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# MOST@Elettra 2.0 Workshop

Trieste  
20-21 Gennaio 2020



## Comitato Scientifico

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Kevin Charles Prince  
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## VENUE

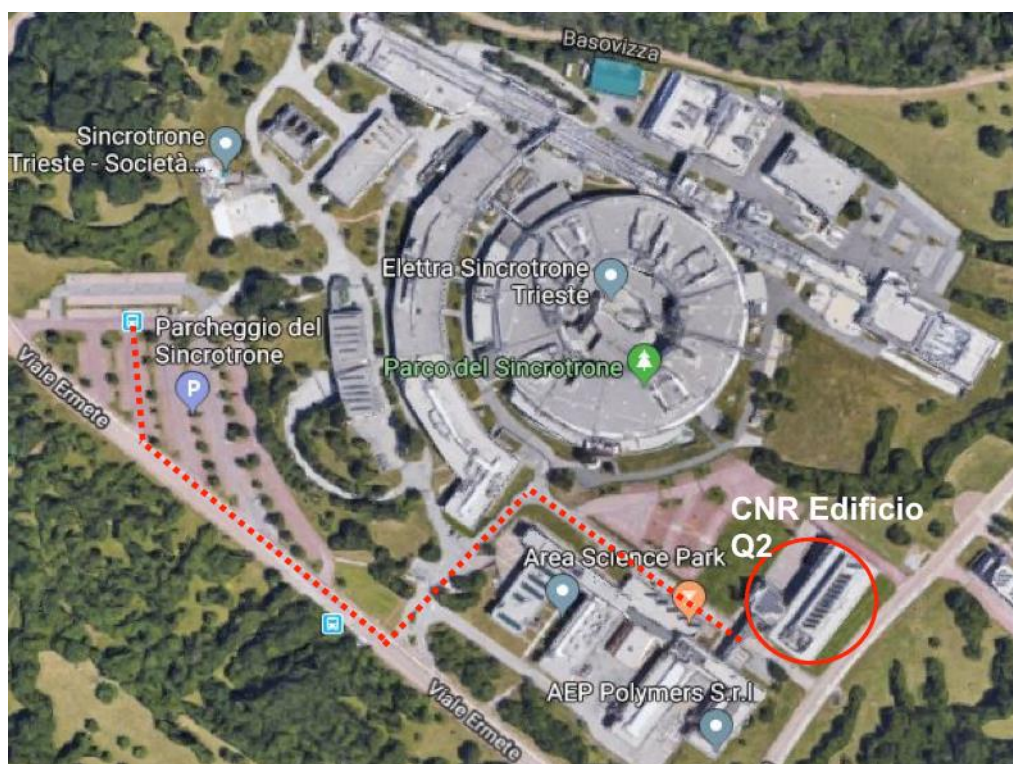
Il workshop si terrà all'interno dell'edificio Q2 nella Sala seminari "Massimo Sancrotti" al primo piano.

La poster session ed il coffe break saranno allestiti nell'edificio Q2 al piano terra.

Nella mappa è indicato il percorso per raggiungere l'edificio Q2 dalla fermata dell'autobus.

Ulteriori informazioni si possono trovare nella pagina web del workshop:

<http://www.elettra.eu/Conferences/2020/MOST/>



## PROGRAM

Monday, 20 January 2020

### Arrival and registration

12:30 Arrival and registration

### Section A

*Chair: M. Coreno*

14:15 *L. Avaldi*  
Opening Speech

14:20 *A. Franciosi*  
Welcome Speech

14:35 *B. Diviacco*  
Status of the Undulator Development

14:50 *M.N. Piancastelli*  
Perspectives for AMO research in the soft x-ray range

15:20 *P. Decleva*  
A dialogue between theory and experiment

15:50 *L. Poletto*  
Innovative instrumentation for ultrafast XUV photon handling: the role of the MOST beamline

### Coffee Break & Poster Session

16:10 Coffee Break & Poster Session

17:10

### Section B

*Chair: A. Ciavardini*

17:10 *F. Fiore*  
Laboratory Measurements of Wavelength and Cross-Sections of Atomic Inner-Shell Transitions from Abundant Elements in Astrophysics

17:30 *P. Bolognesi*  
Radiosensitisers and radiation damage

17:50 *A. Maris*  
Studying isomerism through in silico, XPS and microwave experiments

18:10 *L. Aversa*  
Organic molecules seeded in supersonic molecular beams: a different approach to gas phase analysis and deposition/adsorption on surfaces.

18:30 *A. Cartoni*  
Ion-Molecule Reaction Dynamics

### 20:00 Social Dinner at "Il Tiglio"

Tuesday, 21 January 2020

## Section C

Chair: K. C. Prince

- 09:00 *S. Stranges*  
Upgrade of current experimental methods to benefit from the new Elettra 2.0 photon source in multi-particle detection spectroscopies, and in studying highly reactive materials
- 09:20 *S. Falcinelli*  
Coulomb explosion dissociation processes of simple organic molecules by ionizing radiations in space
- 09:40 *P. Piseri*  
Developing core-level spectroscopy methods on free-nanoparticles: multiple coincidence experiments on clusters from transition metals in a molecular beam
- 10:00 *A.C. Marcelli*  
Characterization of VOCS by spectroscopic techniques

## Coffee Break & Poster Session

- 10:20  
11:20 Coffee Break & Poster Session

## Section D

Chair: S. Turchini

- 11:20 *F. Morini*  
Molecular Dynamics and Electron Momentum Spectroscopy
- 11:40 *S. Coriani*  
Ab initio coupled cluster methods for local, ultrafast and chiral spectroscopies
- 12:00 *M. Stener*  
Origin of Circular Dichroism in noble metal clusters by TDDFT
- 12:20  
Discussion and closing remarks
- 13:20

## **Status of the Undulator Development**

Bruno Diviacco<sup>a</sup>

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The MOST beamline will take light from two variably-polarised undulators, each covering a different photon energy range. The High Energy Undulator, developed for a previous project, has undergone a major refurbishment of the electric parts and the control system. The Low Energy Undulator, a completely new device, is in the initial design stage. The status of the development of the two undulator magnets will be briefly described.

## Perspectives for AMO research in the soft x-ray range

Maria Novella Piancastelli<sup>a</sup>

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The newly implemented MOST beamline will offer some unprecedented opportunities in the field of electron and nuclear dynamics of isolated atoms and molecules with state-of-the-art instrumentation.

In particular, the new beamline will cover the photon energy range 10-2000 eV with high spectral purity, high resolution and variable polarization.

Some examples of the new science made possible by such upgrade are:

1. The total photon bandwidth will be narrow in a range very little explored, namely 1000 – 2000 eV. Studies of double-core-hole states in molecules containing light elements with high intensity and high resolution will be possible, possibly yielding vibrationally-resolved spectra;

2. Inner shells of many atoms will be accessible for the first time under good instrumental conditions, such as e.g. Al K-shell, Si K-shell, Kr L-shell, Xe M-shell etc. Resonant Auger studies of molecules containing silicon will be feasible for the first time.

3. Phenomena such as recoil due to photoelectron emission and photoelectron diffraction have been analyzed either at very low photon energy, below 1000 eV, or a relatively high photon energy, above 2000 eV. The intermediate regime now accessible at MOST has not been explored.

Some instrumental advances will be also suggested, such as the need for a ultimate-resolution electron kinetic energy analyser.

# **A dialogue between theory and experiment**

Piero Decleva<sup>a</sup>

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I will review past results and open problems from collaborations with experimental investigations at Elettra and a few other facilities.

Limitations in the theoretical approaches and current developments will be discussed, with emphasis on accurate treatment of multielectron interactions and nuclear dynamics.

A personal assessment of some experimental limitations and a wish list will be given.



# **Innovative instrumentation for ultrafast XUV photon handling: the role of the MOST beamline**

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The MOST beamline, being capable of complete polarization control, will be a very useful laboratory for the characterization of innovative optical instrumentation in the extreme ultraviolet (XUV).

In my talk, I will review the recent activities done at CNR-IFN Padova in the field of optical instrumentation for photon handling of XUV ultrafast pulses in the femto- and attosecond regime generated through high-order laser harmonics (HHs), with particular attention to the crosscollaborations with the MOST beamline for polarized radiation.

