DAΦNE-Light Laboratory and Activity

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1 Summary

The scientific activity at the DAΦNE-Light laboratory, in 2012, was mainly performed using conventional sources. Due to the not continuous DAΦNE operation, synchrotron radiation was mainly used for check tests. The experimental teams that got access to the DAΦNE-Light laboratory were from Italian Universities and research Institutions, and some of them also from EU countries within the INFN-FAI framework. The experimental activities, performed in 2012, were also dedicated to some upgrades of the beamlines with new instrumentations, the test of the clean-room laboratory for biological sample preparation and also to the completion of the construction of the two new XUV beamlines that will hopefully be commissioned in 2013.

2 Activity

2.1 SINBAD - IR beamline

The experimental activity on the SINBAD IR beamline mainly concerns micro imaging and FTIR (Fourier transform InfraRed) spectroscopy in different research areas, including material science and THz applications, biology, radiobiology, live cell imaging, cultural heritage and geophysics. All these studies are made possible by the imaging capabilities of the IR microscope coupled to the synchrotron source. Due to the problems of DAΦNE, during the last year, researches on the IR beamline were carried out mainly using conventional sources. The institutions involved were mainly Italian teams, due to the late beginning of the EU user access project CALIPSO, that will probably start in 2013. Some of the international collaborations were financed by INFN-FAI fundings. During 2012 the Attenuated Total Reflection (ATR) microscope objective designed to image live biological cells (Fig. 1), partially funded by the Vth INFN scientific Commission, has been realized and first tests are ongoing.

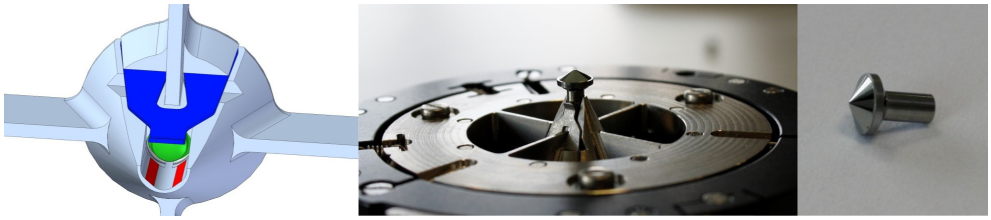

Figure 1: Design and realization of the dedicated ATR objective with a removable Germanium crystal tip.

A powerful 24 V conventional infrared source has been installed on the Vertex interferometer to provide high IR flux on samples when synchrotron radiation is not available. The source has been tested and provides 40% more signal than the standard 12 V globar source, allowing FTIR imaging analysis with improved signal-to-noise ratio and reduced acquisition times. Taking into account the

very interesting results achieved in researches related to astrophysics (radiobiology and dosimetry) and medical applications (cystic fibrosis) different projects have been submitted for funding. Some of the scientific results obtained at the SINBAD IR beamline are here summarized:

1. *The Degradation Process of Lead Chromate in paintings by Vincent van Gogh studied by means of spectro-microscopic methods.*

   C. Miliani, CNR-ISTM - Perugia

   Previous investigations about the darkening of chrome yellow pigments in Vincent van Gogh paintings revealed that this form of alteration is attributable to a reduction of the original Cr(VI) to Cr(III) and that the presence of sulfur-containing compounds plays a key role during this process. In the present work we show how both the chemical composition and the crystalline structure of lead chromate-based pigments influence their stability. For this purpose, artificially aged oil model samples made with in-house synthesized powders of $PbCrO_4$ and $PbCr_{1-x}S_xO_4$ were artificially aged and characterized. Analyses employing UV-visible diffuse reflectance and Fourier Transform infrared (FTIR) spectroscopy were performed on (un)aged model samples in order to obtain additional information on the physicochemical changes induced by the aging treatment (Fig. 2).

