ULiSSE

Ultrabright Light Source Spectroscopy Experiments

A beamline for atomic, molecular, cluster and optical science

- Helena and Seppo Aksela, University of Oulu, Finland
- Peter Hammond, University of Western Australia, Perth, Australia
- George C. King, University of Manchester, UK
- Pascal Lablanquie and Francis Penent, Matiere et Rayonnement, Université P. et M. Curie, Paris, France
-Paolo Milani, Paolo Piseri and Cristina Lenardi, Dipartimento di Fisica, Università degli Studi, Milano
- Michael Mayer, LIXAM, Orsay, France
- Elisabeth Rachlew, Royal Institute of Technology, KTH, Stockholm, Sweden
- Jan-Erik Rubensson, Department of Physics, University of Uppsala, Sweden
- Giacinto Scoles, Sincrotrone Trieste and Princeton Institute for the Science and Technology of Materials, USA
- Stefano Turchini, Nicola Zema, Tommaso Prosperi, Istituto Struttura della Materia, CNR, Rome
- Franco Vecchiocattivi, Dipartimento d'Ingegneria Civile ed Ambientale, Università di Perugia, Italy
- Matjaž Žitnik, Microanalytical Center, "Jožef Stefan" Institute, Ljubljana, Slovenia

- Gas Phase Photoemission Research Team

Specs and dates for FERMI:

- FEL1, 12-31 eV, in 3 years, end 2008

-FEL2, 31-124, in 4.5 years, summer 2010

- Linear vertical, linear horizontal, left and right circular polarised light

- 40-1000 fs pulses

Plan of talk

Science.

1. Non-linear photoexcitation. Examples: two-photon, double excitation of helium, multi-photon ionisation of noble gases, and two-photon double ionization.

2. Pump probe: example of water and core level spectroscopy.

3. Dilute species: clusters.

4. Biomolecules in the gas phase (flying proteins).
Examples, numbers, expected challenges, feasibility with conventional lasers

Instrumentation

Transport optics
Experimental chamber 1.
Experimental chamber 2.

Organization
Preparations (gas phase beamline)
Budget and resources.

Why gas phase?

Deepest understanding of the interaction of radiation and matter.

Fundamental phenomena: correlation, complete experiments, chemical reactions, …

No sample damage problems.

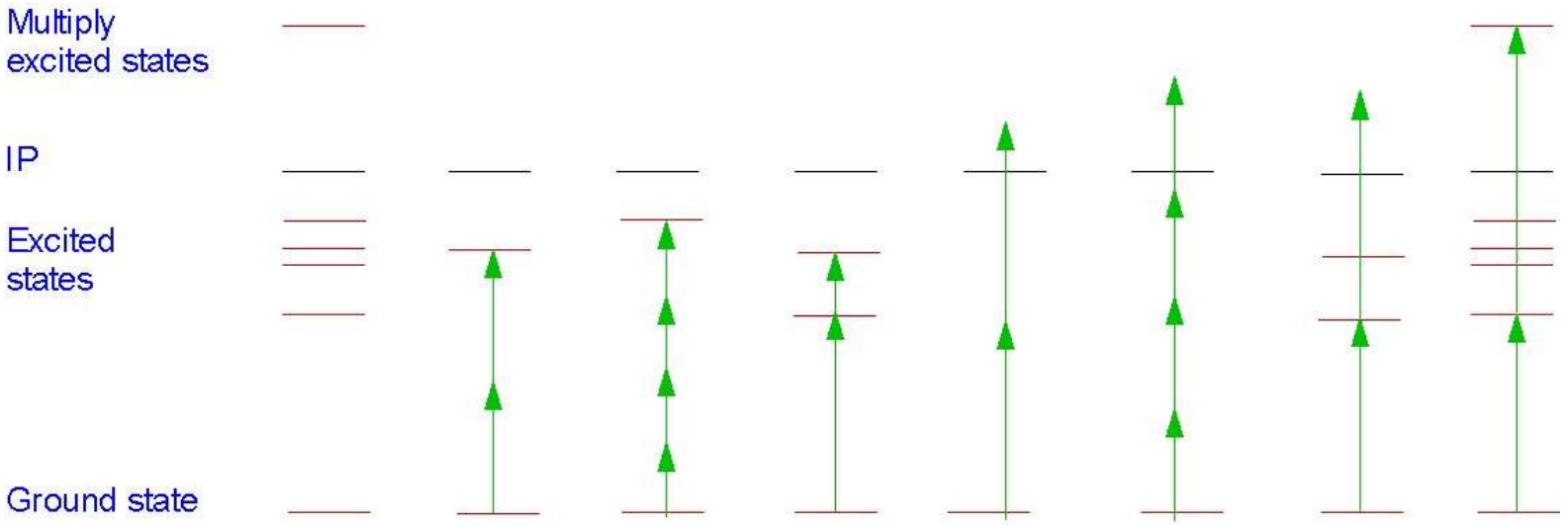
And why FERMI?

Not to do things better: to do things that were impossible before.

Non-linear processes
Low density matter.
Dynamics.

Non-linear photoexcitation schemes

Many optical schemes available:
- one or more colours
- two or n photons
- resonant or non-resonant
- discrete or continuum states

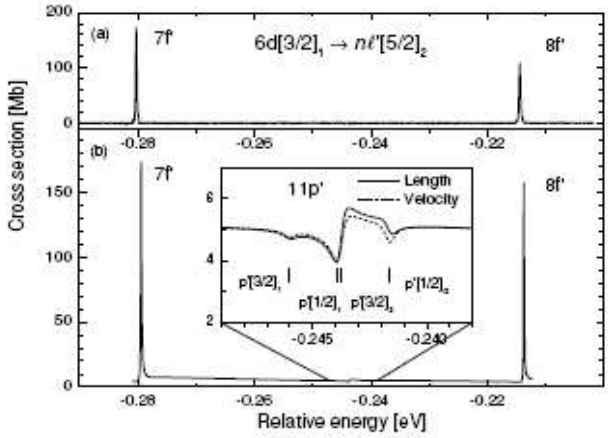


What can we learn about the optical properties of correlated atomic systems?

Non-linear photoexcitation.

Noble gases: what has been done so far?

