3 The Scientific Case

Synopsis

The FERMI FEL source at ELETTRA is designed to supply photons in a spectral range from 100 to 10 nm, covering the region from the VUV to the lower energy soft X-ray regime. FERMI will be much brighter than the existing third generation synchrotron sources with a temporal structure that meets the essential requirements of structural studies with ultra-short, variable polarization pulses of radiation.

FERMI will be realized in two phases: FEL-1, covering the 100 to 40 nm wavelength range, is designed to operate in the time domain in two complementary operating modes: a) high stability and b) high intensity. FEL-2, covering the 40 to 10 nm wavelength range, is designed to operate in the frequency domain (high energy resolution) and with relatively long photon pulses. The FERMI science program is structured to allow users to perform high quality experiments already under the specified FEL-1 initial operation parameters and to proceed to ever more demanding experiments and beam requirements as the source performance is improved.

The coherence properties of FERMI beams allow taking single shot images of complex molecules and performing nano-structures imaging. Samples can be probed in time resolved single shot experiments, of great significance to life sciences as well as to environmental, materials and chemical sciences.

The high peak power can trigger non-linear, multi-photon processes never explored before, unperturbed by any pondermotive effects.

The FERMI average beam power, comparable or slightly higher than that of the best synchrotron light sources, will enable first investigations of dilute samples crucial to the understanding of atmospheric, astrophysical and environmental physics as well as to the characterization of nano-sized materials.

The FERMI short pulse duration properties allow studying ultra-fast dynamic processes such as electronic relaxation, bond formation and breaking reactions or conformational molecular changes.

Teams of world-class scientists, leaders in their respective fields, have proposed a first series of experiments exploiting each of these features that are unique to free-electron-lasers, outlined below.

The extremely high brightness and short pulse duration provided by FERMI will open up a new regime of X-ray microscopy. With present synchrotron-based X-ray microscopes, radiation damage due to chemical changes, diffusion, and local heating, over timescales greater than microseconds, limits the resolution achievable in studying living systems to ~20 nm. This limitation can be circumvented by using intense pulses of duration shorter than that of any process that causes structural changes over time scales longer than the resolution of interest, such as delivered by FERMI. Indeed, flash imaging can be extended at FERMI to atomic resolution, for imaging of single molecules.

The high flux of the FERMI FEL will improve the lateral resolution and increase the data acquisition rate of the full-field X-ray microscope (FFXM). For instance, X-ray fluorescence microscopy may be extended to microscales by exciting high-lying electron levels In such experiments the typically low cross sections will be compensated by the several orders-of-magnitude higher flux available at FERMI. In conjunction with the FFXM, the coherence of the FERMI output radiation also allows using lensless imaging techniques such as phase contrast imaging, micro-tomography and holography.

Small particles, such as nanocrystals and clusters, are different from bulk matter; finite size effects influence effectively all properties of matter. The finite number of constituents and the discrete nature of of phonon, electron, or other quasi-particle densities of states alter the constituent interactions and lead to different geometric and electronic ground state configurations and different dynamical behavior. The results are strong changes in optical, magnetic, chemical and thermodynamic properties. The FERMI spectral range of 100 to 10 nm is one in which plasma absorption processes break down and new physical processes involving core levels become important. Clusters, as a form of matter intermediate between atoms and bulk solids, are ideal samples to study these processes. By varying their size, one can investigate the role of inner- and interatomic, i.e., collective, effects, thus contributing to our understanding of energy deposition, energy transfer, and radiation damage in matter.

3.1 Introduction

Chemical, physical and biological processes are intrinsically dynamic in nature since they are related to electronic and atomic structures that evolve with time. The characteristic time scales span from a few femtoseconds, in the case of electronic processes, to a few tens or hundreds of femtoseconds, in the case of atomic and molecular processes. Furthermore, other phenomena controlling the behavior of critical systems may occur over relatively longer time scales, ranging from a few picoseconds to a few hundreds of picoseconds or more. These phenomena include phase transitions, such as those related to magnetic ordering or to superconductivity. The capability of measuring such processes at the relevant time scales will open totally new perspectives in the way they can be studied. In particular, direct observation of electronic processes, of structural dynamics and of dynamic critical phenomena such as phase transitions, opens up an unexplored landscape in the study of condensed matter physics.

Such perspectives were already evident to the developers of the first coherent sources of femtosecond optical pulses. The availability of ultra-short coherent light pulses has in fact produced remarkable scientific results, recognized by the award of the 1999 the Nobel Prize for Chemistry to Ahmed Zewail for his pioneering work on the application of ultra-short laser infrared spectroscopy to the study of the dynamics of chemical bonds.

Currently available, coherent light sources cover only a limited wavelength range, so that their use is confined to optical and spectroscopic techniques in the infrared, visible and near-ultraviolet range, excluding all measurements needing photons of energy higher that a few eV. There is therefore a strong scientific need for a tunable light source covering the energy range from vacuum ultraviolet (VUV) to X-rays, with a stable and well-characterized temporal structure in the picosecond to femtosecond time domain. To develop such a source international research is moving in three main directions:

1) laser driven light sources using non-linear processes to create very high harmonics,

2) laser "bunch-slicing" techniques based on the interaction between an ultra-short laser pulse and an electron bunch in a storage ring and

3) free-electron-lasers (FEL).

The first two techniques can produce radiation pulses in the femtosecond time domain and in the soft X-ray region, but with low brilliance (i.e. a low useful photon flux on sample). In contrast FELs can produce light pulses with a peak brilliance as much as ten orders of magnitude higher than generated in present third generation synchrotron light sources but with photon energies reaching from the VUV to the hard X-ray region, i.e. from ~10 eV (120 nm) to ~10 keV (0.12 nm) and above.

FEL amplifiers can operate in several different regimes. The most studied ones are SASE (Self Amplification of Spontaneous Emission) and amplification of a coherent input signal generated by a traditional laser harmonic (Seeding). SASE operation can produce very high brilliance but with a pulse temporal structure which is the envelope of a series of micro-pulses with completely random intensity and duration. In contrast, FEL sources based on seeding, while also producing very high brilliance, can deliver coherent radiation pulses with a tailored time profile and intensity. In seeded systems utilizing helical field undulators, one can also fast-tune the polarization of the radiation from linear to circular. For performing reproducible measurements under controlled conditions, seeded FELs therefore represent a superior choice. SASE sources are most useful when the information that one wants to collect does not depend on the pulse temporal structure. They are even indispensable when the wavelength is beyond the range thought practical with seeded systems, due to the lack of suitable laser seeds.

The prospects for the blossoming of a new field of close to fully coherent, ultra-fast X-ray science in physics, chemistry and biology are indeed exciting.

One should nonetheless say that such performances are likely to concern a small minority of the experiments that rely on synchrotron radiation sources. Storage rings are likely to remain the workhorses of synchrotron radiation science for many years to come. By providing X-ray beams with high flux and brightness and outstanding stability, reproducibility and reliability, they will continue to serve the needs of a vast scientific community even as linac-based sources open up new scientific frontiers with their sub-picosecond pulse duration and extremely high peak brightness and coherence.

3.1.1 Required and Delivered Performance of Ultra-intense and Ultra-short Duration Radiation Sources

A common measure of the performance of synchrotron radiation sources are graphs of the time-averaged flux (photons/s/mrad/0.1%BW) and brightness (photons/mm^2/mrad^2/0.1%BW) available for experiments as functions of X-ray energy.

More recently other metrics have been proposed such as the flux density on a small sample. Another metric is the useful flux within the phase space acceptance of a small sample such as a 50-100 micron protein crystal with a mosaicity of several milliradians [1]. With increasing scientific interest in short pulses, the peak (or instantaneous) values of these metrics during the pulse have become important figures-of-merit to complement the generally used spectral curves of flux and brightness.

As far as user requirements are concerned, a contrasting, non-exhaustive list of desired beam properties is:

- as many as 10^{12} X-ray photons in a single ultra-fast pulse;
- pulse intensities not exceeding 10^8 photons with pulses spaced by the relaxation time of the process under investigation;
- auxiliary laser pulses synchronized to within ~20 fs of the X-ray pulse;
- asynchronous operation possible;
- high (~1%) of pulse-to-pulse reproducibility and stability;
- tunable polarization of the radiation;
- multi-colour X-rays on sample.

The performance data of several types of X-ray sources from the point of view of peak brightness and pulse duration are compared in Figure 3.1.1 [2] and Table 3.1.1.

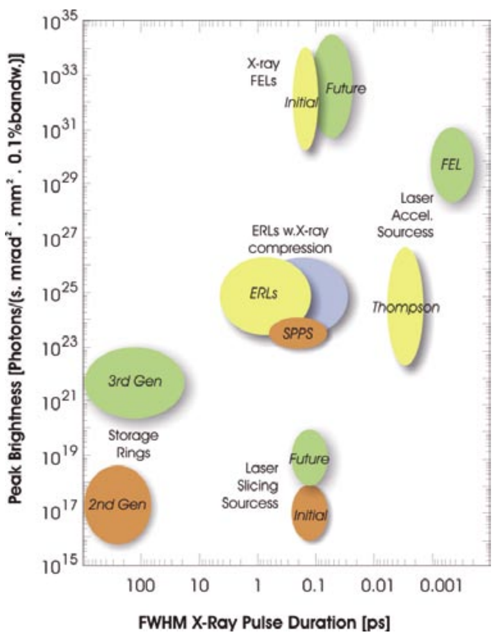

Figure 3.1.1:
Peak brightness and pulse duration ranges of next generation light sources. The time average brightness is the peak brightness times the duty factor [2].

Table 3.1.1: Additional characteristics of X-ray sources.