The presently available techniques to generate circularly polarized harmonics have opened the way to explore ultrafast magnetization and effects linked to chirality. Many HH beamlines require a complete control and characterization of polarization through XUV polarizers/analyzers. The role of the MOST beamline for the development and characterization of such an equipment is crucial, provided: 1) it can cover the primary energy range for HHs, 15-90 eV; 2) it should be very flexible to host experimental chambers taken by the users to host the experimental setup; 3) it is completely characterized from the polarimetric point of view.

Another field where the flexibility of the MOST beamline can be very useful is the measurement of efficiency of innovative experimental set-up for the different polarizations for instrumentation using optics at grazing incidence, e.g. ultrafast monochromator, that are anyway sensitive to the polarization of the incident light and may change the beam polarization at the output.

Finally, I will also talk about possible collaborations with CNR-IFN Padova on the characterization activities of the new beamline, particularly for the full polarimetric characterization of the beamline (that is, the measurements of the Stokes parameters) in the XUV region below 100 eV.



# Synchrotron radiation Measurements of Atomic Inner-Shell Transitions for Astrophysics

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The vast majority of baryonic matter in the Universe is in the form of warm-hot atomic gas, with H and He mostly fully ionized and residual, but fundamental, traces of astrophysically abundant light “metals” (e.g. C, N, O, Mg, Si, S, Al, Fe) in a variety of ionization states. This “metals” interact with the radiation emitted by astrophysical sources through inner- and outer-shell electronic transitions, and leave their imprint on the electromagnetic spectra of these targets, allowing us to diagnose on the physical, dynamical and chemical state of this matter and therefore to shed light on the evolution of the Universe and its assembled structures at all astrophysical scales (from stars to the interstellar medium, galaxies, groups and clusters of galaxies and the diffuse medium between them).

In particular the soft (0.1-2 keV) and hard (2-10 keV) X-ray bands are dense of these electronic transitions, from all ionization stages (from neutral to hydrogen-like), most of which, however, are poorly known both in their absolute resonant wavelength and in strength (cross-section). Moreover, wavelengths and cross-sections of most of these inner-shell X-ray transitions are only known as the outcome of complex theoretical calculations and lack laboratory measurements. This needs to be corrected before large and expensive space observatories with resolving powers  $>500$  in the 0.1-10 keV band, become operative (e.g. the NASA-JAXA X-ray Imaging and Spectroscopy Mission - XRISM, due for launch in January 2022 - or the large ESA mission Advanced Telescope for High Energy Astrophysics - Athena, due for launch in 2031)

Here I will discuss a few examples in which our poor knowledge of either the exact position or strength (or both) of a given transitions, already (i.e. with the instrumentation currently available) hampers our ability to derive fundamental information on, e.g. the energetics of the observed astrophysical phenomenon, the exact amount of material actually involved, its physical and dynamical state, the mechanism responsible for ionization, etc...

## Radiosensitisers and radiation damage

Paola Bolognesi<sup>a</sup>, Laura Carlini<sup>a</sup>, Antonella Cartoni<sup>b</sup>, Anna Rita Casavola<sup>a</sup>, Mattea Carmen Castrovilli<sup>a</sup>, Jacopo Chiarinelli<sup>a</sup>, Lorenzo Avaldi<sup>a</sup>

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Radiosensitisers for enhancing the therapeutic efficacy of cancer treatment continue to be actively investigated, both at the macroscopic level of cells and tissues [1] and at the fundamental level of model systems, considered as isolated species in the gas phase [2,3]. After several years of intensive work from the international community, strengths and limits of these two approaches have become clear. The first, based on ‘trial and error’, can provide realistic responses, while the second, which allows a complete characterization of processes and mechanisms, needs validation in real biological samples. Now it is time to bridge the gap between these two complementary approaches. This implies to apply highly advanced physical chemical methods to the study of both more realistic and complex systems in the gas phase and of species and processes in realistic environment.

In the context of radiotherapy, metallic nanoparticles (NPs) like AuNP, AgNP, PtNP and GdNP have attracted increasing interest for their capacity to enhance radiation damage [4]. The primary interaction with the therapeutic beam leads to the deposition of several tens of keV in the tumor area (K, L and M ionization of the metal atoms). This energy is subsequently redistributed in the surrounding medium via de-excitation of the NPs. Cascade photon and Auger electron emission may ionize surrounding biomolecules as well as neighboring NPs, triggering new processes at lower excitation energies. Examples of these processes triggered by the secondary particles with energy transfer from few eV to few hundreds of eV to NPs are plasmon resonant excitation and metal atom d-shell ionization/excitation. Even though each single event involves a limited energy transfer, their high cross section and large number, due to the amount of secondary particles produced by the primary ionisations, make them very effective among the radiosensitising mechanisms [5]. In addition, they trigger additional damaging processes by water ionization and OH radical formation as well as by dissociative electron attachment, depending on the kinetic energy of the emitted electrons.

In this context which is currently mostly covered by theoretical simulations, both the i) absorption cross section from plasmon excitation (laser or electron collision in laboratory based experiments) to d-shell metal excitation/ionization (tunable synchrotron radiation) and ii) their secondary electron emission need to be studied in NPs with different metals and of different size. Moreover, the effects of the NP coatings and functionalizations have to be experimentally investigated.

The challenges are on one side the production of complex species like NP and large biomolecular clusters and on the other the availability of a tunable and intense VUV and soft-X ray source combined with high efficient instruments which overcome the low density of the target beam and allow to detect electrons in conjunction with other ionisation/decay products. The technical specs of MOST and the end stations that can be designed [6] may offer the possibility to tackle successfully these challenges.

**Acknowledgements.** MAECI Italia-Svezia and Progetto Gruppi di Ricerca Regione Lazio, DESIR.

### References:

- 1 Z. Kuncic and S. Lacombe, *Phys. Med. Biol.* 63, 02TR01 (2018)
- 2 R. Meißner et al., *Nature Communications* 10, 2388 (2019)
- 3 P. Bolognesi et al., *Front. Chem.* 7, 151(2019); J. Chiarinelli et al. *Front. Chem.* 7, 329 (2019) 4 S.J. McMahon et al., *Nanoscale*, 8, 581 (2016)
- 5 A.V. Verkhovtsev et al. *PRL* 114, 063401 (2015)
- 6 L.S. Wang, *J. Chem. Phys.* 143, 040901 (2015)

## Studying isomerism through *in silico*, XPS and microwave experiments

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The chemical-physical properties and the biological activity of a molecule depend on the structural shape and charge distribution of the molecule itself. However the interactions with the surrounding environment can highly influence these features and therefore studies in the isolated phase are needed for their intrinsic characterization. This can be done in a synergistic way, combining gas phase experiments and *in silico* analysis of single molecules.

Here we present several case studies in which, using very high energy radiation (through the gas phase photoemission Elettra synchrotron beamline) and very low energy radiation (through the supersonic expansion microwave spectrometers at UniBo) and complementing results from high level quantum mechanical calculations, an exhaustive description of the molecular behavior was achieved.

We also show that the increase of the power resolution and the use of free-jet techniques at the *MOlecular Science & Technology* (MOST) laboratory could provide additional insights on chemical themes, such as the exploration of potential conformational spaces and the characterization of the intermolecular interactions in weakly bound molecular complexes. Moreover, the opportunity to do measurements with circular polarized radiation in the gas phase, will allow to investigate on enantiomeric equilibria.