Single photon absorption accesses odd states, ΔL=1.
Two photon absorption accesses even states, ΔL=0, 2.
And so forth….
For Ar, Kr, Xe, multi-photon resonant absorption has been reported, as well as two colour, two photon, resonant absorption of Xe:



experiments

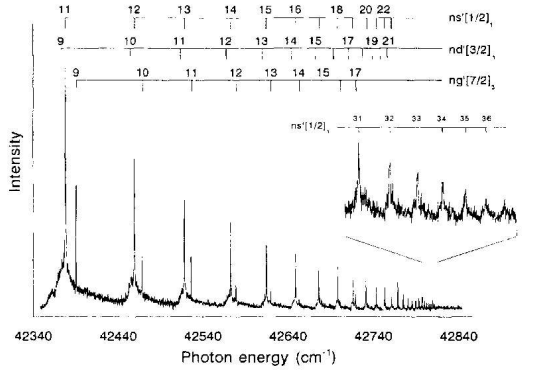


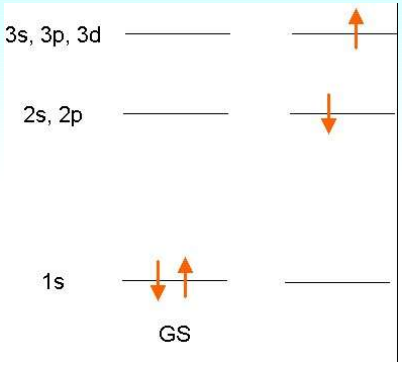
FIG. 1. Three-photon excitation spectrum of autoionizing series in Ar between the $^2P_{3/2}$ and $^2P_{1/2}$ ionic limits obtained with linearly polarized excitation light.

M. Meyer et al, J Phys. B-Atomic Mol. Opt. Phys. **38** (2005) 285

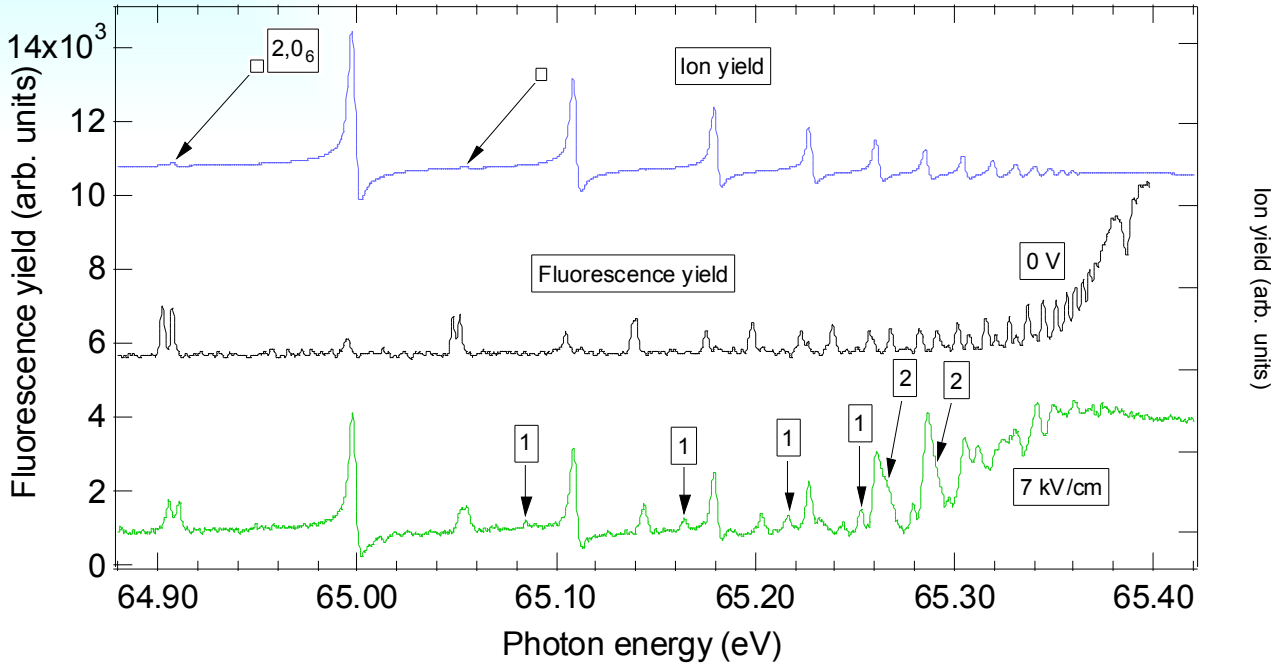
S.M. Koeckhoven et al, Phys. Rev. A **49** (1994) 3322.

Single colour, two photon studies of
- even, doubly excited states
- double ionization
Helium, and other noble gases

The doubly excited states of helium (58-79 eV) are of fundamental importance for understanding correlation. Progress in their investigation has paralleled progress in synchrotron radiation sources.



The lowest doubly excited states can be imagined as having the configuration (2snp+2pns) in a zero order approximation and converge to the second IP of He (the ion is left with one electron in the 2s or 2p level.)

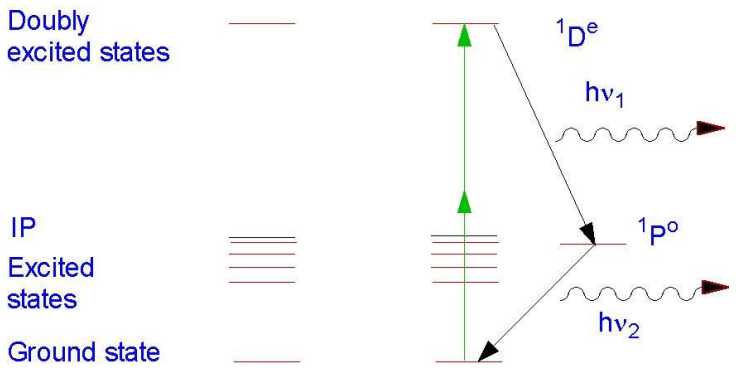


How many singlet Rydberg series are there with low angular momentum for doubly excited He?

For L=0,1,2, ten series below the N=2 threshold:
two $^1S^e$,
three $^1P^o$ (dipole allowed),
one $^1P^e$,
one $^1D^o$,
and three $^1D^e$ series.

How do we want to access them?

The even S and D states can be excited by two photon absorption.
Those decaying by fluorescence can be detected optically; those decaying by autoionization by electrons.