	Maximum Duty Factor	*Laser synchronization*	*Pulse repetition rate*
Storage rings	~10^{-3}	No	10 – 100 MHz
Slicing Sources	~10^{-9}	Limited	1 – 10 kHz
ERLs	~10^{-3}	No	10 – 100 MHz
ERLs w. X-ray pulse compression	~10^{-8}	Yes	10 kHz
SPPS beamline at SLAC	~10^{-11}	No	100 Hz
Warm linac driven X-ray FELs	~10^{-10}	Some	100 – 1000 Hz
Laser Accel. Sources	~10^{-12}	Yes	1 – 10 kHz

3.1.2 Short Review of the Scientific Motivations for Major FEL Projects

Four classes of information, depending on the photon energy, can be extracted from the study of the interaction of radiation with matter.

Electronic processes in the valence band and collective mode excitations in elastic and inelastic scattering processes can be studied using photons with energy between the UV and far VUV regions (wavelength between 200 nm and 40 nm)

Photons in the extremely soft X-ray range (λ~10 nm) allow to taking advantage of the specificity of shallow core levels of chemical elements to obtain phase contrast images, also by microscopy.

Photons with wavelength around 1 nm, comparable to the typical inter-atomic distances, are mainly used in materials science, in particular to study deeper core levels, such as the L2,3 edges of transition metals, and thus of many magnetic systems, superconductors and highly correlated electronic systems. They also allow the study of the K-edges of oxygen and carbon, which are the main constituents of organic and biological materials and are used in technological applications such as nano-fabrication.

From the above one can conclude that radiation sources with wavelength in the UV (200 nm) to soft X-ray (1 nm) range have great relevance for the very large and important fields concerning the study of chemical, physical and material properties suitable for technological applications.

If one adds to the high brilliance, typical of FEL radiation, polarization and control of the beam temporal structure, one sees that it becomes possible to study the mechanisms of structural dynamics of a wide range of materials and material states, covering both hard and soft matter.

To study ultra-fast dynamics (from picoseconds to femtoseconds) in matter, one can use the "pump-probe" (or stroboscopic) technique, based on exciting a sample with a suitable wavelength (pump) followed by probing the excited sample with a radiation pulse, in general of a different wavelength, whose duration is shorter than the characteristic time of the process under observation. The delay time between the pulses is optically controlled so that the short pulse works as a probe of the temporal evolution is of the process under observation. The two wavelengths can be delivered by the same source or from two (appropriately correlated) different sources.

3.1.3 The FERMI@Elettra Project

The FERMI FEL will be built in two phases called FEL-1 and FEL-2.

FEL-1, covering the 100 to 40 nm wavelength range, is designed to operate in the time domain and in two complementary modes of operation: a) high stability mode and b) a high intensity mode.

FEL-2, covering the 40 to 10 nm wavelength range, is designed to operate in the frequency domain (high energy resolution) and with relatively long photon pulses (~ 1 ps).

These design choices will yield a source quite unique among the other FELs under construction or proposed for construction in Europe, USA and Japan.

3.1.4 FERMI@Elettra Photon Parameters

The initial FERMI science program is structured to allow performing experiments with different, and increasingly more demanding photon parameters.

Consequently, in order for high quality experiments to be performable from the very beginning of FEL-1 and FEL-2 operation, classes of experiments are expected to start taking data in the following order:

- Single shot, High Peak Brilliance Experiments;
- Pump-Probe Experiments in both the time and the frequency domains;
- High Energy Resolution Experiments in the frequency, time and non-linear spectroscopy domains.

The idea is illustrated in the following block diagram.

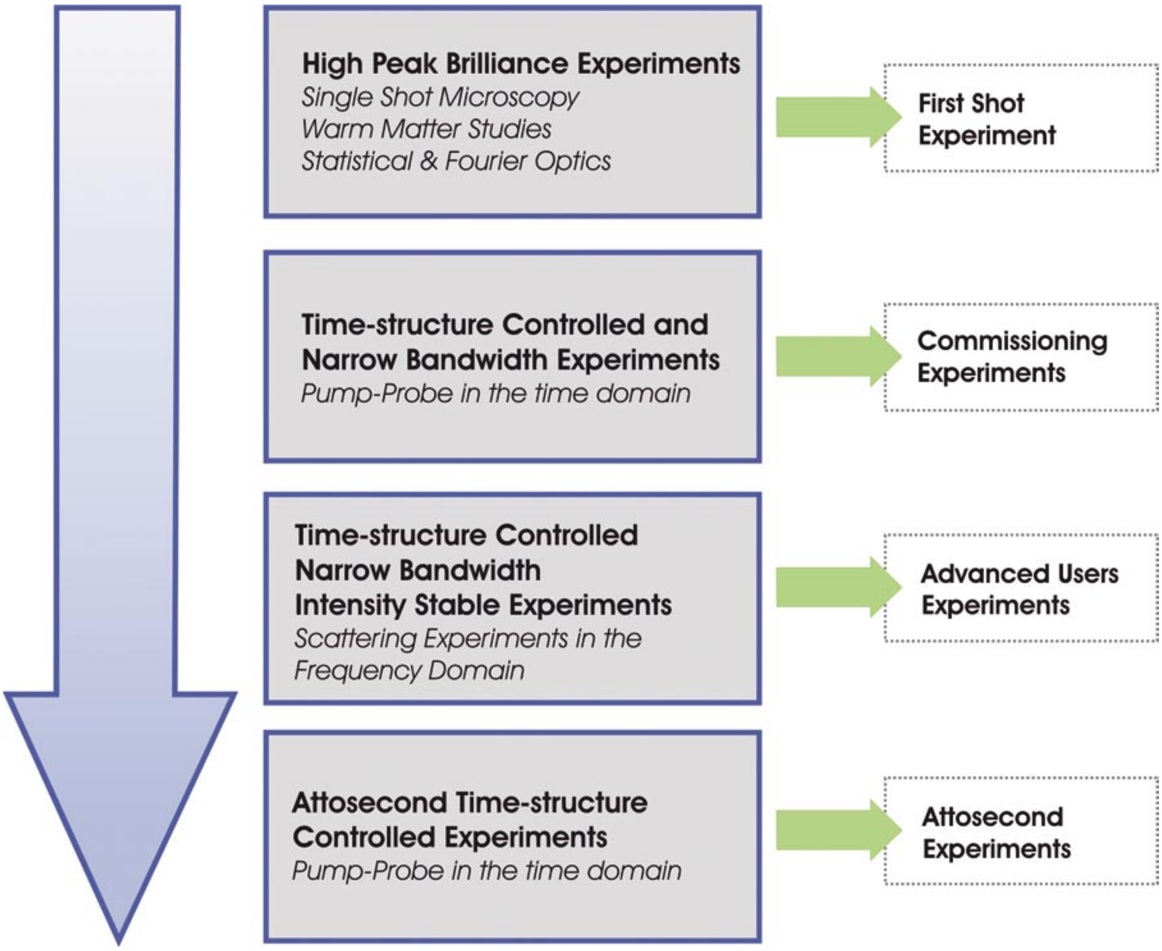

Figure 3.1.2:
Accessible experiments by increasing the FEL performances.

Three different stages of FEL operation have been defined on the basis of beam quality, described by the delivered set of beam parameters: the first, characterised by the "acceptance parameters", defines the end of commissioning, the second is characterised by a "standard parameters" set and the third by having the "advanced parameters" set. The parameter sets for each regime, defining the feasibility of the experiments and therefore driving the technical design of FEL-1 and FEL-2, are listed in Tables 3.1.2 through 3.1.7.

Table 3.1.2: Starting parameters for FEL-1.

Parameter	*Value*	*Comments*
Photon energy range	100 ÷ 40 nm	
Pulse length	50 ÷ 100 fs	
Bandwidth		Incoherent light
Polarization		Not Required
Repetiton rate	10 (50) Hz	Single shot experiments
Peak power (*)	> 2.5 GW	Full Power Requested
Harmonic peak power	Not requested	
Photons per pulse (*)	$> 10^{14}$	
Peak brightness (*)	$> 10^{31}$	Ph/s/mm^2/mrad^2/0.1%bw
Pulse-to-pulse stability		
Pointing stability	< 20 μrad	
Spot size (intensity)	280 μm	
Divergence (intensity)	50 (at 31 eV) μrad	
Beam Properties	Gaussian	
Time jitter	150 fs	

(*) 200 fs pulse length.

Table 3.1.3: Starting parameters for FEL-2.

Parameter	*Value*	*Comments*
Photon energy range	40 ÷ 10 nm	
Pulse length	100 ÷ 200 fs	
Bandwidth		Incoherent light
Polarization		Not Required
Repetiton rate	10 (50) Hz	Single shot experiments
Peak power	1 GW	Full Power Requested
Harmonic peak power	Not requested	
Photons per pulse	$> 10^{13}$	
Peak brightness	$> 10^{31}$	$Ph/s/mm^2/mrad^2/0.1\%bw$
Pulse-to-pulse stability		
Pointing stability	$< 20\ \mu rad$	
Spot size (intensity)	$200\ \mu m$	
Divergence (intensity)	$15\ \mu rad$	
Beam Properties	Gaussian	
Time jitter	150 fs	

Table 3.1.4: Standard parameters FEL-1.

Parameter	*Value*	*Comments*
Photon energy range	100 ÷ 40 nm	
Pulse length	50 ÷ 100 fs	Any value in between is acceptable
Bandwidth	20 meV	Close to TL
Polarization	Linear / Circular	Variable
Repetiton rate	10 (50) Hz	
Peak power	1 ÷ 5 GW	
Harmonic peak power	Few %	
Photons per pulse	$> 10^{14}$	
Peak brightness	$> 10^{31}$ Ph/s/mm^2/mrad^2/0.1%bw	
Pulse-to-pulse stability	20-30%	rms
Pointing stability	< 20 μrad	
Spot size (intensity)	280 μm	
Divergence (intensity)	50 μrad	
Transverse Stability	About 10% spot dimension	
Wavelength Stability	5 10^{-4}	
Beam Properties	Gaussian	
Waist location variation	2 m	
Tuneability	10 ÷ 20%	Around given photon energy
Time jitter	150 fs	

Table 3.1.5: Standard parameters FEL-2.