# Organic molecules seeded in supersonic molecular beams: a different approach to gas phase analysis and deposition/adsorption on surfaces

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Organic molecules are exploited to build innovative organic electronic and/or optoelectronic devices, in which their flexibility permits a fine tune of the electronic/mechanical/chemical properties to match the final device features. Moreover, their functional properties, i.e. the possibility to design the molecule reactivity vs other organic/inorganic compounds further push their application in sensing and biosensing, as well as in achieving inorganic biocompatibility. The comprehension of the fundamental electronic properties is mandatory and photoemission (PES) and X-ray absorption (XAS) spectroscopies are ideal tools for this purpose. While organics are typically analyzed in their solid state form, as thin films or 2D structure, a more comprehensive knowledge can be achieved from the analysis in gas phase, avoiding influence of complex intermolecular or organic/inorganic interactions. Moreover, most of theoretical studies of electronic properties of organics are based on isolated molecules, thus a reliable comparison can be made only with experimental analysis in gas phase. Gas phase PES/XAS of organics is mainly approached by using effusive sources located close to the electron energy analyzer zone, typically leading to significant UHV chamber contaminations, vacuum break due to source material refilling. Another possible issue may come from the rovibrational modes induced by the sublimation/evaporation process, that can negatively increase the width of spectral lines. In different experiments at GASPHASE we investigated the possibility to use supersonic molecular beams seeded by organic molecules (SuMBD) instead of effusive sources. The SuMBD approach has been successfully exploited in several surface science experiments, enabling an unprecedented control of interface chemical/physical processes. Such a highly collimated, dense beam could lead to several improvements in gas phase analysis such as avoid UHV chamber contamination during analysis, or UHV break to refill material in the source. Moreover, the possibility to control the molecule kinetics in terms of translational energy (up to tens of eV) and momentum (by freezing of rovibrational degrees of freedom, with internal energy of about 10K) paves the way for high resolution PES and also to new experiments related to molecule preferential alignment.

# Dynamics of Ion-Molecule Reactions in the Gas Phase

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**Topic:** The study of the reaction dynamics is one of the main goals in chemistry and gives information on kinetic constants and their trend with temperature, thermochemistry and mechanistic insights of the reactions. In this regards, ion-molecule reactions represent a class largely explored by the scientists due to their importance in different fields of chemistry. Ions can be formed in the gas, liquid and solid phase and their reactivity strongly depends on the environment they are embedded in. To explore the intrinsic properties of ions, the gas phase studies represent the right approach. Moreover, gas phase ion-molecule reactions play a crucial role in the chemistry of planetary and satellite atmospheres, in the interstellar medium where the molecules can be ionized by energy sources like cosmic rays. The gas phase reactions are taken into account in the atmospheric models to predict and understand the dynamics of the atmosphere and the climate changes. In these environments, the pressure as well as the temperature can be very low or very high and the ion internal energy and non-thermal reactions should be considered. Hence, the exploration of the reactions at different temperatures and in non-equilibrium regime is needed.

**Research:** the simplest fundamental and widespread ion-molecule reactions are the charge transfer and hydrogen atom transfer (HAT) reactions. Recently we have investigated the latter, exploring the dynamic behavior of the reaction of sulfur dioxide radical cation  $\text{SO}_2^+$  with methane, water and hydrogen, leading to  $\text{HSO}_2^+$  ions. Apart from the relevance of these studies for the general chemistry, they represent models for reactions occurring in the space. The experimental study of these reactions with tunable synchrotron radiation has been supported by an exploration of the reaction dynamics on the potential energy surface with density functional theory (DFT) and variation transition state theory (VTST).

**State of the art:** during the meeting the topic of ion molecule reaction and other outstanding international projects in the gas phase chemistry field will be discussed together with a brief overview of the works performed at the Cipo and GasPhase beamlines and their positive fallout in the scientific community. The “desiderata” to improve the research in this field will be also proposed. It follows the list of the manuscripts published in the last 5 years of research activity at Elettra.

[1] A. Cartoni\*, A. R. Casavola\*, P. Bolognesi, S. Borocci, L. Avaldi “VUV Photofragmentation of  $\text{CH}_2\text{I}_2$ : the  $[\text{CH}_2\text{II}]^+$  Iso-diiodomethane Intermediate in the I-loss Channel from  $[\text{CH}_2\text{I}_2]^+$ ” *J. Phys. Chem. A.* 2015 ,119, 3704. DOI: 10.1063/1.4937425.

[2] M. Satta, P. Bolognesi, A. Cartoni,\* A. R. Casavola,\* D. Catone, P. Markus, L. Avaldi “A joint theoretical and experimental study on diiodomethane: ions and neutrals in the gas phase” *J. Chem. Phys.* 2015, 143, 244312. DOI: 10.1063/1.4937425.

[3] A. Cartoni\*, D. Catone, P. Bolognesi, M. Satta\*, P. Markus and L. Avaldi “ $\text{HSO}_2^+$  formation from ion-molecule reactions of  $\text{SO}_2^+$  with water and methane: two fast reactions with reverse temperature-dependent kinetic trend” (HOT Paper) *Chem. Eur. J.* 2017, 23, 6772-6780. DOI: 10.1002/chem.201700028. Elettra Highlights booklet, ed. 2016-2017. pp. 86-87.

[4] D. Catone, M. Satta\*, A. Cartoni\*, M.C. Castrovilli, P. Bolognesi, S. Turchini, L. Avaldi “Gas phase oxidation of carbon monoxide by sulfur dioxide radical cation: Reaction dynamics and kinetic trend with the temperature” *Front. Chem.* 2019, 7, 140. DOI: 10.3389/fchem.2019.00140. Elettra Highlights booklet, ed. 2018-2019. pp.92-93.

[5] M. Satta,\* A. Cartoni,\* D. Catone, M. C. Castrovilli, P. Bolognesi, N. Zema, L. Avaldi “The reaction of sulfur dioxide radical cation with hydrogen and its relevance in solar geoengineering models” submitted to *JACS*.

[6] 3 manuscripts in preparation

## **Upgrade of current experimental methods to benefit from the new Elettra 2.0 photon source in multi-particle detection spectroscopies, and in studying highly reactive materials.**

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One of the most informative and powerful investigation of radiation-matter interaction of gaseous species interacting with ionizing radiation, as generated by synchrotrons and free electron lasers, can be performed by *multi-particle coincidence detection with momentum vector correlation*. Based on our experience gathered in the last two decades in developing and successfully operating a 3D-ion-momentum-imaging coincidence spectroscopic technique at Elettra, it will be described, as a logical evolution, a desired future upgrade of this method, namely a complete *3D-electron-ion* momentum imaging coincidence detection that can be specifically designed for a large number of detected particles. Various type of molecular sources can eventually be installed in the spectrometer making different types of experiments to be performed.

Recent development activity has also been dedicated to the ARPES-TPES end station, which is currently used at both the GasPhase Photoemission and Circularly Polarized beamlines of Elettra. Its two different setups allow an efficient measuring of all the photoionization dynamical observables, partial cross sections, asymmetry parameters, and dichroism coefficients, these latter in the case of chiral target species. The rotating spectrometer has recently been equipped with a fast 2D position sensitive electron detector and a novel asymmetric fringing field corrector, a home-made development realized in collaboration with Elettra Synchrotron Laboratory, which has largely improved the detection sensitivity and the energy resolution. This apparatus is interfaced with a plasma reactor to study a large variety of highly reactive species, such as free radical and short-lived chemical reaction intermediates, and is compatible with other specifically designed molecular sources, including seeded jet and high temperature devices. Planned upgrades to fully exploit the properties of the MOST beamline of Elettra 2.0, such as, for instance, electron-ion coincidence spectroscopies with this end station, will be envisaged.