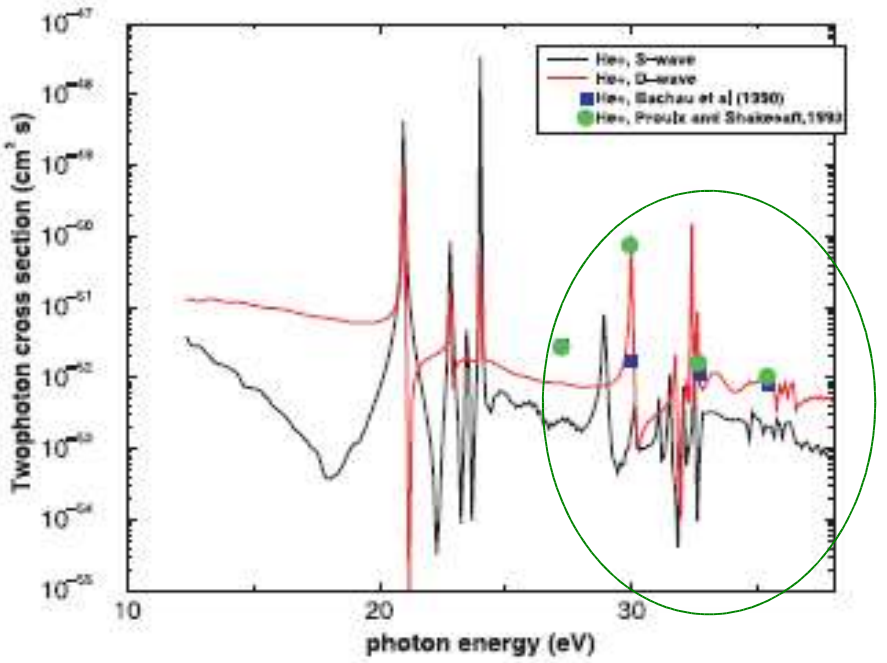
Non-linear photoexcitation, cont

theory

Feasibility

Cross-section is 10^{-50}-10^{-53} cm^4 s.
We estimate count rates of 0.1 to 100 counts/sec, for a 20 micron spot.
Signal: photons or electrons.

Possible experimental problems:
background of large number of charged particles created.
VUV detection: channel plates must be shielded
Electron detection: need moderate energy resolution, high level of discrimination.



L.A.A. Nikolopolous and P. Lambropolous, J. Phys. B: At. Mol. 34 (2002) 545.

Can conventional lasers do it better in the near future?
Probably not, tunability is required.

Two photon double ionization

Above 79.004 eV, helium can be double ionized.

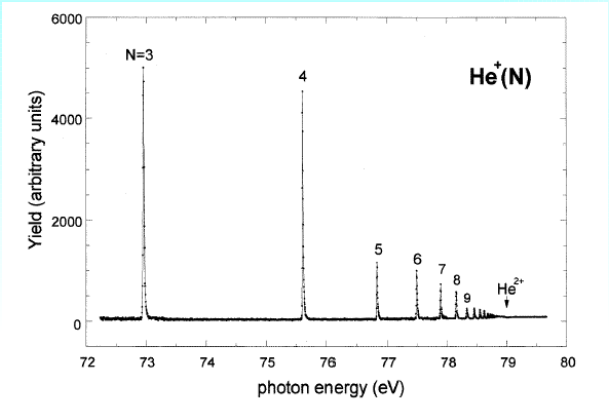
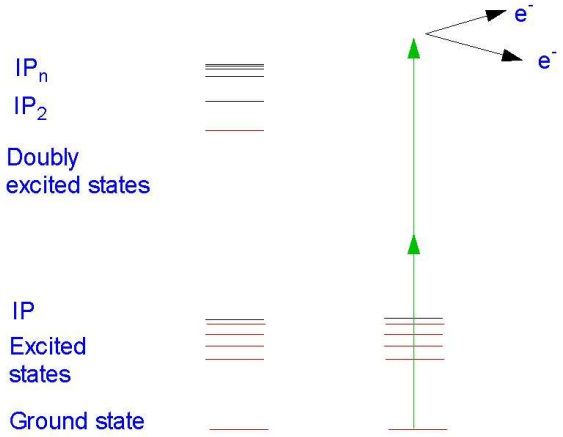


Figure 3. He^+ TPE spectrum covering the energy region from the $N = 3$ ion state threshold through the He^{2+} threshold. The dwell time is 6 s per point.

experiment



Threshold spectra of He up to the double IP.

D. B. Thompson et al, J. Phys. B: At. Mol. Opt. Phys. **31**, 2225 (1998)

Many studies with single photon, double ionization (Avaldi, Schmidt, Becker, King et al, etc). (See talk of J. Ullrich, yesterday). Much interest in two photon, double ionization, calculations available.

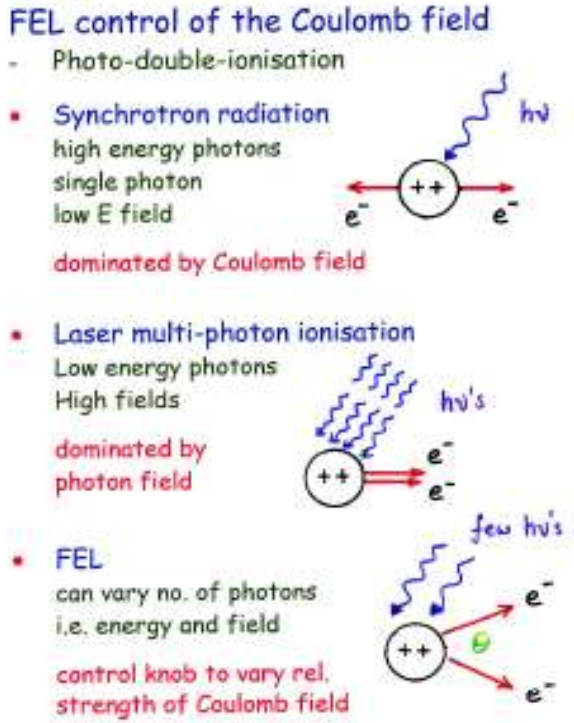
One laser experiment with two photons (Nabekawa et al), ion detection.

Laser experiments with many photons.

J. Colgan and M. S. Pindzola, Phys. Rev. Lett. **88** (2002) 173002.
Yasuo Nabekawa et al, Phys. Rev. Lett. **94** (2005) 043001.

Two photon double ionization, cont.

