

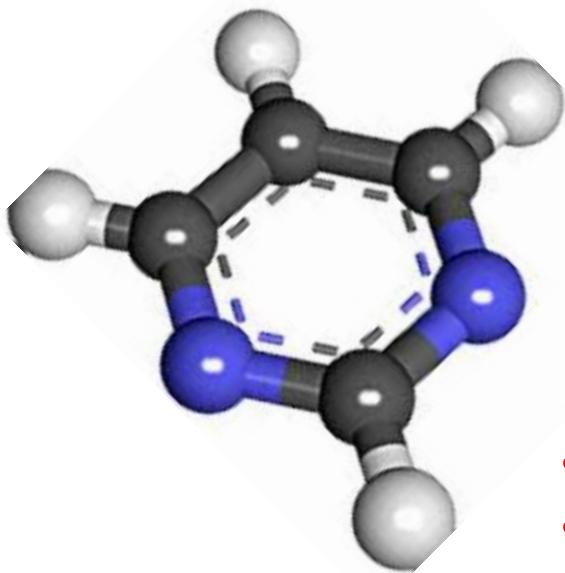


Institute of Structure of Matter

# *Shedding light on atoms, molecules and clusters with novel VUV sources*

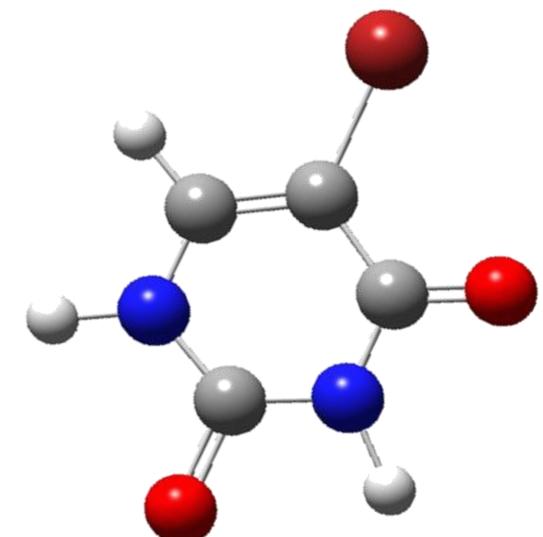
Lorenzo Avaldi

CNR-Istituto di Struttura della Materia  
Area della Ricerca di Roma 1

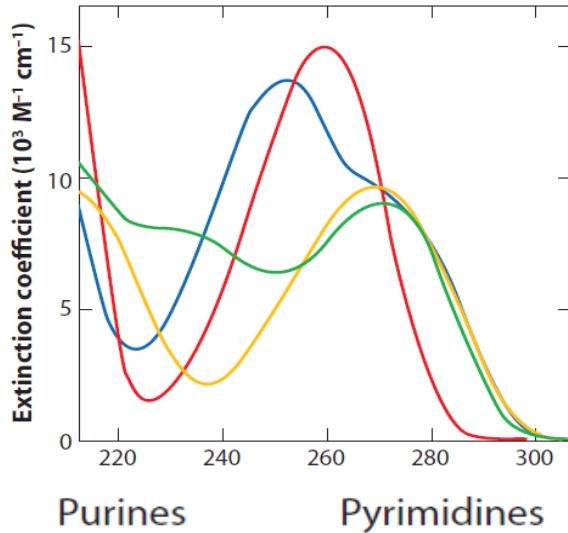


## *Outlook*

- *dynamical energy flow in uracil*
- *ISM and LNF*
  - *SPARC-Lab*
  - *Eurofel Lab*

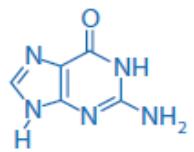


# Time resolved experiments - the question and the approach

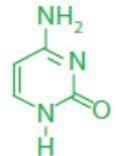


Purines

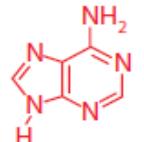
Pyrimidines



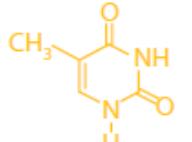
Guanine (G)



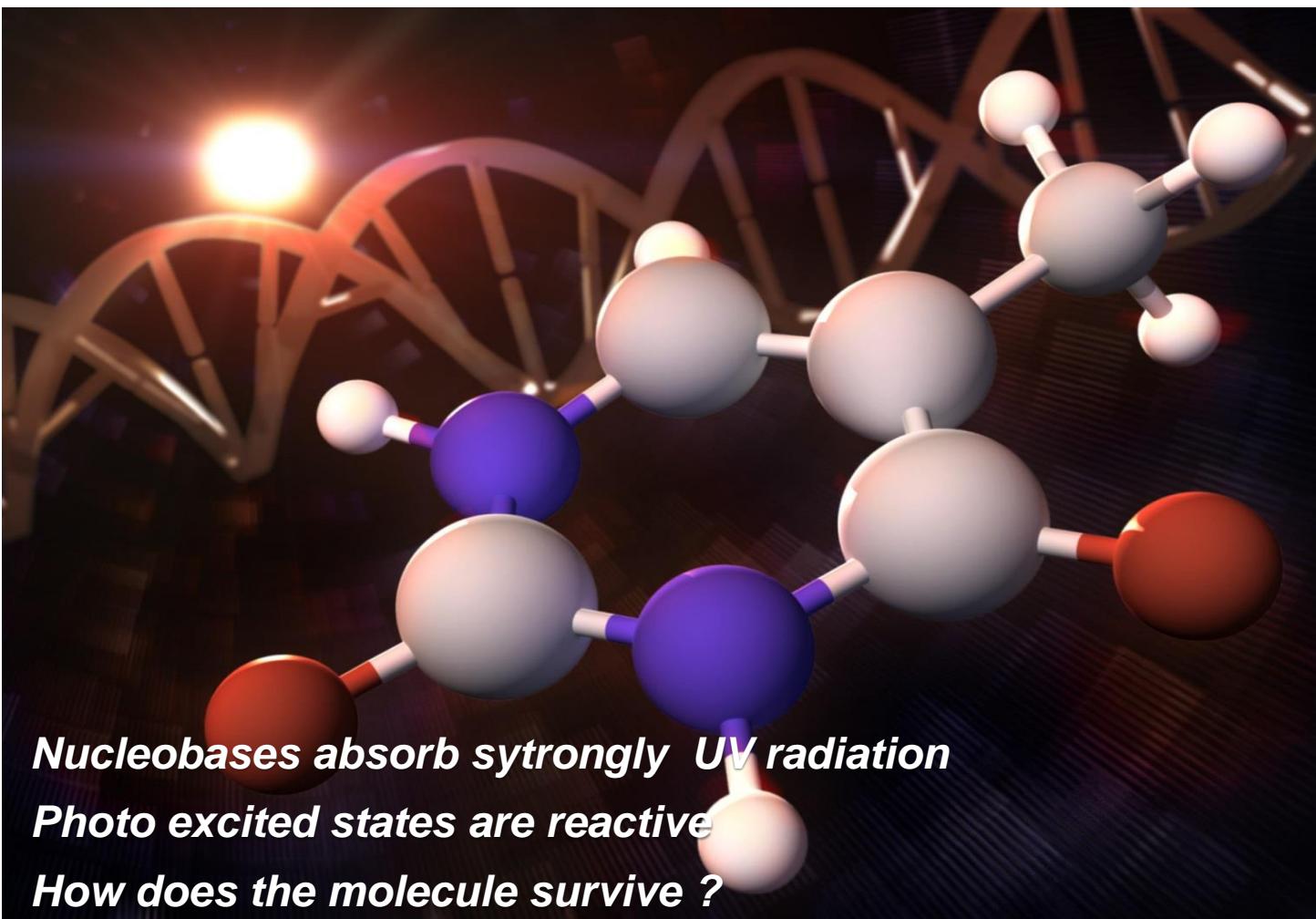
Cytosine (C)

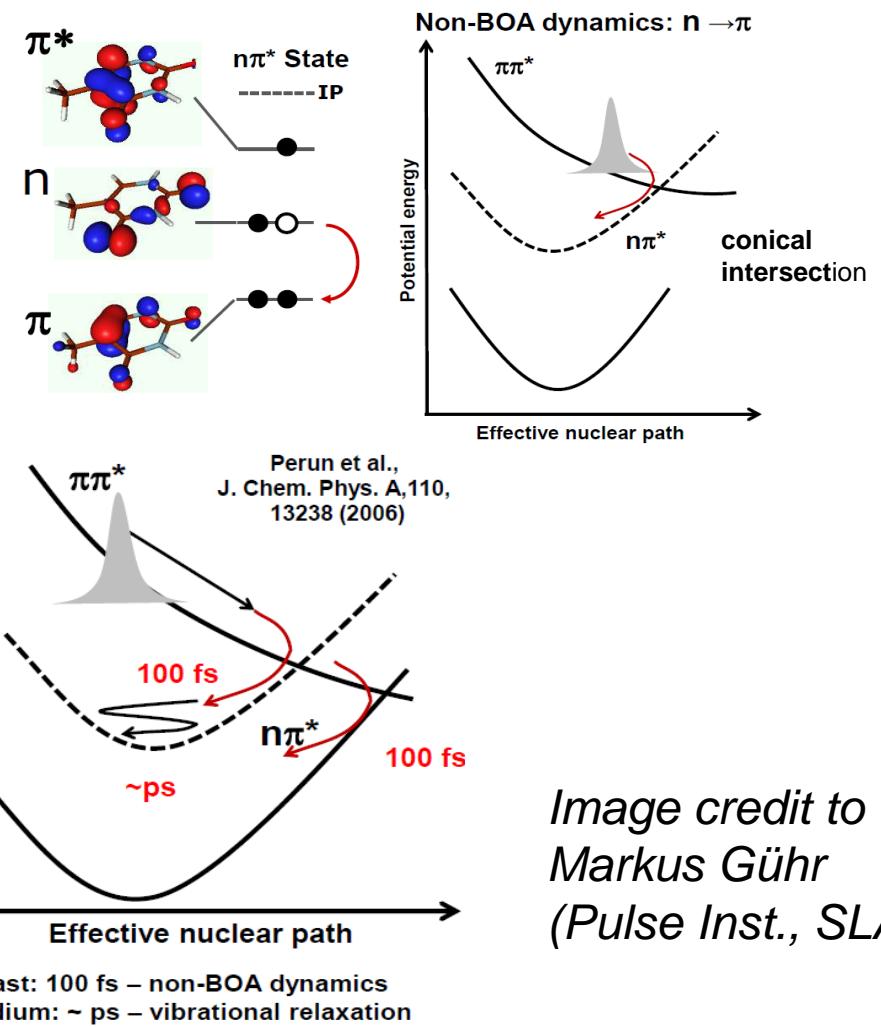
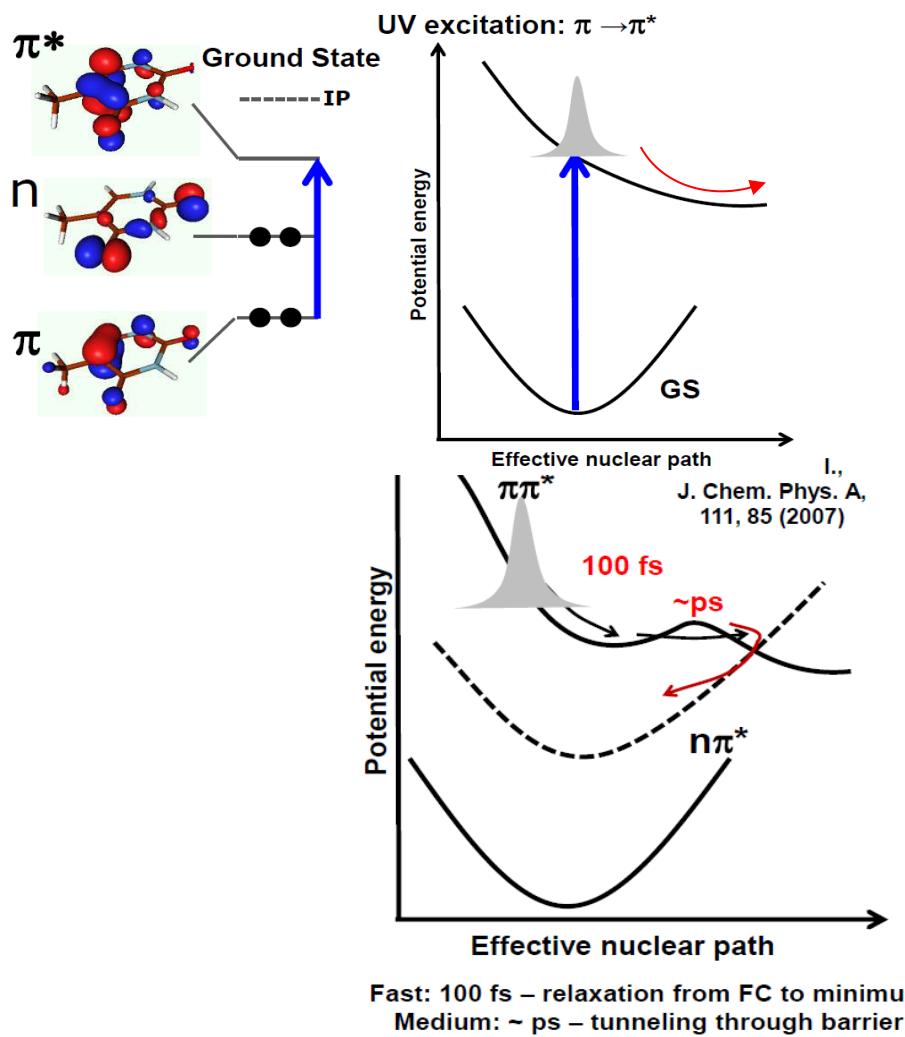