# Coulomb explosion of simple molecules by ionizing radiations in space

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An experimental investigation on the fragmentation dynamics following the double photoionization of simple molecules of astrochemical interest, as carbon dioxide, propylene oxide and N-methylformamide, induced by VUV photons has been reported. Experiments used linearly polarized light in the 18-37 eV (propylene oxide), 26-45 eV (N-methylformamide) and 34-50 eV (carbon dioxide) photon energy range at the Elettra Synchrotron Facility of Trieste (Italy) [1-3]. Ion imaging and photoelectron-photoion-photoion (PEPIPICO) coincidence techniques are used with time-of-flight mass spectrometry (see Fig. 1) [4,5]. In the case of propylene oxide, six different two-body fragmentation processes has been recorded with the formation of  $\text{CH}_2^+/\text{C}_2\text{H}_4\text{O}^+$ ,  $\text{CH}_3^+/\text{C}_2\text{H}_3\text{O}^+$ ,  $\text{O}^+/\text{C}_3\text{H}_6^+$ ,  $\text{OH}^+/\text{C}_3\text{H}_5^+$ ,  $\text{C}_2\text{H}_3^+/\text{CH}_3\text{O}^+$ ,  $\text{C}_2\text{H}_4^+/\text{CH}_2\text{O}^+$  ion pairs. The double photoionization of N-methylformamide occurs producing two main fragmentation reactions, forming  $\text{CH}_3^+ + \text{CH}_2\text{NO}^+$  and  $\text{H}^+ + \text{C}_2\text{H}_4\text{NO}^+$ , while carbon dioxide dissociates by Coulomb explosion of the intermediate  $(\text{CO}_2)^{2+}$  dication into  $\text{CO}^+ + \text{O}^+$  final ions. The relative cross sections and the threshold's energy for all fragmentation channels are recorded as a function of the photon energy. In the case of the double photoionization of propylene oxide, the measure of the kinetic energy released distribution for the  $\text{CH}_3^+/\text{C}_2\text{H}_3\text{O}^+$  final ions with the their angular distributions allowed the identification of a bimodal behavior indicating the possible formation of two different stable isomers of  $\text{C}_2\text{H}_3\text{O}^+$ : acetyl and oxiranyl cations. In the case of  $\text{CO}_2$ , the production of  $\text{CO}^+$  and  $\text{O}^+$  fragments with a high kinetic energy content (2.0 and 3.8 eV, respectively) can explain the lack in the  $\text{O}^+$  expected concentration of the Mars atmosphere as measured by Viking 1 lander and Mariner 6 spacecraft [4]. This energy is large enough in the case of Mars and Titan to allow these fragments to reach sufficient velocity to escape into space. Therefore this process can in principle contribute to the continuous erosion of these planetary atmospheres.

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- [2] S. Falcinelli, F. Vecchiocattivi, F. Pirani, M. Alagia, L. Schio, R. Richter, et al., *ACS Earth and Space Chemistry* **3**, 1862-1872 (2019).
- [3] S. Falcinelli, M. Rosi, F. Pirani, D. Bassi, M. Alagia, L. Schio, et al., *Frontiers in Chemistry* **7**, 621 (2019).
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# **Developing core-level spectroscopy methods on free-nanoparticles: multiple coincidence experiments on clusters from transition metals in a molecular beam**

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Nanoparticles are a much more pervasive and relevant form of condensed matter than the quite recent upsurge of the term nanotechnology would suggest. For about a century they have played an important role in the industrial processes of synthesis and chemical transformation in the gas phase, and have always had a significant impact on natural and anthropogenic atmospheric processes with effects on the environment and on the health of living species.

The key to their relevance is complex and elusive: new chemical and physical properties frequently emerge at the nano-scale, not directly inherited from the atomic and molecular constituents and often absent in the macroscopic analogues. Interaction with a surface or support matrix typically significantly alters these properties by inhibiting them or on the contrary determining their emergence.

The possibility of a bottom-up approach to the investigation of nanometric objects and aggregates with spectroscopic techniques similar to those applied with great impact to the understanding of the physical chemistry of materials and surfaces in extended form, is bound - on the one hand - on the ability to prepare and manipulate the nanoparticles: making them available for experiment as isolated systems, or being able to deposit them to form nano-structured or nano-composite interfaces and thin layers; on the other hand it depends on the development of experimental techniques and apparatus suitable for the specific conditions of the samples that can be obtained: typically extremely rarefied in the case of isolated objects.

The merging of the skills developed at the University of Milan - in terms of the preparation of molecular beam nanoparticles - with those present at Elettra - on gas phase spectroscopy techniques with synchrotron radiation - is realized in a collaboration that across over one decade has carried out a number of pilot experiments and has developed specialized apparatus for core-level - photo-emission and absorption spectroscopy of free nano-aggregates in a supersonic molecular beam.

The state of the art of development along this path and an outlook in the context of the new MOlecular Science & Technology (MOST) beamline are presented as a seed for the discussion of possible new directions and synergies with the members of the Italian community addressed by MOST.

## Characterization of VOCS by means of synchrotron radiation techniques

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Atmospheric pollution from volatile organic compounds (VOCs) produced by human activities contributes to many health issues in industrialised and developing countries. VOCs belong to a wide family of organic compounds characterized by different functional groups, e.g., various aromatic chloro hydrocarbons and perfluorocarbons, such as organic solvent thinners, degreasers, cleaners, lubricants, inflammable liquids. Their presence affects the atmospheric chemistry and ultimately leads to photochemical smog and climate active aerosols. [1]

Actually, also in the area of Occupational Safety and Health and Environmental Protection, VOCs deserve special considerations. They can be released from a variety of solids and liquids during technological processes, e.g., by chemical and petrochemical industries and/or from building products and furnishing materials, but originate also from storage processes, such as breathing and loading losses from storage tanks, leaks from piping and equipment, wastewater streams and heat exchange systems, evaporation of gasoline and diesel fuel, coal combustion, biomass burning, etc..

VOCs pollution occurs also in indoor environments originating from a variety of sources like household products, smoke, burning biomass for cooking, pesticides and carbon compounds.

Many epidemiological studies pointed out the need to identify and quantify the most important human-produced sources of VOC emissions to effectively mitigate air pollution and improve human health. The presence of toxic VOCs as air pollutants in workplaces, has accounted for several deaths in the last decades. Although several sources of VOCs have been successfully contained, others are growing in relative importance. Because the concentration of any pollutant indoors is limited and because of the lack of sensors, the indoor pollution is increasingly regarded as a major treat. For this reason we are interested to develop methods for characterizing VOCs of interest in environmental pollution studies and investigate materials to improve the properties of effective sensing materials for such volatile compounds [2,3].

The use of accurate analytical techniques plays an important role to advance the knowledge of VOCs and their dynamics. MOST with its wide energy range (10-2000 eV), high spectral purity, high resolution (in energy and time); and polarization control: is certainly suitable to perform different experiments with techniques such as XUV, XPS, XANES and mass spectrometry, fundamental to investigate these volatile compounds.

All the above fully justify the interest of a dedicated synchrotron radiation experimental station at MOST to study VOCs and, more in general to characterize and study all Volatile Chemical Compounds (VCC). These systems exhibit different chemistries and each one may follow different pathways from the initial emission through atmospheric degradation, e.g., interacting with UV radiation, to an end product. Moreover, the lifetimes of these volatile compounds range from months to few minutes with oxidation occurring through multiple steps that may ultimately produce CO<sub>2</sub> and water. Models that represent the

chemistry and predict formation of different compounds through complex reactions need to be proposed and investigated to reproduce experimental data.

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# Molecular Dynamics and Electron Momentum Spectroscopy

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**Synopsis** A new analysis of the outer valence (e, 2e) momentum distributions of furan, dimethyl ether, and adamantane has been performed using two complementary approaches. The first relies upon the harmonic oscillator model, while the second uses the principles of the Born-Oppenheimer Molecular Dynamics (BOMD).

In a series of studies, an in-depth investigation of vibrational effects on the electron momentum distributions of the outer valence orbitals of furan [1], dimethyl ether [2], and adamantane [3] is reported. To this aim, two different methodologies have been used. The first one, known as Harmonic Oscillator Quantum Mechanical (HAQM) approach [4], allows us to quantitatively evaluate the role of each normal mode of vibration on a given momentum distribution. The second one uses the principles of Born-Oppenheimer Molecular Dynamics (BOMD) simulations [5] and allows us to average the effects of the temperature over a large number of structures and to take into account non-harmonic effects. The obtained theoretical results have been compared with newly acquired experimental (e, 2e) momentum distributions with improved statistics as compared with that of the available data on the same compounds [6, 7, 8].

Despite their intrinsic difference and the complex nature of the vibrational structure of the targets, both methods provide consistent results and give quantitative insights into the results of the new (e, 2e) experiments. Comparisons between experiment and theory have shown that taking into account vibrational effects leads to a strong enhancement of the low  $p$  component of the momentum profiles and considerably improves the agreement with experiment. This shows also the deficiency of previous explanation that ascribed the discrepancies mostly to distorted waves (see e. g. ref. 8). The analysis based on the HAQM approach has revealed the significant role of vibrational modes associated with the C-H bonds. In line with the Herzberg-Teller principle [9], the influence of these molecular vibrations on the computed momentum profiles has been unraveled by considerations on the symmetry characteristics of orbitals and their energy spacing.