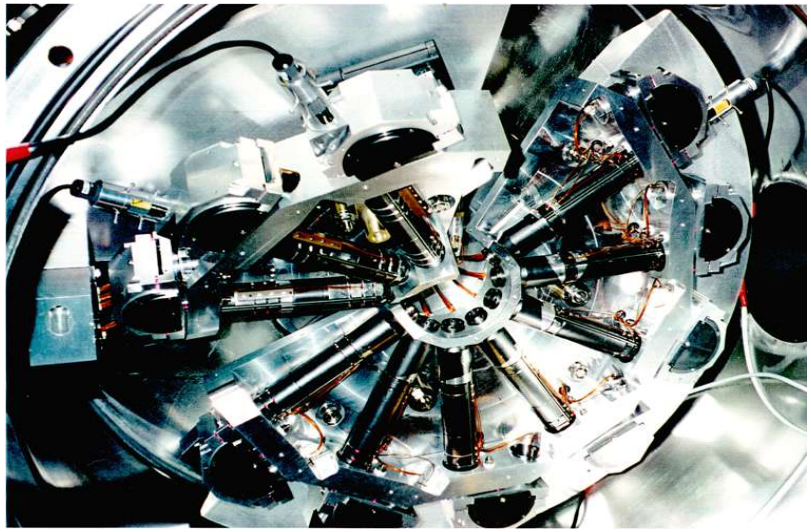
Physics is different for two photon ($h\nu$>39.5 eV)
and many photon ($h\nu$~ few eV) double ionization.
->control of relative field strengths.



Coutesy of George King

Two photon double ionization, cont.

Two electrons are created coherently.
-> measure their momenta.
How will this be done?
Angle resolved coincidence spectroscopy, e.g. chamber of Gas Phase beamline or of Uni Manchester, already available.



Possible experimental difficulties: sea of single photon ionized electrons, KE>14 eV. Need to detect electrons of lower energy. OK.

Will conventional lasers overtake the FEL?
Nabekawa: 24 nJ/pulse, 10 fs pulse, 3 micron spot, 10 Hz. 1.7×10^{13} W/cm^2.
Fermi: 0.1 mJ/pulse, 100 fs pulse, 20 micron spot, 50 Hz. 1.6×10^{14} W/cm^2.
One order of magnitude more power density, and 5000 times more energy.
To compete, conventional lasers must improve by some orders of magnitude….

Probing chemical reactions: photochemistry.

Pump-probe

Pump-probe experiments: probably the largest class of FEL experiments. At most FELs, e.g. VUV FEL, Hamburg, about 25-30% of proposals are for Atomic, Molecular and Optical; largest class is pump-probe.

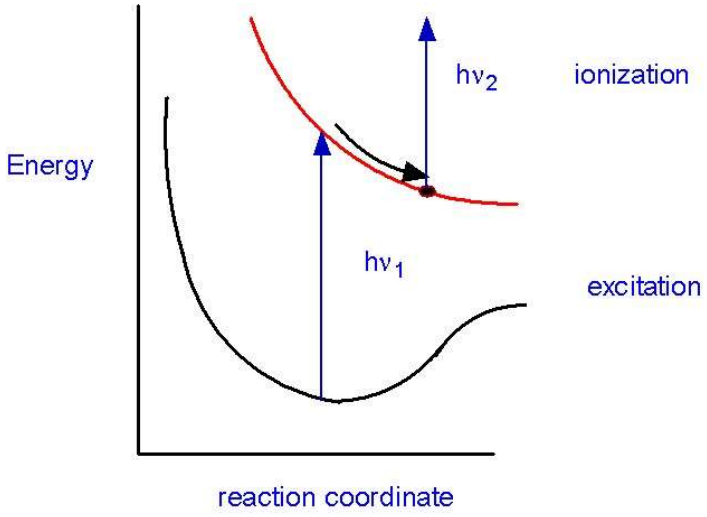
Some examples:

$H_2O + h\nu \rightarrow H_2O^*$

$\rightarrow$ fragments H_2O^+, H^+, OH, H^*

For FEL1 energies, the accessible excited states of water are well-known.

The internal energy of the neutral OH fragment can be probed by Laser Induced Fluorescence, e.g. the A-X transition around 306 nm.



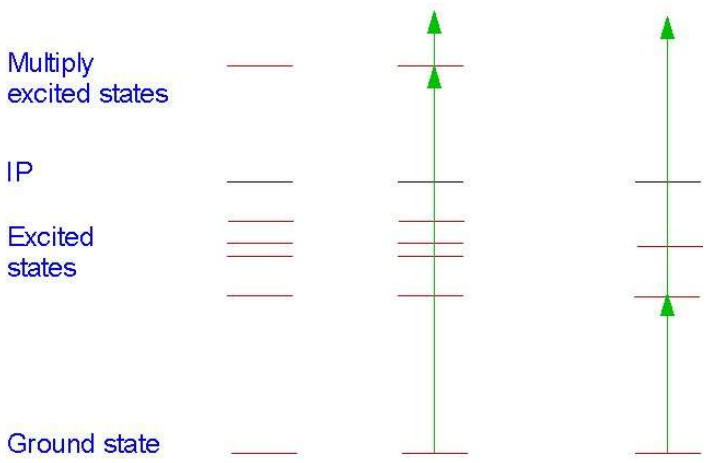
Pump-probe, cont.

Alternatively excite H_2O to a low energy state, e.g. C state, with a laser (2 photon).

Lifetimes: H_2O, 0.5 ps. D_2O, 1.2 ps.
Probe with FEL.
Result: photoelectron spectrum of valence excited water.
Evolution of the reaction into products.

$H_20^* \rightarrow OH+H$

PES spectrum evolves from spectrum of H_20^{*+} to OH^+ and H^+.



FEL pump, laser probe, and laser pump, FEL probe schemes.

Pump-probe, cont.

Feasibility.
Possible technical problems. Optical detection: use slow PMTs to avoid saturation.
Photoemission: possible problems of electron saturation. Need to measure in current mode -> lose advantages of pulse counting.

Will conventional lasers overtake the FEL?
In some fields yes, but not in all. E.g. Aloise et al, PRL 94 (2005) 223002, etc.

These experiments provide insight into the dynamics of bond breaking, angular momentum sharing energetics, internal energy...
-> Complete description of a chemical reaction.
-> Manipulation and control of chemistry.

Pump-probe, cont.

Will the intensity at the third harmonic of FEL2 be useful?
We hope so. We need 284-300 eV in the third harmonic (C 1s.)