Adenine (A)



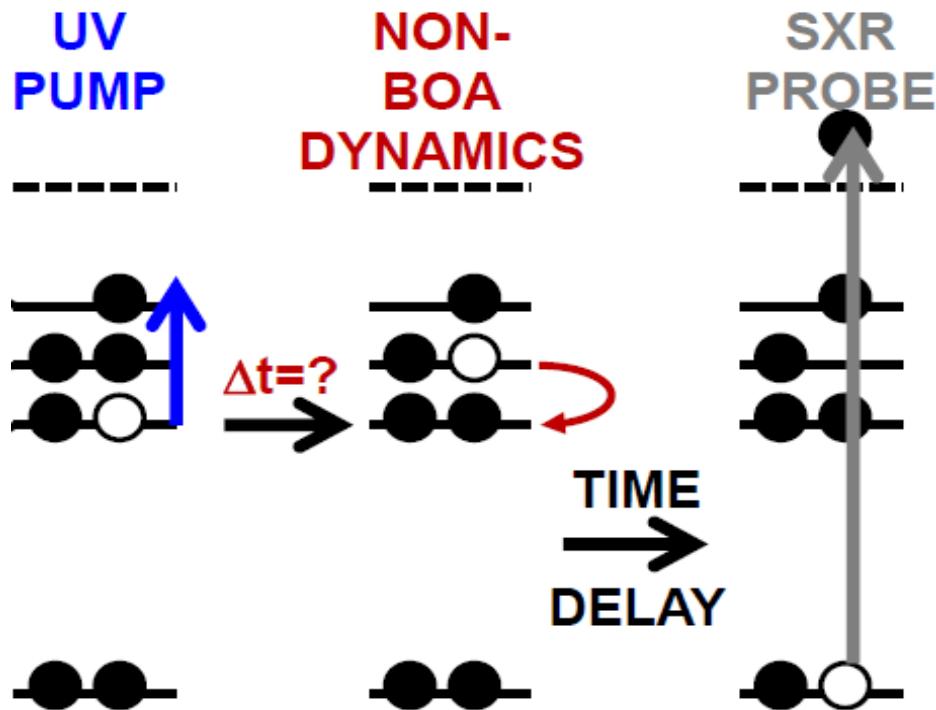
Thymine (T)





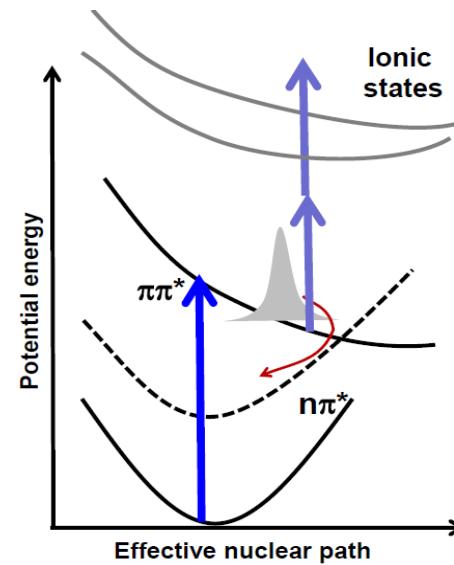
*Image credit to  
Markus Gühr  
(Pulse Inst., SLAC)*

*Our approach : to record inner shell photoelectron spectra as a function of pump-probe delay*



## Advantages

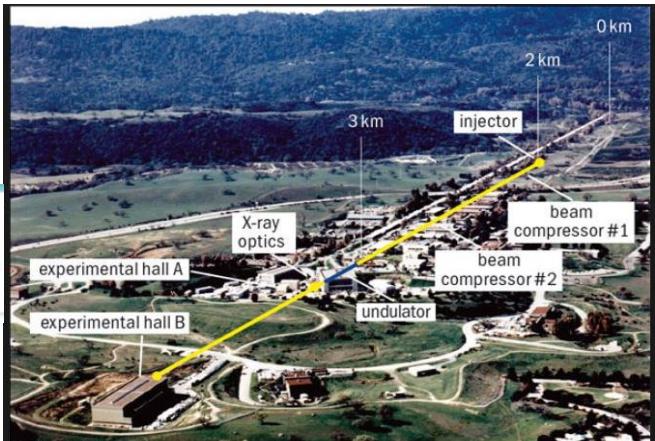
- 1) XPS above threshold ionizes molecule at any nuclear geometry ( no yield reduction due to FC overlap as in optical valence shell ionization)



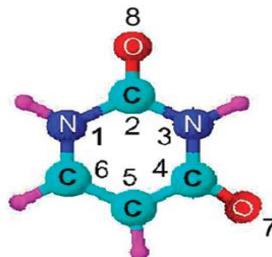
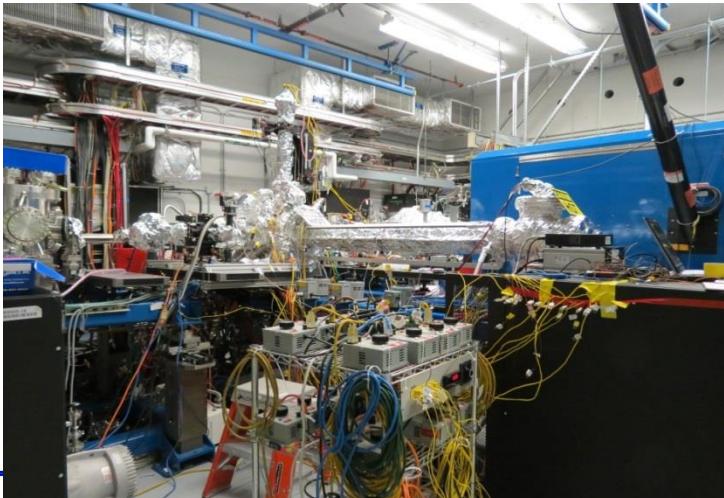
- 2) element and site selectivity

# *Time resolved experiments : where and how*

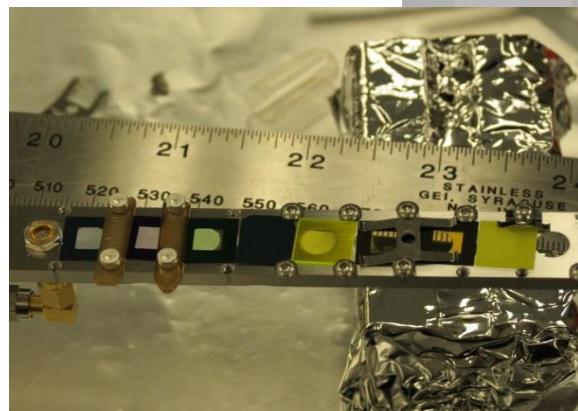
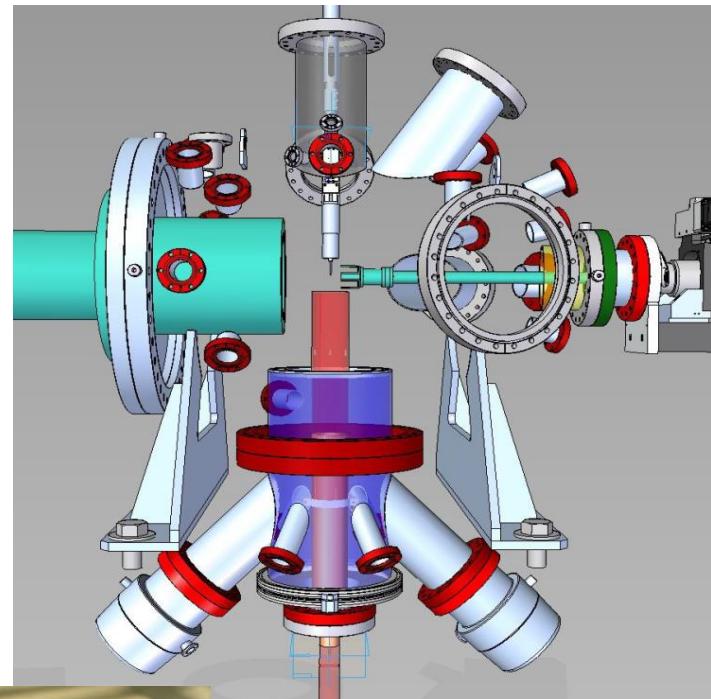
LCLS  $h\nu = 346 \text{ eV}$  (150 pC, 80-100 fs, 120 Hz)