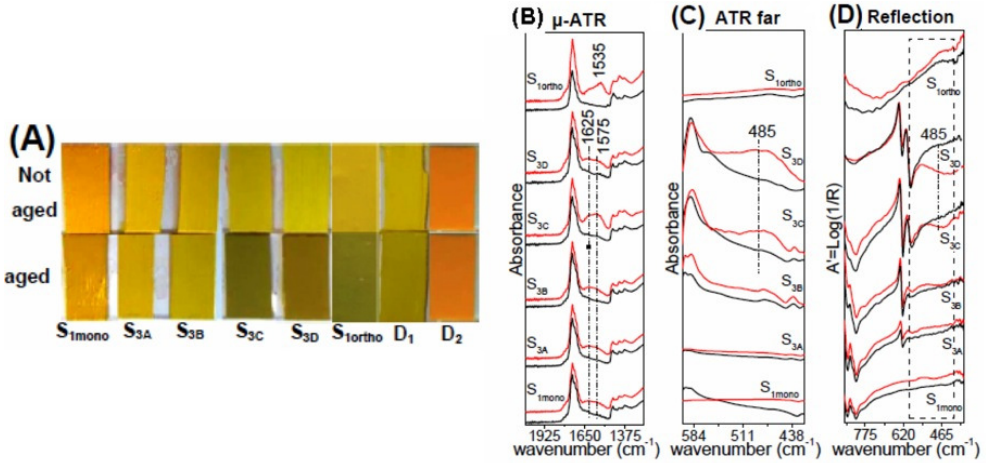

Figure 2: (A) Aged samples, after exposure to UV-A visible light, of paint models containing different amount of sulfate; (B) micro-ATR mid; (C) macro -ATR far; (D) Reflection

These results are a part of a very extended study on yellow paintings of Van Gogh made in collaboration with CNR-ISTM and the ESRF and SOLEIL synchrotron radiation facilities. The results were published on Analytical Chemistry (ACS Publications) and have been cited in many web articles like: http://www.repubblica.it/speciali/arte/recensioni/2013/01/18/news/allarme_i_led_oscurano_il_giallo_di_van_gogh-50792854/ and http://cultura.panorama.it/arte-idee/van-gogh-gialli.

2. *A crystal-chemical study of cordierite, synthesis and stability at variable H_2O and CO_2 concentration: geological and technological applications.*

   F. Radica et al., University of Roma Tre - Dipartimento di Geologia

   Cordierite is a unique case of a microporous mineral stable under geological conditions spanning from the amphibolite facies to UHT metamorphism to crustal anatexis. The interesting

feature of this mineral is its ability to trap different amounts of H_2O and CO_2 as a function of pressure and temperature; the crystal chemical study of cordierite is thus important for both petrological and technological applications. The experimental introduction of volatile components in the structural channels of cordierite has been studied by various authors; they pointed out, particularly for CO_2, the difficulty in reaching the sample saturation and homogeneity, a condition which is crucial for the accurate determination of the volatile content in the specimen. The experimental protocol for this study was developed using a natural, optically transparent, Mg-cordierite as starting material, and silver carbonate as CO_2 source. The experimental apparatus consisted of a non end-load piston-cylinder press housed at INGV (Rome). The reason for this choice is strategic because this apparatus covers a range of pressures and temperatures compatible with those of the lower crust and upper mantle.

The experimental products were analyzed by FTIR spectroscopy, a powerful technique that allows quantifying very low CO_2 concentrations. When using novel bidimensional detectors (FPA detector at INFN-LNF), this technique is also able to provide the distribution of the target molecule, thus allowing to get insight for its diffusion across the specimen. The preliminary experiments so far covered the pressure range from 200 to 700 MPa and temperature range from 700°C to 900°C, with running time up to 48 hours. FPA images showed that carbon dioxide is preferentially distributed along the crystal edges and cracks; in detail concentration along the cracks can be up to five times higher than in the crystal edges (Fig. 3), suggesting that (1) the diffusion of CO_2 across the cordierite matrix is relatively slow under the used experimental conditions; experiments for longer duration time are thus required to address this issue. (2) knowledge of the non-homogeneous composition of the sample is a pre-requisite to get accurate micro-analytical data.