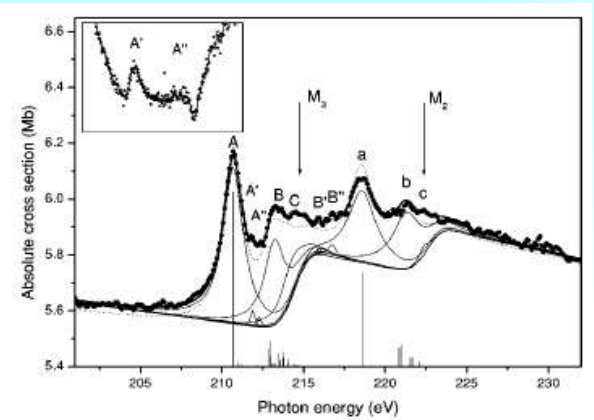
Pump with laser: valence excite, e.g. CO. Probe with FEL.
C 1s spectroscopy of the excited state.

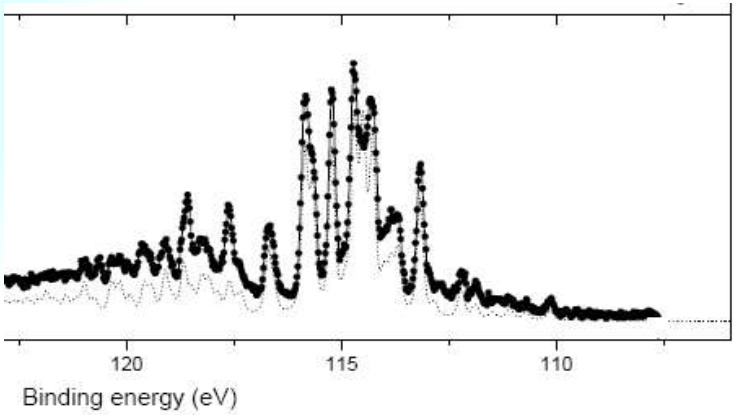
Conventional PES needs spectral purity: need to eliminate first order light.

Also Resonant Auger Raman (RAR) spectroscopy:
sub-natural linewidth. C 1s spectroscopy with 2-20 meV resolution (or analyser limit.)!
High energy electrons, possibly works without harmonic separation.

Pump-probe, cont.

How does Resonant Auger Raman work?





Sankari et al, Phys. Rev. A **67** (2003) 032710.

experiment

Kr $M_{2,3}$ edge broad, 2-3 eV.

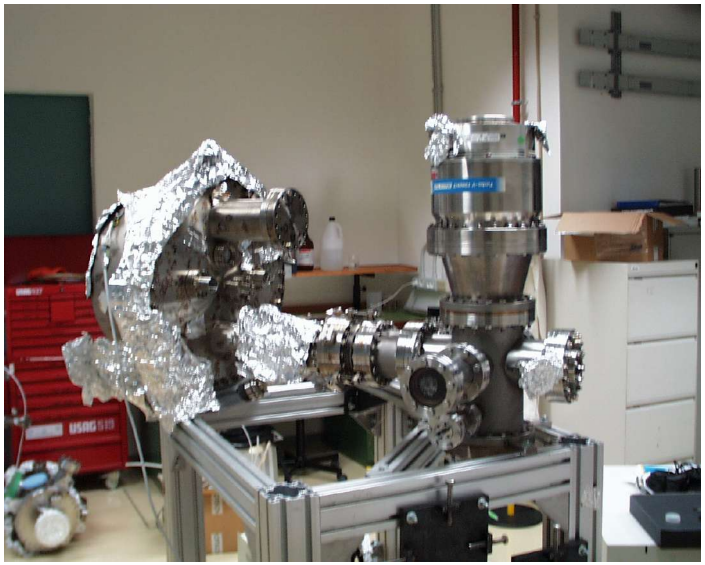
RAR spectrum: sharp peaks, 80 meV.

The numbers for C 1s PES. Third harmonic intensity 1% of fundamental.
spot: 20 microns diameter; third harmonic grating efficiency 10%;
photon density of 3×10^{14} photons/cm^2, 200 fsec pulses,
1 mm interaction length: 10^6 molecules.
All molecules prepared by laser, lifetime longer than FEL pulse,
2 Mbarn cross-section, ->10^3 electrons/pulse.

Pump-probe, cont.

The numbers: on resonance.
as above: 10^6 molecules, 10 times more flux for direct beam.
All molecules prepared by laser, lifetime longer than FEL pulse,
20 Mbarn cross-section, ->10^5 electrons/pulse.
But they are distributed over many more energies,
and over full solid angle.

No problems with saturation of detectors.
Can use hemispherical analyser, available->



Will this be overtaken by conventional lasers?

We expect laser+synchrotron experiments to be more numerous in the next 5 years.
No contest for resolution, count rate of Fermi.

The third harmonics of Fermi will allow experiments at the C 1s threshold.

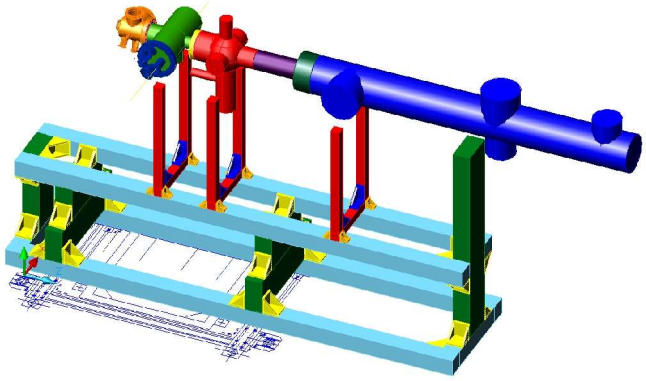
What are the electronic, structural and chemical properties of mesoscopic matter – larger than simple molecules, smaller than solids?

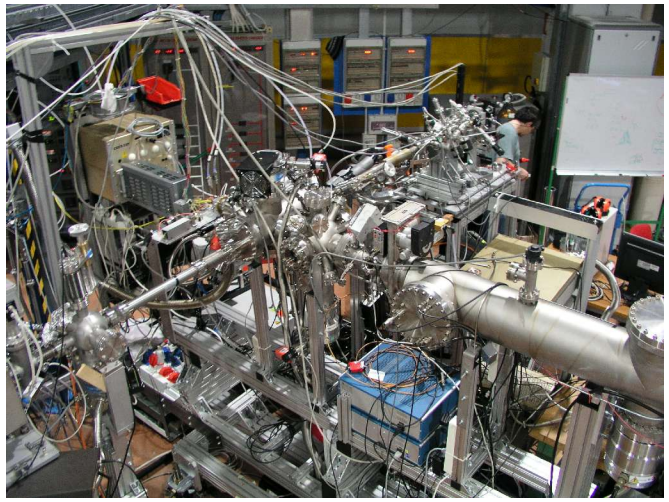
Dilute species: clusters

The Milani group has developed a pulsed plasma source of refractory metal clusters.
Versatile source: metals, oxides, carbon clusters, etc.
Free clusters can be reacted with gases (oxygen, water, hydrocarbons).

