



miras²

microespectroscopía infrarroja con radiación sincrotrón

AN INFRARED MICROSPECTROSCOPY BEAMLINER FOR ALBA

A proposal to the S.A.C.

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AN INFRARED MICROSPECTROSCOPY BEAMLINE FOR ALBA

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Preface

The **miras**² initiative started in 2007, and has now developed into the present proposal for a phase II beamline for the new Spanish Synchrotron Facility ALBA; this has been initiated from the interest and support of many scientists from a wide range of disciplines, with very different approaches to fundamental research and problem-solving in their respective areas. One of the key issues that motivate many of these researchers was the ability to obtain useful information from very small sample domains. To some, Synchrotron Infrared Microspectroscopy (SIRMS) is a completely original technique, to others it represents a significant advance over previous limitations in IR microspectroscopy, but to many it offers a powerful and versatile solution that allows them to successfully approach previously inaccessible problems, with important consequences for the consolidation of knowledge in a wide range of scientific disciplines.

mirar *transitive verb* **to look**

miras *2nd person singular (tu) present perfect* **you look**

“miras” *acronym* (orig. ca. 2007) **microespectroscopía infrarroja con radiación sincrotrón,**

...which translates as ... **synchrotron infrared microspectroscopy**

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1. Introduction

The **miras²** initiative proposes to build at ALBA a world-class beamline for Infrared Microspectroscopy using the combination of both edge radiation (ER) and bending magnet (BM) sources from the same extraction port. This dual source configuration will allow the construction of two end-stations designed to operate simultaneously.

This facility will offer the highest level of sensitivity attainable at diffraction-limited spatial resolution in the mid-IR range, and will support applications of analytical microspectroscopy to disciplines ranging from medicine through biology, food science, chemistry, environmental science, geology, physics, forensic science, and archaeology to cultural heritage.

The design of the optical transfer system will benefit from experience gained and shared with colleagues' worldwide in particular at the ESRF and SOLEIL. The beamline will be designed for optimum performances in both the mid-IR and far-IR, with a suite of detectors taking advantage of competitive performance in the widest spectral range. The IR instruments located on the end-stations will combine the best available technology for both single-point microspectroscopy and infrared imaging spectroscopy, which currently would involve two alternative instruments. The wide range of disciplines represented in the expressions of interest calls for a versatile suite of sample environments and sampling methods coupled with off-line facilities for sample preparation and results analysis.

The ability to acquire high quality IR spectra, in measurement times of seconds, from materials on a length scale of a few microns owes its impact to the high information content of the IR spectrum coupled with wavelength-limited spatial resolution (2 – 10 μm). The synchrotron source achieves this performance by delivering up to 10^3 times more IR light onto a 3 μm spot than a conventional infrared source such as a *globar*. The prospect of "world-beating" performance is not in this instance directly related to the IR flux delivered at a micro-spot by the present beamline design. However, the flux generated at ALBA will be comparable to that achieved by leading competitor synchrotron facilities. The signal-to-noise ratio (S/N) in synchrotron infrared microspectroscopy (SIRMS) spectra is commonly limited by the noise related to beam instability. According to the recent achievements in newly opened synchrotron facilities, such as SOLEIL and DIAMOND, a positional feedback system might not be necessary. Given that best practice on achieving beam stability will be incorporated into this beamline design we can expect important enhancements in the S/N ratio exceeding those predicted by the flux advantage. We are fortunate to be in a position to benefit from the experience of colleagues currently planning and/or designing SIRMS beamlines elsewhere in Europe (e.g. ESRF, SOLEIL) and the rest of the world (e.g. NSLS, Australian Synchrotron).

We therefore confidently aim to provide a world-class beamline at ALBA with a first-rate working environment appropriate for the very wide range of disciplines which it will serve, enabling advancements in areas such as: the study at sub-cellular resolution of phenomena related to disease states and their diagnosis and treatment; the mapping of solid state and catalytic reactions in micro-crystals, the characterisation of microscopic areas of nanoscopic thin films important in lubrication, wear, colloid chemistry and high throughput screening; studies on diverse phenomena in polymeric and hybrid systems, interphase structure and morphology; amongst the many others specifically mentioned in this proposal. Taken together these activities will contribute significantly to health, quality of life and prosperity in Spain.

1.1 A brief history of synchrotron infrared microspectroscopy

Infrared (IR) spectroscopy is probably the most widely used characterization technique for chemical analysis due to its high versatility, non-destructive sampling possibilities, and rich information, given that an IR spectrum contains multiple signals that are highly characteristic absorption bands from a single molecular species. This high information content from IR spectra allows the operation of databases and the “fingerprint” approach to unequivocal chemical identification. On the other hand, IR spectra are also highly sensitive to the molecular environment, and can provide information related to chemical and structural changes, valuable for the study of numerous processes that occur in the materials of interest.

IR + MS = IRMS
infrared spectroscopy + microscopy = infrared microspectroscopy

The first references in the literature on the combination of microscopy and IR spectroscopy appeared before the Second World War, but it was not until the early 1950s that the first successful applications of the technique for the characterization of microscopic samples emerged^{1,2}. Infrared microscopy, or infrared microspectroscopy (IRMS) as it is often called, only became fully commercially available in the early 1980s, due to significant technological advances in Fourier transform infrared spectroscopy, and related data processing hardware and software.

Infrared Microspectroscopy generates chemical and structural information from a precise microscopic volume, and in many cases the interrogation of such tiny volumes is fundamental to the understanding of the chemical and physical properties of the vast range of materials that are organised on a microstructural level.

Modern IR microscopes employ reflective Cassegrain or Schwartzchild objectives and condensers which focus the IR radiation on the sample and collect the transmitted or reflected light for delivery to the detector, generally a cryogenically cooled mercury cadmium telluride (MCT) device. Variable apertures are situated at one or more conjugate image planes to allow specific selection of the area to be studied. The development of sophisticated software and hardware in these systems, such as the use of computer controlled xy translation stages, allow not only the characterization of specific points on a sample, but also enable the analyst to generate infrared spectral maps of whole areas of a sample, providing spatial or topological chemical and structural information over selected regions of a given specimen. With specialised optics such as attenuated total reflectance (ATR) objectives, grazing angle objectives, etc., the study of a wide range of materials at the microscopic level is now almost routine.

The spatial resolution of the microscope can be controlled by changing the size of the apertures. However, the highest spatial resolution of an infrared microscope is not defined by the size of the field apertures, but rather by the diffraction limit of the radiation. The resolution limit, Δl , or the minimum resolvable separation of two points on the sample, can be described by the Rayleigh criterion, which is given by Abbe³ as

¹ R.M. Badger, R. Newman (1951) *Rev. Sci. Instrum.* 22, 935

² E.R. Blount (1951) *J. Opt. Soc. Am.* 51, 547

³ E. Abbe (1873) *Mikrosk. Anat.* 9, 413

$$\Delta l = \frac{0.61\lambda}{NA} \quad (\text{Eq. 1})$$

where λ is the wavelength of the infrared radiation, and NA is the numerical aperture of the microscope system. Over the mid-infrared region, between 4000 and 400 cm^{-1} , the wavelength varies between 2.5 – 25 μm . So if we consider a microscope with an ideal numerical aperture of 1, we would find at 1000 cm^{-1} , a maximum spatial resolution of around 6 μm . However, if we close the field apertures down to 6 μm in a typical IR microscope, the result we obtain is very poor. This is because the amount of infrared radiation passing through such a small aperture is too low, and the signal to noise (S/N) ratio falls dramatically. Due to the aforementioned noise limitations, the best spatial resolution available in an IR microscope is generally quoted as around 10 μm , but this should be considered more as a “practical limit”, independent of wavelength considerations. Indeed the time required for measurements at this “aperture limited resolution” increases the measurement time significantly in order to obtain adequate S/N in the spectra, often making mapping and imaging experiments prohibitively long.

Williams⁴ first reported the use of accelerator-based sources for IR spectroscopy over 20 years ago. Synchrotron radiation obtained from a bending magnet in a storage ring provided a highly coherent broadband IR source, which covered the whole IR region. Its extraordinarily high brightness has been demonstrated to provide more than three orders of magnitude improvement in intensity^{4,5}, and its almost linear broadband spectral coverage over the whole IR region makes it an ideal IR source⁶.

The importance of this discovery was soon recognised, and the improved beam stability of newer synchrotron sources along with a manageable beam size allowed it to be efficiently coupled to an IR microscope. The first IR microscopy beamline was built in 1993 at Brookhaven National Laboratory, New York, USA^{7,8,9}. The use of synchrotron sources has lifted IRMS to new levels of sensitivity and spatial resolution, with a spectacular impact across a wide range of life and physical sciences. At present there are more than twenty IR microscopy beamlines, active or under development, throughout the world, as can be seen in **Appendix I**. Indeed, every 3rd generation synchrotron source operates at least one SIRMS beamline, and many operate several.

The access to higher sensitivity and spatial resolution via synchrotron infrared microspectroscopy has opened up a whole new line of studies over a wide area of scientific disciplines. In recent years, growth of the SIRMS technique (or **MIRAS**, in Spanish) has been spectacular precisely due to its great success in diverse fields, ranging from biology and biomedicine, forensics and industrial analysis, archeometry and cultural heritage, to polymer and ceramic materials science, geology and astrophysics, amongst others.