Electron spectrometer : 2 m long magnetic bottle (R. Feifel, Uppsala University)



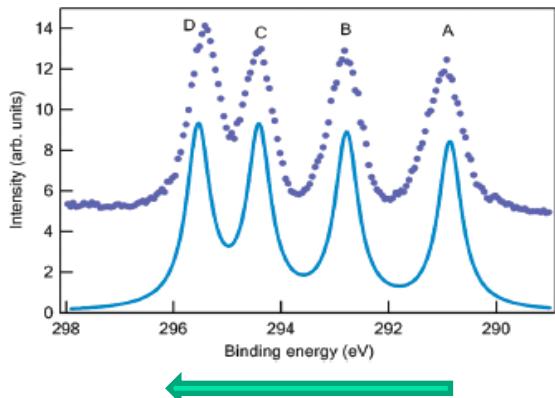
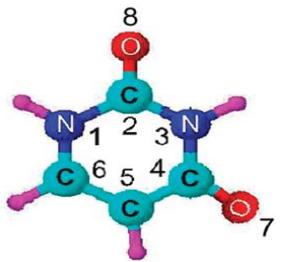
Uracil molecules  
evaporated in an  
inductive oven at  
 $140^\circ$  (density  
 $10^{11} \text{ cm}^{-3}$ )



Alignment tools

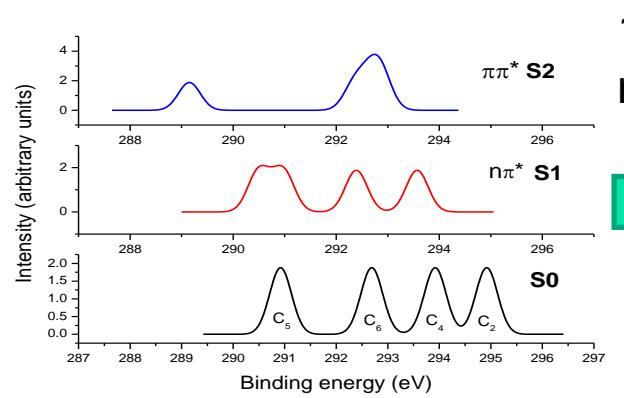
# *Calculations and simulations*

## Simulation of the experiment

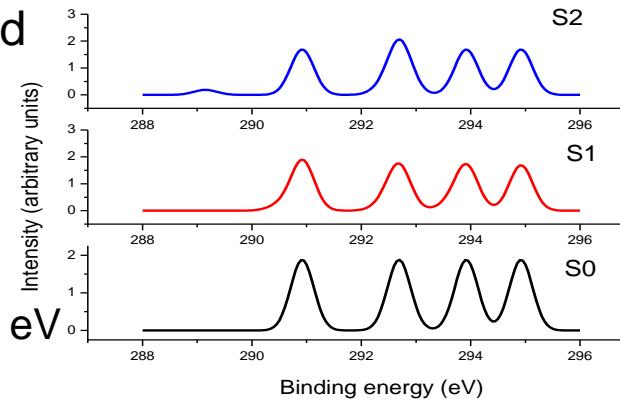


C 1s	BE (eV)	ΔE (eV)	label
C <sub>5</sub>	291.0	-	A
C <sub>6</sub>	292.8	1.8	B
C <sub>4</sub>	294.4	3.4	C
C <sub>2</sub>	295.4	4.4	D

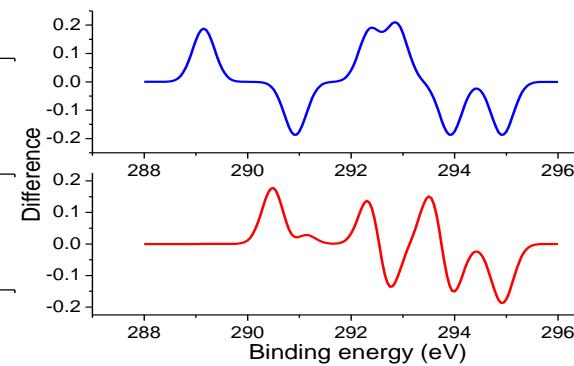
O. Takahashi, Hiroshima University, Japan  
 K. Ueda, Tohoku University, Sendai, Japan



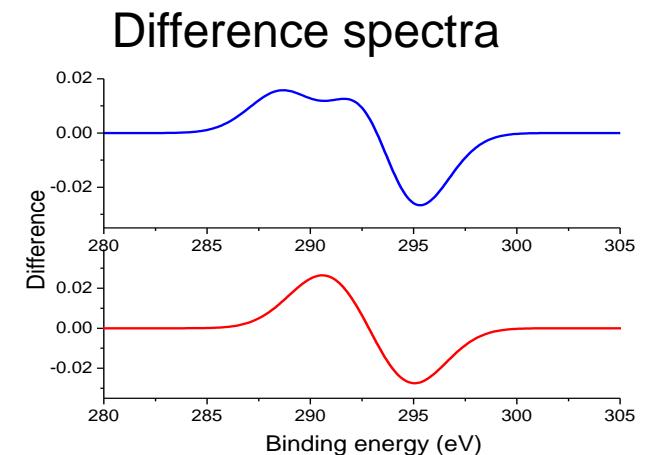
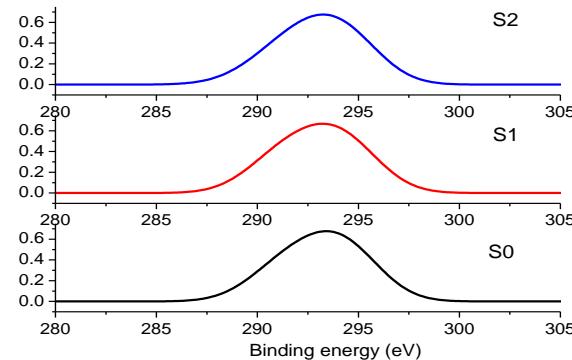
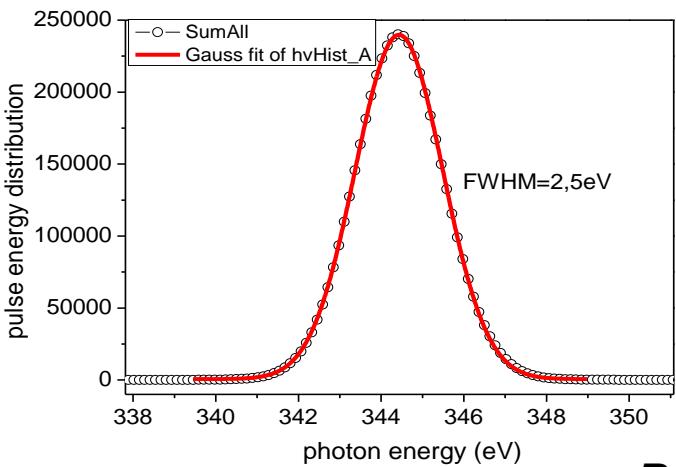
10 % excited molecules  
 FWHM = 0.5 eV



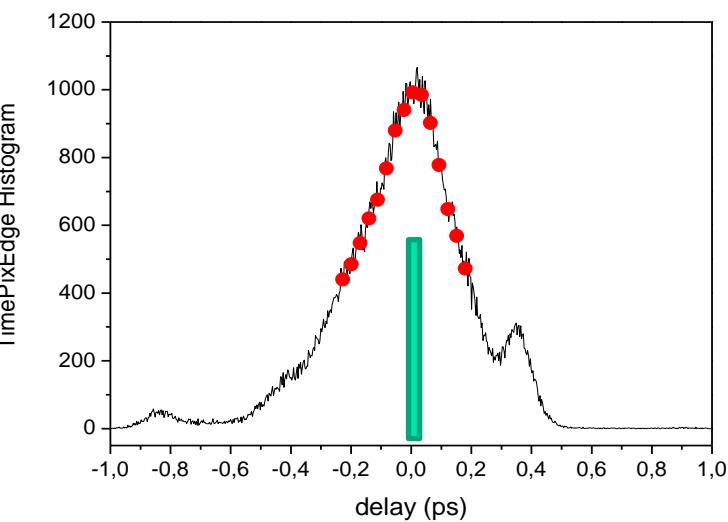
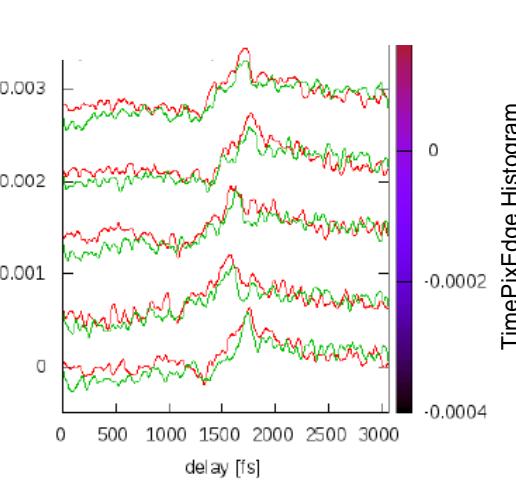
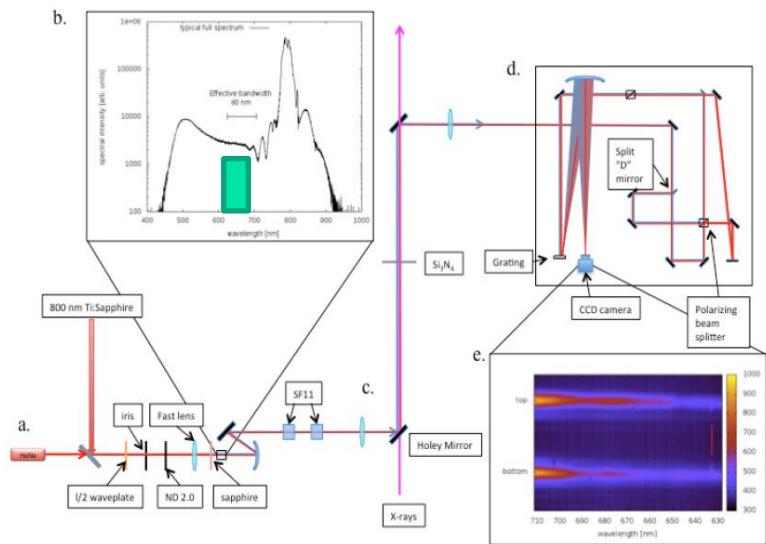
## Difference spectra