Parameter	*Value*	*Comments*
Photon energy range	40 ÷ 10 nm	
Pulse length	100 ÷ 200 fs	Any value in between is acceptable
Bandwidth	5 meV	Closed to TL
Polarization	Linear / Circular	Variable
Repetiton rate	10 (50) Hz	
Peak power	0.5 ÷ 1 GW	
Harmonic peak power	Few %	
Photons per pulse	$> 10^{12}$ in 1 meV BW	
Peak brightness	$> 10^{31}$ Ph/s/mm^2/mrad^2/0.1%bw	
Pulse-to-pulse stability	About 50 %	rms
Pointing stability	$< 20\ \mu$rad	
Spot size (intensity)	About 200 μm	
Divergence (intensity)	15 μrad	Not restrictive
Transverse Stability	About 10% spot dimension	
Wavelength Stability	10^{-5}	rms
Beam Properties	Gaussian	
Tuneability	10-20%	Around given photon energy
Time jitter	150 fs	

Table 3.1.6: Advanced Parameters FEL-1.

Parameter	*Value*	*Comments*
Photon energy range	100 ÷ 40 nm	
Pulse length	50 ÷ 100 fs	Any value in between is acceptable
Bandwidth	About 20 meV (FWHM)	Close to TL
Polarization	Linear / Circular	Variable
Repetiton rate	50 Hz	
Peak power	1 ÷ 5 GW	
Harmonic peak power	Few %	
Photons per pulse	$> 10^{13}$	
Peak brightness	$> 10^{31}$ Ph/s/mm^2/mrad^2/0.1%bw	
Pulse-to-pulse stability	5 %	rms
Pointing stability	$< 20\ \mu$rad	
Spot size (intensity)	280 μm	
Divergence (intensity)	50 μrad	
Transverse Stability	About 10% spot dimension	
Wavelength Stability	$5\ 10^{-4}$	rms
Beam Properties	Gaussian	
Waist location variation	2 m	
Tuneability	10 ÷ 20%	Around given photon energy
Time jitter	150 fs	

Table 3.1.7: Advanced Parameters FEL-2.

Parameter	*Value*	*Comments*
Photon energy range	40 ÷ 10 nm	
Pulse length	100 ÷ 1000 fs	Any value in between is acceptable
Bandwidth	> 5 meV	Closed to TL
Polarization	Linear / Circular	Variable
Repetiton rate	50 Hz	
Peak power	0.3 - 1 GW	
Harmonic peak power	Few %	
Photons per pulse	> 10^{13} in 1 meV BW	
Peak brightness	> 10^{31} Ph/s/mm^2/mrad^2/0.1%bw	
Pulse-to-pulse stability	About 20 %	rms
Pointing stability	< 20 μrad	
Spot size (intensity)	About 200 μm	
Divergence (intensity)	15 μrad	Not restrictive
Transverse Stability	About 10% spot dimension	
Wavelength Stability	10^{-5}	rms
Beam Properties	Gaussian	
Tuneability	10 ÷ 20%	Around given photon energy
Time jitter	150 fs	

3.1.5 Scope of the Science with FERMI@Elettra

The FERMI FEL source will cover the range wavelength range from VUV to the lower energy portion of the soft X-ray region. Therefore, in order to provide new scientific opportunities, it must be much brighter than the existing third generation synchrotron sources and have the temporal structure needed for studies requiring ultra-short pulses with variable polarization. In addition, experimentalist will have a further variety of operational options provided by the possibility of bringing into the FEL experimental hall, photon beams extracted from the adjacent ELETTRA synchrotron radiation source.

The available range of scientific applications covers several fields of hard and soft matter science:

- chemical reaction dynamics;
- study of the electronic structure of atoms, molecules and clusters;
- biological systems;
- inhomogeneous materials on a microscopic scale;
- geophysics and study of extra-terrestrial materials;
- material properties under extreme conditions (pressure, temperature, etc.);
- surfaces and interfaces;
- nano-structures and semiconductors;
- polymers and organic materials;
- magnetism and magnetic materials;
- superconductors and highly correlated electronic materials.

3.2 Science Case

3.2.1 Exploiting the Main Photon Parameters

The laser-like properties of the FERMI FEL output radiation, coherence, high peak and average power and ultra-short pulse, will unlock the gates to new scientific frontiers, allowing one to perform new classes of experiments, not feasible using incoherent synchrotron radiation sources.

Coherence will open up a new era for imaging, where samples can be probed in time resolved single shot experiments. Coherent imaging has great potential in life sciences as well as in environmental, materials and chemical sciences.

High peak power at soft X-ray photon energies triggers non-linear, multi-photon processes in a regime never explored before, unperturbed by any pondermotive effects, which scale with the square of the inverse frequency and thus complicate tremendously the understanding of such reactions when using optical lasers.

High average power, comparable or slightly higher than that of present synchrotron sources, in pulses far shorter than available from synchrotrons, enables studying for the first time dilute samples of paramount importance in atmospheric, astrophysical, environmental physics as well as in the characterization of nano-size materials. Moreover, it allows access to fundamental reactions governed by small cross sections.

Ultra-short time properties will open the door to visualize ultra-fast nuclear and electronic dynamics such as in electronic relaxation, bond formation and breaking reactions or in conformational molecular changes.

The interest in the science described above is confirmed by the first and second call for proposals, for the initial round of experiments at FERMI, having been responded to by world-class teams of scientists – leaders in their respective fields of study. The letters of intent from these teams are presented in the accompanying appendix.

In the following sections the scientific goals to be pursued in this first round of experiments is briefly described.

3.2.2 Ultra-fast Coherent Imaging and Nano-spectroscopies

The extremely high brightness and short pulse duration of VUV- and X-FELs allow one to explore a new regime of X-ray microscopy. With current synchrotron-based X-ray microscopes, the optics for which have steadily been improving, the highest resolution achieved on living systems has reached a limit of ~20 nm, imposed by radiation damage. The damage is caused mainly by chemical changes, diffusion, and local heating over timescales greater than microseconds [3,4]. This resolution barrier can be overcome by using intense pulses of duration shorter than that of any process causing structural damage. [5]. Indeed, the concept of flash imaging can be extended to achieve atomic size resolution [6] for the imaging of single molecules.

The experimental method of choice to perform imaging with resolution of ~20 nm to <0.2 nm, is single-particle diffraction [7,8]. While, for given resolution, other methods require less dose (and hence induce less damage) [9], diffractive imaging does not require any optics and hence does not impose any technological limit to the resolution.

At FERMI, the long-term research program in ultra-fast, time-resolved, coherent diffraction imaging has three main aims:

a) determine the ultimate limits of imaging with FEL radiation,
b) study the interactions of matter with X-ray pulses,
c) develop a program of high-resolution, biological imaging.

Extending diffraction imaging to the ultimate goal of atomic resolution with future X-ray FELs will require much learning and the development of new experimental techniques. This extension demands an ultra-fast, bright, coherent source leading to new science in its own right, capable of high-resolution single-shot imaging beyond the radiation damage limit, time-resolved high-resolution imaging of the interaction of FEL pulses with matter, and high-resolution time-resolved soft-X-ray imaging of the interaction of particles with optical laser pulses, for example, to study alignment of particles with high-field lasers.

To achieve these goals the FERMI science program has approved the proposal of a team that will bring to Sincrotrone Trieste new technologies it has been developing over the last several years, including:

(i) high-efficiency multilayer, submicron focusing optics,
(ii) a unique diffraction camera based on a multilayer mirror filter,
(iii) beam-splitting and pump-probe imaging methods,
(iv) injection techniques to guide particles, under vacuum, into the FEL beam,
(v) robust image reconstruction methods, and
(vi) diagnostics and alignment aids.

The multilayer systems were developed for high-power operation and are extremely stable at temperatures as high as 500 °C. They have been tested under high peak power conditions at the FLASH soft-X-ray FEL. The team is tooled-up to fabricate multilayer optics operating at near-theoretical efficiency with atomic spacing dimensional control across large areas. The group novel diffraction camera uses one such multilayer mirror with a change in d spacing by a factor of two over a transverse distance of 25 mm. The multilayer optics operates at normal incidence for wavelengths from 3 nm to 32 nm.

The team will carry out high-resolution, two-dimensional imaging of biological materials beyond the radiation damage limit by flash imaging in a single shot, which is expected to produce the highest achieved resolution images of cells and sub-cellular structures in an unmodified state. Another major field of investigation will be the study of the interaction of FEL pulses with atomic clusters and particles, for the validation of molecular dynamics and hydrodynamics models [6,10,11,12,13].

The team is also developing particle injection systems based on electrospray to be integrated into the FERMI end-station. Such systems will deliver particles from solution or atomic clusters of noble gases into the interaction region of the focused FEL beam, allowing to study the interaction of clusters and particles with the radiation pulse, to explore the dynamics of Coulomb explosions and the resolution limits that can ultimately be achieved. Three-dimensional imaging of reproducible samples injected into the beam will exploit algorithms specially developed to produce imaging of molecules with atomic size resolution.

3.2.3 Full Field X-ray Microscopy and Lensless Imaging

The Full-field X-ray Microscope (FFXM) will benefit from the high flux of the FERMI FEL, allowing a gain in achieving higher lateral resolution, as well as a faster acquisition rate. A challenging possibility for x-ray fluorescence microscopy can be explored, at micro-scales, exciting the high-lying electron levels. The typically low cross sections will be compensated by the several orders-of-magnitude higher FERMI flux.

In conjunction with the FFXM, the coherence of FEL radiation is fundamental to lensless imaging techniques such as phase contrast imaging, micro-tomography and holography. Recent coherent light scattering experiments have shown that phase information can be retrieved by iterative algorithms applied to an over-sampled diffraction pattern [14,15], or through a mask-based, holographically formed interference pattern [16]. In addition, extension of oversampling methods to three-dimensional imaging has been experimentally demonstrated on micron-sized, nanostructured, Ni arrays at a resolution of 50 nm (see Figure 3.2.1).