⁴ G.P. Williams (1982) *Nucl. Instr. and Meth.* 195, 383

⁵ W.D. Duncan, G.P. Williams (1983) *Appl. Opt.* 22, 2914

⁶ G.L. Carr, P. Dumas, C.J. Hirschmugl, G.P. Williams (1998) *Il Nuovo Cimento* 20, 375

⁷ J.A. Reffner, P.A. Martoglio, G.P. Williams (1995) *Rev. Sci. Instrum.* 66, 1298

⁸ G.L. Carr, J.A. Reffner, G.P. Williams (1995) *Rev. Sci. Instrum.* 66, 1490

⁹ G.L. Carr, M. Hanfland, G.P. Williams (1995) *Rev. Sci. Instrum.* 66, 1643

1.2 The Scientific Impact of SIRMS

Since the introduction of the SIRMS technique, numerous advances have been made in diverse scientific fields, and the research results published in highly specialised journals, with a important impact at an international level. There is already a prolific literature base in many fields. The graph in Figure 1.1 represents an approximate distribution of publications by broad research area over the last 10 years.

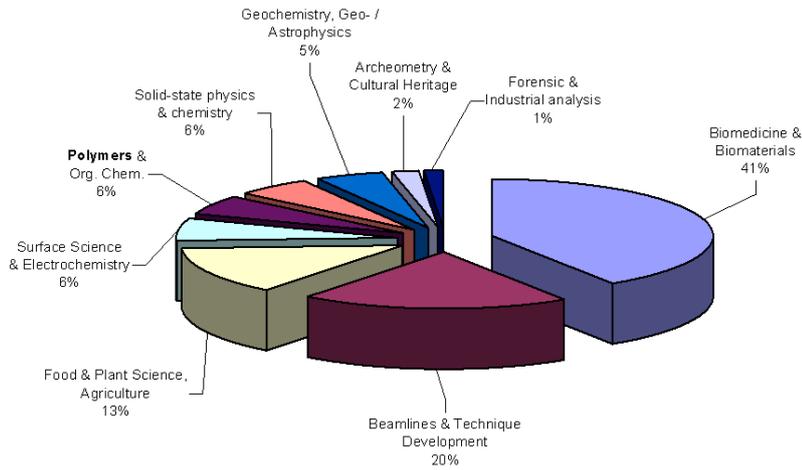


Fig.1.1 Approximate distribution of publications on SIRMS

Within the application areas of SIRMS, biomaterials and biological or biomedical applications, including the areas of food and agriculture, account for over 50% of the publications to date. However, many research groups have started to introduce the technique in new areas, and are already producing an important impact in the scientific and technological literature.

The number of articles published annually that employ SIRMS are growing rapidly, and can be currently estimated¹⁰ at over 1.5 manuscripts per week, with a prediction of between 70 – 80 registered articles in 2009.

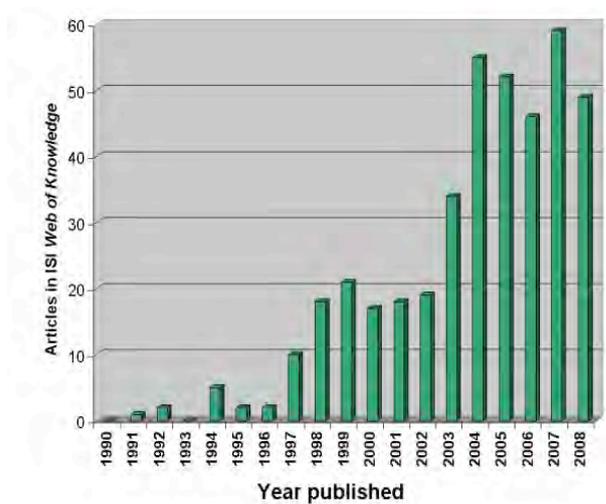


Fig.1.2. Number of articles registered in the database ISI Web of Knowledge.

The potential impact of synchrotron infrared microspectroscopy on the quality of life in Spain and on the Spanish economy can be visualized in terms of the diverse areas of activity in the

¹⁰ It should be noted that not all of the manuscripts with SCI ratings are found with the ISI database search.

Spanish scientific community, ranging from biology and biomedical studies, medical diagnosis, food science and forensic science to high throughput screening in materials, catalytic chemistry, polymer science, environment, geochemistry, and archaeology and cultural heritage.

1.3 The Spanish User Community

To date the number of research groups in Spain that use or have used SIRMS has been limited to a handful. This has been due to a number of reasons, notably the lack of nearby facilities, and the heavy oversubscription of IR beamlines at newly inaugurated European facilities¹¹.

However, the rapid expansion of the technique throughout the world stimulated us to organise a monographic workshop¹², miras.2008, the *1st Spanish Workshop on Synchrotron Infrared Microspectroscopy*. Details of the Workshop can be found at the following internet website: www.ictp.csic.es/miras2008.

The miras.2008 Workshop was celebrated in Madrid on the 14th - 15th of April, to introduce the technique and its current applications, and demonstrate the future possibilities of an IR beamline in ALBA to diverse groups of the Spanish scientific community from Universities, CSIC (Spanish Scientific Research Council), Institutions and Private Companies. During the workshop, 8 invited lectures were given by international experts from the USA, France, Germany, United Kingdom and Spain. A round-table discussion and a poster presentation session were also held. As a consequence, various research groups in Spain expressed their intention to exploit the technique in their future research. Some statistical data taken from the answers of delegates to a questionnaire is presented in **Appendix II**.

One of the decisions taken at miras.2008 was the creation of a webpage to inform the Spanish scientific community of the miras² initiative; www.miras2.es came live at the end of January 2009, providing a means for scientists to make contact and express their interests.

A questionnaire¹³ was posted on the website, in which we specified several broad scientific areas in line with the current trends in SIRMS in the world. We also invited people to specify a series of options related to their experimental interests, in order to give us an initial feel for the requirements of the potential user community.

Between 15th February – 15th March 2009, we received around 70 EXPRESSIONS OF INTEREST, and the distribution of interests expressed is shown in Figure 1.3a, along with the answers of the potential users to the different options, in Figure 1.3b.

Finally, the proposal has received numerous letters of support from Industry

¹¹ After the closure of LURE (Paris) in 2003, the nearest operative IR beamlines available were ANKA and BESSY (Germany), and SLS (UK). In 2008, the new SMIS beamline at SOLEIL came online, and is heavily oversubscribed making access difficult for prospective users. The requested beamtime to allocated beamtime ratio in 2008 was approximately 3:1!

¹² This event was supported by the Spanish Ministry of Education & Science through a project lead by AUSE (the Spanish Synchrotron Users Association), and was sponsored by the C.S.I.C., the I.C.T.P., and the companies Bruker, Perkin-Elmer and Thermo.

¹³ See **Appendix III** for an example questionnaire

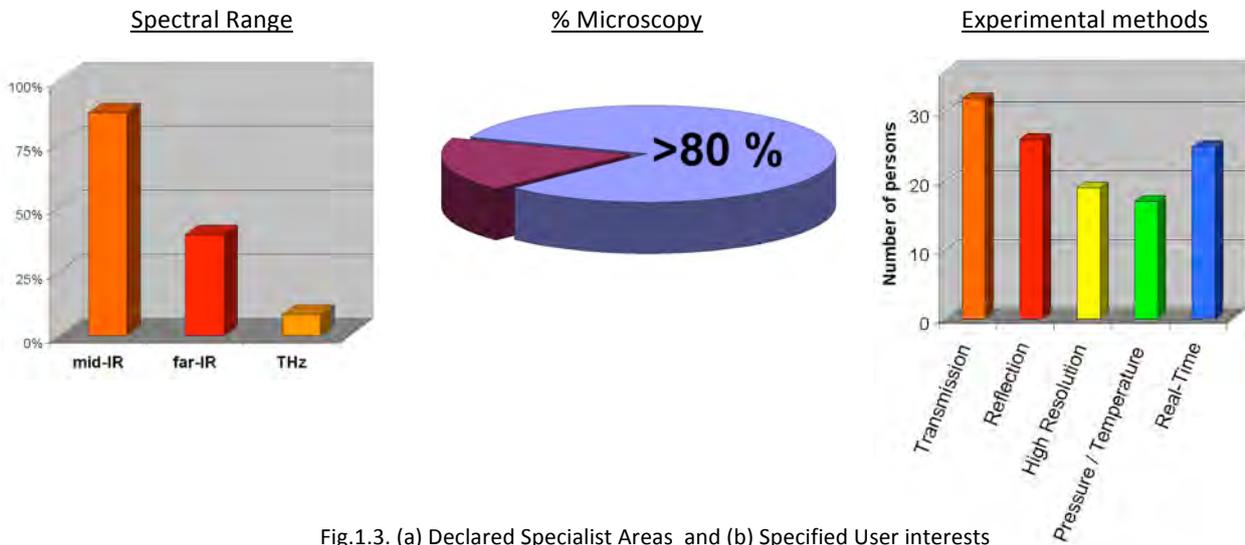
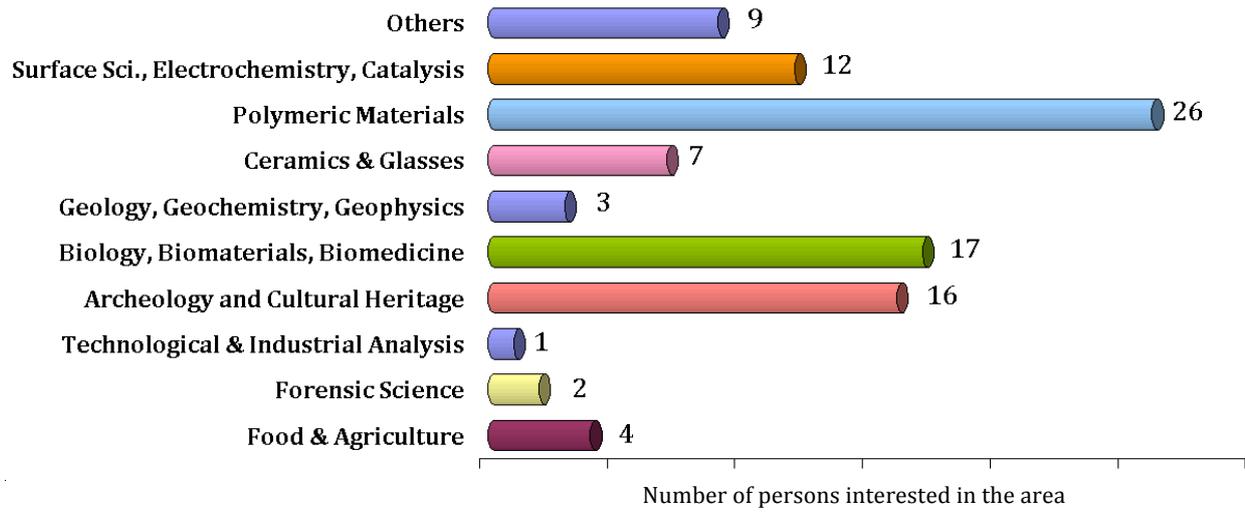