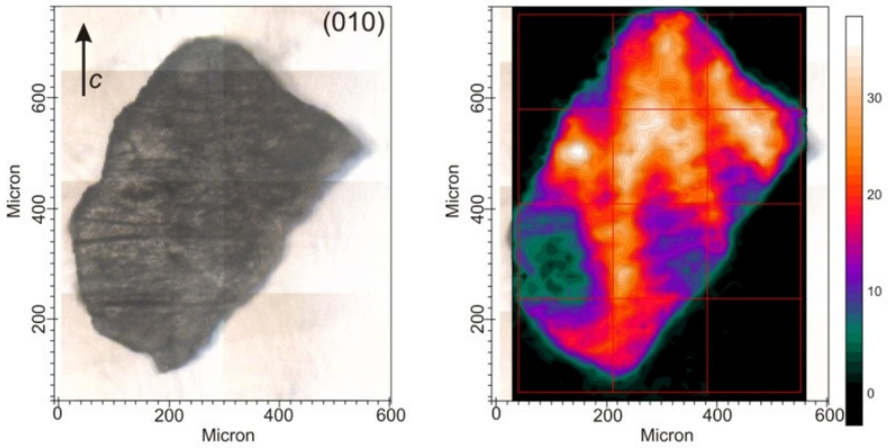

Figure 3: Visible (left) and infrared image (right) of the CO_2 distribution of a 90 μm thick cordierite slab (CRD_PR35) treated at 700 MPa and 800°C for 15 hours. The chromatic intensity is proportional to the CO_2 concentration, intensity units in the right picture are arbitrary.

3. *Fourier transform InfraRed micro-spectroscopy (micro-FTIR): a useful method to evaluate the effects of CFTR modulators in cells.*

   G. Bellisola, University of Verona

   Translational research on cystic fibrosis (CF) aims at developing diagnostic tools to iden-

tify CFTR (Cystic Fibrosis Transmembrane conductance Regulator) mutants, at increasing knowledge on the pathophysiology of CFTR protein and at developing therapeutic molecules targeting the corresponding defective CFTR protein responsible for multi-organ alterations in CF people. Recently, research efforts have been awarded with the first drug approved by US FDA for the therapy of underlying CFTR defect. In this contest, the availability of both new validated CFTR biomarkers and of corresponding biomarker assessment techniques has become a research priority. Actual methods to measure CFTR biomarkers suffer from some limitations. For instance, the results of sweat chloride sometimes can be affected by concomitant diseases or therapies and sweat test cannot be applied to test drugs in *ex vivo* CF cell systems. The *in vivo* measurements of trans-epithelial nasal potential difference (NPD) or the *ex vivo* intestinal current measurements (ICM) reference bioassays result uncomfortable, scarcely practicable and are not widely available to perform multiple assessments as usually required in clinical trials. Methods such as the measurements of trans-membrane potentials in single cells by patch-clamp and/or by trans-membrane potential-sensitive fluorescent $DiSBAC_2(3)$ probe are time consuming and have high variability. Therefore, CF research still focuses on the development of more reliable and comfortable methods necessary to monitor changes induced by drugs targeting CFTR protein/activity, respectively.

The biomolecular and structural composition of a cell as well as biochemical changes induced by drug treatment in the samples can be studied by Fourier transform InfraRed (FTIR) spectroscopy and microscopy (micro-FTIR). This non destructive, high sensitive and reproducible spectroscopic technique allows to obtain in a few seconds an IR spectrum reflecting qualitative and quantitative information on different molecules and their interactions in the sample. Therefore, an IR spectrum can be a useful biomarker to identify and compare the responses of CFTR defective cells to drug molecules. This global information can be acquired at the different levels of spatial resolution in samples without the use of specific probes and with minimal sample manipulation. In association with unsupervised multivariate data treatment methods subtle differences induced by drugs can be objectively identified in the corresponding dataset.