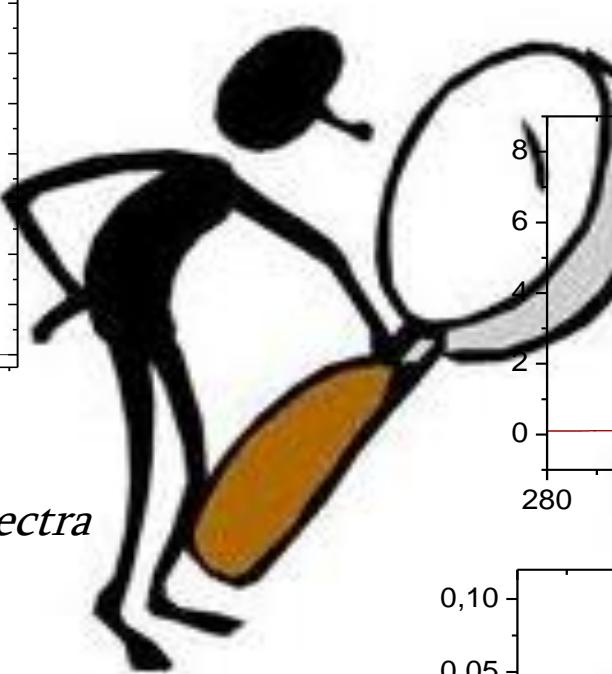
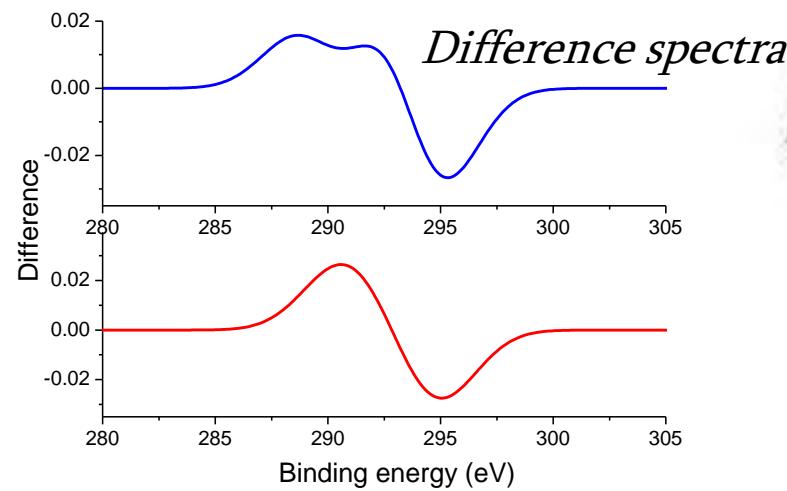
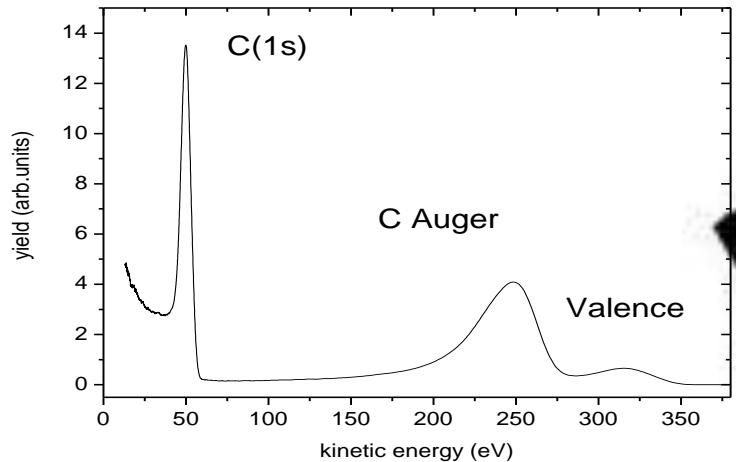
## LCLS SASE Fel : spectral width + spectral jitter



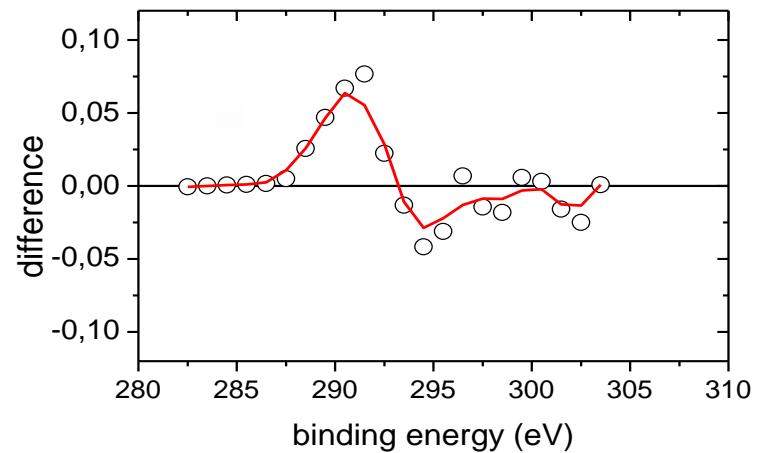
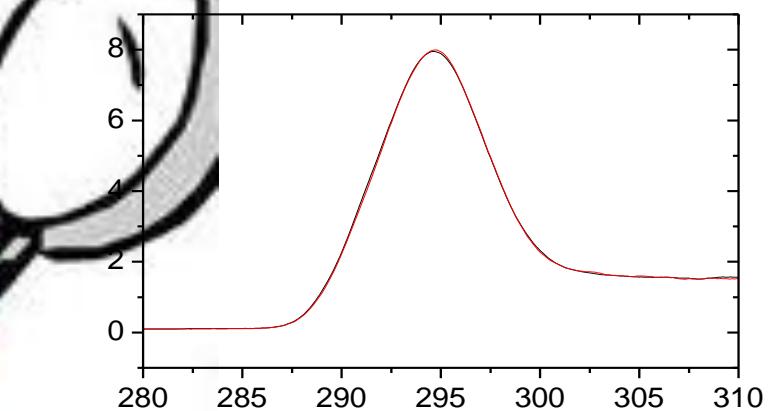
*Pump-probe : measurement of actual delay shot by shot to take into account the time jitter between XFEL and UV laser*

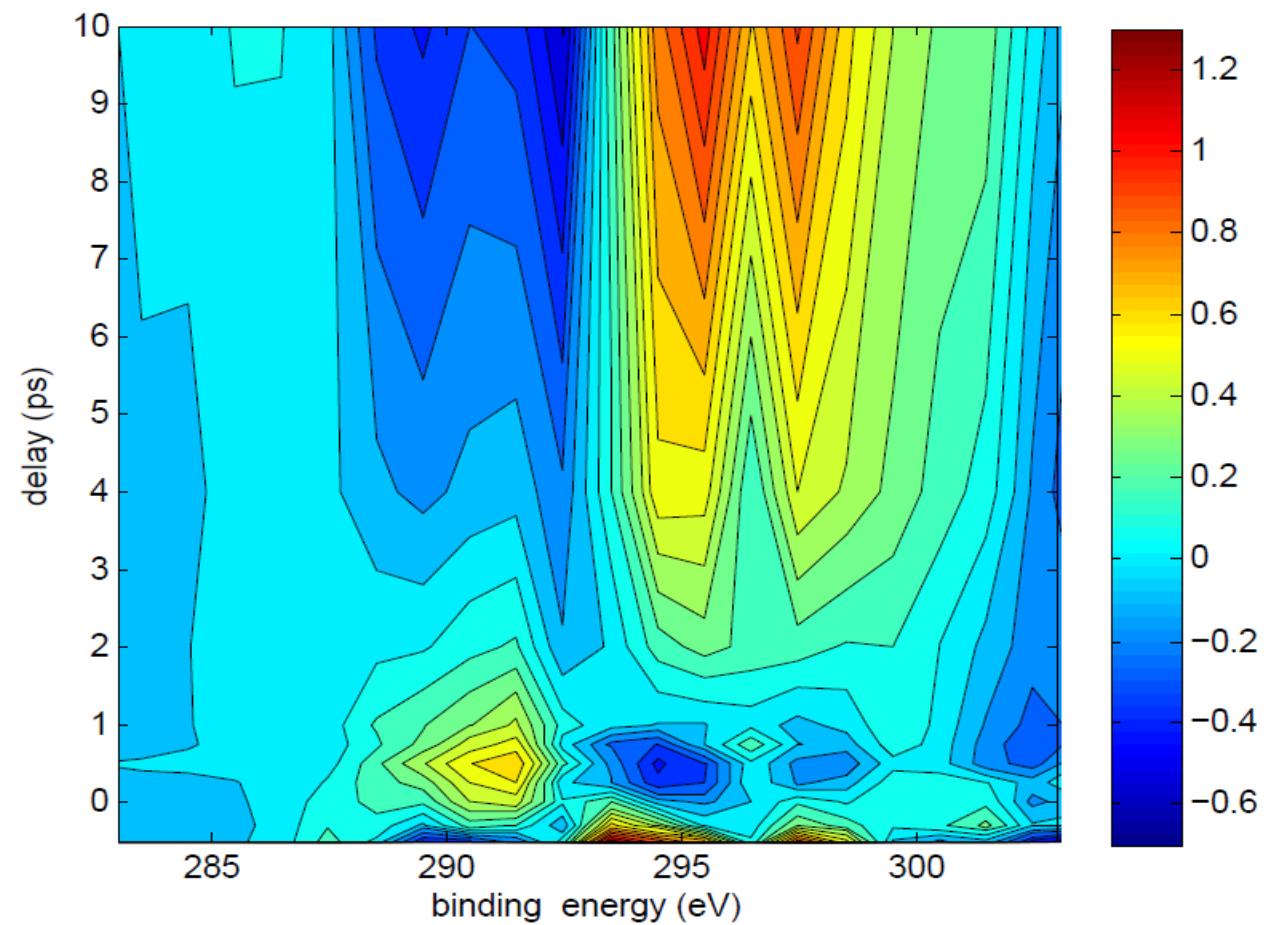
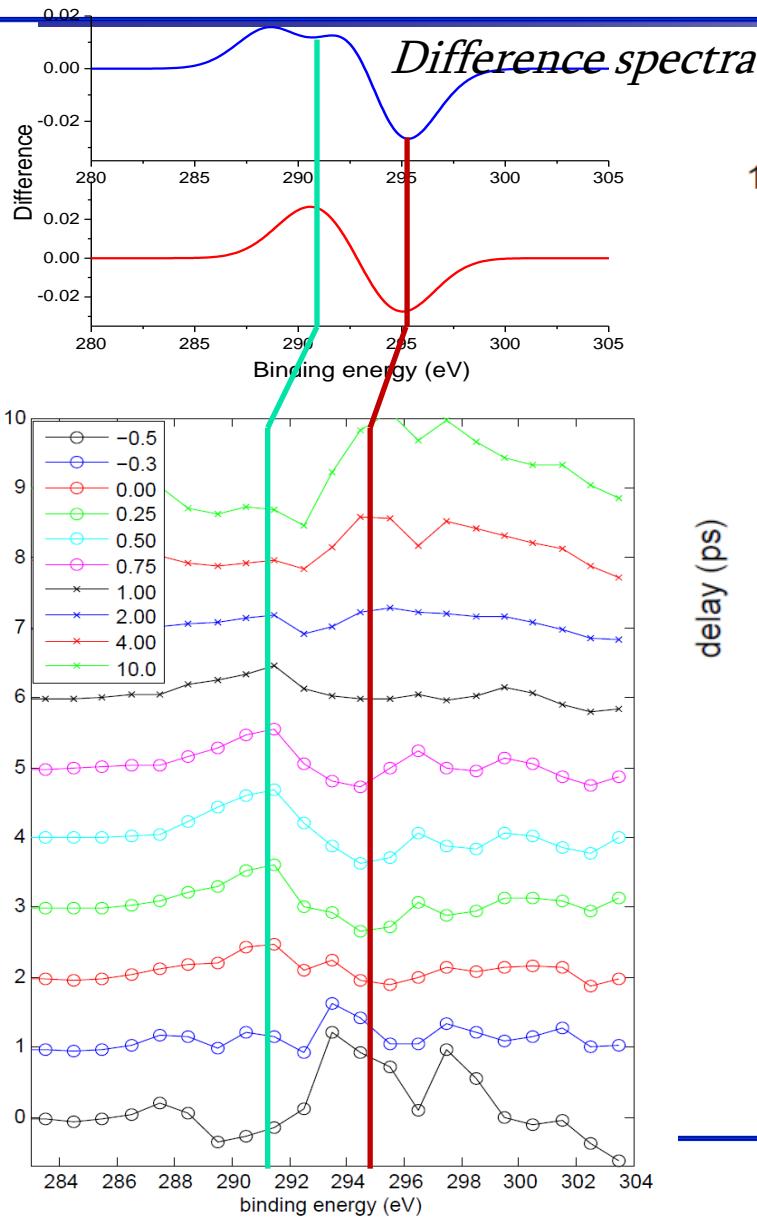