Since lensless imaging does not require focusing systems, affected by inherent technological constraints that limit the resolution, the coherence and intensity of the FERMI FEL open up unprecedented

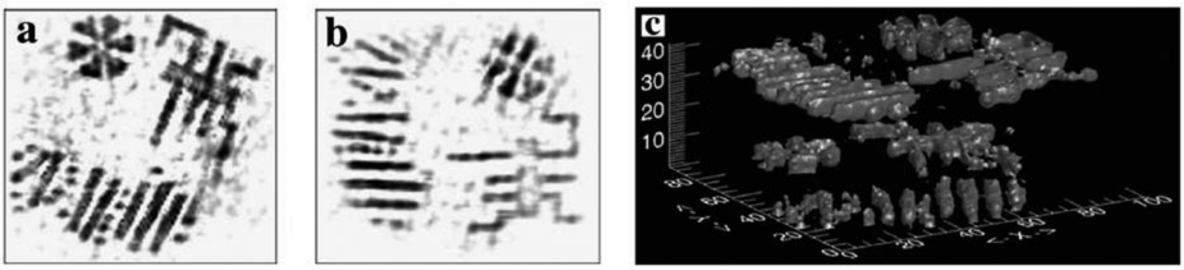

Figure 3.2.1:
The reconstruction of a 3D nanostructured material at 50 nm resolution. (a), (b) The reconstructed top and bottom layered pattern. (c) The reconstructed 3D structure displayed in iso-surface rendering [17].

opportunities. First pilot experiments using a 32 nm beam at DESY have demonstrated a lateral resolution of 60 nm. For FEL-2 at FERMI, imaging samples at the diffraction limit of 10 nm can be envisaged.

A team led by Sincrotrone Trieste researchers is proposing to design and implement on one of the two FEL beamlines a "beam-tailoring" optical approach to lensless microscopy to explore new regimes of FFXM and lensless imaging. The planned research includes implementation of non-conventional optics, along with the development of next generation detectors tailored to the demands of 'one-shot' microscopy.

The beam tailoring requirement for this line of research is simply demagnification of the beam spot delivered by the source to the FFXM. Technical challenges for the experimenter are

a) source displacement as a function of beam energy,

b) shot-to-shot, longitudinal bunch position jitter compatible with spot sizes of <10 μm,

c) preservation of the spatial coherence of the FEL beam.

The experimental station can easily accomodate the optical elements for FFXM and the same detector can be used also for lensless imaging. The main experiment components are: (i) transport system for samples, sample holder and precise manipulation stage, (ii) stage for the optical elements, (iii) fast detector to monitor the diffraction pattern and (iv) long working distance optical microscope for pre-alignment of the sample with the FEL beam, placed behind the focusing optics to ensure optimal illumination of thin samples (e.g., cell-type structures). The detector must have a central hole or be otherwise shielded from the direct FEL beam. The sample stage is particularly critical, because it must allow reproducible feeding of identical samples after each shot.

The source characteristics required for the microscopy branch of the FEL microscopy beamline, including the FFXM, are as follows:

Parameters considered for the first harmonic:

Bunch length 200 fs

Energy bandwidth ≈ 3 meV

Peak Power 0.4 GW (2 10^{13} ph/s) down to 40 nm (10-30 eV) FEL-1 (80 mJ)

Peak Power 0.15 GW (2 10^{12} ph/s) up to 10 nm (30-120 eV) FEL-2 (30 mJ)

Source geometry

FEL-1:

Source waist 280 μm (FWHM≈160 μm)

Divergence* (σ): 140μrad @ 10 eV; 70μrad @20 eV; 50μrad @30 eV

FEL-2:

Source waist 210 μm (FWHM≈120 μm)

Divergence* (σ): 65μrad @ 30 eV; 33μrad @ 60 eV; 22μrad @ 90 eV; 15μrad @ 120 eV

* (Divergences are diffraction limited).

3.3 Low Density Matter - Atomic, Molecular and Cluster Physics

3.3.1 Cluster and Nanoparticle Spectroscopy

Small particles are different from bulk matter; finite size effects influence all properties of matter. In particular, the finite number of constituents and the discrete nature of phonon, electron, or other quasi-particle densities of states alter the constituent interactions and leads to different geometric and electronic ground state configurations as well as influencing the dynamical behavior of nanoscale matter. This results in strong changes of optical, magnetic, chemical and thermodynamic properties [18].

Although a large variety of such effects has been studied in recent years, in many cases a deeper insight was hampered by the lack of adequate light sources for spectroscopy of gas phase nanoparticles. The FERMI FEL will allow performing much broader, in-depth studies in the several areas discussed here below.

Electronic structures of nanoparticles

Examples of important quantum size effects in small particles are the highly discrete electronic density of states in metal clusters [19], the metal/nonmetal transition in divalent metals [20], the indirect/direct band-gap transition in silicon clusters [21], the general increase of the band-gap in semiconductor clusters [22], or the increase of the magnetic moment of ferromagnetic clusters [23]. For other properties like superconductivity only some evidence for related effects have been found in small particles [24]; the question of down to what size "classical" superconductivity exists is completely open.

Even a seemingly easy problem such as the total valence bandwidth in nanoparticles, is not yet solved. The calculated and measured bandwidths of simple structures such as sodium clusters differ significantly [25]. The situation is even worse in the case of d-bands of transition metals that determine important properties such as magnetism or chemical reactivity. In that case, bandwidths and positions are often unknown. The same applies to dynamic properties such as ultra-fast electronic relaxation processes after d-band or shallow core state excitation. The related spectroscopic features such as line shapes (with phonon and low energy electronic contributions) or satellite structures (strong correlations as for the "6 eV satellite" in nickel) constitute an entirely unexplored, yet interesting and important, field of research - no gas phase experiments on size-selected clusters exist at all.

The reason for this lack of knowledge, despite the wealth of existing photoelectron spectroscopy results concerning free clusters and nanoparticles, is that the limited photon energy of standard laser systems allows studying electronic states only down to ~5 eV below the Fermi energy. This limitation prevents measuring the full valence electron structure as well as, for example, performing photon energy dependent spectroscopy across shallow core edges (resonance photoemission [26]), data that would greatly contribute to the understanding of the evolution of the electronic structure as a function of cluster size.

The beam intensities available at 3rd generation synchrotron radiation facilities are still far below what is required for meaningful gas phase experiments. Size-selective spectroscopy at the FEL light source will therefore allow measurements of unprecedented significance and will undoubtedly lead to a deeper understanding of the electronic structure of nanoscale metals and semiconductors, as well as of electron correlation effects in solids in general.

Femtosecond dynamics and pump-probe spectroscopy

To follow the temporal evolution of intra-molecular, photo-induced processes, femtosecond pump-probe techniques are the only means of resolving, in real time, relaxation processes and nuclear motion. To date such measurements cover the range of conventional femtosecond lasers. Higher harmonic generation has been used to form ultra-short pulses, even in the attosecond time range, at VUV wavelengths [27]. Since the Nobel awarded work of Zewail and others [28], femtosecond real-time spectroscopy has been applied in many fields of chemistry and physics. The group of Stienkemeier has successfully combined femtosecond lasers with helium nano-droplet isolation experiments, and pump-probe techniques are routinely performed using standard lasers in the IR, VIS and UV range. The multiple aspects of this work are summarized in a recent review article in J. Phys. B [29]. Elementary excitations of superfluids, desorption and energy relaxation in nano-clusters, wave packet propagation in small molecules, bond formation processes, as well as quantum interference oscillations requiring resolution down to the attosecond range have been carried out. The group of v.Issendorff has also applied fs pump-probe spectroscopy to study electron emission and electron-phonon coupling in highly excited sodium clusters [30].

However, the number of photons per pulse, as much as a factor of 108 smaller than that available from an FEL, prevented carrying out sophisticated experiments in dilute systems. FEL high intensity femtosecond pulses will therefore be the first useful tool for studying time resolved ESCA (usually associated with high binding energies) photoelectrons, photo-absorption and photoemission.

Studies at ultra-low temperatures

HElium NanoDroplet Isolation (HENDI) has become a standard technique to form neutral and charged molecules, clusters and nanostructured complexes at ultracold temperatures. Here a beam of superfluid helium droplets (HeN, 102 < N < 108) is produced and doped with molecules and clusters, or with the respective charged entities of interest. The droplets cool the embedded species to 380 mK at which temperature, even for larger species, only vibrational ground states are populated. Because atoms or molecules can be picked-up from different sources sequentially, otherwise unfeasible experiments can be done under ultra-low temperature conditions. The nano-droplets act as an ultra-cold trap in which the weak interaction with the superfluid helium environment guarantees minimal matrix perturbations. The well-collimated beam trapped particles traveling in ultra high vacuum provides a stable regenerating target even for complex, radiation-damage-sensitive molecular structures. FERMI XUV radiation will extend optical techniques with these dilute targets to desired higher excitation energies.

Thermodynamics of nanoparticles

Caloric curves describe the relation between the internal energy and the temperature of a thermodynamic system. Knowledge of the caloric curve provides an exhaustive insight into the thermodynamics of the system, by revealing the different thermodynamic potentials as well as phase transitions such as boiling, melting and structural transitions.

Note that the thermodynamics of small systems strongly differs from that of the bulk. On one hand they involve surface effects that typically lower melting points and latent heats [31-33] while in small clusters with specific crystalline structures such effects are reversed [34]. On the other hand, there are substantial differences between the textbook thermodynamics of infinite systems and that of clusters, due to the limited number of degrees of freedom of the latter. In particular, in infinite systems the singularities that indicate phase transitions are broadened, and specific effects such as negative heat capacities can be observed [35]. The experimental method to access caloric curves of small clusters uses the laser fragmentation pattern of mass selected and thermalized clusters [31]. The temperature influence is visible in the fragmentation pattern and can be compared to a controlled variation of the energy using a laser. The fragmentation spectra relate energy and temperature and therefore serve as caloric curves of mass selected clusters. Strongly bound systems like group 3 metals or noble metals, that are of high general interest, cannot be studied yet due to the lack of high intensity lasers with photon energies of 3 to 4 times the atomic binding energies.