2.2 DXR1 - Soft X-ray Beamline

The DAΦNE soft X-ray beamline, DXR-1, is mainly dedicated to soft X-ray absorption spectroscopy. The X-ray source of this beamline is one of the 6-poles equivalent planar wiggler devices installed on the DAΦNE electron ring (0.51 GeV) for the vertical beam compaction. The 6 wiggler poles and the high storage ring current (higher then 1 Ampere) give a useful X-ray flux for measurements well beyond ten times the critical energy. The useful soft X-ray energy range is 900 eV - 3000eV where the lower limit is given by the Beryl crystals used in the double-crystal monochromator and the higher limit is given by the wiggler working conditions. Some check tests were performed on all the elements of the beamline because after the long 2011 DAΦNE shut down a first beamline realignment was performed at the end of 2011 and ended in 2012 when the beam condition became more stable. In order to control the new working conditions also some XANES measurements were performed in october 2012 in the presence of good and stable beam conditions (Fig. 4).

Some recent experimental results achieved on data taken some years ago were presented in 2012 at the Symposium on Synchrotron Radiation in Natural Science held in Krakow (Poland):

1. *Valence of constituents of selected rare earth silicides -XANES and LAPW numerical study.*
   Pavel ZAJDEL - University of Silesia, Institute of Physics, Katowice, Poland

   The inter-metallic rare earth (RE) silicides call a lot of attention due to their uranium based members, frustrated geometry and interesting magnetism. Although the electronic structure

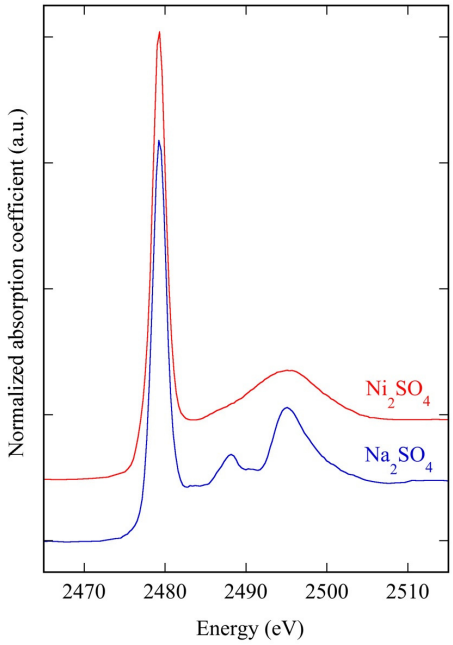

Figure 4: Normalized XANES spectra of Ni_2SO_4 and Na_2SO_4 reference compounds.

and magnetism are primarily determined by the rare earth and the RE-Pd/Rh hybridization it is interesting to verify the role of silicon as ″passive″ spacer. The investigation of the chemical environment and electronic structure of Si and Pd using X-Ray Absorption Fine Structure related to two different families of samples is reported. The XAS experiments were performed at the DAΦNE-Light Laboratory of the Laboratori Nazionali di Frascati. Data were collected at room temperature, in the transmission mode. Two families of silicides were chosen for the study. The similarities and differences caused by different rare earth in the same matrix for RE_2PdSi_3 series, where RE=Ce, Nd, Td, Dy, Ho, Er are shown. The compounds crystallize in an AlB_2-type structure (space group P6/mmm). The RE ions occupy the Al-equivalent positions, while nonmagnetic Pd and Si atoms should be statistically distributed on B sites.