Fig.1.3. (a) Declared Specialist Areas and (b) Specified User interests

2. Areas of Scientific Interest

It is often quite complicated to organise or categorise into clear-cut research areas the diverse scientific interests, since many key themes are for obvious reasons multidisciplinary. Thus the election of a particular “category” for a particular research theme is relatively subjective, as can be deduced from the scientific cases and expressions of interest presented in this document. That said, several key areas have been identified and are presented below. The full list of the persons involved in the research in the Scientific Cases and Expressions of Interest presented in this proposal is given in **Appendix IV**, and includes 182 people from 56 Research Groups/Departments in 15 Universities, 11 CSIC Institutes and 5 Mixed and Other Research Centres.

Further, the proposal has received a number of supporting letters from 5 major Industrial Companies, 1 R+D+i Foundation, 3 Specialised Groups and 1 CSIC Institute. These can be found in **Appendix VI**.

2.1 Life Sciences and Biomedicine

life science *noun*. Any of several branches of science, such as biology, medicine, anthropology, or ecology, that deal with living organisms and their organization, life processes, and relationships to each other and their environment¹⁴. Also called *bioscience*.

Our understanding of life processes has an enormous impact on well-being and quality of life. In this respect, the application of advanced characterization technologies at the forefront of current progress of is fundamental importance, and necessary for the provision of new information in many areas of the life sciences.

Vibrational spectroscopy carries a high level of molecular information and is able to detect subtle biochemical changes within tissues^{15,16}. One of the main challenges for the biological materials community is the development of new and creative methods for acquiring, processing, and interpreting biomolecular information arising from tissues, and from individual cells¹⁷ or cells in a microscopic environment, with cellular and sub-cellular resolution^{18,19}. In this respect, SIRMS is a powerful technological platform for developing cutting-edge research that will open the way to a large number of biological and biomedical applications where high spatial resolution and high quality information are required²⁰. The ability to study a single live cell with or without an external perturbation^{21,22} is a fundamental issue, and at present acquiring infrared spectra in such conditions, where only a few cells are available for analysis or diagnosis, can only be achieved at synchrotron facilities.

Let us take as an example cancer. The screening and early diagnosis of cancer is an issue of worldwide impact. As an example, let us consider just one theme: **cervical cancer diagnosis**.

In developing countries cervical cancer is now the most common cause of death from malignancy in women. In the European Union the figures are alarming: in 2004 approximately 31,000 women in the EU25 developed cervical cancer and almost 14,000 died from the disease²³. Current screening methods rely on the cytopathological analysis of exfoliated cells, which is labour-intensive, of debatable reproducibility and highly subjective to the criteria of the observer^{24,25}. This results in alarmingly high false-negative rates, up to 25% in some cases²⁶.

¹⁴ The American Heritage® Dictionary of the English Language, Fourth Edition, Copyright © 2006 by Houghton Mifflin Company.

¹⁵ Mantsch, H.H. et al. (2002) Vibrational Spectroscopy and Medicine: An alliance in the making. *Vibrational Spectroscopy* 30, 31-41

¹⁶ Jackson, M. and Mantsch, H.H. (1996) Biomedical infrared spectroscopy, in "Infrared Spectroscopy of Biomolecules" (Wiley-Liss, ed.), pp. 311

¹⁷ M. Diem, M. Romeo, C. Matthäus, M. Miljkovic, L.M. Miller, P. Lasch (2004) Comparison of Fourier Transform Infrared (FTIR) Spectra of Individual Cells Acquired Using Synchrotron and Conventional Sources. *Infrared Physics and Technology*, 45: 331-338.

¹⁸ Jamin, N. et al. (1998) Highly resolved chemical imaging of living cells using synchrotron infrared microspectrometry. *Proc. Natl. Acad. Sci.* 95, 4837-4840

¹⁹ Holman, H.Y.N. et al. (2000) IR spectroscopic characteristics of cell cycle and cell death probed by synchrotron radiation based Fourier transform IR spectromicroscopy. *Biopolymers* 57, 329-335

²⁰ L.M. Miller, P. Dumas (2006). Chemical imaging of biological tissue with synchrotron infrared light. *Biochim Biophys Acta.* 1758 (7): 846-87

²¹ H. N. Holman, K. Bjornstad, M. P. McNamara, M.C. Martin, W.R. McKinney, E.A. Blakely (2002) Synchrotron Infrared Spectromicroscopy as a Novel Bioanalytical Microprobe for Individual Living Cells: Cytotoxicity Considerations *J. Biomedical Optics*, 7(3), 417-424

²² Jamin, N. et al. (2003) Chemical heterogeneity in cell death: combined synchrotron IR and fluorescence microscopy studies of single apoptotic and necrotic cells. *Biopolymers* 72, 366-373

²³ Arbyn M, Raifu AO, Autier P, Ferlay J., Burden of cervical cancer in Europe: estimates for 2004, *Ann Oncol.* 2007, 18(10):1708-15

²⁴ Lyall H, Duncan ID. Inaccuracy of cytologic diagnosis in high grade squamous intraepithelial lesions (CIN3). *Acta cytol* 1995; 39: 50-4.

²⁵ Williamson SL, Hair T, Wadehra V. The effects of different sampling techniques on smear quality and the diagnosis of cytological abnormalities in cervical screening. *Cytopathology* 1997; 8: 188-95

Although the incidence of cervical cancer in Spain is of the lowest in Europe, the rapid changes in population demography urgently require new approaches. Screening methods based on IR spectroscopy offer potential advantages over screening by conventional cytology, which include faster and less subjective analysis, reduced cost and the potential for automation, and are the subject of new developments^{27,28} in cervical^{29,30} and endometrial³¹ carcinoma. The ability to obtain spectra of the highest quality at cellular and sub-cellular level will allow the development of powerful training sets for chemometrics³² or neural-network (ANN)³³ based protocols which may allow the early identification of cell abnormalities.

Important advances in the application of SIRMS to other oncology-related areas are being made in, for example, head and neck³⁴, lung³⁵ and prostate^{36,37,38} cancer, the study of drug-based and radiation therapies for cancer treatment^{39,40}. It is relevant to point out that the vast majority of Spanish Universities and CSIC Institutes with Biology or Molecular Biochemistry Departments have at least one group that investigates some aspect of cancer. Spain also has centres of excellence with exclusive dedication to cancer research, such as the Spanish National Cancer Research Centre (CNIO)⁴¹ in Madrid, the Cancer Research Centre⁴² in Salamanca, and the Catalan Institute of Oncology⁴³ in Barcelona.

Other areas of biomedical interest of SIRMS include the study of neurological diseases⁴⁴ such as Alzheimer^{45,46}, Parkinson⁴⁷ or Scrapie⁴⁸, skin and bone disease (osteoporosis^{49,50,51} and

²⁶ J.J. Terrádez Raro, F. Coloma Colomer, P. Navarro Conde, J. Gasull Ibáñez, Cervical cancer screening in public health system in Valencia Community and Pap test limits, *Revista Española de Patología* (2005), 38(1), 3-7

²⁷ Tobin M.J., Rutten F., Chesters M.A., Chalmers J., Symonds I., Fisher S., Allibone R., Hitchcock A. (2002) Investigating the potential for infrared microanalysis in cancer screening. *European Clinical Laboratory* 21 (4) 20-22

²⁸ Tobin, M.J., et al., *Infrared microscopy of epithelial cancer cells in whole tissues and in tissue culture, using synchrotron radiation*. Faraday Discussions, 2004. 126: p. 27-39

²⁹ Faolain, E.O., et al., *Potential of vibrational spectroscopy in the early detection of cervical cancer: an exciting emerging field*. Opto-Ireland 2005: Optical Sensing and Spectroscopy, 2005. 5826: p. 25-36

³⁰ Walsh, M.J., et al., *IR microspectroscopy: potential applications in cervical cancer screening*. Cancer Letters, 2007. 246(1-2): 1-11

³¹ Kelly, J.G., et al., *Derivation of a subtype-specific biochemical signature of endometrial carcinoma using synchrotron-based Fourier-transform infrared microspectroscopy*. Cancer Letters, 2009. 274(2): p. 208-217.