# Results

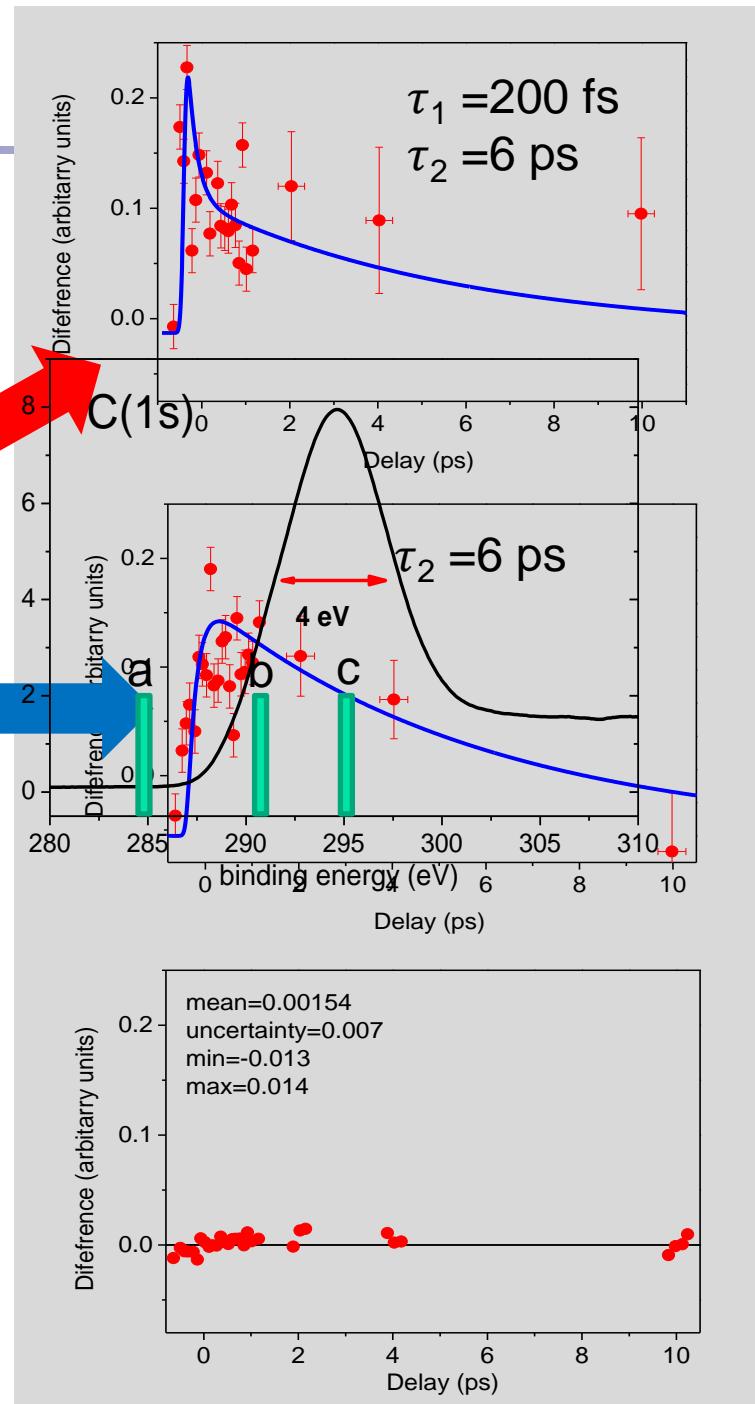
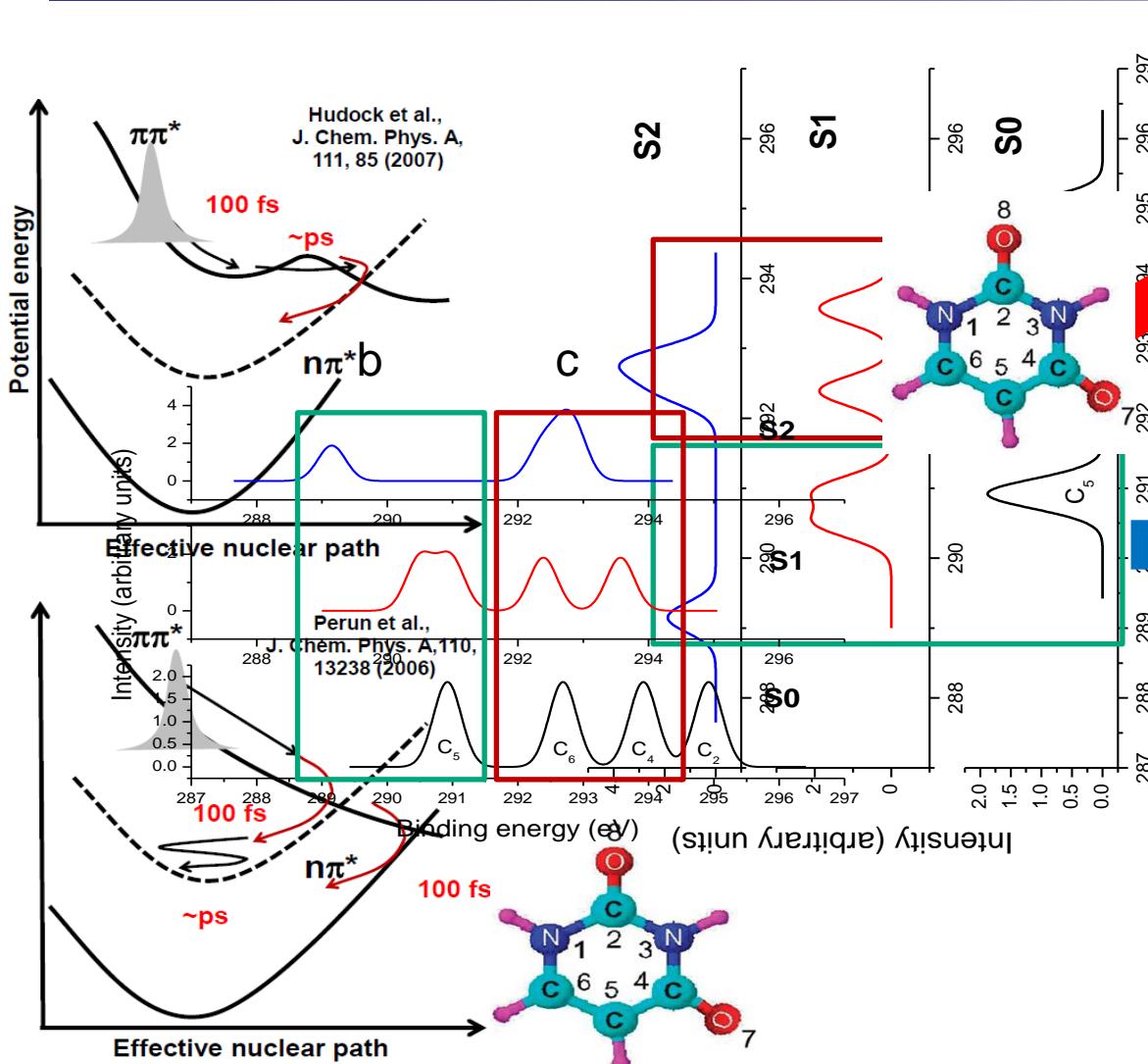


delay 500 fs





# Resorting on shot-to-shot delay (slots 30fs\*n )



## *Conclusions*

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X-ray photoelectron and Auger electron spectroscopies have been used to investigate energy relaxation in UV excited uracil → **Advent of seeded Fel's**

Fast and slow dynamics have been observed : fast dynamics attributed to nuclear dynamics (vibrational relaxation in the  $\pi\pi^*$  state) + slow dynamics due to tunneling (coupling of electronic states via conical intersection)

To be proved/disproved by molecular dynamics calculations

## **A high-resolution VUV beamline @ SPARC-Lab**



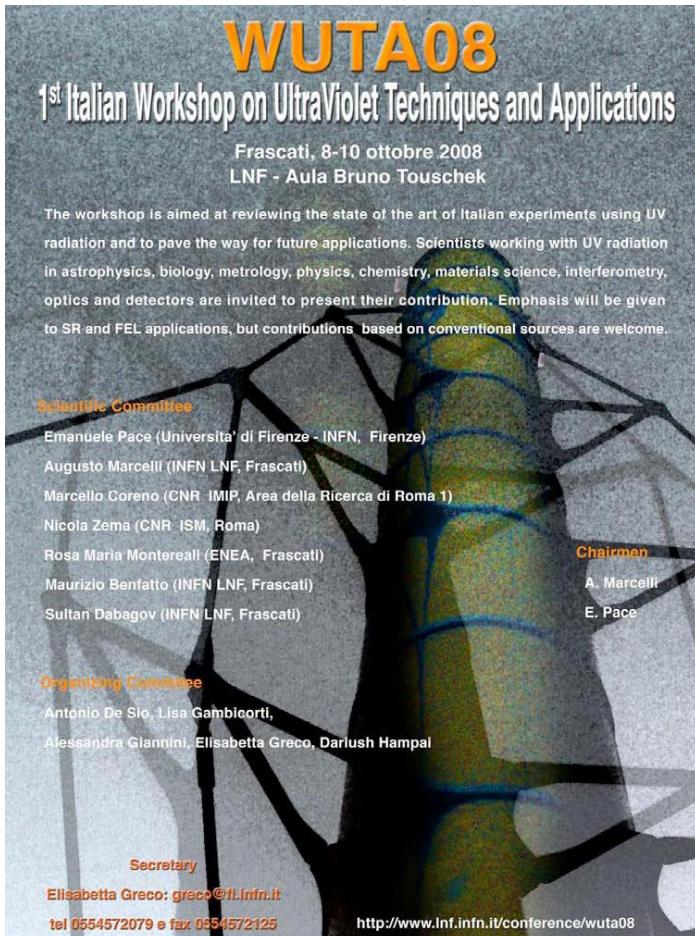
- wavelength range (with high harmonics) 250-40nm
- repetition rate: 1-10 Hz
- radiation spectrum «slightly» tunable
- higher harmonics linearly polarized sources with high temporal and spatial coherence
- pulse duration: 100 fs

A. Marcelli, INFN – LNF  
E. Pace INFN, Università di Firenze  
M. Coreno, CNR-ISM  
L. Poletto, CNR-IFN, Padova

Two possible uses of monochromators:

- As monochromators for SPARC to monochromatize the beam before the experimental chamber: increase the spectral purity of the fundamental (i.e. increase the FEL resolution), select high-order FEL harmonics and suppress the fundamental, filter out the background
- As spectrometers for the analysis of the radiation after the interaction FEL/sample

## The scientific case (October 2008)



**WUTA08**  
1<sup>st</sup> Italian Workshop on UltraViolet Techniques and Applications  
Frascati, 8-10 ottobre 2008  
LNF - Aula Bruno Touschek

The workshop is aimed at reviewing the state of the art of Italian experiments using UV radiation and to pave the way for future applications. Scientists working with UV radiation in astrophysics, biology, metrology, physics, chemistry, materials science, interferometry, optics and detectors are invited to present their contribution. Emphasis will be given to SR and FEL applications, but contributions based on conventional sources are welcome.