2.3 DXR2 -UV branch Line

The synchrotron radiation (SR) photon beam from a wiggler installed on the DAΦNE storage ring is split by a grazing incidence Au-coated mirror (θ_i = 40 mrad, cut-off energy about 800 eV), in order to provide the X-ray and UV beamlines. The reflected UV radiation travels through the UV beamline and ends in a 63 mm diameter MgF_2 window. The UV-VIS beamline operates on an extended spectral range from 120 nm to 650 nm, spectral regions commonly referred to as Visible, UV-A, UV-B and UV-C. There are three experimental stations: one operates in the VUV (UV-B and UV-C) region between 120 nm and 200 nm (monochromatic radiation), the second covers the range 200-650 nm (VIS, UV-A, UV-B) with monochromatic radiation and the third covers the same spectral range but in white light or broadband typically for experiments of irradiation or aging. The same spectral range can be also covered by conventional light sources like gas discharge lamps that have emission spectra not continuous as synchrotron radiation, but have particularly

intense emission lines (see Fig. 5).

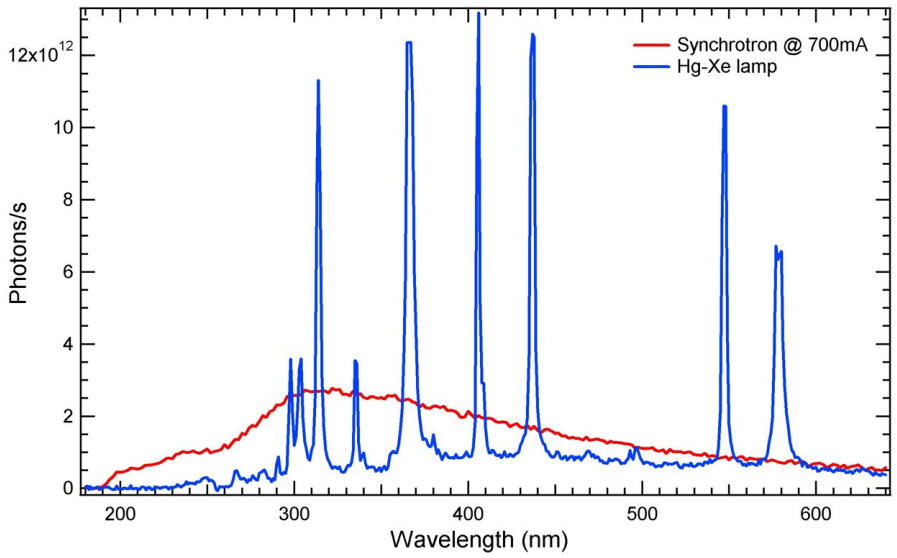

Figure 5: Emission spectrum of the Hamamatsu 500 W Hg-Xe lamp compared to the synchrotron radiation spectrum in the UV-VIS range measured with a 700 mA electron current circulating in the storage ring.

The three stations can also be used in test operations and calibration of components of optical systems even of large size, of photon detectors having standard sizes and of thin layers or multilayers. It is possible to carry out measurements of reflectivity, transmissivity and absorption of thin layers. This beamline is particularly suitable for experiments of photochemistry and photobiology related to the characterization of inorganic and organic materials, the alteration of organic molecules and inorganic complexes as an effect of irradiation experiments and aging. The UV region of this beamline has been used for photochemistry experiments to study molecules of astrobiological interest. Also bacteria, which were tested on board in the International Space Station, showing no evidence of radiation damaging, were exposed to UV radiation in order to investigate the effects on such radiation resistant systems. The interest of this research is to find, if it exists, the effective dose that can induce a damage, i.e., the surviving threshold. This experiment is still going on, exploring a wide range of photon doses and exploiting the synchrotron radiation beam intensity in order to simulate prolonged exposures or life conditions on other space environments, like Mars. This kind of experiments was also performed in combination with the use of the SINBAD IR beamline to monitor in real time the UV irradiation effects. An on-going project for a photochemical facility at the DAΦNE-L laboratory combines the UV and the IR beamlines. Such a facility takes advantage from the capabilities of the two synchrotron radiation beam-lines: the first one, operating in the visible-UV range, is used as a strong excitation and irradiation light-source in which both intensity and spectral range can be selected to fulfill the experiment requirements while the infrared beamline provides FTIR micro-spectroscopy and imaging. An optical fiber allows the UV irradiation of samples directly into the FTIR interferometer or microscope. Fast photochemical reactions can be analyzed in real time, letting unveil inter-phases not normally observable by analyzing the reagents and products of the reaction itself. Complex unstable systems can be irradiated and analyzed without changing the sample condition (morphology, humidity etc.). The accessible