³² Martin, F.L., et al., *Identifying variables responsible for clustering in discriminant analysis of data from infrared microspectroscopy of a biological sample*. Journal of Computational Biology, 2007. 14(9): p. 1176-1184

³³ Lasch, Peter; Haensch, Wolfgang; Lewis, E. Neil; Kidder, Linda H.; Naumann, Dieter, Characterization of Colorectal Adenocarcinoma Sections by Spatially Resolved FT-IR Microspectroscopy, *Appl. Spectrosc.*, 2002, 56(1), 1-9

³⁴ Conti, C., et al., *Microimaging FTIR of Head and Neck Tumors. IV*. Microscopy Research and Technique, 2009. 72(2): p. 67-75

³⁵ Sule-Suso, J., et al., *Sensitivity of single, in vitro growing lung cancer cells to gemcitabine measured with synchrotron based fourier transform infrared microspectroscopy*. EJC Supplements, 2005. 3(2): p. 51-51

³⁶ Gazi, E., et al., *Imaging ToF-SIMS and synchrotron-based FT-IR micro spectroscopic studies of prostate cancer cell lines*. Applied Surface Science, 2004. 231: p. 452-456.

³⁷ Gazi, E., et al., *A study of cytokinetic and motile prostate cancer cells using synchrotron-based FTIR micro spectroscopic imaging*. Vibrational Spectroscopy, 2005. 38(1-2): p. 193-201

³⁸ Paluszkiwicz, C., et al., *SR-FTIR spectroscopic preliminary findings of non-cancerous, cancerous, and hyperplastic human prostate tissues*. Vibrational Spectroscopy, 2007. 43(1): p. 237-242

³⁹ Chio-Srichan, S., et al., *Photosensitizer effects on cancerous cells: A combined study using synchrotron infrared and fluorescence microscopies*. Biochimica Et Biophysica Acta-General Subjects, 2008. 1780(5): p. 854-860

⁴⁰ Liu, C.J., et al., *Enhanced x-ray irradiation-induced cancer cell damage by gold nanoparticles treated by a new synthesis method of polyethylene glycol modification*. Nanotechnology, 2008. 19(29)

⁴¹ <http://www.cnio.es/ing/index.asp>

⁴² <http://www.cicancer.org/index.php>

⁴³ http://www.iconcologia.net/index_eng.htm

⁴⁴ Kneipp, J., et al., *In situ identification of protein structural changes in prion-infected tissue*. Biochimica Et Biophysica Acta-Molecular Basis of Disease, 2003. 1639(3): p. 152-158

osteoarthritis), diabetes⁵², tropical diseases such as malaria⁵³, and numerous *in-vitro* studies related to novel treatment strategies^{54,55}. These are but a few of the challenges that SIRMS allows researchers, physicians and/or pathologists to approach.

Finally, SIRMS holds great potential for studies in other bioscience areas, such as bioinspired biomaterials design, synthetic biocompatible materials and hybrids, for diverse applications such as tissue engineering, biodegradables for controlled drug release, and many more innovative research areas. Further, the ability to work in an open laboratory situation provides ideal conditions for novel types of cellular analysis employing new technologies, such as microfluidics systems⁵⁶. More about specific instrumental developments relevant to the life sciences can be found in Section 2.7.

⁴⁵ Leskovjan, A.C., et al., *Synchrotron-based imaging detects metal and plaques in a mouse model of Alzheimer's disease*. 2007 IEEE 33rd Annual Northeast Bioengineering Conference, 2007: p. 54-55.

⁴⁶ Miller, L.M., et al., *Synchrotron-based infrared and X-ray imaging shows focalized accumulation of Cu and Zn co-localized with beta-amyloid deposits in Alzheimer's disease*. Journal of Structural Biology, 2006. 155(1): p. 30-37

⁴⁷ Szczerbowska-Boruchowska, M., et al., *Biomolecular investigation of human substantia nigra in Parkinson's disease by synchrotron radiation Fourier transform infrared micro spectroscopy*. Archives of Biochemistry and Biophysics, 2007. 459(2): p. 241-248

⁴⁸ Kretlow, Q. Wang, M. Beekes, D. Naumann, L.M. Miller (2008). Changes in Protein Structure and Distribution Observed at Pre-Clinical Stages of Scrapie Pathogenesis, *Biochim Biophys Acta* 1782(10):559-65.

⁴⁹ Huang, R.Y., et al., *In situ chemistry of osteoporosis revealed by synchrotron infrared microspectroscopy*. Bone, 2003. 33(4): p. 514-521

⁵⁰ Miller, L.M., et al., *Alterations in mineral composition observed in osteoarthritic joints of cynomolgus monkeys*. Bone, 2004. 35(2): p. 498-506

⁵¹ M.E. Ruppel, L.M. Miller, D.B. Burr (2008). The effect of the microscopic and nanoscale structure on bone fragility. *Osteoporosis Int.* 19(9):1251-65

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2.1.1 Scientific Cases

SYNCHROTRON BASED FTIR SPECTROSCOPY IN THE DIAGNOSIS OF CANCER

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Over the last few years, Synchrotron based-FTIR (S-FTIR) spectroscopy has become an established tool to study single cells⁵⁷. Furthermore, our recent work on the characterisation of the scattering properties of single cells⁵⁸, and nuclei⁵⁹ has helped to separate physical from biochemical properties of single cell spectra. This should now facilitate the characterisation of spectral biomarkers for cancer diagnosis and to study the effects of chemotherapy drugs on cancer cells. The clinical application in cancer diagnosis could be twofold. First the development of an automated system that could scan cytology and, by extension, tissue samples confirming or ruling out a cancer diagnosis. Second, to help pathologists on those samples that contain few cells that are suspicious but not diagnostic of cancer to better characterise these cells.

Single cells in cytology samples would be studied using synchrotron FTIR spectroscopy. Mie scattering would then be corrected and the final spectral data would be used to characterize spectral biomarkers for cancer diagnosis. Similarly, spectral biomarkers that correlate with cell sensitivity to chemotherapy drugs would also be characterized.

Our preliminary data obtained at ESRF and SOLEIL synchrotrons have shown it is possible to correct Mie scattering properties of cells⁵⁸ and single, isolated cell nuclei⁵⁹. We are now furthering this work by studying the use of synchrotron FTIR spectroscopy in the diagnosis of cancer using tissue samples.

Based on our previous work on the effects on FTIR spectra of cells following the addition of chemotherapy agents⁶⁰, we are now studying how the interaction of chemotherapy drugs could affect Mie scattering in cancer cells in order to separate physical properties of cells from the biochemical processes caused by drugs.

An important issue in cancer diagnosis using FTIR spectroscopy is standardization of protocols in order to confirm that the same spectral results are obtained at different synchrotrons and using different bench top spectrometers. Therefore, having a new infrared beamline at ALBA Synchrotron will help to provide not only extra beam time in Europe in this rapidly growing area of research, but also help towards the standardization of data collection by adding a third new generation synchrotron in Europe after SOLEIL and Diamond.

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Collaborators: Dr N. Stone, Gloucestershire Royal Hospital (UK), Dr G. D. Sockalingum, University of Reims (France), Dr A. Kohler, Nofima (Norway).

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DISEASE PATTERN RECOGNITION IN SINGLE CANCER CELLS – A "CELLOMICS" APPROACH.

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Cancer is the one of the leading causes of death. Surgery, radiation, and chemotherapy, alone or in combination, are the known modalities of treatment. Multidrug resistance (MDR), resistance to multiple and structurally uncorrelated drugs, is known to be a serious hurdle in chemotherapy⁶¹. Identification of resistant/sensitive phenotype in cancer cells from a patient can enhance the efficiency of the therapy and can thus lead to individual patient basis treatment plan. Therefore, development of simpler, cost-effective and less time-consuming methods for identification of resistant/sensitive phenotype in cancer cell lines or cell response to drugs has significant interest in cancer therapy. Infrared spectroscopy can be such a method because it is rapid, sensitive, and gives a "molecular fingerprint" of the studied sample. Several successful FTIR studies for discrimination of Pap smear and other exfoliated cells have been reported⁶². Studies on apoptosis⁶³, identification of MDR and sensitive phenotypes in a cancer cell lines^{64,65,66}, cancer cell response to chemotherapy⁶⁰, and cell migration⁶⁷ have also been described, showing the potentials and applications of this approach. A synchrotron IR microspectroscopy source provides diffraction-limited spatial resolution with high signal-to-noise. With this ultra-bright source of infrared photons, specific chemical information can be obtained from single cells^{18,57}.

Rapid identification of cell status by less time-consuming and more reliable methods is an emerging concept because it can be extremely useful in the management and treatment of diseases. Our aim is to use Synchrotron FT-IR microscopy for single cell analysis in order to (a) perform cell typing and differentiation between sensitive and resistant human cancer cell lines, (b) monitor the response of cancer cells to an external effect like an antitumour drug, and (c) analyse cells and their micro-environment. Cell typing and interaction with drugs have been demonstrated by FTIR monitoring of cell populations. SR-microscopy can be a good technological platform for developing high-throughput single cell analysis in combination with cell microarray devices.

It is foreseen that SR-FTIR will reveal relevant biochemical and structural information at the single cell level. This information will be useful to determine a cell status or define a biological function. In the case of typing it expected to reveal that the method could differentiate not only between different cell types but also cells that exhibit a resistance phenotype like MDR due to an over-expression of membrane proteins. For cell-drug interaction, we anticipate that spectroscopic marker bands can be found and that they can be correlated to the cell sensitivity. Furthermore, IR functional imaging close to the diffraction limit with an ultra-bright source will undoubtedly reveal high quality spatial and structural information of the main common biomolecules (proteins, nucleic acids, lipids, carbohydrates) present in cells, which exhibit characteristic spectral signatures. We also foresee that the results obtained will be useful for the development of high throughput rapid single cell analysis systems (in the forms of smears, cytopinned) based on the combination of synchrotron FT-IR microscopy with a cell micro-array (CMA).