Chemistry of molecular clusters and nanocrystal interfaces

Reactions at interfaces, such as aerosols or nanocrystal surfaces, have emerged in recent years as an important issue in fundamental and applied molecular science. Aside from the intrinsic interest in surface reactions, gas phase reactions cannot explain all measured data. A case that has received considerable attention originated from the measurement of large amounts of Cl2 produced by the reaction of radicals with solvated NaCl molecules, in the laboratory [36] and in the marine troposphere. The results could only be explained by the reaction of the radicals with chloride ions accumulated at the surface of the water droplets. A recent “perspective” article in Science highlights the importance of understanding these processes at the water interface [37].

3.3.2 Ultra-fast Cluster Interactions

The understanding of the interaction of high intensity, short-wavelength, short-pulse radiation with matter is essential for virtually all future FEL experiments and even more important for flash imaging of nanosized particles. The FERMI FEL will supply photons in the very interesting spectral regime ranging from 100 to 10 nm in which plasma absorption processes break down and new physical processes involving core levels become important. Clusters as a form of matter intermediate between atoms and bulk solids are ideal samples to study these processes. By varying their size the role of inner- and inter-atomic collective effects can be investigated. These studies will contribute to our understanding of energy deposition, energy transfer, and radiation damage in matter that is essential to plan future experiments. Furthermore, clusters and nanoparticles irradiated by intense FEL pulses exhibit a wealth of interesting non-linear physics covering atomic and cluster physics, biochemistry and plasma physics.

Initial experiments at the FLASH facility at DESY provide an insight into the absorption processes and the ionization dynamics with ultra-fast, intense VUV-pulses in rare gas clusters. The results for single shot imaging of gas phase nanoparticles hold great promise for various types of time-resolved structure determination. These studies are the first steps into a new interdisciplinary field with many fundamental open questions.

The FERMI FEL with its seeding scheme will provide unique possibilities for these studies, such as reproducible and well-controlled pulse shapes (which are extremely helpful for all non-linear studies) and stable synchronization to external lasers.

To make these studies possible experimenters and ELETTRA beamline scientists will work together to develop and build tools for investigating ultra-fast processes in gas phase particles, in particular

- gas phase, molecular beam apparatus with pulsed sources of rare gases and metal clusters,
- time-of-flight based electron and ion spectrometers for the kinematics and momentum analysis of ionization products,

- angle-resolving XUV spectrograph with a 2D position sensitive detector,
- a 2D-scattering detector for high repetition rate experiments on gas phase samples,
- specialized optics for pump–probe experiments with high power density beams.

The experimental team also plans to address, among others, the following topics of interest for FERMI:

1. Time resolved ionization dynamics – Multiple ionization of clusters is expected to proceed on at least two different time scales. The electrons leave the cluster within a few fs, while the Coulomb explosion, i.e., ion motion, takes place on a time scale in the range of several hundred fs to ps, depending on the cluster size. Experiments with optical lasers give strong evidence that the ionization dynamics is sensitive to pulse length and shape [38, 39]. Cluster dynamics will be studied with pump-probe techniques by measuring the intensity of scattered light as a function of the time delay. The measurement can be done by splitting the FEL beam into a low intensity pump pulse (2-5% of the total intensity) and a high intensity probe pulse. In this way the pump pulse inducing the initial non-linear processes will be only a minor contribution to the total scattered signal. Assuming tight focusing into a 5 μm spot, a power density of more than 1014 W/cm^2 can be achieved even in the pump pulse. In addition, two-colour pump-probe experiments, making use of the first and third harmonics of the FEL, are ideally suited for this application because they are automatically synchronized. Furthermore, pump-probe studies with a femtosecond-IR laser as pump and the FEL as a probe yields the angular distribution of the scattered light on a 2D-detector to provide information on the time evolution of electron density with nanometer spatial resolution.
2. The role of inner-shell electrons – Theoretical studies predict that the photo-absorption of atoms in clusters can be substantially smaller than that of isolated atoms, if inner shell electrons are involved [39]. The reduced absorption is due to bleaching, as the Auger decay rates of delocalized valence electrons in clusters are reduced.
3. Slowing down the Coulomb explosion – According to theory [40], the positive charges accumulate preferentially in the outer part of the clusters while the inner part stays almost neutral. This effect can possibly be used to slow down the Coulomb explosion when clusters or macromolecules are embedded in a large He droplet. The ionization dynamics can be investigated with time resolved scattering and with time of flight mass spectroscopy.
4. Production of high harmonics of VUV radiation.

According to recent theoretical work, processes involving the vibration of inner-shell electrons [41] might allow to efficiently generate high harmonics by VUV radiation.

3.3.3 Spectroscopic Studies of Atoms, Ions, Neutral Molecules and Reaction Intermediates

Non-linear optics in absorption and ionization; double ionization – FERMI will allow exploring non-linear optical systems that were hitherto inaccessible with lasers, particularly shallow core levels. Noble gases atoms are the simplest ones to investigate in such experiments. Much work has been done with conventional lasers on Ne, Ar, Kr and Xe [42]. Fewer experiments have been done on He for two reasons: the energies required are higher due to the higher ionization potential of He, and He is less easily polarized than the other noble gases, resulting in lower cross-sections. Several key experiments are planned for FERMI, namely:

- Two-photon resonant absorption at the doubly excited states of He, to access even states. Comparing rates from estimated cross-sections with the FERMI parameters indicates that the flux density is sufficient.

- Multi-photon, double ionization of He and of the other rare gases is an experiment of considerable interest [43]. Double ionization is a basic process in atomic and molecular physics, in which a single energetic photon injects two coherent electrons into the continuum. The origin of the process lies in the electron–electron correlation in the initial state. Since the first observation of of high ion yields by double and multiple ionization using intense, linearly polarized photon pulses, only a few experiments have been performed to elucidate the mechanism behind these processes. At intensities such as provided by FEL sources, Parker et al. [44] have predicted interesting phenomena to occur, including single-photon-induced double ionization. They show, for example, that the electron pair in the continuum behaves as a single correlated wave-packet that absorbs and shares energy in units of the energy of the exciting field, like in the ATI process.

- Basic non-linear interaction between atoms and strong electromagnetic fields can be studied in a clean way for the first time because the pondermotive potential will be negligible when using high photon frequencies. Many-electron processes become increasingly important at higher frequency, an with ultra-short photon pulses. Two-photon, inner-shell ionization is another interesting test case for which theoretical predictions are already at hand.

- Pump-probe, two-colour experiments will use the FEL beam in combination with a beamline laser. Important processes include auto-ionization, fragmentation, and conformational changes. The main differences between the two approaches are the amount of internal energy in the excited state, and the spectroscopic methods applicable in the probe step.

- Dilute species: neutral cluster beam spectroscopy – Using the source developed by the Milani group [45], refractory metal clusters and their oxides will be characterized to elucidate the relationship between size and electronic structure. The interaction of free clusters with atomic and molecular species such as oxygen, hydrogen, water and hydrocarbons will be characterized as a function of mass and production conditions. The most used techniques will be time-of-flight mass spectrometry and fluorescence spectroscopy; test runs have been carried out at ELETTRA, and more are planned on free clusters and condensed samples.

- Dilute species: macromolecules – The proposal is aimed at studying the secondary structure of biomolecules using circular dichroism (CD). Circular dichroism in optical absorption is a standard method of determining protein folding for the wavelength range down to about 180 nm. The intensity changes are small, about 10^{-3} to 10^{-4}, and the amount of detailed information is limited (the spectra typically show a few wiggles over a 60-70 nm wavelength range). Nevertheless the basic structures of helix, coil and sheet can be distinguished. Experiments with FERMI will provide structural information about free macromolecules, potentially more detailed than with UV/visible absorption circular dichroism, because the spectral range is much broader. The technique can also be used for general ion spectroscopy.

3.3.4 Spectroscopic Studies of Reaction Intermediates

Most information available to date on excited states of ions has been obtained by the application of conventional photo-electron spectroscopy. States accessible by this technique are only a fraction of the total, and most of the literature is concentrated on the spectroscopy of stable species. Information about reactive intermediates is much more limited as the species need to be prepared in situ, and therefore generally a high sensitivity method is required. High sensitivity laser techniques - even via multi-photon processes - offer access only to the lowest states of cations. High resolution data are available for stable molecules and some reactive intermediates. [46] Variable photon energy studies using conventional photo-electron spectroscopy are few in number and the data are fragmentary [47]. Information comes also from discharges by emission, an environment in which states excited by collisions are important; the method is limited to states that fluoresce. A route, which leads to highly excited states or to states not accessible through conventional photo-electron spectroscopy is, for example, resonant Auger spectroscopy, for which the selection rules are different [48]. Such studies on radicals are virtually nonexistent. In natural environments excited states are produced and play important roles, as they can be formed by collisions. The concentrations are necessarily small since, because of the high internal energy content, such states are very reactive. In case of dissociation, excited states can be a source of fast neutral or ionic fragments (in their ground or excited state), also very reactive.

FERMI will allow accessing higher lying states of reactive intermediates through the application of well-developed and highly sensitive techniques. The relevant intensities are often increased by near-resonant, auto-ionization of highly excited states [46] in which case states not accessible by direct ionization from the ground state or levels outside of the Frank-Condon region become observable. The experimental arrangement (section 3.4) will be designed to detect all particles produced in the absorption event, so both fragmentation and (auto) ionization dynamics will be studied. The addition of a synchronized, tunable laser allows further extending such studies by either preparing the initial state of the radical using a visible, UV or VUV photon – i.e., above or below the first ionization potential – or by directly measuring the auto-ionization lifetimes by varying the delay between the two lasers.

