An innovative photochemical facility at DAΦNE-L

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Abstract. An on-going project for a photochemical facility at the DAFNE-L laboratory at the Frascati National Laboratories of INFN (National Institute of Nuclear Physics) is presented. Such a facility takes advantage from the combined capabilities of two different synchrotron radiation beam-lines. The first operates in the visible-UV and is used as a strong excitation and irradiation light-source in which both intensity and spectral range can be selected to fulfil the experiment requirements. The second is an infrared beamline equipped by FTIR micro-spectroscopy and imaging facility. An optical fiber allows UV irradiation of samples directly into the FTIR interferometer or the microscope. Thus, fast photo-chemical reactions can be analysed in real time, letting unveil inter-phases not normally observable by analysing the reagents and products of the reaction itself. Complex unstable systems can be irradiated and analysed without changing the sample condition (morphology, humidity, irradiation etc.). Preliminary experiments, validating most of the facility capability, will be presented.

1. Introduction

Synchrotron Radiation (SR) is a powerful instrument to investigate the physical properties of the matter. In particular, by using spectroscopic analyses - from X-ray to infrared spectral ranges - aggregation states, chemical bonds and spatial structures can be studied. Due to its peculiar features (intensity, brilliance, polarization, continuous spectrum, etc.), SR represents also an ideal light-source to simulate irradiation conditions present on Earth and in many astrophysical environments.

Ultraviolet (UV) radiation is widely used in experiments studying the degradation of organic or biological materials, in applications were the radiation modify the molecular bonds and therefore the material properties. It is of great interest to achieve real-time monitoring in order to have information on the evolving process and to infer the behaviour of the molecules.

Infrared (IR) SR is widely accepted as an advantageous source for all spectroscopic applications requiring both high brilliance and high signal-to-noise ratio, with the broadest emission band among all radiation sources (from ~ 0.5 mm to 0.5 μm wavelength). These advantages of IR SR apply to a large choice of experimental techniques and investigations, mostly on micro-spectroscopy and micro-imaging, spanning from solid-state physics to biology, radiobiology, environmental science, Earth and space science.
2. Synchrotron radiation at DAΦNE-Light

The INFN DAΦNE storage ring is a 0.51 GeV e+/e- collider, where a routinely circulating current larger than 1A provides a very high photon flux in the low energy region (1.24 meV – 4 keV). The DAΦNE-Light SR facility has three operating beamlines, working both in parasitic and dedicated mode: DXR-1 (soft X-ray), DXR-2 (UV-VIS) and SINBAD (IR), and two XUV beamlines under commissioning [1]. In this work we will present a photochemistry facility that was arranged by bringing the UV-VIS beam from DXR to the FT-IR spectrometer of the IR beamline, to achieve real time and in situ monitoring of chemical reactions for radiobiology, astrobiology and space applications.

The UV and IR beamline optical setup are here briefly discussed. A grazing incidence Au-coated mirror (θ=40 mrad, cut-off energy ~ 800 eV) reflects part of the beam extracted from a wiggler and deflects it towards a 38 mm diameter MgF₂ window in the UV beamline [2]. The optical layout of the whole apparatus consists of three light channels: white beam, monochromatic (180-650 nm) and monochromatic vacuum UV (120-300 nm), allowing measurements in a very wide spectral range, i.e., from 120 nm up to 650 nm (2-10 eV). The experimental chamber at the end of the optical system was designed to perform any kind of optical experiments: reflectivity, absorption, scattering, detector calibration, etc.

The IR radiation is collected from a bending magnet of the electron ring under a 35 mrad (H) x 45 mrad (V) solid angle and transmitted by an optical system consisting of six Au coated mirrors to two end stations at about 25 m distance [3, 4]. The first end station is a Bruker Equinox 55 interferometer, suitably modified to work under vacuum, covering a spectral range from 10 to 15000 cm⁻¹ (1.24 meV to 1.8 eV) with a maximum spectral resolution of 0.5 cm⁻¹. The second one is a Vertex70v coupled to a Hyperion 3000 IR microscope and equipped with a 64x64 pixel Focal Plane Array (FPA) detector to perform chemical imaging of biological tissues, cells and other samples with a diffraction limited spatial resolution. The beamline instrumentation includes also a Diffuse Reflectance unit (DRIFT), a diamond Attenuated Total reflection module, a low and high temperature (4-500K) cryostat and a diamond anvil cell for measuring the IR properties of samples at high-pressure up to 30 GPa.