Team members: Dr. Ganesh D. Sockalingum (University of Reims)
 Dr. Josep Sulé-Suso (Keele University, UK)

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BIOMOLECULES ON SURFACES

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The study of self-assembled monolayers of molecules provides fundamental information, which can be developed in to several scientific-technological applications in the nanotechnology and biotechnology fields. Therefore, the aim of the present Project is to study the interaction of single amino acids on metallic and mineral surfaces, and their chemical reactivity, by means of infrared microspectroscopy. Also, due to their simple structure, amino acids can be used as good model systems to study biomolecule-surface interactions, which can assist in the understanding of more complex systems. It has been found that a number of amino acids self-organize to form well-ordered two-dimensional structures on metal surfaces⁶⁸. The second aim of the project is to explore the catalytic properties of surfaces in the field of the origin of life, which could be involved in peptide bond formation between two amino acids (aa-aa), and therefore the chemical reactivity of these molecules on both metallic and mineral surfaces.

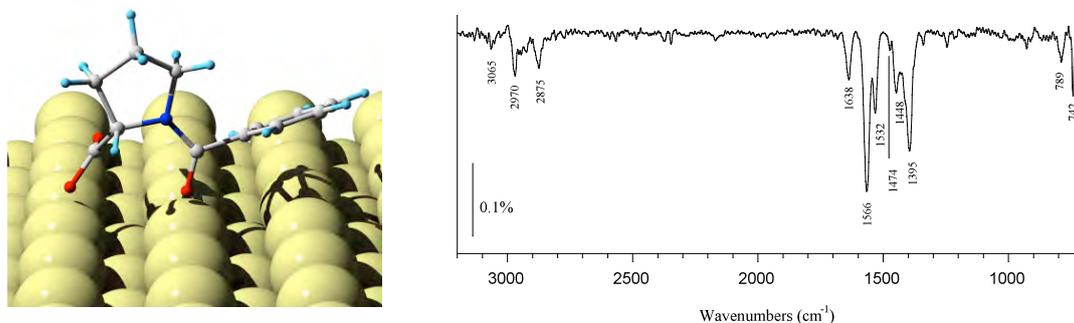


Fig.2.1 Molecular configuration and IR spectra of the chiral amino acid S-Proline on Cu (110)

We aim to study the adsorption of amino-acids on surfaces by mid-infrared synchrotron microspectroscopy, to search for chemical information on the biomolecule-surface interaction, such as the chemical state when the molecule adsorbs on the surface, chemical bonding between molecules after surface reaction process (information on the functional groups involved), whether the adsorption is homogeneous on heterogeneous mineral surfaces. We are particularly interested in the reactivity of the molecule on the surface under different experimental parameters: temperature, solvent, pH, UV irradiation processes, etc. We also aim to study mineral surfaces acting as catalysts for a pre-biotic chemistry reactions.

The high brilliance of a synchrotron IR source, high spatial resolution and high sensitivity are the three main advantages that can help us to follow biomolecule interaction processes on both metallic surfaces and minerals, which have complex non-homogeneous surfaces.

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SYNCHROTRON INFRARED IMAGING OF NORMAL AND PATHOLOGICAL HUMAN AORTIC TISSUES

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Ectasia and aneurysms of the ascending aorta are important but frequently underestimated health problems in Western countries. Many patients present asymptomatic aneurysms of the aorta or other arterial locations. To date, no non-invasive predictive diagnostic test exists and mortality rate in these aortic pathologies remains alarmingly high⁶⁹. Thus, new methods capable of giving an early diagnosis of these pathologies could be useful to reduce mortality and morbidity reported in aortic aneurysms. In fact, characterisation of the different aortic tissue types is an important issue in view of evaluating the stage of the aortic disease as this is an important factor for the surgical indication. For the last decade, FTIR spectroscopy has been successfully applied for the in-vitro analysis of biological tissues^{70,71,72}. These studies made use of the molecular information that is contained in the spectra in the form of a "fingerprint" to identify markers for diseases. The main advantages of this approach are that it is non destructive, requires minimal sample preparation, no staining, and offers both structural and morphological information. Thus, spectral imaging can be performed based on the intrinsic molecular information present in the analysed tissue and has been shown to be complementary to histopathological methods⁷².

The spectroscopic studies reported so far on coronary arteries and aortas have been based essentially on the identification of atherosclerotic plaque composition^{73,74}. The novelty in our study lies in a different approach, which probes the whole aortic wall section from the adventice to the intima (see Fig. 2.2). The main objective of this study is to use the potential of synchrotron based FTIR microscopy as an *ex vivo* diagnostic method for investigating human ascending aortic tissues. The high quality spatially-resolved chemical information obtained should reveal compositional and structural differences between normal and aneurismal tissues, mainly in the secondary structure of proteins. These marker bands can then be useful for diagnostic purposes.

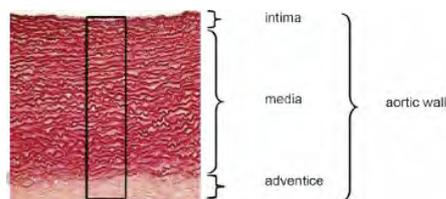


Fig.2.2 A stained section of an aortic tissue showing the three layers composing the aortic wall; the intima, the media, and the adventice

Biopsies of aortic tissues can be studied in the form of 10-20 μm thick cryosections that are deposited on IR transparent windows (ZnSe and CaF_2). Infrared point-by-point mapping performed at a spatial resolution of 3-6 μm can produce an image of the tissue and obtain precise information from the three regions of the aorta (Fig. 2.2).

In preliminary studies⁷⁵ we have shown that structural and compositional differences between the different tissue types specially in absorption regions assigned to fibrous proteins like elastin and collagen – two major proteins of

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the extracellular matrix that are essential components of the aortic wall in association with smooth muscular cells. Although interesting, these data were obtained with a poor spatial resolution. Synchrotron IR microscopy will give us access to data of high sensitivity and high spatial resolution that will shed new light on tissue modifications. This will give new insight into the local degradation of collagen and elastin structures and to correlate them with pathological situations (dilated tissues). Furthermore, image analysis by multivariate statistical analytical methods is expected to reveal spectral patterns that could be useful for classification of tissue types. In the long term, we intend to develop an approach based on the coupling of synchrotron FTIR microscopy and tissue micro array (TMA) that will enable rapid analysis and classification of micro-biopsies (< 500 µm size) with high throughput and high information content. The synchrotron source will be an interesting technological platform for such novel developments.

Team members: Dr. Ganesh D. Sockalingum (University of Riems)
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 Dr. Josep Sulé-Suso (Keele University, UK)

***IN VITRO* VALIDATION OF BIOLOGICAL MOLECULES WITH NOVEL PLASMONIC NANOSTRUCTURES**

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Our interest in using synchrotron Infrared radiation is to study the optical properties of novel plasmonic nanostructures in order to produce label-free, real-time biosensors for detection of biological molecules⁷⁶. In this sense, it is possible to prepare novel detection systems based on nanostructures with sustaining multimode localized surface plasmon resonances (LSPR), which are highly sensitive to internal morphology. High spatial resolution IR radiation will allow validation of proteins (e.g., antibodies) and nucleic acids in biological fluids with these nanoparticle-structured systems.

Team members: Dr. Pablo Botella Asunción and Dr. Patricia Concepción Heydon

NEW NON-VIRAL VECTORS BASED ON BIOCOMPATIBLE CHOLESTERIC LIQUID-CRYSTAL POLYMERS FOR THE CARRIAGE AND DELIVERY OF BIOMACROMOLECULES AND INSOLUBLE DRUGS AS A STRATEGY

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Gene therapy is a strategy based on the use of nucleic acids as drugs or therapeutic targets. It implies the incorporation of the nucleic acids in the cell nucleus in order to increase the number of genes, to block or to silence their expression, or with the intention of repairing possible mutations. Vectors in gene transfer can be viral and non-viral. Among the latter are those based on lipids (complex formation, cationic lipids and classic liposomes), and those based on polymers (polypeptides, polyethylenimine, dendrimers, etc.). Lipoplexes and polyplexes, based on the interactions of DNA with lipids or polymers, have been used.

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Thermotropic cholesteric liquid-crystal polymers (CLCP), chiral in nature, synthesised and isolated in our lab⁷⁷, have shown interesting behaviour for application in the field of gene therapy. Our CLCPs have proved to be biocompatible with macrophages and fibroblast cellular lines with a viability > 50% after 24 and 48 hours.

CLCPs exhibit helical macromolecules which self-associate in helical "cages" able to trap smaller molecules inside. They also interact with lipids⁷⁸ of different nature and effective charge⁷⁹ to form poly-lipoplexes. Our polymers do not need to be grafted to the lipid molecule, such as PEG-ylated liposomes do. Instead they insert spontaneously into the bilayer via hydrophobic forces. Added to the liposome, their structure is maintained, as observed by x-ray diffraction, using synchrotron radiation source at EMBL/DESY (Hamburg)⁸⁰.

Thus they can act as nanocarriers for the the transport and controlled delivery of active components and biomacromolecules such as nucleic acids, proteins/peptides and anti-oxidizers, among others. They have been applied with success to the design and synthesis of new non-viral vectors⁸¹ with transfection capacity in in tumoral cell lines and in mice.

We are interested in the microspectroscopic study of the behaviour of these CLCPs vectors with diverse active components and agents, and possibly in selected cellular environments. We consider the possibilities of synchrotron IR microspectroscopy with cellular and sub-cellular spatial resolution essential to this purpose.