The use of the laser-FEL combination provides other possibilities. For example, photo-dissociation of state-selected ions can be studied. Pulsed-field ionization of long-lived high-n Rydberg states of neutral radicals is a convenient route to prepare molecular ions from radicals in one or more selected rovibronic states. After initial excitation, the Rydberg electron is removed by a weak pulsed field to leave the pre-selected quantum state of the ionic core unchanged. FERMI FEL radiation in the 12.0-18.0 eV range can produce a Rydberg state of a radical or complex, which upon pulsed field ionization yields an ion in the selected quantum state. A synchronous pulsed UV laser can then be used to photo-dissociate the state-selected ions. The cation fragment can be detected by velocity-map imaging which allows determining the relative quantum yields of the various product channels, and their spatial anisotropies, each as a function of the initial parent quantum state and the photolysis wavelength.

As a first study, the double ionization of ozone by two-photon absorption (FEL-1 photons) will be studied as a function of the photon energy. Two- and three-body dissociation processes of O_3^{++} will be investigated for the first time including the detection of the neutral fragment. The 3D electron-ion-neutral velocity image will then be measured as a function of the field power density. A similar detailed study of the double photo-ionization of O_3 by single-photon absorption (using FEL-2) will be done for comparative purposes.

Recently the application of short pulse, high intensity, visible-IR lasers has stimulated strong experimental and theoretical interest in the multiple ionization process [49]. FERMI allows examining strong field effects at shorter wavelengths. By varying the pulse length, intensity and photon energy (also beyond the single photon multiple ionization limit), the importance of these effects can be examined in detail. The excitation region of particular interest is the range accessible by FEL-1. At higher energies many-electron atomic/molecular processes are predicted to dominate [49]. The capability of tailoring the electronic structure of small molecules (by using selected radicals or other reactive intermediates) offers the unique possibility of studying the role of molecular structure in high-field multiple ionization.

3.4 Scattering Spectroscopies

Time-resolved resonant scattering with coherent radiation can be applied to the study of complex dynamics in disordered systems by means of the “speckle” technique. This technique analyzes the temporal correlations among the scattered photons from incident, spatially coherent radiation. Due to the characteristics of the FERMI radiation it will be possible to access as yet unexplored space-time scales. Interesting examples include the study of critical fluctuations under equilibrium conditions of polymers, colloidal suspensions and liquid crystals [50], the non-equilibrium dynamics during phase separation and the spinodal decomposition of liquid systems, including magnetic and glass systems, magnetic domain dynamics in thin films and multi-layers [51], the study of stripes in high-Tc superconductors and phase separation in manganites [52].

3.4.1 Time-resolved Resonant Scattering of Disordered Systems

One of the current goals of condensed matter physics is the measurement of collective dynamical properties that are due to atomic, electronic and magnetic-density fluctuations. These fluctuations are responsible for specific vibrational, electronic and magnetic elementary excitations, which are often related to many macroscopic properties in condensed matter systems. The experimental challenge is to measure the dynamical structure factor S(Q,E) (or, in time resolved experiment, its Fourier transform F(Q,t)) in the largest region of energy (E) (or time t) and momentum transfer (Q) spaces. The specific research interest is the study of S(Q,E) associated with the collective dynamics in systems without translational invariance: glasses, liquids, and dense fluids. This aim, of great interest for basic and applied research, has been pursued using visible light, x-ray and neutron scattering.

Operating the FERMI photon source between 40 nm and 10 nm will probe regions of (E,Q) space not otherwise accessible for kinematic reasons, with the sufficient intensity to meet the energy and angular resolution requirements. The ultra-short and polarized nature of the FEL radiation pulse opens a completely new field of investigations that will extend and complement the research activity that will start at the IUVS beamline under construction at ELETTRA and at other similar experimental stations.

3.4.2 Resonant Inelastic X-ray Scattering

The FERMI project aims to achieve transform-limited, mJ, soft x-ray pulses for the first time. An enormous advantage of using a transform-limited source is that the x-ray pulse produced can be highly monochromatic. For example, a 1 pico-second long pulse has a bandwidth of only 2 meV. With such a source, an instrument for resonant inelastic x-ray scattering (RIXS) in the photon energy range from 30-120 eV is possible that will dramatically outperform counterparts on third-generation synchrotron sources.

Inelastic x-ray scattering is a photon-in/photon-out method with compelling fundamental advantages over methods such as angle-resolved photoemission, which measure the out-going electron. These advantages are:

(1) an energy resolution which is not limited by the core-hole lifetime;

(2) the considerably greater sampling depth of the out-going photon compared to an electron;

(3) the ability to exploit high incident photon number that would cause space charge blowup of the electron emission, limited only by considerations of radiation damage to the sample;

(4) the ability to work in biologically important solutions or in applied fields.

With the capability to tune to the resonant energy of the L and M absorption edges of many important constituent atoms, the technique is the soft x-ray equivalent of the well-known and powerful Raman technique.

The resonant method allows access to excitations otherwise forbidden by selection rules; it provides element and site-specific information; and it can significantly increase cross-sections to permit measurement of weak collective electric and magnetic excitations. The FERMI photon range encompasses the M-edges of transition metals, allowing the experimenter to study the physics of electron dynamics in highly correlated electron systems – a major frontier of condensed matter physics today. In such systems, the traditional description using single electron-like quasi-particles breaks down, and fundamentally new states of matter occur. A new instrument at FERMI can measure the dynamics of spin-charge separation and the excitation spectrum of high-Tc superconductors or colossal magneto-resistive materials to test theoretical models.

In the most complex systems there are poorly understood interplays between the fluctuations associated with spin, charge, orbital, and lattice degrees of freedom that can be separated and studied with the resolution and high flux of this instrument.

3.5 Non-linear Spectroscopies

The second round of experiments with the FERMI FELs, using the advanced parameter set, will exploit photon intensities that will give access to novel, in-depth studies of non-linear phenomena.

3.5.1 VUV Non-linear Optics in Condensed Matter

The theoretical description of nonlinear effects in solids is a formidable task, and important difficulties have delayed any accurate calculations for many years. Even at the simplest level of approximation – treating electrons as independent particles interacting with the electromagnetic field in the long wavelength limit and neglecting local field effects – the calculation of nonlinear coefficients is cumbersome. Moreover, many-body effects might be important; in fact, note only recently is theory able to reproduce ab initio the systematics of the linear response in solids, including these effects, using either many-body perturbation theory [54] or, even more recently, time-dependent density functional theory [55].

One important nonlinear process is second harmonic generation. Although several calculations of the corresponding susceptibility have been performed for various semiconductors in the visible range, a consistent picture has not emerged from these calculations [56]. For instance, the question of the importance of excitonic or local field effects is not yet settled. Attempts have been made in the low energy range only [57, 58]. Ab initio calculation of nonlinear properties must now be extended to the XUV region.

The unique properties of FERMI@Elettra extend into the XUV region the techniques for nonlinear optics in condensed matter already developed in the visible. The investigations of non-linear optics in condensed matter will develop from a FERMI end-station dedicated to this task and will benefit from the collaboration of an international group of partners of complementary experience, expertise and interests. Continuous, close theoretical support to the experimenters will be provided via a novel approach to the use of numerical simulation as a design tool for optimization of experiments. The first experiments will be in the fields of two-photon absorption (TPA) in solid targets, second harmonic generation (SHG) in condensed media and transient phenomena.

In general, nonlinear optical effects can be readily observed by using coherent sources of radiation. In the XUV region of the spectrum such sources were not directly available until recently. At present two kinds of coherent UV sources are available, namely soft X-ray lasers [50] and multiple harmonic generation in gaseous targets from visible laser pulses [51]. The intensity delivered by these systems is generally not suitable for performing nonlinear optical experiments. Only very recently FEL radiation has been used in the EUV [52]. To date, in fact, very few experiments are reported using such sources, the nonlinear medium being in general a gas jet expanding into vacuum. Experiments on two-photon absorption in He gas have been reported as a tool for autocorrelation of high-harmonic coherent pulses [53].

From the point of view of nonlinear optics, gas systems suffer from several limitations. a) the center-symmetry of the medium allows only nonzero odd nonlinear susceptibility terms, b) albeit variable, the matter density of gaseous nonlinear media is always low, and this fact may reduce the efficiency of the nonlinear process, c) gaseous targets are intrinsically unstructured, therefore no effects related to the presence of medium discontinuities can be observed.

No experiments, to our knowledge, have been so far attempted in the XUV range on nonlinear optical effects in condensed matter. The reason for this is mainly due to the lack of sufficiently intense short pulses of coherent laser radiation in the XUV region. The high brilliance, coherent FERMI source will remove this limitation.

Despite absorption, there are various reasons for attempting nonlinear optical experiments on solids in the XUV region. First, non center-symmetric material systems may be selected which have a nonzero, second order susceptibility £q(2) that drives more intense, non-linear effects. Then, the presence of well-defined material-vacuum and/or material-material buried interfaces allows surface and bulk effects to be discriminated and may also switch on interaction with collective material excitations.

3.5.2 The UNUS Project

The UNUS Project is conceived around a single end station for FERMI to be designed and built specifically for nonlinear optical experiments, with aim of extending and testing for the first time our knowledge of nonlinear properties of condensed matter in the XUV region. For this challenging task experiments must be modeled theoretically and simulated numerically to guide and optimize the experiments.

Beam intensity, polarization, short duration, monochromaticity and temporal coherence of FERMI radiation offer exciting possibilities for nonlinear optical experiments. In particular, nonlinear optical phenomena are effective when the optical fields become comparable with the atomic field strength (≈ 108 V/m) associated with the relevant electronic levels. This condition imposes a minimum value for the brilliance on sample of the order of 1015 W/m^2 for FEL operation at 31 eV. Short duration of the FEL pulses, besides helping in obtaining high intensities, is per se an attractive feature that allows time resolved measurements in so far unexplored temporal domains with x-ray pulses. The most promising time duration for coherent pulses is in the tens of fs where a sufficient resolution is achievable on most electronic collective excitations in condensed matter.

Operationally, the first set of experiments will proceed along the three lines: two photon absorption, harmonic generation in condensed matter and transient phenomena

- Two photon absorption: This technique makes use of "virtual" intermediate electronic states to reach the final state. It will be used within the VUV and XUV range of FERMI as applied for instance to 3p shells of 3d metals, to 4f shells of some noble metals and also to K shell excitation of selective light elements. The latter possibility has particular relevance to the analysis of electronic bonds. By continuously tuning the FEL radiation, one could develop a two-photon NEXAFS [59] for dipole-forbidden final states, thus offering an original perspective in the simulation and solution of local structure around an absorbing site.