UV-grade fiber optics was used to couple the two beamlines, bringing the UV SR beam from the DXR-2 beamline to the FTIR interferometer (v. Fig.1a), in order to exploit their advantages. The accessible wavelength region for photochemical experiments is 180-400 nm. Two optical
configurations are under development: the first makes use of the SR white beam; the second brings monochromatic SR on the sample. A fiber optics is arranged at the entrance of the DXR-2 beamline, where an off-axis parabolic mirror can be put at 45° incidence angle to fold and focus the SR white beam at the fiber input.

A couple of 3 mm diameter Suprasil micro-spheres is arranged in front of the fiber optics entrance to match the beam aperture with the fiber aperture. A 10-m long fiber transfers the collected white beam through a vacuum feed-through directly on the sample inside the interferometer. The last part of the fiber is naked and inserted in a capillary to allow a fixed position to illuminate vertically the sample. The distance between the fiber output and the sample can be changed to have circular and uniform spotlight matching the size of the sample. The fiber optics bringing the white beam can be easily replaced by the fiber bringing monochromatic SR, whose entrance side is arranged in air at the exit slit of a VIS-UV monochromator. Even in this case, a couple of Suprasil micro-spheres collimates and re-focuses the monochromatic beam at the fiber entrance matching its acceptance. The fiber end inside the FTIR interferometer does not intercept the IR beam. For IR diffuse reflectance, the sample is located inside the DRIFT tool (Praying Mantis by Harrick Scientific; v. Fig.1c).

A different setup is conceived to irradiate samples having micrometric size with UV light at the IR microscope. This arrangement allows real-time imaging or microanalysis of processes occurring under UV irradiation. In this case, UV irradiation can not be vertical: the fiber optics is arranged laterally with an angle of about 20° producing a non-uniform elliptical spot. However, the size of the spotlight and the related non-uniform photon flux on the sample can be easily estimated.

3. Experimental

The optimal throughput of the UV optical system strongly depends on the optical coupling between the fiber entrance and the parabolic mirror focusing the white beam, or the monochromator exit slit for the monochromatic beam. The fiber-to-fiber optical coupling at the vacuum feed-through of the FTIR interferometer is also crucial. To assess these optical couplings as well as the fiber transmission on a long distance, we used a UV-grade (solarized) 10-m fiber optics to bring the UV radiation emitted by a Hamamatsu 500 W Hg-Xe lamp to a sample inside the FTIR interferometer. The large aperture beam from the source was focused by means of a couple of spherical mirrors. The aperture of the focused beam was not optimized for the fiber acceptance; therefore, we put a couple of sapphire micro-spheres at the entrance of the fiber optics in order to test their effectiveness.

![Emission spectrum of the Hamamatsu 500 W Hg-Xe lamp compared to the SR spectrum emitted in the UV-VIS range by an electron current of 0.7 A circulating in the storage ring.](image)

Figure 2. Emission spectrum of the Hamamatsu 500 W Hg-Xe lamp compared to the SR spectrum emitted in the UV-VIS range by an electron current of 0.7 A circulating in the storage ring.
After some preliminary tests, we realized that the mechanical optical coupling at the vacuum feed-through on the interferometer was not compliant with the optical alignment required to maximise the UV flux on the sample. The position of the two fibers inside the feed-through is not fixed: even very small mismatching may cause a decrease of the already small throughput. We decided to put another couple of sapphire spherical lenses in between the two fibers in order to collect the radiation even if the two fibers were not perfectly aligned. The optical transmission improved from roughly 10% up to 72%, providing the lamp spectrum reported in Fig.2. The photon flux at the main lines is of the order of $10^{11}$ photons/s in the spotlight, while the integrated flux of the emission spectrum from 200 nm to 400 nm is of the order of $10^{14}$ photons/s in the spotlight.