Team members: Dr. Mercedes Pérez Méndez, Javier Sanguino Otero

HETEROGENEITY OF HYBRID AND BIOHYBRID NANOSTRUCTURED MATERIALS

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It is of great importance to know the homogeneity and distribution of organic functions in hybrid materials prepared by chemical treatments of the surface of inorganic solids with organic compounds. This is the case of i) grafting reactions (example: silica and silicates treated with organosilanes coupling agents), ii) intercalation compounds (example: alkylammonium species inserted into layered silicates), and iii) adsorption of organic species on porous solids (example: polysaccharides adsorbed on sepiolite).

IR spectra coupled to microscopy images can be useful to distinguish between phases containing organic aggregates and the hybrid with homogeneous distribution of the organic compound covering the solid surface.

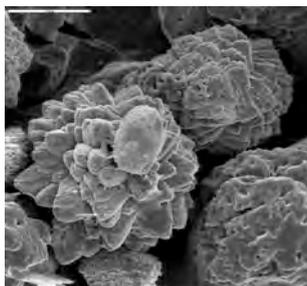


Fig.2.3. SEM micrograph of CaCO₃ crystals obtained on films prepared from 1% chitosan after 8 h of exposition to CO₂⁸². Scale bar 50 μm.

⁷⁷ Spanish Patent ES2125818-A1 and US Patent n° 6,165,382-A

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⁸⁰ Méndez, Pérez, M., Berenguel, Marsal, R., Funari, S.S., "Structural Characterization of the Interaction Between Cholesteric Liquid-Crystal Polymers and Molecules of Biological Interest", *HASYLAB Annual Report*, 2003, 11150

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Of particular relevance is the case of bio-hybrid materials^{83,84}. One of the most salient examples concerns to the characterization of bio-nanocomposites based on the combination of biopolymers (polysaccharides and proteins) with silicates belonging to the clay minerals family (montmorillonite, hectorite, sepiolite,..). By a controlled drying process, these materials can be conformed as foams in which MIRAS can be decisive to distinguish the nature of materials defining the surface of the macropores. Also related with this topic is the study of natural bio-hybrids (nacre, ivory, bone), as well as intermediate bio-inspired developed by biomineralization processes.

Synchrotron infrared microspectroscopy is an essential experimental tool, since it can provide fundamental high quality, high spatial resolution structural and chemical information non-destructively from microscopic zones in diverse bio-inspired systems.

Team members: Prof. Eduardo Ruiz-Hitzky Dr. Pilar Aranda, Dr. Margarita Darder, Francisco Fernandes, Bernd Wicklein

2.1.2 Expressions of Interest

TIME-RESOLVED STUDIES OF CONFORMATIONAL CHANGES IN MEMBRANE PROTEINS

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STUDY OF THE STRUCTURE OF CHROMATIN IN SPERM WITH AND WITHOUT GENETIC DAMAGE

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MEASUREMENT OF NORMAL AND CANCEROUS CELLS BY FTIR MICROSPECTROSCOPY

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STUDY OF PROTEIN FOLDING PHENOMENA

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STUDY OF AMYLOID PEPTIDES

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⁸⁴ M. Darder, P. Aranda, E. Ruiz-Hitzky, Bionanocomposites: a new concept of ecological, bioinspired and functional hybrid materials Adv. Mater. 19, 1309-1319 (2007)

2.2 Food and Agricultural Sciences

Another important area in biological materials, which deserves separate consideration, is that related to Food Science and Agricultural applications of synchrotron infrared microspectroscopy⁸⁵. There has been important growth in recent years in publications in this area related to diverse subjects in the field, some examples being chemical imaging of plant cell microstructures^{86,87}, seeds^{88,89,90}, grains^{91,92}, seaweed⁹³, mapping nutrient-induced biochemical changes in algal cells^{94,95} and phytoplankton⁹⁶, monitorization of processes such as plant growth and development⁹⁷, degradation^{92,98} and cooking⁹⁹, monitorization of organic contaminants in plants^{100,101}, studies on nutrition and feed science¹⁰², and the elucidation of endosperm protein secondary structure in diverse sources of animal feedstocks^{103,104}.

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The food and agricultural science & technology community in Spain is powerful. The Spanish Food Industry is the top industrial sector, accounting for around 17% of the GNP of Spanish industry. Companies in the sector closely collaborate with research groups, and there are over 50 Institutes and Departments dedicated to improving the quality and efficiency of biological materials throughout the food chain, see **Appendix IV**. This community is yet to be awakened to the advantages of SIRMS. However, there are several themes that have already received expressions of interest.

2.2.1 Scientific Cases

ANALYSIS OF PLANT MICROSTRUCTURE BEFORE AND AFTER SUB- AND SUPERCRITICAL PROCESSES TO DETERMINE THE EXTENT OF THE EXTRACTION PROCESS AND THE CHEMICAL DISTRIBUTION OF THE COMPONENTS

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The interest of our research group is to obtain information related to quantity, composition, structure and distribution of chemical components and functional groups in tissues of a particular plant (rosemary, oregano, etc.), and to test the effectiveness and selectivity of a supercritical extraction process towards some specific components. Sub- and supercritical fluid processes have been developed as an environmentally friendly way to selectively extract valuable components (lipids¹⁰⁵, carbohydrates¹⁰⁶, carotenoids¹⁰⁷, polyphenols¹⁰⁸, etc.) from natural matrices. The ability of supercritical fluids to extract such valuable components is related to their diffusivity and solvating power that allows selective extraction of components distributed in a tissue. The knowledge of the composition before and after sub- and supercritical processes in terms of quantity and distribution inside a tissue or cell can help to explain the complex processes occurring during the extraction and therefore to optimize the process towards the compounds of interest. Since the synchrotron radiation-based Fourier transform infrared microspectroscopy (SR-FTIR) is an advanced bioanalytical technique capable of exploring the chemistry within microstructures of plant without destruction of the intrinsic structures of a tissue⁸⁶, it will be a valuable tool to optimize such extraction processes and to understand the extent of the cellular damage produced during the process.

Team members: Dr. Elena Ibáñez Ezequiel, Prof. Alejandro Cifuentes Gallego, Dr. Carolina Simó Ruiz, Dr. Virginia García-Cañas, Dr. Miguel Herrero Calleja, Dr. José Bernal del Nozal, Dr. José Antonio Mendiola.

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¹⁰⁸ I. Rodríguez-Meizoso, F.R. Marin, M. Herrero, F.J. Señoráns, G. Reglero, A. Cifuentes, E. Ibáñez. Subcritical water extraction of nutraceuticals with antioxidant activity from oregano. Chemical and functional characterization. *J. Pharmaceut. Biomed. (Special Issue: Analysis of Nutraceuticals)* 41, 1560-1565 (2006)

STUDY OF OLIVE OIL ADULTERATION, OXIDATION OR DEGRADATION WITH ADVANCED SPECTROSCOPIC TECHNIQUES

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Currently, infrared spectroscopy is one of the most common spectroscopic techniques used in the food industry. With the rapid development in infrared spectroscopic instrumentation software and hardware, the application of this technique has expanded into many areas of food research¹⁰⁹. In addition, olive oil is an economically important product in the Mediterranean countries. It has a fine aroma and a pleasant taste, and it is also known for its health benefits. The quality of olive oil ranges from the high quality extra virgin olive oil to the low-quality olive–pomace oil (or raw residue oil). Extra virgin olive oil is obtained from the fruit of the olive tree (*Olea europaea* L.) by mechanical press and without application of refining processes. Its acidity¹⁰⁵ cannot be greater than 0,8%. Due to its high quality, it is the most expensive type of olive oil and in fact the most expensive vegetable oil. For this reason, it is sometimes mislabelled or adulterated. Adulteration involves addition of cheaper oils. The most common adulterants found in virgin olive oil are refined olive oil, olive pomace oil, seed oils (such as sunflower¹¹⁰, soy, corn and rapeseed oils) and nut oils (such as hazelnut and peanut oils). In some cases, besides the economic fraud, adulteration may cause serious harm to health.

Also of importance for our research group is the evaluation of degradation effects on olive oil and virgin olive oil due to oxidation processes produced by their exposition to daylight and heat, for instance during frying of food, and the distribution of the oxidised oil within in the fried food structure. High spatially resolved spectroscopic methods will be valuable in this respect. Olive oil contains high amounts of monounsaturated fatty acids^{111,112,113,114,115,116}, which are important lipid molecules, and the information obtained from the crystal structures may have two meanings: (a) to relate the crystal structures with physical properties of the unsaturated fat microcrystals contained in the oil and (b) to highlight the structural nature of individual molecules through comparable studies of various specimens, i.e., different samples of heated oils with varying temperature, or oxidised oil samples.

To contribute to a better understanding of all of these mechanisms, we would like to use infrared microspectroscopy at ALBA synchrotron to monitor the oil structure changes as a function of the purity alteration or oxidation processes, with a view to developing an accurate, reliable and robust analytical methodology. These studies could have further applications in the characterization of fish and marine oils, and especially, in the control of the oxidation of these unstable and valuable edible oils.