- Harmonic generation in condensed matter: Higher harmonic generation (HHG) has been explored for more than two decades, and coherent radiation has been generated in the VUV and XUV from gaseous samples starting from visible laser pulses [60-63]. UNUS will study the nature of the intrinsic nonlinearities in optical response in condensed matter in the VUV to XUV photon energy range by measuring the nonlinear susceptibilities in condensed matter.

- Transient phenomena – XUV or VUV photo-excitation of materials can be readily obtained in a conventional synchrotron beamline provided that a) time separation between pulses is consistently larger than the lifetime of the transition being measured and b) the intensity of the (monochromatized) exciting pulse is sufficiently high. This last condition is very seldom true in practice and very few fluorescence photons per bunch are generally obtained [64]. This implies the use of photon counting techniques with sophisticated timing systems to obtain the decay parameters of the fluorescent signal. The pulsed excitation provided by FERMI can be exploited in transient studies by probing unexplored ranges of characteristic de-excitation times of systems under high intensity VUV excitation. In this respect the investigation of temporal properties of the radiative (e.g. fluorescence, phosphorescence and luminescence) and non-radiative (e.g. Auger and photoelectric emission) de-excitation channels could become a natural topic to be studied.

3.6 Exploiting the Schemes to Produce Intense EUV and Soft X-ray in the Attosecond Time-domain

Zholents and Fawley have proposed [65] producing isolated soft x-ray pulses pulses of ~100 attosecond duration using electrons selected by their previous interaction with a few-cycle, intense laser pulse. They call this process "seeded attosecond x-ray radiation (SAXR)." In principle, SAXR allows excellent temporal synchronization between the attosecond x-ray probe pulse and a pump source that can be the same few-cycle pulse or another signal derived from it. Thus, it is conceivable to track the temporal evolution of atomic or molecular states during a single optical cycle in the process of laser-assisted photoionization.

As a specific example they choose 2 nm as the x-ray source wavelength to eventually produce 1-nm wavelength attosecond radiation. However, as long as an intense, coherent source is available, attosecond pulse generation at both longer and shorter wavelengths is also possible with the same scheme. In particular the harmonic cascade of FEL-2 of FERMI is well suited to performing the first experimental verification of this scheme. A sample layout is in Figure 3.6.1.

Figure 3.6.1:
A schematic of the components involved in attosecond x-ray pulse production.

SAXR requires an ultra-relativistic electron beam, a few-cycle, intense optical laser pulse and an intense pulse of coherent x-ray radiation, together with a number of magnetic undulators and transport elements.

3.7 Instrumentation R&D

FERMI, like more conventional synchrotron light sources, is planning an R&D campaign focused on developing instrumentation specially dedicated to the exploration of ultra-fast processes. The main instrumentation items are briefly discussed in the following paragraph.

3.7.1 Sub-picosecond Streak Camera

The sub-picosecond resolution Streak Camera (SPSC) FERMI project calls for a system with 500 fs temporal resolution, 10-100 nm photon wavelength range, with an efficiency of > 10^{-6}. The 500 fs temporal resolution for x-rays, is challenging. The resolution of streak cameras has slowly improved over the years from around 2 ps in 1990 [66] to the best achieved so far 800 fs [67]. This improvement mainly resulted from the reduction of jitter in triggering of the camera by use of an improved design of photoconductive switch and from improved laser stability. The temporal range is also challenging; however, it can be achieved by use of a variable sweep rate. The SPSC would have a wide temporal window and a narrow temporal window mode. These modes would be used respectively for finding the beam in time, and for high temporal resolution measurements.

The camera will be designed to be read at up to the FERMI-FEL, 50 Hz repetition rate. The requisite dynamic range of the camera depends on whether the system is used in single shot or in the accumulation mode; the R&D goal is to develop the more challenging, single shot capable device.

Applications of such a camera range from measuring the separation of pulses created by an X-ray beam splitter, to measuring the decay of x-ray fluorescence from a plasma. The baseline dynamic range design value is 103. This sets the required number of electrons per temporal resolution element and thus determines the space charge broadening of the beam.

The streak camera is shown schematically in Figure 3.7.1. X-rays hitting the transmission photocathode produce the electron beam, consisting mainly of low energy secondaries. The width of the electron energy distribution and its mean energy mainly depend on the work function of the material, the best being CsI or KBr, with an energy spread of around 1 eV. However, because these materials are easily radiation damaged, gold, having a higher work function and consequently higher energy spread but being radiation hard, will also be considered for the application. The emitted electrons are accelerated in a field of up to 25 KV/mm, established between the photocathode and a mesh or a slit. The accelerated electrons are then deflected by a time varying electric field, and focused unto a detector plane by a magnetic lens.

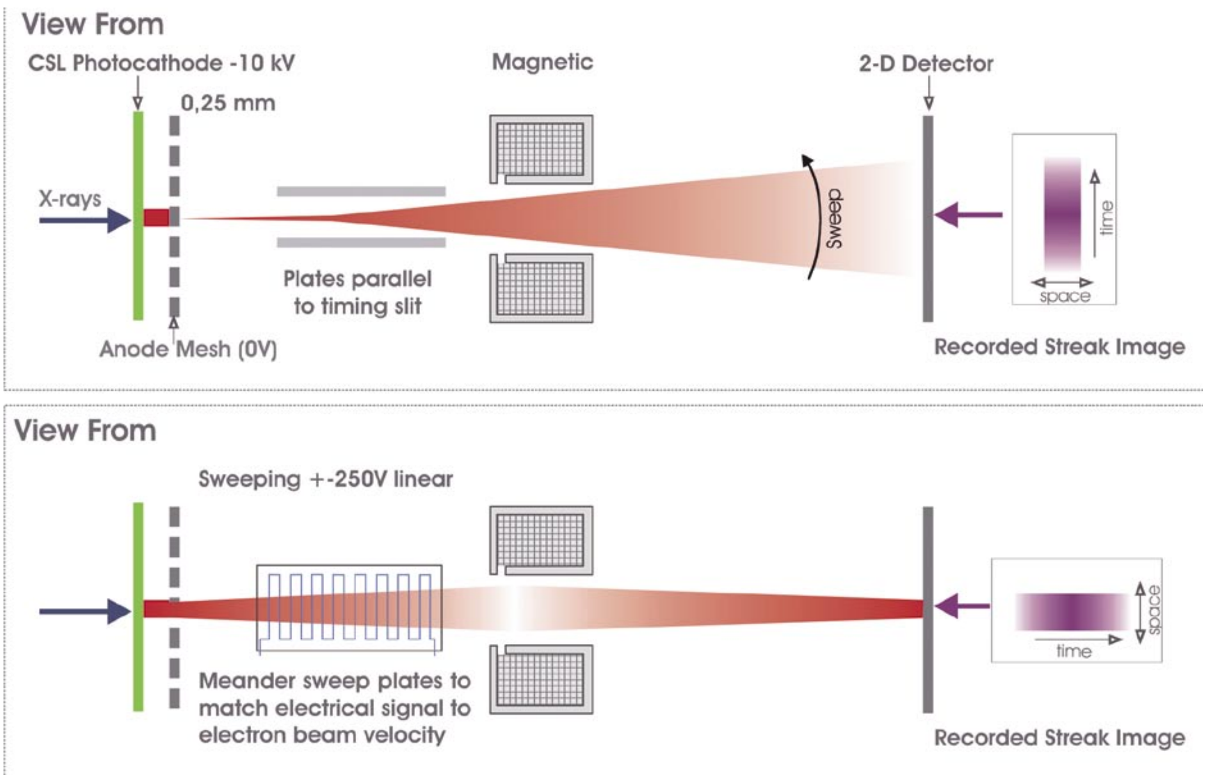

Figure 3.7.1: General arrangement of the streak camera components.

3.7.2 Detection and Diagnostic of Ultra-short EUV and Soft-X-ray Photon Pulses

There are currently two interesting methods for the temporal characterization of XUV pulses. The first one is the extension of the auto-correlation technique, developed for measuring visible pulses, into the X-ray region. Auto-correlation requires splitting the pulse into two replicas which are then recombined in a suitable nonlinear medium, where the nonlinear process is sensitive to their temporal overlap. Examples of such nonlinear processes are second-harmonic generation in a nonlinear crystal (for visible pulses), two-photon ionization, or index variation in a Kerr medium. A serious drawback of this method is that the efficiency of nonlinear processes depends on pulse intensity, and if the intensity is too low the method is not applicable. The generalized cross-section for two-photon ionization decreases rapidly with wavelength; for example, for argon at 53 nm, it is only 2.1×10^{-52} $W^{-2}cm^{6}$. To measure a statistically significant auto-correlation over reasonable number of pulses, a few nJ of focused X-UV radiation are sufficient. Single-shot measurements instead require a thousand-fold increase in pulse energy. The auto-correlation method does not give complete information about the pulse temporal shape, the auto-correlation trace being symmetric by definition.

A second class of measurement techniques, also suited for pump-probe measurements, is based on the cross-correlation of the X-ray pulse with a longer wavelength (visible or infrared) probe pulse. In this case the single-photon XUV process becomes the limiting factor. Again for argon at 53 nm the corresponding ionization cross section is 8×10^{-20} cm^2, and ~ 5 fJ of XUV energy per pulse would provide a detectable signal, while single-shot capability requires pulse energies greater than 5 nJ.

This second method will be first tested using femtosecond X-ray pulses obtained by high-order harmonic generation (HHG) in noble gases. The technique will then be used to measure the duration of the most energetic FEL X-ray pulses.