wavelength region for the photochemical experiments is 180-400 nm. Two optical configurations are available: the first makes use of the synchrotron radiation (SR) white beam while the second brings monochromatic SR on the sample. A different setup was conceived to UV irradiate samples of micrometric size in 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. After some preliminary tests, we realized that the optical coupling at the vacuum feedthrough on the interferometer is very critical. 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 are not perfectly aligned. The optical transmission improved from roughly 10% up to 72%, providing the spectrum reported in Fig. 5. The photon flux at the main lines of the UV lamp is of the order of 10^{11} photons/s/nm in the spotlight, while the SR integrated flux from 200 nm to 400 nm is of the order of 10^{14} photons/s/nm in the spotlight. In order to fully assess the methodology and the optical system tests using the Hg-Xe lamp as UV source and nucleobases as samples were made. Pure nucleobases, as adenine, uracil, pyrimidine and cytosine, and the same nucleaobases in presence of inorganic mineral matrices, were irradiated using the UV white beam and real-time FTIR analysis, making use of the diffused reflectance technique, was used to monitor their degradation. A 500 W Hg-Xe lamp was optically coupled to a 10-m UV-grade optical fiber illuminating the organic sample. IR radiation was sent on the sample inside the FTIR interferometer of the SINBAD beamline and the diffused/reflected 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 IR spectra from Uracil are shown in Fig. 6 as an example.

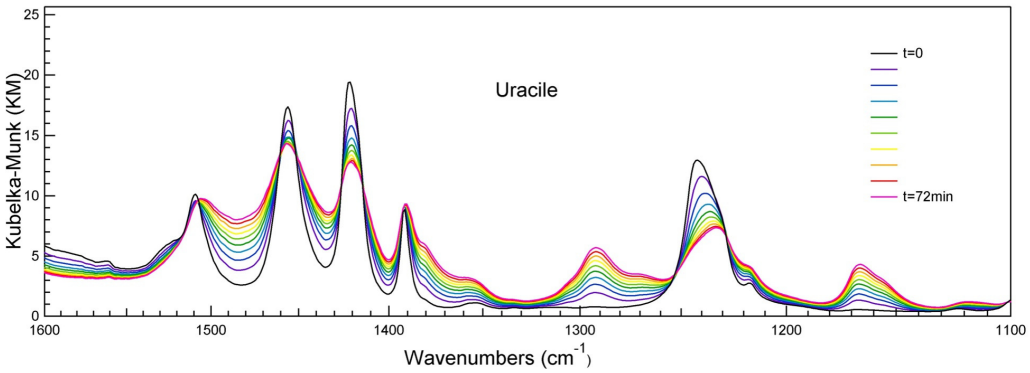

Figure 6: FTIR spectra of the degradation process of uracil molecule after UV irradiation.

The interaction between electromagnetic radiation and bio-molecules in heterogeneous environments is a prebiotically relevant process. Minerals may have a pivotal role in the prebiotic evolution of complex chemical systems, mediating the effects of electromagnetic radiation, influencing the photostability of bio-molecules, catalyzing important chemical reactions and/or protecting molecules against degradation. In particular, nucleobases are relevant bio-molecules to investigate both in the prebiotic context, because they are coding components of nucleic acids, and from the standpoint of the survival of biological systems in space conditions. Experimental results confirmed the high intrinsic photostability of such molecules, because a rather low probability of interaction

between UV radiation and nucleobases was estimated, and furthermore indicate that cytosine and hypoxanthine have a greater photostability compared to adenine and uracil, both pure and adsorbed onto magnesium oxide and forsterite.