Team members: Dr. F. Javier Señoráns, Dr. Guillermo Reglero, Dr. Diana Martin, Dr. Carlos Torres, Dr. Tiziana Fornari, Dr. Susana Santoyo, Dr. Laura Jaime, Dr. Luis Vázquez, Dr. Pilar Luna, Dr. Monica Rodriguez

¹⁰⁹ Da-Wen Sun (Editor). INFRARED SPECTROSCOPY FOR FOOD QUALITY ANALYSIS AND CONTROL. Elsevier. 2009. ISBN-13: 978-0-12-374136-3

¹¹⁰ E.J. Hernández, G.D. Mabe, F.J. Señoráns, G. Reglero, Tiziana Fornari High-Pressure Phase Equilibria of the Pseudoternary Mixture Sunflower Oil plus Ethanol plus Carbon Dioxide *Journal of Chemical and Engineering Data* 53 (2008) 2632-2636

¹¹¹ T. Fornari, L. Vázquez, C. F. Torres, E.Ibáñez, F. J. Señoráns and G. Reglero Countercurrent Supercritical Fluid Extraction of Different Lipid-Type Materials: Experimental and Thermodynamic Modelling *Journal of Supercritical Fluids* 45 (2008) 206-212

¹¹² C. F. Torres, T. Fornari, D. Tenllado, F. J. Señoráns and G. Reglero A predictive kinetic study of lipase-catalyzed ethanolysis reactions for the optimal reutilization of the biocatalyst *Biochemical Engineering Journal* 42 (2008) 105–110

¹¹³ C. F. Torres, G. Torrelo, F.J. Señoráns, G. Reglero A two steps enzymatic procedure to obtain sterol esters, tocopherols and fatty acid ethyl esters from soybean oil deodorizer distillate *Process Biochemistry* 42 (2007) 1335-1341

¹¹⁴ C. F. Torres, A.M. Toré, Tiziana Fornari, F. J. Señoráns, G. Reglero Ethanolysis of a waste material from olive oil distillation catalyzed by three different commercial lipases: A kinetic study *Biochemical Engineering Journal* 34 (2007) 165–171

¹¹⁵ Luis Vázquez, C. F. Torres, Tiziana Fornari, F. J. Señoráns and G. Reglero Recovery of Squalene from Vegetable Oil Sources using Countercurrent Supercritical Carbon Dioxide Extraction *Journal of Supercritical Fluids* 40 (2007) 59-66

¹¹⁶ C. F. Torres, L. Vázquez, F.J. Señoráns, G. Reglero Study of the analysis of alkoxyglycerols and other non-polar lipids by liquid chromatography coupled with evaporative light scattering detector *Journal of Chromatography A* 1078 (2005) 28-34

CHARACTERIZATION OF CELLULAR DAMAGE AND ELUCIDATION OF ANTIMICROBIAL ACTION MECHANISMS AND CHARACTERIZATION OF TOXIC AND ACTIVE/BIOACTIVE MIGRANTS OF INTEREST IN MICROBIOLOGY AND FOOD SCIENCE

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There is great interest in the determination of the mechanisms of action of biocides^{117,118}, particularly nanostructured biocides such as chitosan^{119,120}, silver and natural extracts-based systems. This currently means identification, inside cells or on the cell membranes, of the presence of these components. There has been some literature developed in which FTIR-based techniques have been used, coupled in some cases with chemometric methods, for gaining information on such systems. Nevertheless, synchrotron radiation-based Fourier transform IR (SR-FTIR) microspectroscopy shows great advances in this area since it is a rapid, direct, non-destructive and bioanalytical technique¹⁰². The technique takes advantage of the synchrotron light brightness and the small effective source size and is capable of exploring the molecular chemistry within the microstructures of a biological tissue without the destruction of inherent structures at ultra-spatial resolutions within cellular dimensions.

In another context, an area in which we are highly active¹²¹ is the migration of toxic substances from packaging and coating plastics and ultrathin and nanofiber based substrates^{122,123,124,125}. This is a very relevant issue in intended and non-intended migration¹²⁶ of packaging components, and becomes essential both from a food safety viewpoint and for the development of novel active and bioactive technologies¹²⁷. In this area, conventional FTIR spectroscopic techniques do not reach sufficient sensitivity levels, and in cases where ultrathin or nanofibers are used, the spatial resolution of analysis becomes very relevant. Again, in this context, synchrotron radiation-based Fourier transform IR (SR-FTIR) microspectroscopy shows potentially significant advantages that will allow our group to reach higher levels of understanding in the characterization of migration processes and kinetics.

Team members: Dr. Jose Maria Lagarón, Dr. Maria Jose Ocio, Dr. Amparo López-Rubio, Dr. Carla Soler

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¹²⁵ Torres-Giner, S., Ocio, M.J., Lagaron, J.M., Development of active antimicrobial fiber based chitosan polysaccharide nanostructures using electrospinning, 2008, Engineering in Life Sciences 8 (3), pp. 303-314

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ANALYSIS OF CARBOHYDRATES COVALENTLY BOUND TO FOOD PROTEIN BACKBONES

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Previous studies carried out by our research group have demonstrated that glycans covalently bound to food protein backbone by both post-transcriptional process *and Maillard reaction (non-enzymatic glycosylation also called glycation)* determine their functionality (1-5). Commonly, characterization of structural glycans of proteins involve tedious and time consuming enzymatic or chemical hydrolysis processes prior to analysis. Under chemical hydrolysis conditions the carbohydrates bound to proteins may be degraded making difficult their identification. Therefore, to make the structural analysis avoiding the carbohydrate breakdown is desirable and fundamental for characterization of glycoproteins and glycated proteins. Since the synchrotron radiation-based Fourier transform infrared microspectroscopy (SR-FTIR) is an advanced non-destructive technique capable of exploring the chemistry of complex molecules, it can be a feasible and powerful tool to confirm changes in protein structure due to either deglycosylation or glycation which of interest for our group.

Team members: Dr. M^a Dolores del Castillo Bilbao, Dr. Javier Moreno Andujar, Dr. Miryam Amigo-Benavent, Dr. Jose Manuel Silván Jimenez

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2.2.2 Expressions of Interest

CHARACTERIZATION OF METABOLITES AND/OR MACROMOLECULES UNITED TO TOXIC METALS

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We are very interested in the characterization of metabolites and/or macromolecules (proteins & carbohydrates) united to toxic metals (Hg, Cd) and the understanding of the nature of the metallic species in plant tissues and cells, in order to optimise fitotechnology development programmes. It would be very interesting to have high micron-scale resolution, and be able to determine in real-time changes produced in microscale experiments (plantules) at short treatment times.

MICROSPECTROSCOPIC CHARACTERISATION OF FOODSTUFFS

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2.3 Environmental and Geological Sciences

Much of geochemical and environmental research requires carefully controlled sample environments that can accurately mimic the conditions in which the materials of interest can be found, or the environment to which the materials have been exposed. In many cases, of particular interest is the use of high pressures and high temperatures^{128,129}. High pressure research with SIRMS has been considered in Section 2.7 of this document.

Amongst work in the environmental field, *in situ* and *in vivo* biomineralization studies have provided an insight into exciting new research possibilities in geobiology. Novel IR methods and algorithms for the analyses of IR spectra have been developed and applied to determine biomineralization mechanisms and kinetic rates using the changes in the IR spectral features on cyanobacterial cells¹³⁰. The quantification of the mechanisms and kinetics of *in situ* and real-time variations in the biogeochemical environments around microbial cells and their effects on the organic functional groups on cell surfaces will be key areas for future developments. Other interesting key environmentally related themes include the investigation of toxicological effects of chemicals^{131,132}, corrosion^{133,134}, and pollution¹³⁵.

2.3.1 Scientific Cases

SYNCHROTRON BASED FTIR SPECTROSCOPY IN THE STUDY OF THE MECHANISM OF STABILIZATION/SOLIDIFICATION OF WASTES USING CEMENT POLYMER CONCRETES

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One of the most extended procedures for the treatment of toxic and hazardous waste is stabilization/solidification, S/S. The technology is based on obtaining monolithic materials by means of the use of pozzolanic compounds (cement, blast furnace slag, etc.). Recently the substitution of cement materials by sulphur and sulphur polymers has opened new possibilities not only for the confinement of the wastes into stable structures

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¹³⁰ Benning, L.G., et al., *Molecular characterization of cyanobacterial silicification using synchrotron infrared micro-spectroscopy*. Geochimica et Cosmochimica Acta, 2004. 68(4): p. 729-741

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¹³⁵ Schafer, T., et al., *Spectromicroscopy mapping of colloidal/particulate organic matter in Lake Brienz, Switzerland*. Environmental Science & Technology, 2007. 41: p. 7864-7869

but for the possible uses of those materials^{136,137,138,139}. The proponent research group is carrying out several research projects, funded by LIFE/EU and National Programs in relation with the use of S-polymeric materials in process to stabilize liquid mercury, mercury-contaminated soils and natural radionuclide-containing wastes. The knowledge of the S-polymerization mechanism would contribute to a better understanding of the S/S process and would allow the design of new application for these materials.

The experiments to be performed are based on the study of S and STX (a polymer) mixtures by means of IR spectroscopy and synchrotron microscopy. The samples were obtained at different temperatures (100-300°C) using several complementary techniques, especially differential scanning calorimetry. XRD studies of pure sulphur and modified sulphur (STX) have been carried out. Diffractograms of sulphur correspond to the orthorhombic phase S_α. The modified sulphur, a plasticized concentrate called STX, is first formulated from a polyolefin and elemental sulphur and it exhibits a diffractogram similar to the pure sulphur but with a lower crystallinity. Besides, diffraction lines appearing at 2θ = 22.8 and 27.8 correspond to the β phase of S. The morphological aspect of modified sulphur and reticular structure can be seen in Figure 2.4a, which consists of monoclinic crystals (β phase). The morphological appearance corresponds to a compact structure of polymeric materials (Fig 2.4b).