Aim: clarify relationship between size and properties.

Well prepared experiment: measurements started on Gas Phase beamline (June 2003), and on condensed clusters on other beamlines. Long term project initiated.



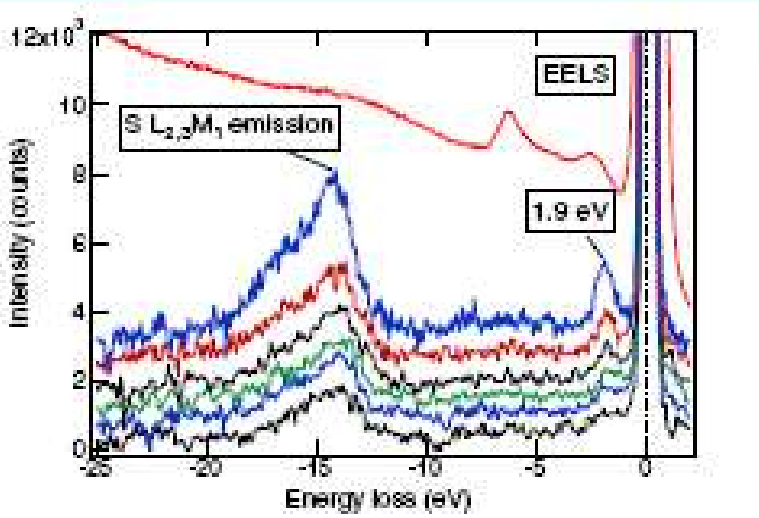


CESYRA: The source. Left schematic, right, mounted on the Gas Phase Beamline

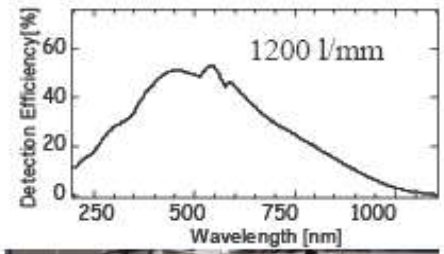
Dilute species: clusters, cont.

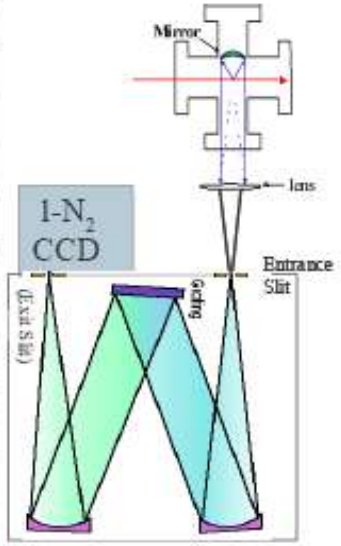
Main techniques: TOF mass spectroscopy, visible/VUV fluorescence.

Photon-in, photon-out avoids many problems of charged particle spectroscopy.
Resonant scattering gives the excitation spectrum for optically forbidden transitions.



K. C. Prince et al, J. Phys.: Condens. Matter **16**, 7397-7404 (2004).





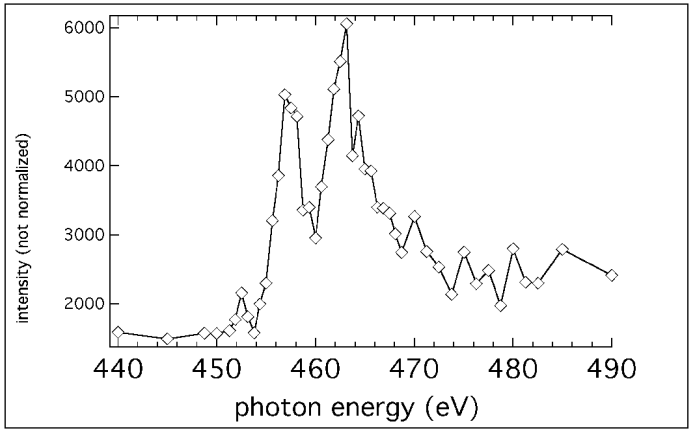
Visible fluorescence apparatus at Gas Phase.

Dilute species: clusters, cont.

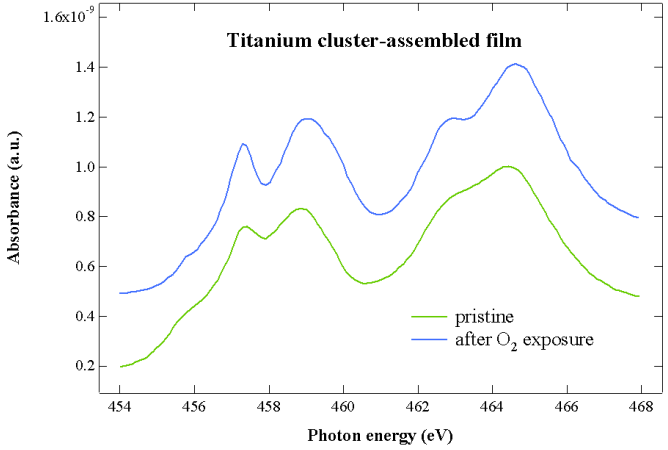
Why Fermi?

Pulse structure well suited (10 Hz).
Very dilute.
Natural resolution is well adapted.
Can use third harmonic for carbon nanoparticles.

Will this be overtaken by conventional lasers? No: energy, intensity, tunability not right. Overtaken by SR? No, temporal mismatch.



Spectra at
Ti 2p, not 3p.