2.4 New XUV beamlines

In 2012, the new XUV laboratory has continued its construction, based both on the detailed plans approved by the SRL Committee and on available resources. Aim of this laboratory is to host two bending magnet beamlines covering the photon energy range from 30 eV to 1000 eV. One beamline will cover the low energy part of this interval (30-200 eV) and is called LEB (Low Energy Beamline), the other will cover the energy range from 60 eV to 1000 eV and is called HEB (High Energy Beamline). Both beam lines are in UHV and directly connected to the vacuum of the main DAΦNE ring. All the safety protocol and control systems are ready and tested. Since the beginning of the year, the two beam lines were ready to start commissioning with synchrotron light. The commissioning did not even start in 2012 because stable and continuous DAΦNE working conditions are clearly required. The complex procedures of commissioning of the two XUV beamlines will start as soon as the necessary beam conditions will become available. Meanwhile, the two *state of the art* end stations, whose construction was nearly completely funded without using resources from the DAΦNE-L laboratory were implemented and successfully used. Both experimental set-up have been equipped with commercial laboratory sources (X-ray lamp and He-discharge lamps), electron sources and all the needed tools to perform not only detailed tests on their functionality but also experiments. The tests of the experimental chambers were also used to perform experiments on SEY (Secondary Electron Yield) reduction versus electron bombardment, surface conditions and carbon deposition, which are the objectives of the IMCA-NTA Project (see this annual report for a detailed description of this activity) and were done in collaboration with R. Larciprete (ISC-CNR) and R. Flammini (IMIP-CNR), who are associated to that project. During 2012, a state of the art micro-Raman station was set up. This was done in order to enrich the available techniques and experimental apparata offered by the DAΦNE-L laboratory to its users community. Such ancillary equipment has been founded combining DAΦNE-L and IMCA-NTA economic resources. The XPLORA micro-Raman Instrument from Jobin-Yvon was installed in the laboratory as shown in Fig. 7.

Figure 7: The new micro-Raman instrument XPLORA from Horiba Jobin-Yvon installed in 2012.

Already some test experiments have been done to commission the instrument and see its potentialities. An example is given in Fig.8 where the Raman spectra measured on C film grown at room temperature on polycrystalline copper by magneton sputtering, before and after thermal annealing at 800 °C are shown.

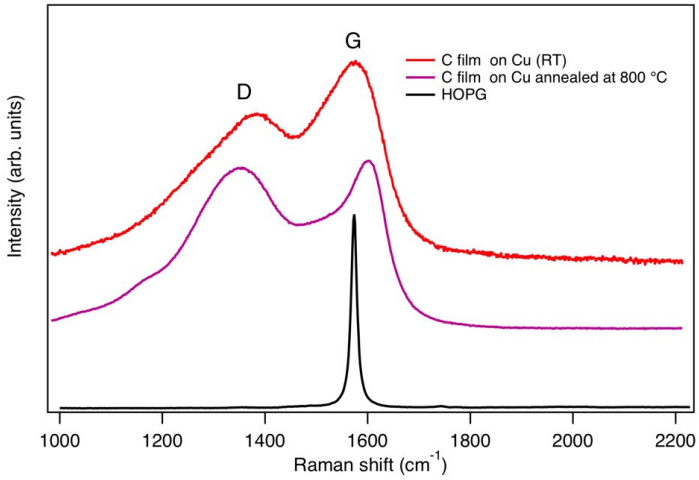

Figure 8: Raman spectra measured on C film deposited at RT by magnetron sputtering, before and after the thermal annealing at 800 °C. For comparison the bottom curve shows the Raman spectrum of HOPG.