In order to fully assess the methodology and the optical system we made a test by using the Hg-Xe lamp as UV source and nucleobases as sample. The experiment was aimed to irradiate pure nucleobases, as adenine, uracil, pyrimidine and cytosine, with UV white beam and to monitor their degradation by real-time FTIR analysis, making use of the diffused reflectance technique.

The 500 W Hg-Xe lamp was optically coupled – as described in the previous paragraph – to a 10-m UV-grade fiber optics illuminating the organic sample. IR radiation was sent on the sample inside the FTIR interferometer of the SINBAD beamline and the diffused/reflective beam was collected by means of the Praying Mantis optical tool. The FTIR spectra of the nucleobases were acquired every 10 minutes during the two-hour exposition to UV light. The spectra reported in Fig.3 show the effects of UV irradiation on the uracil molecules, i.e., a variation of the molecule roto-vibrational modes indicating the occurring degradation. Real-time monitoring allows to infer the behaviour of the irradiated molecules through the degradation curve, whose fitting allows to estimate more precisely their life-time and cross section. Starting from the spectrum of the uracil molecules (blue line in Fig.3, see [5]) we observe the emergence of new bands centred at 1170 cm$^{-1}$ and 1290 cm$^{-1}$, the enhancement of the large band at 700-900 cm$^{-1}$ and the quenching of the bands around 1000 cm$^{-1}$ and 1244 cm$^{-1}$.

Figure 3. IR absorption spectra of the uracil molecule showing its degradation under UV irradiation. The bands around 1007 cm$^{-1}$ and 1244 cm$^{-1}$ are related to vibrational modes of the aromatic ring, while the bands at 763 cm$^{-1}$ and 828 cm$^{-1}$ are due to the bending of the C=O bond and of the CH bond respectively. The new emerging large peaks centered around 1150 and 1290 cm$^{-1}$ are likely due to breaking of C=O bonds into C–O during UV irradiation.

Being the proof of concept positive, we put the optical fiber at the exit slit of the VIS-UV monochromator in order to use the SR as UV radiation on the sample, because the optical system at the entrance of the DXR-2 beamline, as discussed above, was not yet available. We got the spectral flux of the SR exiting the fiber output (see Fig.2), after having adapted the numerical aperture of the
monochromator to the fiber acceptance. The result of this first attempt, at 700 mA as electron current in the DAFNE storage ring, provides the spectral SR flux and allows a direct comparison between the lamp and the SR as VIS-UV sources. This is clearly a preliminary result showing that in the spectral region of interest for biological and photochemical experiments (200-300 nm) we gain a factor of 2 as photon flux, but lamps are still competitive. However, we would expect an improvement of factor of 4 as radiation flux, because of a factor of 2 gained by coupling the optical fiber at the entrance of the DXR-2 beamline and another factor of 2 from the nominal electron current in the DAFNE storage ring that is 1500-1800 mA (not available at the time of this experiment). The expected spectral flux will be comparable to that of the UV lamp limited to the emission peaks, but the continuous spectrum of SR is a great advantage at any other wavelength and if photon flux integrated over spectral bands is required.

4. Conclusions
We have discussed the project of a new photochemical facility at the DAFNE-L laboratory at the National Laboratories of Frascati of the INFN, which combines the existing UV and IR SR beamlines in order to use SR for both UV irradiation of organic and inorganic materials and FTIR technique for real-time monitoring of the processes. Absorption spectroscopy, microscopy and imaging combined with simultaneous intense UV irradiation will be available to better understand the physical and chemical properties of biological molecules, organic materials, inorganic compounds. The overall concept and the optical design of the facility have been completed and work is in progress to improve the performance of the experimental apparatus.

5. References

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