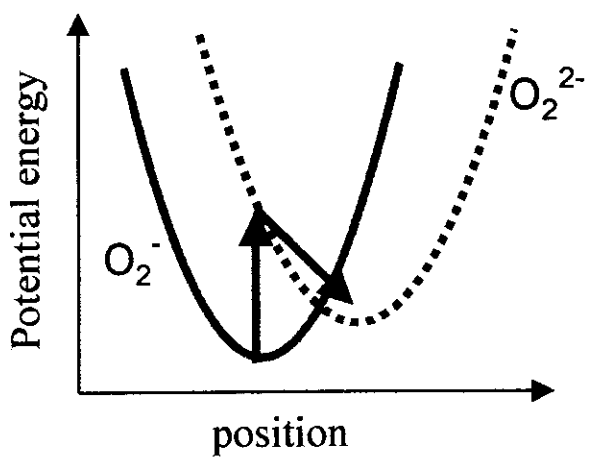


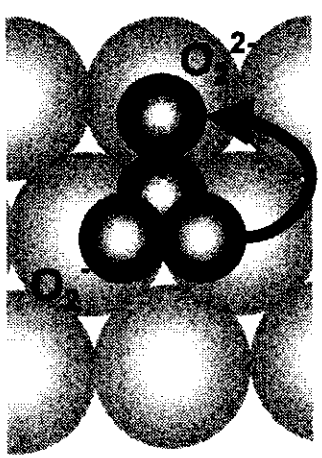
1) step: Thermalization of electron gas



For thin gold films: max. temperature at about 200 - 400 fs after excitation
(W.S. Fann et al., PRB (1992))

2) step: adjustment into new equilibrium position





Summary

•phase-matched high harmonic generation to produce ultrafast XUV-pulses

•realized time-resolved photoemission to study fs-dynamics on surfaces

•directly observe a bond-change between oxygen and platinum on a subpicosecond timescale