For comparison the Raman spectrum of highly oriented polycrystalline graphite (HOPG) is also reported. The C film spectra show the D (disordered) and G (ordered or graphitic) bands at 1380 and at about 1580 cm^{-1} typical of carbonaceous materials. The D band is absent in the HOPG spectrum. The thermal annealing reduces the width of the D and G bands indicating a higher degree of ordering of the C network.

3 List of Conference Talks

1. E. Pace ″Innovative photochemical facility at DAΦNE-Light synchrotron source″, SRI2012: 11th International Conference on Synchrotron Radiation Instrumentation , Lione (FR), July 9-13, 2012.

2. M. Cestelli-Guidi, ″In vivo skin leptin modulation after 14 MeV neutron irradiation: a molecular and FT-IR spectroscopic study″, ISSBB - Italian Society for Space Biomedicine and Biotechnology - Brindisi 25-27 October 2012.

4 List of other contributions to Conferences

1. P. Zajdel (oral presentation), A. Kisiel, A. Szytula, P. Starowicz, J. Goraus, J. Konior, A. Banas, A. Balerna, G. Cinque and A. Grilli ″Valence of constituents of selected rare earth silicides -XANES and LAPW numerical study.″, ISSRNS 2012 11th International School and Simposium on Synchrotron Radiation in Natural Science, Krakow, Poland May 20-25, 2012.

5 Publications

1. P. Savchyn, I. Karbovnyk, V. Vistovskyy, A. Voloshinovskii, V. Pankratov, M. Cestelli Guidi,C. Mirri, O. Myahkota, A. Riabtseva, N. Mitina, A. Zaichenko, and A. I. Popov, ″Vibrational properties of $LaPO_4$ nanoparticles in mid- and far-infrared domain″, J. Appl. Phys. **112**, 124309 (2012)

2. M. Cestelli Guidi, C. Mirri, E. Fratini, V. Licursi, R. Negri, A. Marcelli and R. Amendola, ″In vivo skin leptin modulation after 14 MeV neutron irradiation: a molecular and FT-IR spectroscopic study″, Anal Bioanal Chem **404**, 1317 (2012)

3. S. Lupi, A. Nucara, A. Perucchi, M. Cestelli Guidi, E. Chiadroni, M. Ferrario, M. Ortolani, L. Baldassarre, D. Nicoletti, C. Mirri, F. M. Vitucci, P. Di Pietro, U. Schade and P. Calvani, ″A survey of the Italian research in solid state physics by infrared spectroscopy with electron-beam sources″, J. of Phys.: Conf. Series **359**, 012001 (2012)

4. L. Monico, K. H. Janssens, C. Miliani, G. Van der Snickt, B. G. Brunetti, M. Cestelli Guidi, M. Radepont, and M. Cotte, ″The Degradation Process of Lead Chromate in paintings by Vincent van Gogh studied by means of spectromicroscopic methods″, Anal. Chem. doi: 10.1021/ac3021592 Publication Date (Web): October 10, 2012

5. M. Cestelli Guidi, S. Yao, D. Sali, C. Sabine, A. Marcelli and C. Petibois ″Experimental ATR device for real-time FTIR imaging of living cells using brilliant synchrotron radiation sources″, Biotechnol. Adv. (2012), doi:10.1016/j.biotechadv.2011.11.009

6 Other pubblications

1. A. Mottana, A. Gorghinian, M. Cestelli-Guidi, A. Marcelli, ″Esame gemmologico qualitativo integrato con misure quantitative in microspettroscopia di fluorescenza dei raggi X, e in s pettroscopia vibrazionale dei raggi infrarossi, identificazione delle pietre preziose e dei leganti.″, Splendore Marciano, M. L. Sebasatiani and P. Crisostomi, ISBN 978-88-95047-14-0, Edizioni Nova Charta, 2012.