3.7.3 Optical Component Development

The experimental program at FERMI will require the development of a new generation of optical components tailored to the ultra-brilliant, ultra-fast FEL output radiation. The main areas and items of interest to be developed, possibly on different time scales, are the following:

Spectral analysis of EUV FEL radiation

The information about the FEL spectrum is essential both during the development and characterization of the source, and for defining the experimental conditions for the users. Since the FEL is operated at low repetition rate, the spectrum must be obtained on-line, using a single shot.

A single-shot online EUV and soft X-ray spectrometer is an essential instrument for the FEL facility.

Time-compensated broad-band monochromators.

A filter tunable over the whole spectral region covered by both FEL-1 and FEL-2 may be required to suppress background radiation outside the FEL spectral band and high-order harmonics. The filter can be a broad-band grating monochromator. The design must preserve the FEL pulse time duration and produce an output beam with the smallest possible dispersion. As in the previous case, a tunable EUV and soft X-ray filter will be needed by many users and should therefore be part of the FERMI FEL beamlines.

Optical systems for focusing the FEL beam

Focusing of the FEL beam on sample is required by almost all experiments. The development of focusing for all kinds of FEL operating modes is therefore essential.

Beam-splitters for EUV ultra-short pulses

Beam-splitters for ultra-short intense EUV pulses are crucial items for many experiments and need developing. A short-term goal is to build a prototype of such a time-compensated beam splitter for visible-UV, ultra-short pulses, using grazing-incidence gratings in a time-compensated configuration. The task will be performed in close collaboration with ULTRAS-Politecnico Milano. The prototype will be tested and operated with visible-UV radiation, in air, to demonstrate its feasibility. The same configuration, with the appropriate choice of gratings, can be used for all wavelengths in the 3-100 nm range, covering the whole spectral range of both FEL-1 and FEL-2.

Time-compensated high-resolution monochromators

Although the FEL intrinsic spectral resolution is high, some proposed experiments require even higher resolution. High-resolution monochromators to respond to this asks for the study and design of time-compensated configurations.

3.7.3.1 Time-compensated Instruments for Handling FEL Radiation

The use of grazing-incidence optics for the EUV intense FEL radiation is chosen to ensure safe operation of the optics and high efficiency of the instrument.

In particular, the use of reflective grazing-incidence gratings as beam handling devices for EUV ultra-short pulses offers many advantages but also raises design issues related to the preservation of the pulse time duration. Only the zero-order beam has the original ultra-short pulse duration, since the grating acts like a mirror, while the duration of the diffracted orders is altered. The total difference in optical paths of rays diffracted by N grooves at wavelength l is DOP=Nml, where m is the diffracted order.

The effect becomes dramatic in the femtosecond time scale: considering a 200 grooves/mm grating illuminated over a 30 mm length, the total number of grooves involved is 6000, corresponding to a maximum delay in the first diffracted order of 240 mm, i.e. 800 fs at l=40 nm.

The effect therefore reduces both the time resolution capability and the peak intensity of ultra-short pulses. In addition, the grating introduces also spectral broadening, since the different spectral components of the pulse are diffracted in different directions.

It is nevertheless possible to design time-compensated configurations by using two gratings in a subtractive and compensated dispersion configuration. In such a configuration, the second grating compensates both the time difference and the spectral broadening introduced by the first one [68].

3.7.3.2 Focusing of the FEL Beam

The FEL beam must be focused on the sample resting in the experimental chamber. Since different power densities and/or different illuminated areas are required, different spot sizes on sample are required. Focusing in the 4-100 nm wavelength range is efficiently done by grazing-incidence mirrors.

Several solutions can be proposed. One example is the use of a pair of deformable cylindrical mirrors in the Kirkpatrick-Baez configuration, whose radius of curvature can be varied between infinite (plane mirrors, no focusing) and a given value. A different choice calls for several (2 to 4) ellipsoidal mirrors with different radius of curvature.

The proposed solutions take into account that the minimum focal spot size is limited by diffraction to $\approx 2.44 \cdot \lambda \cdot f/\#$ where λ is the wavelength and f/# the numerical aperture of the beam. For example, a 20 μm spot at 40 nm requires $f/\# \approx 200$, i.e. an angular aperture of 5 mrad. Taking into account the intrinsic divergence of the FEL beam and the actual distance between the FEL source and the mirror, the exit arm of the mirror must be quite short (~ 0.5-1 m). The mechanical mounting of the optics has therefore to be carefully studied to avoid interference between the focusing optics and the diagnostic instruments around the sample.

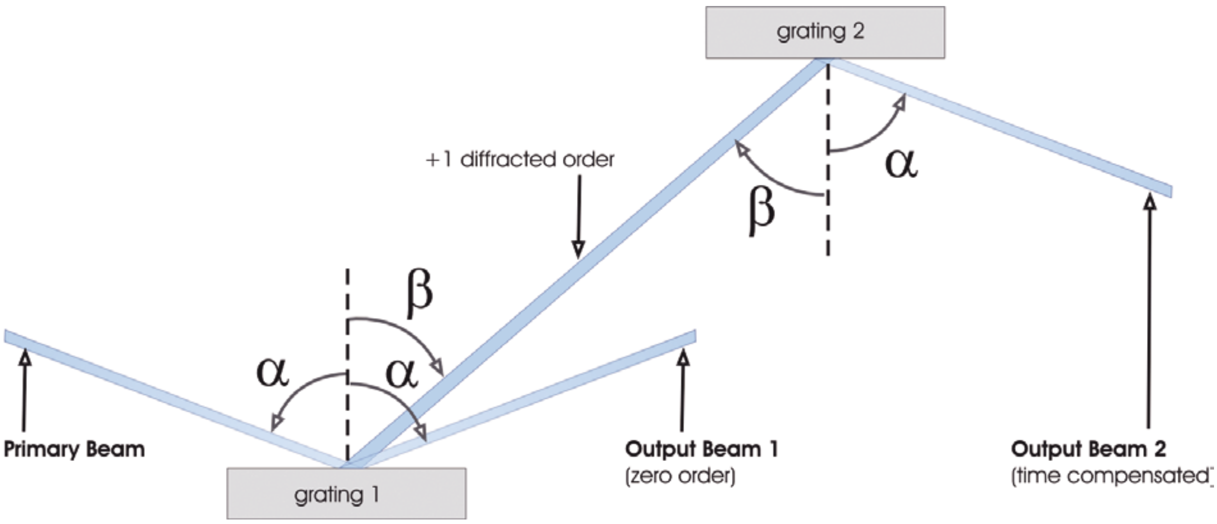

Figure 3.7.2:
Layout of a time-compensated beamsplitter.

3.7.3.3 Beam Splitter in the Visible-to-UV Range Using Grazing-incidence Plane Gratings

A simple beam-splitter consists of a diffraction grating: the incident beam is diffracted into several output beams, corresponding to the zero order and the other, diffracted orders. To preserve the temporal structure of the incoming radiation a time-compensated configuration using two gratings in subtractive and compensated dispersion must be used [69]. The layout is shown in Figure 3.7.2. The gratings are mounted in the so-called Z-configuration, with the incidence angle on the second grating equal to the diffraction angle from the first one; consequently, the diffraction angle from the second grating is equal to the incidence angle on the first one, so that the output beam is parallel to the input one. In such an arrangement, the rays with a longer optical path from the first grating have a shorter optical path from the second grating, and vice versa. Furthermore, also the spectral dispersion of the non-monochromatic radiation is almost compensated by the Z-configuration, since the second grating has a subtractive spectral dispersion with respect to the first one.

A schematic of the prototype to be realized is shown in Figure 3.7.3. The optics will be mounted on a breadboard of approximately 1 m × 0.4 m. The optical system consists of two gratings and three plane mirrors. All optics are operated at grazing incidence, with incidence angle in the range 80°-86°. The two gratings are rotated along with the input wavelength in order to work at constant subtended angle $\alpha+\beta$ and maintain the direction of output beam 2 fixed, parallel to the input beam. Mirror M1 must also reflect the zero order in a fixed direction and is therefore also is rotated and translated along with the wavelength. To select the delay between output beam 1 and 2, Mirrors M2 and M3 can be rotated and translated.

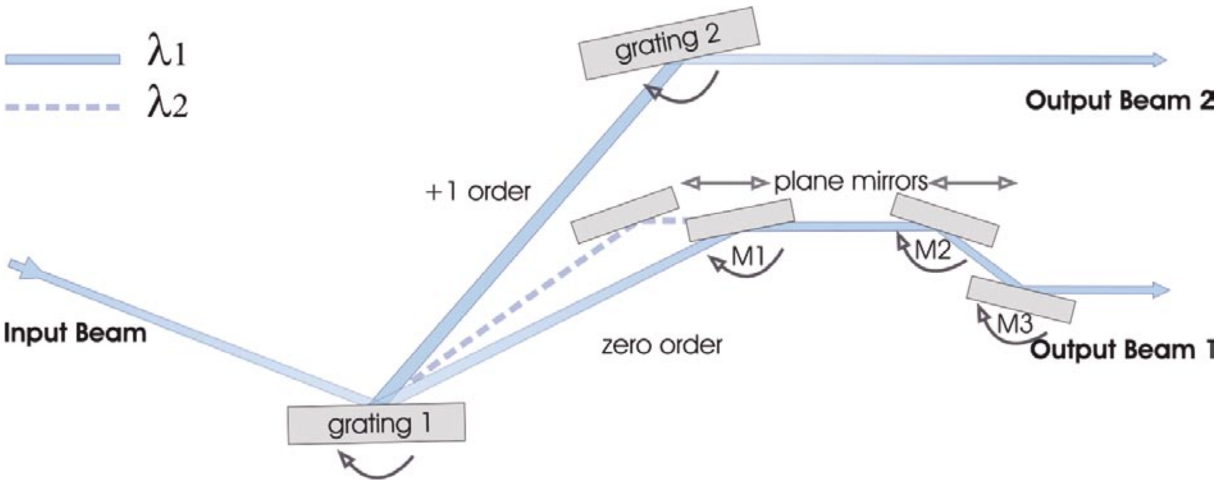

Figure 3.7.3:
Schematic of the beam-splitter to be realized.

3.8 References

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