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# Ab initio coupled cluster methods for local, ultrafast and chiral spectroscopies

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The massive investments in advanced light source facilities working in the x-ray frequency range has increased the popularity of X-ray-based spectroscopic techniques to probe molecular systems. At the same time, it has stimulated the development of quantum-chemical theory and computational tools to simulate such spectra. Theory and simulation tools are essential components to unambiguously relate experimental measurements to both structural and dynamical properties of the probed system.

The accurate description of core excited states presents some additional challenges, compared to that of valence excited states, challenges that have for a long time prevented the application of electronic structure methods, like the coupled cluster ones, that are considered among the most reliable and accurate to describe excited state.

During the last decade, we have tried to rectify this situation, developing ab initio approaches, rooted on the coupled cluster ansatz, to address X-ray spectroscopic techniques like X-ray absorption (XAS) [1-10], emission (XES) [11-13], circular dichroism (XCD) [12], resonant inelastic x-ray scattering (RIXS) [11-13], photoelectron (XPS) [14], that are applied to probe both the electronic ground state and electronic excited states in a pump-probe [5,8,10,14] set up. An overview of their performance and capabilities will be presented.

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# Origin of Circular Dichroism in noble metal clusters by TDDFT

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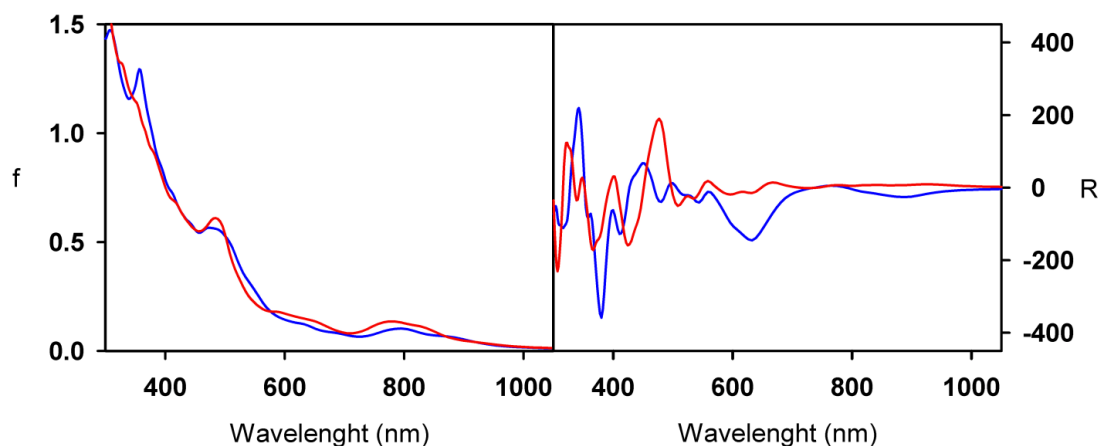
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The origin of Circular Dichroism (CD) of a class of atomically precise noble metal alloy clusters,  $\text{Ag}_{24}\text{Au}_1(\text{DMBT})_{18-2x}(\text{BINAS})_x$  (DMBT = 2,4-dimethylbenzenethiolate) has been studied by time dependent density functional theory (TDDFT) calculations and compared with on experimental results from the group of Thomas Bürgi (Geneve University). In order to impart chirality to the achiral  $\text{Ag}_{24}\text{Au}_1(\text{DMBT})_{18}$  cluster, a chiral ligand, R/S-1,1'-[binaphthalene]-2,2'-dithiol (R/S-BINAS) was incorporated. The icosahedral  $\text{Ag}_{12}\text{Au}_1$  core undergoes a transition from achiral to chiral by increasing the number of incorporated BINAS ligands. The CD spectroscopic measurements, in conjunction with DFT calculations, suggest that the CD response in  $\text{Ag}_{24}\text{Au}_1(\text{R/S-BINAS})_x(\text{DMBT})_{18-2x}$  originates from transitions from metal-ligand occupied orbitals to ligands virtual orbitals. This work suggests that the chiroptical spectroscopic techniques such as circular dichroism represents a useful tool to understand the nature of electronic transitions in ligand protected metal clusters.

Finally we will discuss the ability of TDDFT to describe the CD for large chiral bare gold nanotubes in presence of plasmonic transitions.



Photoabsorption oscillator strength ( $f$ , left box) and Circular Dichroism rotatory strength ( $R$ , right box) calculated at the TDDFT/LB94/TZV level for two geometries of the  $[\text{Ag}_{24}\text{Au}(\text{DMBT})_{10}(\text{BINAS})_4]^-$  cluster anion.

## POSTER SESSION

- P1:** **Laura Carlini**, CNR– ISM Roma  
*“Peptide bond formation and decomposition in linear and cyclic dipeptides”*
- P2:** **Alessandra Ciavardini**, CERIC – ERIC Trieste  
*“Peptide bond formation and decomposition in linear and cyclic dipeptides”*
- P3:** **Emanuele Coccia**, Università degli studi di Trieste  
*“Role of coherence in ultrafast spectroscopies on single molecules and nanostructures”*
- P4:** **Sergio D’Addato**, Università di Modena e Reggio Emilia e CNR - NANO  
*“Magnetic and plasmonic metal@oxide, core@shell nanoparticles: a fundamental case study for advanced synchrotron radiation techniques”*
- P5:** **Alessandro D’Elia**, Università degli studi di Trieste e CNR - IOM  
*“XUV investigation of free metal cluster and nanostructured films”*
- P6:** **Cesare Grazioli**, CNR – IOM Trieste  
*“ULLA: end-station for photoionization spectroscopy of free organic molecules”*
- P7:** **Ambra Guarnaccio**, CNR – ISM Potenza  
*“Photoionization and electronic structure of  $\pi$ -conjugated organic molecules for organic photovoltaics”*
- P8:** **La Mattina**, EMPA, Dübendorf, Switzerland  
*“Charge induced structural reconstruction at buried STO/YBCO interface”*
- P9:** **Valeria Lanzilotto**, Università di Roma La Sapienza  
*“XPS micro liquid-jet of melamine in aqueous solution”*
- P10:** **Aurora Ponzi**, Institut Ruđer Bošković, Zagreb, Croatia  
*“Calculation of MFPADs profiles for different excited states of acetylacetone”*
- P11:** **Javad Rezvani**, INFN Roma  
*“Shaping of Synchrotron radiation beams by spherically bent optical devices”*
- P12:** **Luca Schio**, Università di Roma La Sapienza e CNR – IOM Trieste  
*“Photoelectron and nuclear dissociation dynamics of gas phase molecules studied with Synchrotron Radiation”*
- P13:** **Andrea Sterzi**, EMPA, Dübendorf, Switzerland  
*“WO<sub>3</sub> hydrogenation probed by high pressure photoemission”*
- P14:** **Daniele Toffoli**, Università degli studi di Trieste  
*“Development of a CIS/TDDFT B-spline Scattering Code for Molecular Ionization Processes in the Weak and Strong-Field Regimes”*
- P15:** **LDM beamline**, Elettra Sincrotrone Trieste  
*“The Low Density Matter beamline at the FERMI Free Electron Laser”*



# P1 - Peptide bond formation and decomposition in linear and cyclic dipeptides

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**Synopsis** The peptide bond formation and decomposition is studied by photoelectron spectroscopy, time-of-flight mass spectrometry and photoelectron-photoion coincidence (PEPICO) spectroscopy in a series of isolated linear and cyclic-dipeptides. Interesting cyclization mechanisms are observed.

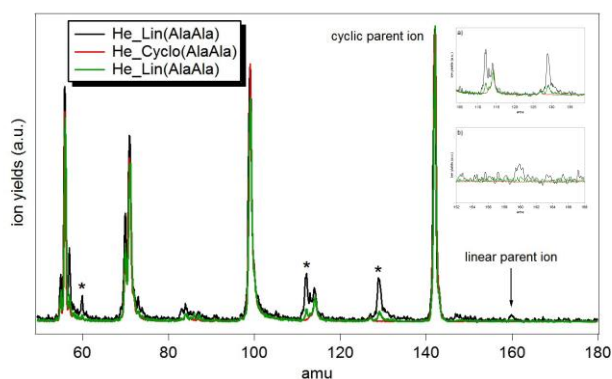
It has been proposed that a dynamic chemical process [1,2], which involves the coupling of the condensation of  $\alpha$ -aminoacids into peptides with the peptide degradation 'returning' individual aminoacids, may have provided an effective mechanism for reshuffling and building up the complexity of aminoacid sequences preceding the emergence of life. These processes rely on peptide bond formation and cleavage mechanisms, respectively, and can be influenced by the presence of activating agents, chemical precursors or the delivery of energy in a proper environment.