**Scientific Committee**  
Emanuele Pace (Università di Firenze - INFN, Firenze)  
Augusto Marcelli (INFN LNF, Frascati)  
Marcello Coreno (CNR IMP, Area della Ricerca di Roma 1)  
Nicola Zemà (CNR ISM, Roma)  
Rosa Maria Montereali (ENEA, Frascati)  
Maurizio Bentatto (INFN LNF, Frascati)  
Sultan Dabagov (INFN LNF, Frascati)

**Organizing Committee**  
Antonio De Sio, Lisa Gambicorti,  
Alessandra Giannini, Elisabetta Greco, Darlush Hampal

**Secretary**  
Elisabetta Greco: [greco@fi.infn.it](mailto:greco@fi.infn.it)  
tel 0554572079 e fax 0554572125  
<http://www.infn.infn.it/conference/wuta08>

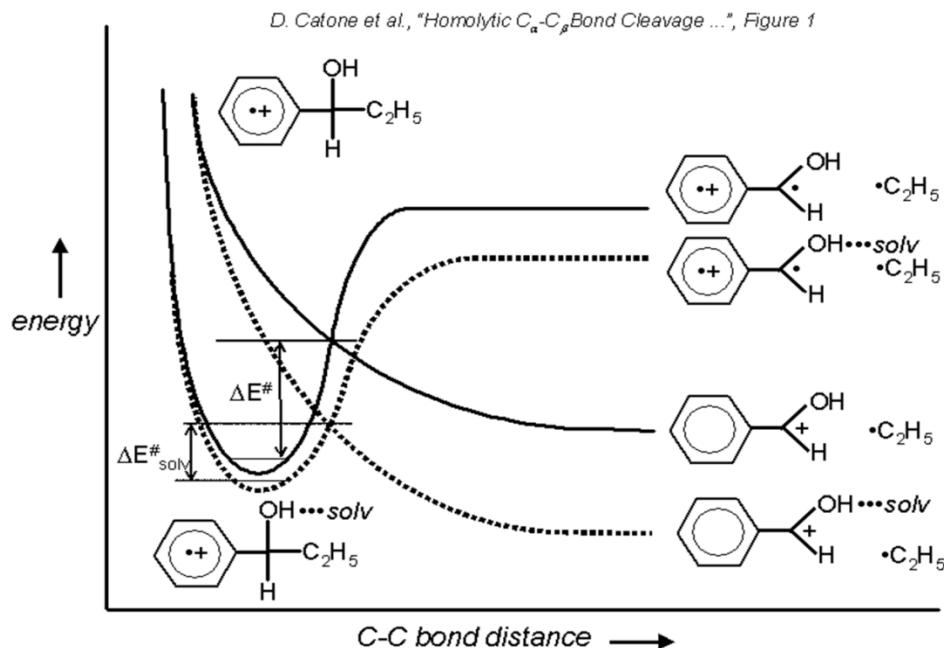
### Topics

- Atomic and molecular physics
- Astronomy
- Nanostructure
- Anelastic scattering
- Biology and astrobiology
- UV induced damaging
- Photochemistry
- Quantum coherence and entanglement

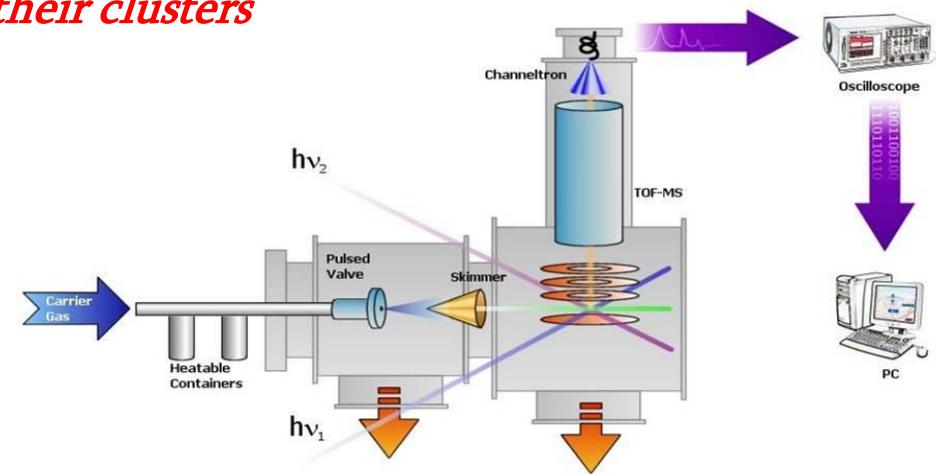
## Electronic properties of biomolecules and their clusters

Solvent-free environment :

- easier modeling of different intermolecular forces
- results comparable with theoretical calculations



**Figure 1.** Pictorial crossing between the two lowest-energy electronic states of  $[(\text{BZC}_2\text{H}_5)_R]^+$  (full lines) and  $[(\text{BZC}_2\text{H}_5)_R \cdot \text{C}_{\text{solv}}]^+$  (broken lines).

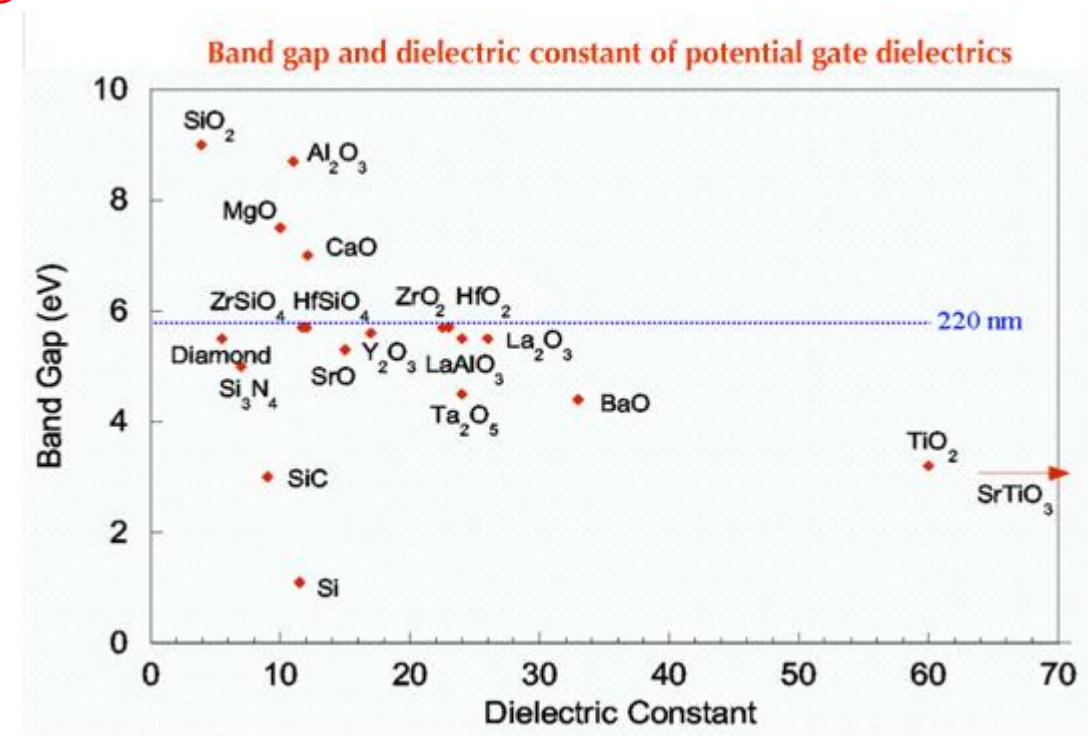


Variable polarization and  $\lambda < 150$  nm from SPARC extends investigation to  $\sigma$ -bonded systems like sugars and non aromatic aminoacids and implement valence photoemission techniques for the study of chiral recognition.

Ref. Marcello Coreno

## Raman spectroscopy on isolated building blocks of nanostructured films

Raman spectroscopy is among most popular methods for characterization of nano-structured systems. The ability of the VUV-FEL to shift the wavelength of scattered light from visible into deep UV will allow to probe new electronic transitions well within the 7-10 eV range for classes of cluster materials such as nano-carbons and potential gap dielectrics from metal oxides



Correlation map between band gap and dielectric constant in many insulators and semiconductor materials. The dotted line points out the gap value of 220 nm ( $\sim 5.64$  eV).