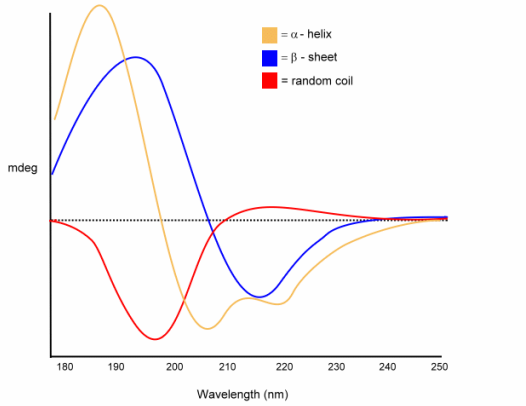
NEXAFS spectra at the L edge of titanium clusters of 350-400 atoms. Left: free clusters, 10 min/pt. Right: cluster assembled film.

What is the secondary (folding) structure of a free bio molecule?

Dilute species, biomolecules

Circular dichroism (CD) in the near UV is a standard tool for secondary structure determination/control of large molecules. [I(left)-I(right)]/I~0.001-0.0001.

+ Sample in solvent, structure is "true" structure.
- Sample in solvent, wavelength range limited to 180-250 nm circa.
- low info content (few peaks).



CD spectrum and secondary structure of proteins.

"Conventional" CD is best for: monitoring conformational changes due to a perturbation, quality control etc.

Less good for absolute structure.

Being extended to 120 nm (Daresbury, Brookhaven etc.)

Dilute species, biomolecules, cont.

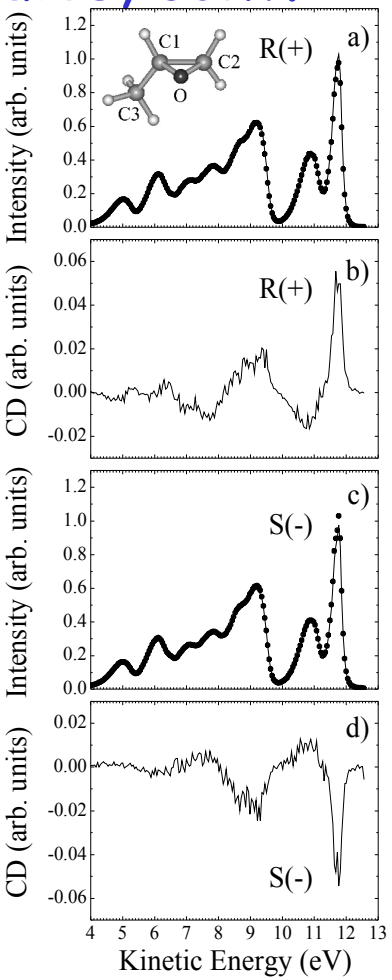
Recently natural CD of small chiral molecules investigated. Optimal conditions: CD signal=[I(left)-I(right)]/I~0.04.

Can we use Fermi to obtain structural (folding) information?

Higher energy
-> no windows
-> molecules in vacuum.

Free molecules
-> range extended above the IP
-> potentially larger info content

Fig. 1

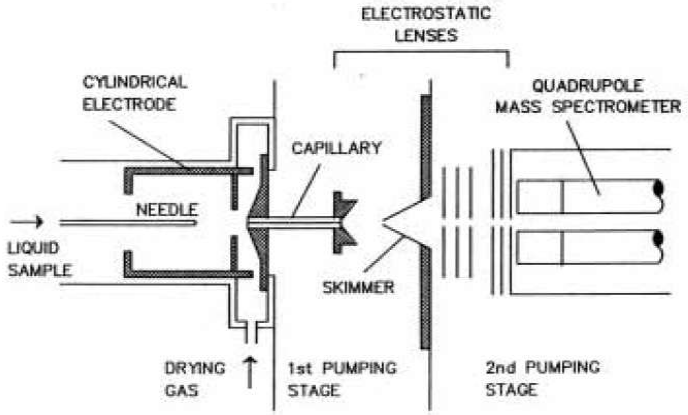


S. Turchini, N. Zema, G. Contini, G. Alberti, M. Alagia, S. Stranges, G. Fronzoni, M. Stener,P. Decleva, and T. Prosperi, Phys. Rev. A **70**, 014502 (2004)

Dilute species, biomolecules, cont.

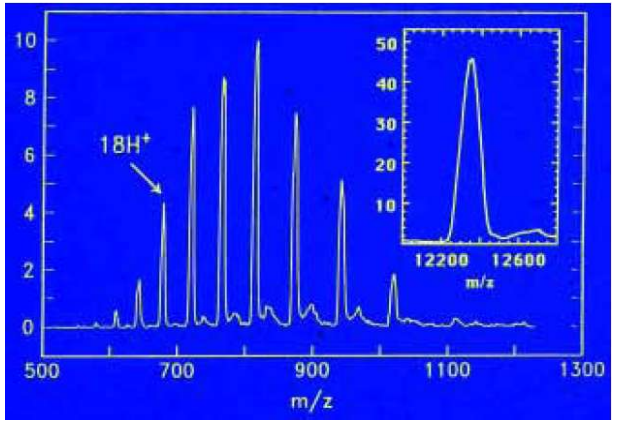
How can we vaporise large molecules?

Electrospray/nanospray:
Vaporisation of large molecules,
often with multiple charges,
with minimal fragmentation.



Second electrospray apparatus of J. Fenn. From Nobel lecture, 2002.

Sophisticated algorithms
allow determination of mass.

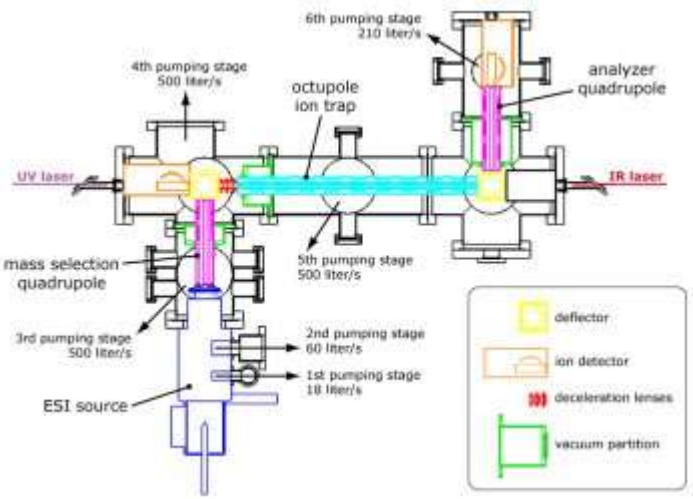


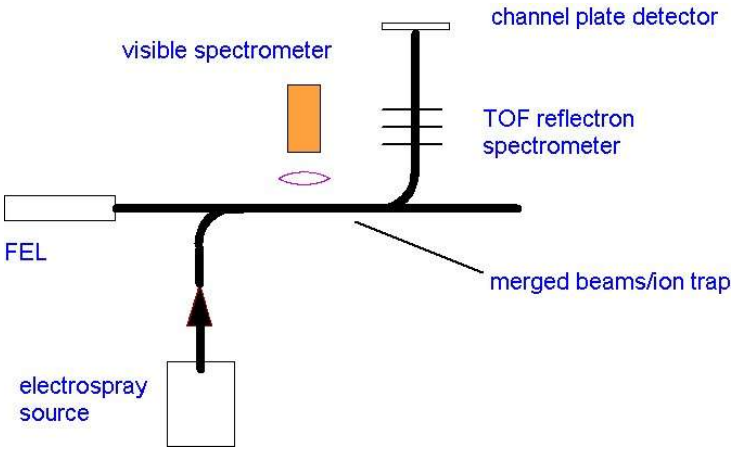
Dilute species, biomolecules, cont.