Our group has undertaken a study of the peptide bond formation and degradation on the simplest aminoacids, the cyclic (c) and linear (l) dipeptides in the gas phase, by photoionisation and ion collision experiments. In the poster, we will present preliminary results on the study of c- and l- GlyGly, AlaAla, GlyPhe, GlyAla and of l-PheAla by mass spectrometry and PEPICO experiments.

The mass spectra of the l- species have shown a common pattern of fragmentation, with i) dominance of the m/z peak attributable to the cyclic structure, ii) very strong similarities between the measured mass spectra in l- and c-structure, with the associated observation that iii) parent ion and fragments attributable to the l-species, if present at all, diminish with time until they disappear. All of this suggests that cyclisation phenomena may happen in the l-species at some stage of the experimental procedure, driven by either the temperature in the condensed phase or the 'electrostatic forces' in the unstable zwitterion produced in the sublimation, or due to the fast rearrangement of the highly reactive cation following ionisation.

In the l-AlaAla molecule, for example, a careful characterisation of the mass spectrum (Figure 1) as a function of the temperature as well as the IR spectra of the sample analysed before and after thermal evaporation, consistently indicate a temperature induced cyclisation in the condensed phase, prior to sublimation. Different scenarios may arise in other samples, suggesting that a complex and not easily predictable chemistry occurs already at the stage of simple dipeptides and the limit of feasibility for the study of polypeptides produced in gas phase by thermal vaporation is very rapidly reached. In the framework of the MOlecular Science and Technology (MOST), the implementation of an end-station, which combines an ElectronSpray Ionization Source with electron and ion spectroscopies will allow to make a step forward in the study of peptide chains in their natural conformation, controlling molecular stability, preventing the linear dipeptides cyclization or

decomposition and, eventually, increasing the peptides chain elongation.



**Figure 1.** The mass spectra of *l*- and *c*-AlaAla at photon energy 21.22 eV are reported in black and red, respectively. The *l*-AlaAla spectrum collected after 24h at the same sublimation temperature (green) clearly shows the disappearance of the parent ion and associated fragments (indicated by the \*). In the inset a) and b) are shown the amu range 105-140 (associated fragments) and 152-168 (parent ion), respectively.

**Acknowledgment:** MAECI Italia-Svezia and Progetto Gruppi di Ricerca Regione Lazio, DESIR.

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## P2 - Photoionization of excited states at the GasPhase beamline: a pump-probe study of a dye molecule in the gas phase

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Synchrotron light sources provide pulsed, ionizing radiation that is suitable for probing processes on the picosecond time scale. Pump-probe spectroscopy with VUV synchrotron radiation is a powerful tool for understanding of the photoionization process and the underlying dynamics of atomic and molecular system [1]. (TRPES), with a fs laser to excite the states and synchrotron VUV radiation as probe. Probe photon energies in the VUV region are highly useful in elucidating photophysics and photochemistry of molecules, because they allow one-photon ionization of low-lying excited and ground states as well as the ionization of photoreaction products [2]. In the experiments described here, the target was the dye molecule Coumarin-6. Coumarin dyes have been widely studied and used in a large number of chemical and physico-chemical applications like inkjet printing, heterojunction solar cells, fluorescent microcrystals and molecular dots etc [3]. The valence electronic structure of coumarin-6 excited by a 390 nm fs laser was probed by synchrotron radiation photoelectron spectroscopy. The laser pulse was produced by doubling the fundamental frequency of a Ti:Sapphire laser system at 83 MHz repetition rate, and synchronized with VUV synchrotron pulses at 26 eV. Figure 1 shows the valence photoelectron spectra of coumarin-6 in the ground state (black line) and the spectrum taken after excitation with the laser at time delay 250 ps (red line). After excitation, a peak was found at 1.98 eV above the first ionization potential. This long-lived feature (> 2 ns) was assigned to a triplet state [4] populated after a fast decay of the first excited state.

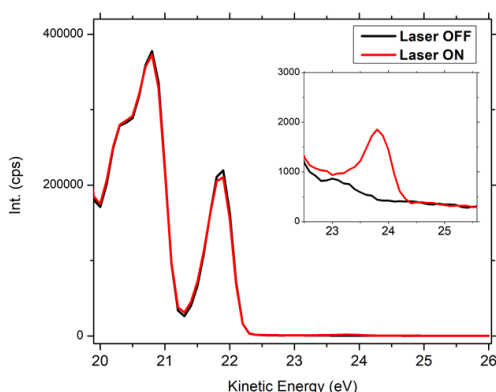


Figure 1. Valence photoelectron spectra taken at 26 eV from the ground state (black line), and after excitation with laser (red line). Inset: enlarged view.

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## P3 - Role of coherence in ultrafast spectroscopies on single molecules and nanostructures

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Ultrafast spectroscopy is a powerful tool to investigate, control and manipulate quantum coherence in molecules and complex systems [1-2]. Detection of electronic and vibrational coherence in biological systems and in plasmonic nanostructures is a matter of stimulating and open debate [2-3]. Recently, specific ultrafast spectroscopy techniques could probe a single molecule [2]. To understand the outcomes of such experiments, theoretical and computational approaches are required, able to include all the important features of the simulated system. Using a recently developed computational approach coupling the theory of open quantum systems, by means of stochastic Schrödinger equation [4], with a quantum-chemical description of the molecular target, we have simulated a two-pulse experiment on the TDI and DNQDI fluorophores [5], both investigated experimentally [6-7]. We study which kind of information can be inferred from the evolution of the TDI and DNQDI fluorescence as a function of the delay time and phase shift between the two pulses. A complete rationalization of the experiments has been carried out, leading to a clear description of the appearance of electronic [4] and vibrational [5] coherence in a two-pulse spectroscopy on single molecule. Moreover, we show that electronic decoherence can be thought as a further design element of molecular nanoplasmonic systems [3]: metal nanoparticle effects on the absorption of light by a nearby molecule may be strongly affected (even qualitatively, i.e., suppression vs enhancement) by molecular decoherence.

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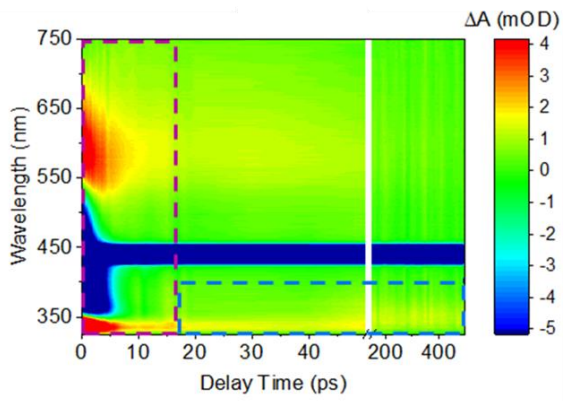
## **P4 - Magnetic and plasmonic metal@oxide, core@shell nanoparticles: a fundamental case study for advanced synchrotron radiation techniques**

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Synthesis, study and applications of NanoParticles (NPs) have been playing a major role in material science and technology over the last 20 years. Realization of NPs with chemical methods is nowadays mainstream, because of the cost effectiveness and scalability. Nevertheless, physical synthesis with a bottom-up approach presents some advantages, especially when a “fine tuning” of the NP properties is required. Physical synthesis can be single-step and ligand-free, and these characteristics can result in a more accurate analysis of the NP structure and of their electronic and magnetic behavior. During the last years we developed a laboratory for the NP synthesis with a magnetron-based gas aggregation source and a quadrupole mass filter. The versatility of the NP source allowed us to prepare and study different types of NPs. Moreover, co-deposition and sequential layer deposition methods have been used to obtain core@shell NPs. These methods gave us the possibility of realizing non-native oxide shells [1], and to investigate metal@metal oxide core@shell NPs by varying independently the core diameter and the shell thickness.