*Raman Imaging...!*

*Ref. Claudio Marcelli*

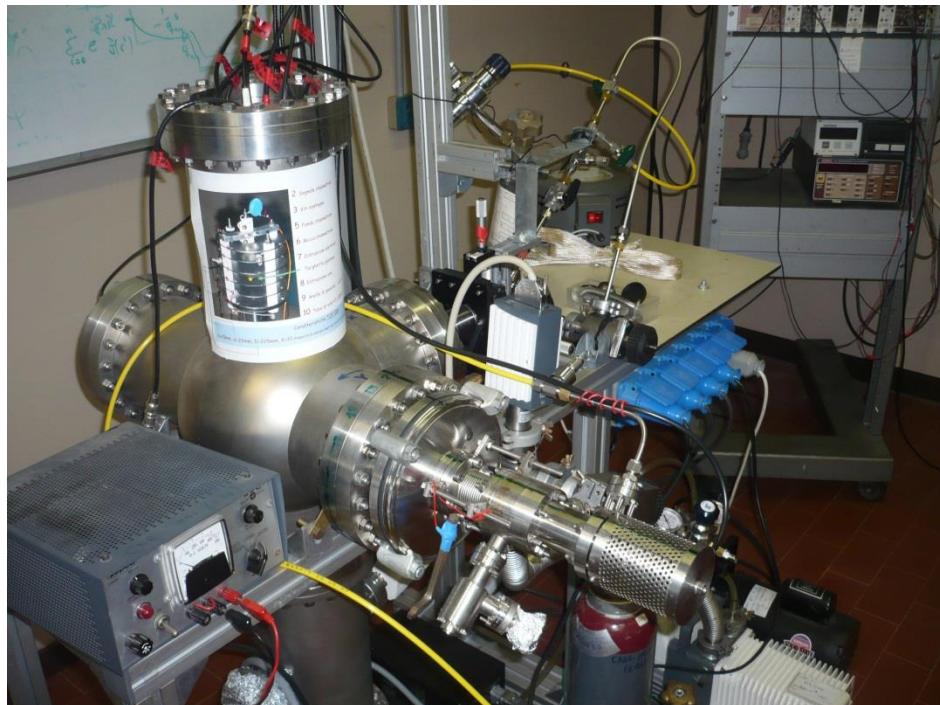


## Monochromator

High-resolution high-spectral purity 5m McPherson  
Normal Incidence  
UV-VUV monochromator  
from SRS-Daresbury,  
beamline 3.2



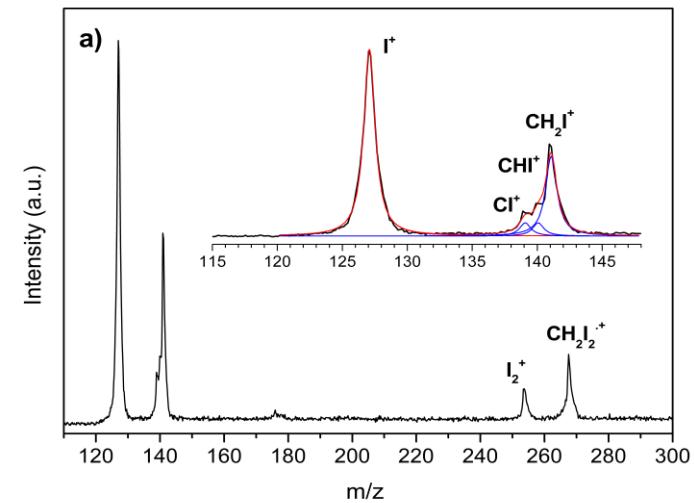
wave (nm)	SEEDED	SASE	slit aperture (mm)			
	FEL resolution	FEL resolution	0.4	0.2	=FWHM	DT (ps) max resolution
250	180	200	3750	7500	10.0	12000
150	300	200	2250	4500	3.0	6000
100	450	200	1500	3000	1.2	3600
75	600	200	1120	2250	0.7	2700
50	910	200	750	1500	0.3	1800
30	1510	200	450	900	0.1	1080



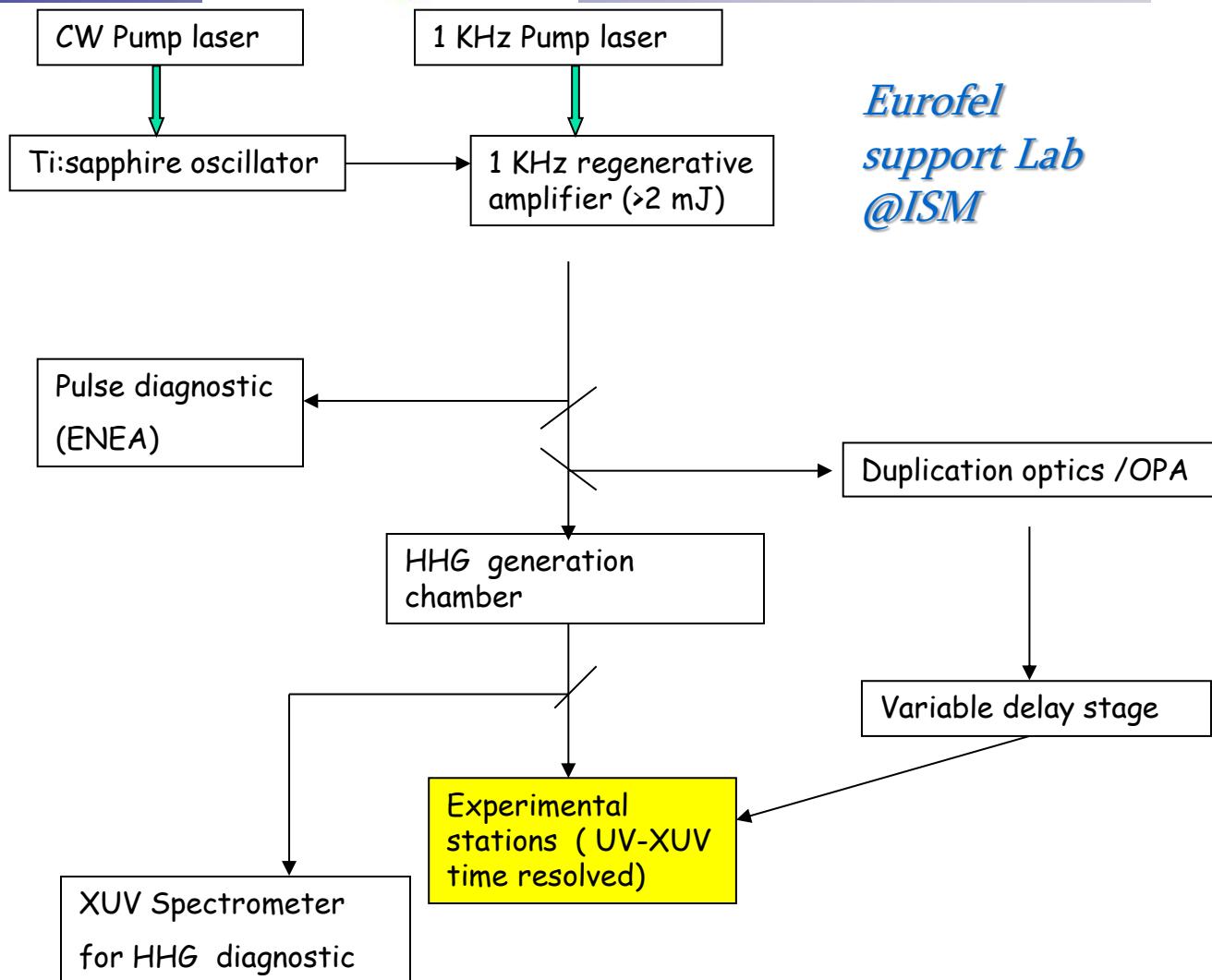
## TOF-300 set-up

Test with rare gas discharge lamp  
[21.22 eV (He I), 16.67 eV (Ne I) and 11.62 eV (Ar I)]

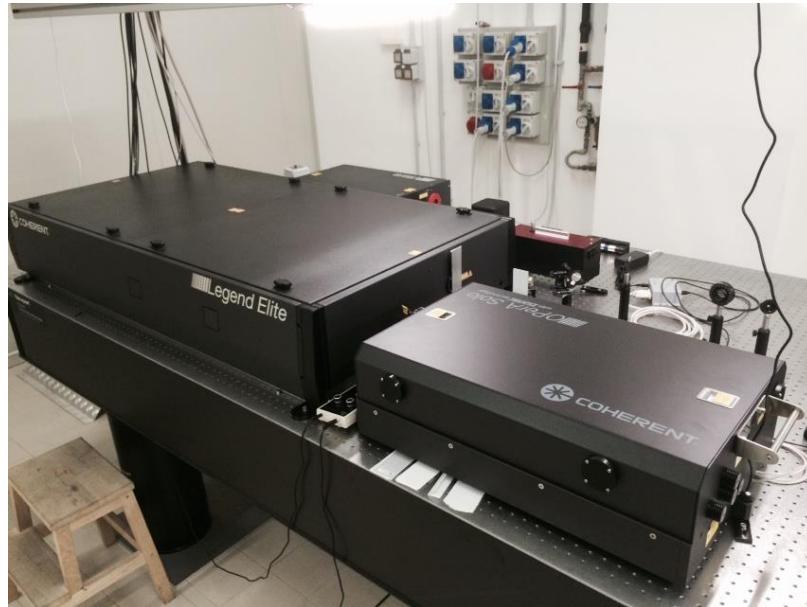
$\text{CH}_2\text{I}_2$  diiodomethane



“(2012) Il consorzio EuroFEL nasce da un approccio globale..... L’infrastruttura di ricerca distribuita su più sorgenti diverse tra di loro permetterà la realizzazione di linee di luce tra loro complementari, con la possibilità di aprire l’infrastruttura nel suo complesso a campi di ricerca non tradizionali e quindi a nuove utenze.... **Il tempo di luce disponibile presso le linee di FEL è e rimarrà limitato e quindi esperimenti preparatori e complementari da svolgersi presso linee di luce di sincrotrone e laboratori CNR saranno essenziali per garantire un utilizzo efficiente da parte della comunità scientifica CNR e più in generale italiana delle nuove sorgenti pulsate.”**



*Eurofel  
support Lab  
@ISM*



## Laser parameters

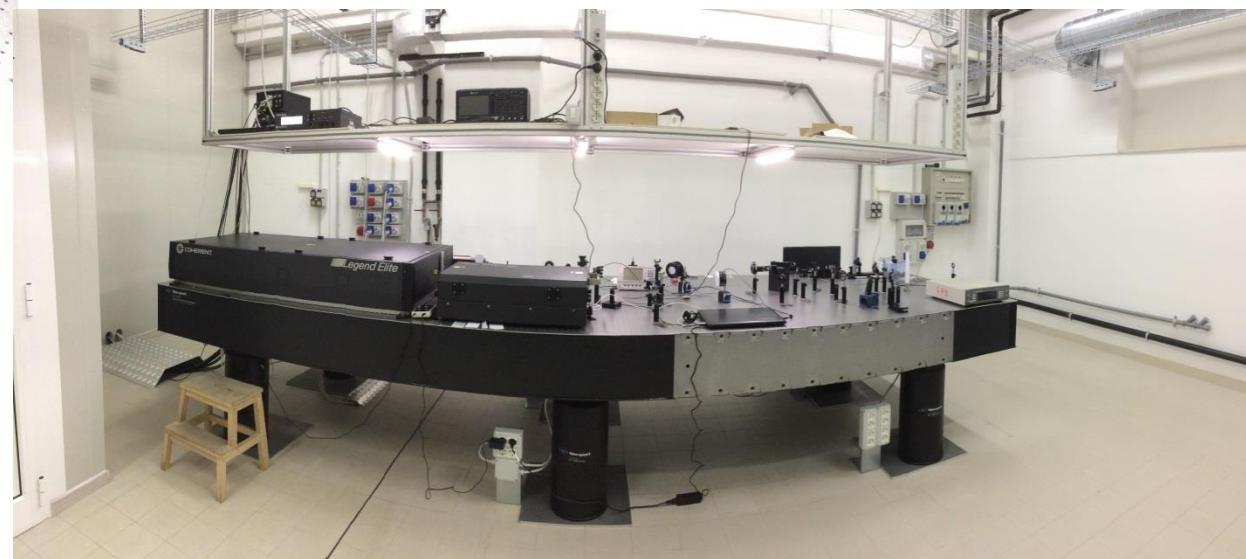
32 fs, 4.6 mJ/pulse max energy per pulse, 1 kHz