Merged beam/ion trap.
Collect all signals: ions, visible fluorescence, scattered photons, electrons.

Dichroism may occur in ion yield (cross-sections), fragmentation patterns, optical yield, elastic scattering, etc.

Nanospray set-up for spectroscopy,
with unfree lasers,
T.R. Rizzo et, PPCM, EPFL.





Dilute species, biomolecules, cont.

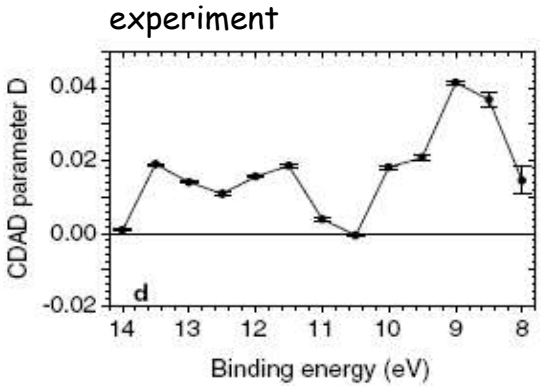
The measurement:
hν well above threshold
Search for dichroism in all signals
(ion yield, fragmentation, fluorescence).
Large energy steps, e.g. 1 eV.

Some numbers:
molecule such as an amino acid
beam diameter 2 mm
ion trap
2 kV acceleration in electrospray

-> 10^4 molecules, from a solution of 100 μmol/l all ionized in one pulse.
-> detect parent and daughter ions, form ratio.
-> several seconds accumulation for each polarization.
-> normalization to pulse intensity required.
-> not sensitive to source stability.

However we want to go to bigger molecules…

Dilute species, biomolecules, cont.



Böwering et al. PRL 86 (2000) 1187.
Bromocamphor.

Possible technical problems/developments.

We are extrapolating: chirality must be due to secondary not local structure.
Precise normalization preferred.

Electron detection.

Possible: orient the molecules using lasers?
(Spence and Doak, PRL **92** (2004) 198102).
Perhaps gives a large increase in CD signal.

Complementary to single molecule x-ray diffraction experiments.
(Neutze et al, Nature **46** (2000) 752).

Technical design

Beam transport.
-first optical element: plane deflection mirror (radiation protection),
grazing incidence (to transmit higher harmonics);
not graphite and equipped with in situ cleaning for FEL2,
translatable in a vertical direction to select fresh areas.

- beam transport to the experimental station, choice of "direct" light (reflections from mirrors only) or higher order light (second or third harmonic), e.g. high efficiency, low dispersion gratings interchangeable with mirrors.

- removable beam splitter for extracting two beams (zero, pos/neg first orders), time delay adjusted mechanically (Δl=15 microns corresponds to 50 fs) time structure (pulse duration) conserved; designs available [Poletto et al, App. Phys. B **78** (2004) 1009].

Technical design, cont.

Spot size:
choice of focusing: unfocused, focused 1:1 (about 100 microns)
and maximum focusing, minimum spot size about 20 microns -> large demagnification.
-> last mirror close to sample.

Pulse intensity monitor: each pulse individually measured in intensity
(for example by a gas cell, or end of beamline monitor);
if possible, pulse length monitor.

Differential pumping stage, pressure differences of 10^5, non-getterable gases,
10^8, getterable gases. High pressure will rarely be used: a safety precaution.

Technical design, cont.

Apart from existing chambers and detectors, two new chambers will be constructed.

Chamber 1. For non-linear optics, pump-probe, clusters.

Sources:
Pulsed supersonic beam source (reduce gas load, cool beam)
Effusive source
Vapour sources
Pulsed discharge cluster source (CESYRA)

Ultra High Vacuum
Modular design of vacuum vessel
New detector: wavelength and time resolved VUV spectroscopy.

Chamber 2. Flying proteins.

Technical design, cont.

Existing systems:

Multi coincidence chamber
Coincidence chamber, Uni Manchester
Hemispherical analyser, 150 mm, 6 multipliers

Existing detectors:

Time resolving total fluorescence yield detectors (channel plate based)
Total fluorescence yield detectors (YAP based)
UV/vis fluorescence spectrometer

Project preparation

Preparative studies.

Pump-probe: the Gas Phase beamline is initiating a program of pump-probe activity: laser + SR.
Goal: use existing expertise to develop a scientific program in two colour experiments.
Complementary to Fermi: time scales much longer. Rep rate higher, and peak power lower.

Guaranteed access to SR via CNR-Elettra contract: allows programmed testing of detectors, experiments etc.

Milani group cluster source has an approved long term project (2 years).

Funding

e-, hν, p, etc are important quantum particles.
The most important fundamental particles are the $ and the €.

Contributions of partners are in labour, equipment and know-how.

Total cost of the project: € 2,231,000.

ULiSSE
A strong international team to build an Atomic, Molecular and Optical beamline.

Non-linear optics Pump-probe Clusters Biomolecules

Helena and Seppo Aksela,
Peter Hammond,
George C. King,
Pascal Lablanquie and Francis Penent,
Paolo Milani, Paolo Piseri and Cristina Lenardi,
Elisabeth Rachlew,
Jan-Erik Rubensson,
Giacinto Scoles,
Stefano Turchini, Nicola Zema, Tommaso Prosperi,
Franco Vecchiocattivi,
Matjaž Žitnik,

The Gas Phase Beamline Research Group.

Complementary expertise Experienced third generation users

……and now the commercial break.

15th December 2005 Workshop on Ultrafast processes