On the other hand, experiments involving the use of Synchrotron Radiation have been demonstrated to be essential in the comprehension of the fundamental properties of molecules, clusters and more generally nanostructures. Recently, our group concentrated on the magnetic [2] and plasmonic properties of this class of NPs. For instance, the coupling of wide band gap oxides with suitable plasmonic NPs has shown to be effective in providing materials with a light absorption range extending over the full solar radiation spectrum. This represents a promising strategy to obtain efficient functional materials, which convert solar into chemical or electric energy, relevant for a wide range of applications, like sensors, photocatalysts or photovoltaic devices. The localized surface plasmon resonance (LSPR) decay, occurring on femtosecond time scales, involves a relevant energy transfer to the oxide, which may lead to modifications of the material properties on much longer time scales. Recent experiments involving time-resolved spectroscopies have been performed on Ag NPs embedded in a reducible wide bandgap oxide, namely CeO<sub>x</sub> [3], showing that a high absorbance in the visible range can be obtained, and we identified a long-living excited state induced by LSPR decay, that we tentatively ascribed to a transient occupation of Ce 4f levels. This experiment, occurring in the visible range, is planned to be extended to soft X-rays, and by using time-resolved XAS it will be possible to induce chemical selectivity to the absorption mechanism, for a better understanding of the electronic states involved in the energy transfer process. We therefore believe that a high brilliance soft X-ray beamline like MOST will be important for our research areas.



**Figure 1:** FTAS map of Ag NPs embedded in a CeO<sub>2</sub> matrix, obtained using a pump at the LSPR (440 nm), below the CeO<sub>2</sub> band gap. The red box highlights the Ag NPs LSPR-related features at ultrashort times, while the blue box marks the signal ascribed to electron injection from Ag NPs to the CeO<sub>2</sub> film [3].

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## **P5 - XUV investigation of free metal cluster and nanostructured films**

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A Pulsed Microplasma Cluster Source (PMCS), has been used to produce clusters beam of vanadium and vanadium oxides. This versatile Cluster source can be used to produce nanostructured (NS) materials and isolated nanoparticles in the gas phase. Studying free cluster is necessary to understand how properties of matter evolve from atomic features to those of bulk materials. On the other and production and study of NS material is crucial for the technological application and therefore the possibility to tune the stoichiometry and electronic structure is of paramount importance. New advancements in cluster production and free cluster investigation and detection will be presented.



## P6 - ULLA: end-station for photoionization spectroscopy of free organic molecules

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### Abstract.

Photon flux and energy resolution achievable at undulator beamlines, such as the Gas Phase beamline at the Elettra storage ring (Trieste, Italy) [1], enable studies of the energy dependence of photoionization processes on isolated molecular targets over a large energy range. It is then possible to address the specific effects that follow selective excitations of inner-shell electrons. However, this kind of measurements often suffers from an intrinsic low signal level attainable from rarefied low-vapor-pressure targets such as biomolecules [2].

Our studies address biphenylene, pteridine and metal-containing phthalocyanines. These highly conjugated organic molecules are all characterized by a rich photochemistry, which also makes them particularly interesting for pharmacological purposes. Our synchrotron radiation experiments provide insights into their electronic structures, whose detailed knowledge is of great value when planning further investigations on their excited states at novel ultrafast light sources. By comparison with the results of Density Functional Theory (DFT) calculations, we could identify the characteristic contributions of chemically non-equivalent carbon atoms in the x-ray photoelectron spectra as well as in the core hole absorption spectra of these molecules, and to correctly assign them.

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## P7 - Photoionization and electronic structure of $\pi$ -conjugated organic molecules for organic photovoltaics

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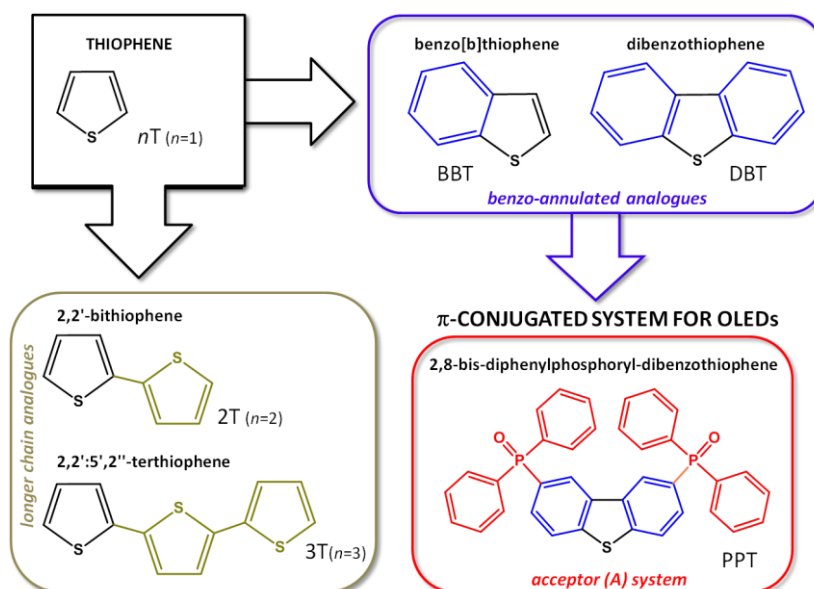
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$\pi$ -Conjugated molecular systems are of growing interest in the field of organic electronics [1], due to the possibility to combine building block molecules to form more complex structures tuned to the desired device efficiency and performance in OLEDs [2]. In a typical device, the photoactive material is made by donor (D) and acceptor (A) counterparts designed by combining their electron donor and acceptor properties connected (or not) by covalent bonds through proper  $\pi$ -bridge linkers (D- $\pi$ -A) [3]. Thiophene-containing molecules [4] are well-known electron donors which are considered suitable donors/ $\pi$ -bridges for D- $\pi$ -A molecular systems, capable to improve the light harvesting efficiency and charge transport properties, facilitating the electron migration from the donor to the acceptor counterparts. Furthermore, the introduction of  $\pi$ -conjugated ring-annulated moieties, such as benzene, simultaneously extends the  $\pi$ -conjugation and improves the stability of the resulting thiophene-based electron-donors and  $\pi$ -bridges for the assembling of organic electronic materials.

The study here presented is an excursus focused on our experience about electronic structure characterization of simple thiophene-containing building block molecules (Thiophene (T) [5, 6], Bithiophene (2T), Terthiophene (3T)) and of thiophene benzo-annulated building blocks such as benzo[b]thiophene (BBT) and dibenzothiophene (DBT) [7]. All the molecular structures of cited molecules have been reported in Figure 1.

Taking advantages from their gas phase photoemission and photoabsorption properties, the final goal is the comprehensive electronic structure characterization of some technological interesting complex systems like the 2,8-bis(diphenylphosphoryl)dibenzo[b,d]thiophene (PPT) (see Fig. 1). The PPT is a promising ambipolar host-guest material recently introduced in OLEDs [8] and formed by two diphosphine oxide moieties functionalizing the small dibenzothiophene (DBT) core. The phosphine oxide groups act as breaking points of  $\pi$ -conjugation between the core and the outer groups, leaving the electronic structures of the compound practically matching those of the central DBT moiety [8].

In summary, we will present a combined experimental and theoretical excursus related to the gas phase electronic structure of simple thiophene-based, benzo-annulated thiophene building blocks and a more complex acceptor  $\pi$ -conjugated system (PPT) employing X-ray photoelectron spectroscopy (XPS) and near-edge x-ray absorption fine structure (NEXAFS) spectroscopy performed at GasPhase beamline of Elettra-Sincrotrone in Trieste (Italy).



**Figure 1.** Sketches of all molecules related to the present study.

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## **P8 - Charge induced structural reconstruction at buried STO/YBCO interface.**

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Selected complex oxides can be stacked in multi-layer epitaxial heterostructures exhibiting an enhancement or even new properties with respect to the parent compounds. The electronic reconstruction or the strain at interface in these structures is expected to induce modifications of the electrical properties, i.e. changing in the electronic density of state. Here we investigate about the transport properties of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  (YBCO) thin film at the interface with  $\text{SrTiO}_3$  (STO) dielectric insulator. We use soft-X-ray angle-resolved photoelectron spectroscopy (SX-ARPES) to access electronic states at buried STO/YBCO interface. We studied for the first time by SX-ARPES the Fermi surface of YBCO thin film and its modification due to the STO/YBCO interface. Complementary investigation by means of resonant photo-emission spectroscopy across the Ti L<sub>2,3</sub> absorption edge was performed to study electronic states of the insulating STO near the YBCO interface.