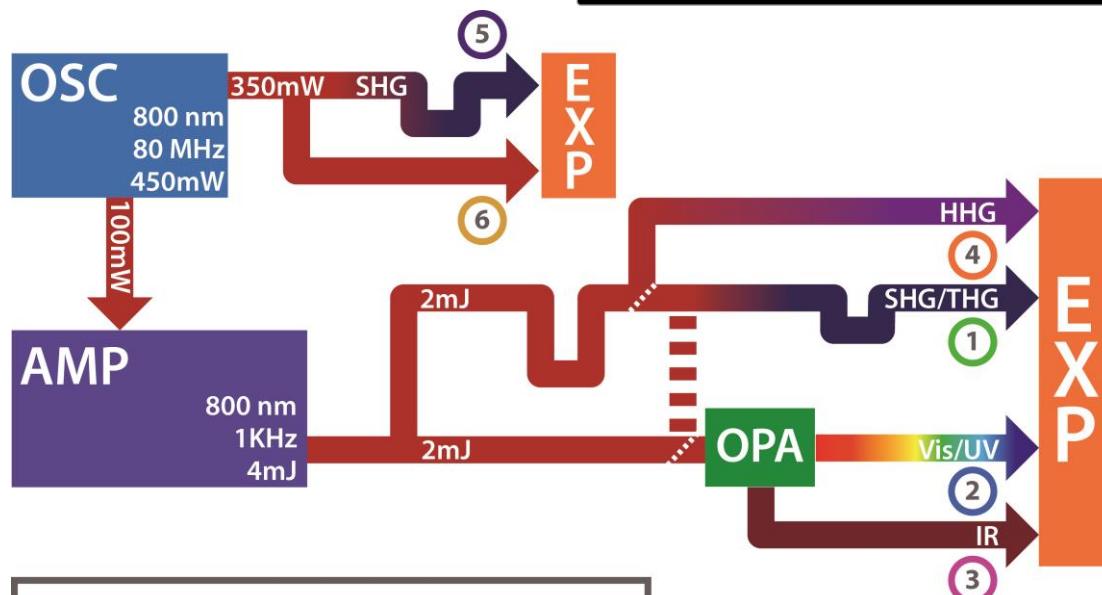
Optical parametric amplifier (OPA)

240 – 15000 nm

Output  $\geq 220 \mu\text{J}$  for 1 mJ input

Input (800 nm: 2 mJ)





Pump	1	1	4	4	4	5
Probe	2	3	2	3	1	6

## Monochromatic beamline for ISM-Roma

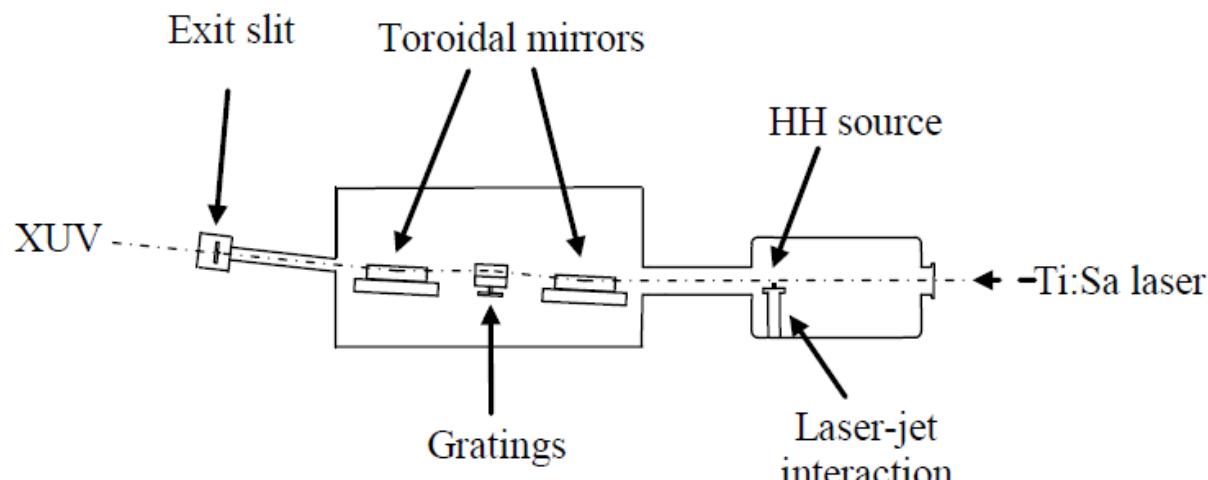
Luca Poletto and Fabio Frassetto

CNR – Institute of Photonics and Nanotechnologies, Padova (Italy)

### Laser parameters

32 fs, 4.6 mJ/pulse max energy per pulse, 1 kHz

XUV spectral region	Output bandwidth	Time response
15-90 eV	0.15-0.2 eV @50 eV	100 fs



**Fig. 1.** Schematic of the monochromator

<b>Mirrors</b>	Toroidal
Arms	600 mm
Grazing angle	3°
Radii	22900 mm × 62.8 mm
Coating	Gold
Coated area	60 mm × 10 mm
Maximum acceptance angle	5 mrad × 5 mrad
<b>Gratings</b>	3 plane grating
Constant subtended angle	160° (tentative)
Coating	Gold
Ruled area	40 mm × 10 mm
<b>Grating #1</b>	
Spectral region	30-90 eV
Groove density	600 gr/mm
Blaze angle	2°
<b>Grating #2</b>	
Spectral region	25-45 eV
Groove density	246 gr/mm
Blaze angle	1.6°
<b>Grating #3</b>	
Spectral region	15-30 eV
Groove density	150 gr/mm
Blaze angle	1.2°
<b>Exit slit</b>	
Width	> 50 μm, manual actuator Normally kept at 100 μm
Height	2 mm

Table 1. Parameters of the monochromator with the gratings in the CDM.

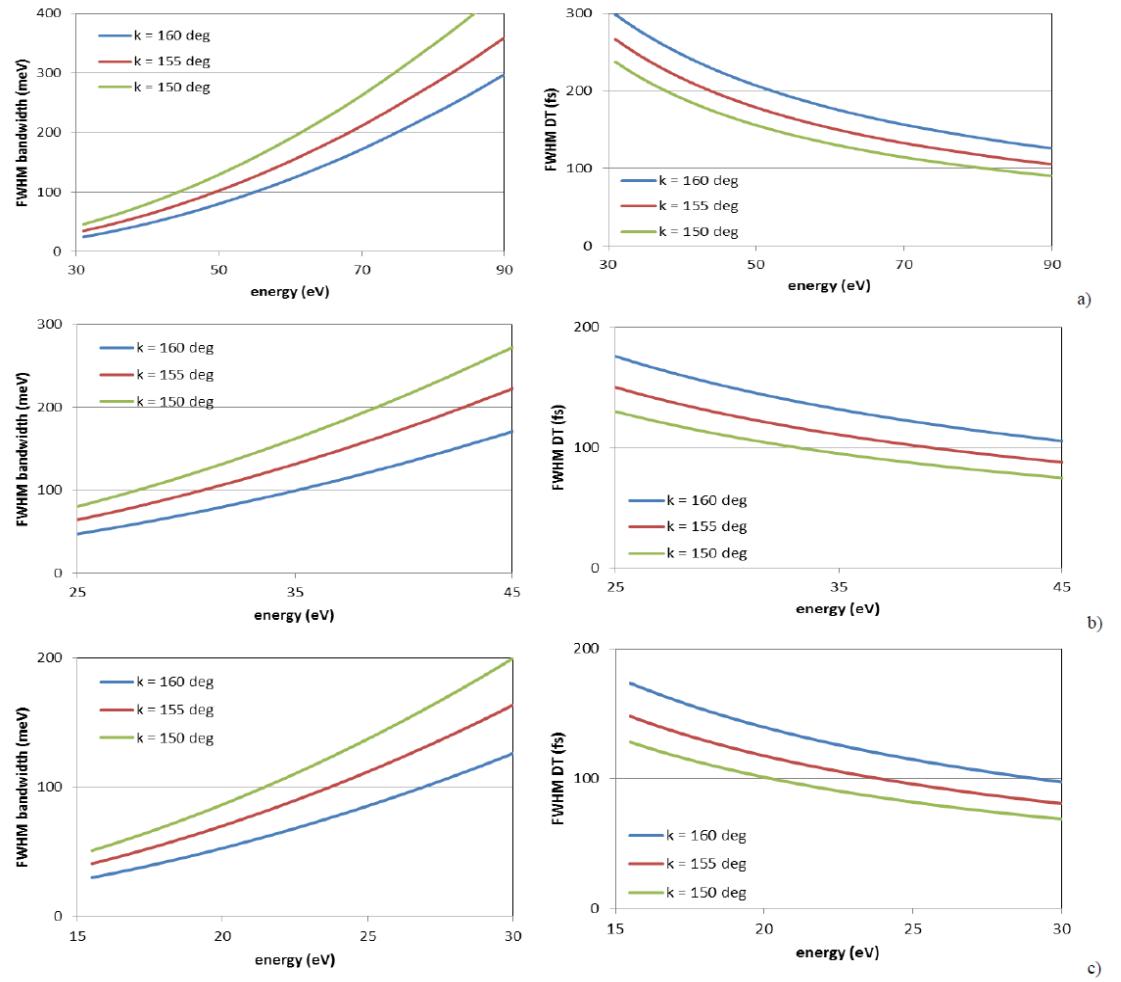


Fig. 2. FWHM bandwidth on 100-μm slit, 50-μm XUV source size and FWHM pulse front-tilt with 3-mrad full divergence: a) 600 gr/mm grating; b) 246 gr/mm grating; c) 150 gr/mm grating.

# ***ACKNOWLEDGMENTS***

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**Area di Ricerca Roma 2**



CNR - ISM  
Istituto di Struttura  
della Materia

*M. Coreno, P. Bolognesi, D. Catone, P. O'Keeffe, S. Turchini,  
N. Zema, D. Rau, S. Colonna, C. Quaresima, A. Cricenti, A.  
Paladini, S. Priori, M. Brolatti, M. Luce*

**Area di Ricerca Roma 1**



**Sincrotrone Elettra - Area Science Park-**



**Area di Ricerca Potenza**





# *Studies of dynamical energy flow in molecules using covariance mapping*



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Patrick O'Keefe  
**Lorenzo Avaldi**  
Valerio Rossi Albertini



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Brendan Murphy  
Li Fang  
Nora Berrah

Emily F. Sistrunk Jakob  
Grilj  
Brian K. McFarland  
Markus Koch  
Markus Guehr

Catalin Miron

PULSE



Robert Richter  
Kevin Prince



東北大学  
TOHOKU UNIVERSITY

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Kyoshi Ueda



John Bozek  
C. Bostedt  
Ryan Coffee  
S. Carron



Peter v.d. Meulen  
Peter Salen  
Mats Larsson



Melanie Mucke  
V. Zhaunerchyk  
M.N. Piancastelli  
John Eland  
Raimund Feifel



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