## P9 - XPS micro liquid-jet of melamine in aqueous solution

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In the past few years, "soft" photocatalysts are emerging as a new class of materials for solar fuel production[1]. Among them, carbon nitride polymers (p-CNH) have been holding the stage since 2009, when Wang *et al.* have shown their ability to produce H<sub>2</sub> from water under visible light irradiation[2]. Despite the mesoscopic structure, recent theoretical investigation has shown that the water-splitting mechanism behind p-CNH can be explained in terms of a photochemical reaction essentially confined on a single molecular unit[3]. At the basis of this reaction, also known as proton-coupled electron transfer (PCET), there is the formation of a hydrogen-bonded complex between the p-CNH heterocycle with water molecules.

In a perspective to experimentally observe the PCET reaction, we have employed the XPS micro liquid-jet technique to study the local electronic structure of p-CNH N-functional groups in the aqueous environment. As model system, we have used the melamine molecule, which is one of the building blocks of p-CNH. In solution, the core level shift between the two non equivalent N atoms (NH<sub>2</sub>, N=C) is halfway between the case of the isolated molecule and that one of the crystalline melamine. By combining biased classical molecular dynamics calculations together with quantum simulations of the XPS spectra, we will attempt to disentangle all possible contributions responsible for the experimental results.

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## P10 - Calculation of MFPADs profiles for different excited states of acetylacetone

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Acetylacetone is a prototype system for studying intra-molecular hydrogen bond interactions. In the ground electronic state, photoionization studies have provided evidence of temperature induced keto-enol tautomerism. In our previous study on this molecule [1], we followed the dynamics of the excited states. It remains to be explored the possibility to discriminate between different excited states through the Molecular Frame Photoelectron Angular Distributions (MFPADs) profiles.

MFPADs are highly characterizing signatures of the final ionic states. In particular, they are really sensitive to the nature of the final state which is embodied in the corresponding Dyson orbital. The use of Dyson orbitals, computed through the Complete Active Space Self-Consistent Field method, allows a correlated description of the initial and final ionic bound states. Dyson orbitals are coupled to accurate one particle continuum orbitals obtained as a continuum solution of the Kohn-Sham Hamiltonian built from the DFT ground state density [2, 3].

The calculation of MFPADs profiles to differentiate excited states can open the way to the possibility of a clear discrimination for all the cases where the recognition of excited states is otherwise tricky.

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## P11 - Shaping of Synchrotron radiation beams by spherically bent optical devices

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Third generation synchrotron radiation sources and free-electron laser (FEL) sources providing highly brilliant X-ray beams will allow to investigate the structure and dynamics of matter from atomic distances to meso- and macro- dimensions. Generating a small and an intense spots is a critical issue to optimize the experiment on different type of samples [1,2].

The experimental demands of the new powerful sources require the development of new optical elements capable to focus and/or shape the beam as well as to filter the radiation spectrum, to shift and control the energy of the emitted light. In particular, the propagation of UV and soft x rays through compact focusing devices is a strategic, but extremely challenging issue, in particular for the next generation of coherent UV and X-ray sources. New optical devices and dedicated experimental setup have to be designed and tested.

In our case, synchrotron radiation sources have been used to characterize the properties and the angular distribution at the exit of flat and spherically bent Micro-Channel Plate (MCP) devices with different radii of curvature. Experiments performed both at BESSY (Berlin) and Elettra (Trieste) have shown that beams with energy ranging from 450 eV to ~ 2 keV can be focused by thin spherically bent MCPs with curvature from 30 to 50 mm. Experimental data point out that the spot or the circle of least confusion is obtained at distances smaller than R/2 between the detector and these thin devices. Moreover, data point out a clear focusing phenomenon with an increased flux density in this focal spot. All experimental results can be explained in the terms of the wave theory for radiation passing through a polycapillary system [3,4].

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## P12 - Photoelectron and nuclear dissociation dynamics of gas phase molecules studied with Synchrotron Radiation

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Gas phase small molecules interacting with electromagnetic radiation are valuable model systems to study fundamental aspects of photoemission processes. Accurate experimental measurements, combined with state-of-the-art *ab initio* theoretical predictions, can allow, for instance, a deeper understanding of the complex role played by electron correlation in molecular photoionization. Recent work, exploiting the unique features of Synchrotron Radiation and performed with specifically designed experimental setups, provided accurate values of dynamical photoionization observables, i.e. partial cross sections, photoelectron angular distributions, and dichroism coefficients, over a wide photon energy range. The specific case of epichlorohydrin, chosen as prototype chiral molecule, whose valence photoionization dynamics was investigated in the Cl 3*p* Cooper minimum region, will be described in detail. Here, the emphasis is put on the importance and the final state specificity of the electron correlation effects, and the accuracy of their theoretical description by current state-of-the-art *ab initio* methods.

Furthermore, case studies of molecular dissociation dynamics will be given, where 3D-multi-particle coincidence detection is used to provide detailed information on appearing potentials of fragment ions, as well as their yields, kinetic energies and angular distributions, as a function of photon energy. Special emphasis is given to dissociation energetics and dynamics of dication species of relevance in atmospheric chemistry and astrochemistry, formed by XUV and soft x-ray excitation. Perspective of investigations that will be allowed by future experimental upgrades will be envisaged.

## P13 - WO<sub>3</sub> hydrogenation probed by high pressure photoemission

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Hydrogen intercalation into oxides is at the origin of various electronic, optical, and chemical effects relevant for catalysis, photocatalytic water splitting and several other applications [1-3]. In this respect, to investigate hydrogen-induced changes in the oxides electronic structure is of paramount importance. Standard photoemission techniques are incompatible with the atmospheric pressure required for the hydrogen sorption to take place [4]. To circumvent this limitation, we developed a membrane holder for high-pressure X-ray photoemission spectroscopy of oxides deposited on Pd films [5]. The specimen holder is installed into the GasPhase experimental chamber, enabling the first synchrotron-base photoemission investigation of the membrane surface with the hydrogen chemical potential of 1 bar. By performing high-resolution experiments, we reveal valence band structure changes upon hydrogen exposure. Moreover, by exploiting the unique tuneability of the synchrotron radiation, we can probe the hydrogen and oxygen partial density of states in H<sub>x</sub>WO<sub>3</sub>.

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## **P14 - Development of a CIS/TDDFT B-spline Scattering Code for Molecular Ionization Processes in the Weak and Strong-Field Regimes**

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We report on the development of a CIS/TDDFT least-squares B-spline basis set approach to the study of molecular ionization processes in the weak and strong-field regime. The novelty of the approach is due to an efficient implementation of two-electron integrals between multicentric symmetry-adapted B-spline functions. As such, the code is therefore capable of describing ionization events on medium- sized molecular systems. Further *in-fieri* developments include the use of correlated wave functions for the initial and final target states. Applications to small polyatomics in both linear and strong-field ionization regimes will be presented.

## **P15 -The Low Density Matter beamline at the FERMI Free Electron Laser**

### *LDM beamline – Elettra Sincrotrone Trieste*

The light pulses produced by the seeded Free Electron Laser FERMI in Trieste have superior qualities (cleanness, repeatability, coherence, variable polarization) which open new perspectives in the study of atoms, molecules and clusters. The Low Density Matter beamline (LDM) covers many areas of research, from nanoparticle spectroscopy, dynamics, extreme irradiation, and imaging to precision time-resolved spectroscopy, nonlinear spectroscopy, and dichroism of atoms and molecules. Interchangeable pulsed sources allow the production of jets of atoms, molecules, radicals, and clusters thereof (notably: helium droplets and metal clusters, that can further be doped with other species). Pump-and-probe experiment can be performed, using the FEL alone or in combination with an IR users' laser (SLU). The LDM beamline is open to external user since its commissioning, in 2012. The end station houses a velocity map imaging spectrometer, a time-of-flight mass spectrometer, and a scattering detector, and has accommodated other detectors from external users. The modular design of the beamline guarantees the necessary flexibility to those experiments which may require a non-standard configuration.

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