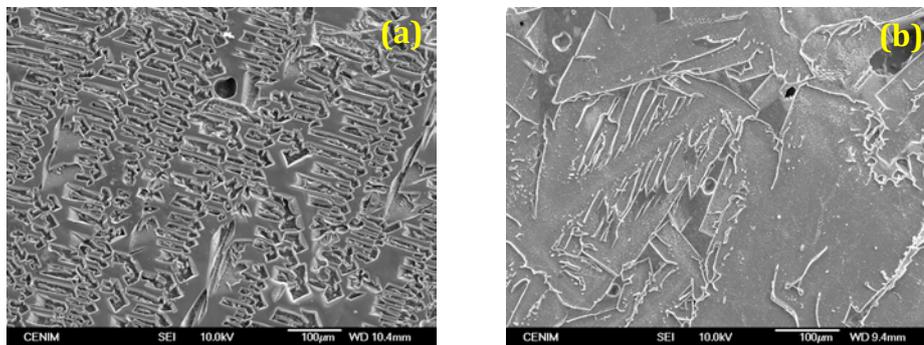


Fig. 2.4.- SEM images for modified sulphur (a) and the mixture of sulphur + sulphur modified at 150° C (after cooling) (b)

In comparison with the previous one, it can be observed, that the pure sulphur filled up the voids in the modified sulphur structure and, as a consequence, a continuous structure is formed. The FTIR spectrum of modified sulphur shows vibrational bands corresponding to organic compounds at 3037 – 2930 cm⁻¹ which correspond to stretching modes of C-H associated to C=C. Bands at 1448 and 1372 cm⁻¹ can be attributed to C-H bond deformation, and finally a narrow strong band at 467 cm⁻¹ corresponds to stretching of S – S.

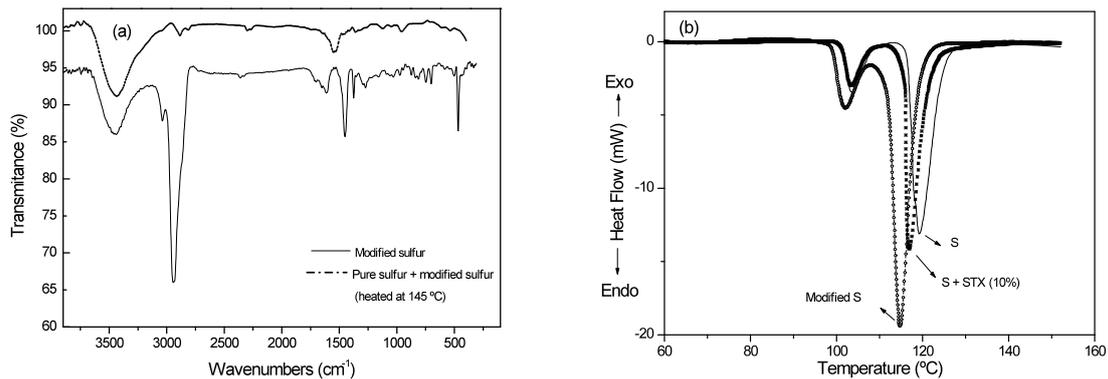


Fig. 2.5. FTIR spectra of the modified sulphur and the mixture (S+STX) (a) and DSC curves of pure sulphur, modified sulphur and mixture S +STX (heating rate 5°C/min) (b)

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A spectrum of the mixture of pure sulphur and modified sulphur exhibits a large decrease in the intensity of bands corresponding to organic compounds. This can be attributed to the partial elimination of these compounds during the polymerization of sulphur (Figure 2.5a). In the DSC curves, two endothermic effects can be observed which correspond to melting of alpha and beta phases respectively. In the case of the mixture (S+STX) and modified sulphur, peaks temperature is shifted at lower values and the enthalpies associated to both effects are smaller than those corresponding to pure sulphur (Figure 2.5b).

However, these data are not sufficient to allow us to elucidate the interaction mechanism between sulphur and modified sulphur is. We think that the combination of IRS and synchrotron microscopy might provide us with more powerful evidence.

The proponent researchers belong to the Environment and Recycling group of CENIM-CSIC. This group is presently involved in several research Projects in which the "Laboratory of Environment Radiactivity and Radiology Vigilance" of the Energetic, Environmental and Technological Research Centre (CIEMAT) also participates.

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REAL-TIME MONITORING OF CARBONATION REACTIONS OF CEMENT BASED MATERIALS

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Due to the action of CO₂ on the mineralogical compounds of Portland Cement (PC), transformation of portlandite into calcium carbonate occurs. This causes the modification of the material microstructure and, consequently, of the mechanical and durability properties¹⁴⁰. During Calcium Aluminate Cement (CAC) carbonation, CAH₁₀, C₂AH₈ and C₃AH₆ also react with CO₂ to give calcium carbonate and aluminium hydroxide. Carbonation in the absence of alkalis normally increases the compressive strength of CAC¹⁴⁰ concrete. In contrast, some degradation processes are related to the presence of alkalis contained in aggregates or other external sources. Alkaline hydrolysis, i.e. carbonation in presence of alkalis, is a catalytic-like process leading to the destruction of the affected concrete¹⁴¹.

Three varieties of CaCO₃ are liable to appear: calcite; aragonite; and vaterite¹⁴². Moreover, three varieties of aluminium hydroxide (AH₃) are also likely to occur: bayerite; nordstrandite; and gibbsite. At first, carbonation process usually generates both carbonates and aluminium hydroxides of amorphous or microcrystalline nature. IR techniques are most suitable to detect such compounds¹⁴³.

On top of that, formation of these phases commonly take place in external areas instead of in the main structure, making more interesting the comparison between those differentiated micro-areas. Due to the high brightness and high collimation of the beam, SR-FT-IR microspectroscopy allows focusing on areas of a few microns and also obtains spectra with a very good signal-noise ratio. The technique gives the possibility to identify phases from very small samples and to achieve data of minor compounds offering information on the processes due to the chemical reactions taking place.

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DEVELOPMENT OF CEMENT WITH LOW ENVIRONMENTAL IMPACT. ALKALINE CEMENTS.

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Portland cement-based products (primarily concretes) are the world’s most commonly used building materials. Due to its huge production world-wide, the Portland cement industry is faced with problems of an economic (use of increasingly scarce and expensive fossil fuels), energetic ($T > 1400\text{-}1500\text{ }^{\circ}\text{C}$) and environmental (1 t of cement \cong 1,5 t prime materials \cong 0,8 t CO_2 , accounting for 7 % of total world-wide CO_2 emissions) nature. Major international concern over how to reduce CO_2 emissions has given rise, within the scientific community, to a growing interest in the development of materials and technologies able to reduce the impact of Portland cement and advance toward a more sustainable construction industry.

We are working to develop more earth-friendly materials^{144,145} such as the so-called **alkaline cements**, produced by alkali activating silico-aluminous materials^{146,147,148}. The latter may be natural prime materials (dehydroxylated clays, feldspars...) or industrial waste (blast furnace slag, fly ash...) ^{149,150}. The aim of such research is to develop new cement materials similar to, or in certain respects (strength and durability)^{151,152,153} even better than, Portland cement-based concretes, i.e., more energetically and environmentally sustainable^{154,155} cements for use in civil engineering.



Fig.2.6 Alkali activation of fly ash

Alkali activation is a chemical process (see, Fig.2.6) in which natural or industrial materials (with amorphous or vitreous structures), are mixed with alkaline solutions, set and hardened to yield a product with good binding properties. At moderate temperatures (60-90 $^{\circ}\text{C}$), the main reaction product from alkali activation of aluminosilicate materials is a sodium aluminosilicate hydrate gel (N-A-S-H) main responsible of the good

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2.4 Polymeric Materials Science

Vibrational spectroscopy and microspectroscopy has been for many years a fundamental tool in the study of polymeric materials, and quite sophisticated experimental techniques and approaches are described in numerous reviews and recent monographic texts^{160,161,162}. It is thus quite surprising that relatively few papers have appeared to date in the literature describing the use of SIRMS for the study of polymeric materials¹⁶³. The ability to obtain spatially resolved IR spectra from different types of domains in polymeric materials has been illustrated in various heterogeneous polymer systems^{164,165}. Some processes such as crystalline polymorphism^{163,166,167}, additive migration¹⁶⁸, cross-linking¹⁶⁹, phase separation¹⁷⁰ and surface structuring¹⁷¹ have been monitored. Finally the 2D imaging of microscopic chain orientation phenomena in fibres and composite films has been investigated, either by exploiting the natural polarization properties of the synchrotron source^{163,167} or by employing polarisation modulation techniques^{172,173}.

In Spain the polymer industry is the largest and most important chemical industry, and polymer research in both the CSIC and University laboratories is intense, ranging from the development of highly competitive materials based on commodity polymers, through composite and hybrid materials, to innovative biopolymers, nanomaterials and environment-responsive polymeric systems, to mention but a few. The potential user community is very large and highly active, as illustrated by the significant number of scientific cases and expressions of interest received in this area.

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2.4.1 Scientific Cases

SYNCHROTRON IR MICROSPECTROSCOPY STUDIES ON DIVERSE MULTIPHASE POLYMERIC SYSTEMS

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Polymeric materials are normally extrinsically multiphase systems, such as polymer blends, composites or hybrid materials, which incorporate organic or inorganic components in a polymeric matrix in order to enhance, or fine-tune the polymer properties. Alternatively, they can be intrinsically multiphase (crystalline, semicrystalline or amorphous), or they can be induced through their manufacturing or processing history to generate multiple phase structures (orientation, epitaxy, etc.). Indeed, as an example, in many manufactured polymeric products the macromolecular chains are aligned or oriented in some way; polymeric fibres tend to have directional (longitudinal) stiffness imparted by chains preferentially aligned along the fibre long-axis, whereas in many film and moulded products the macromolecular chains are typically biaxially oriented with respect to the surface plane. In semicrystalline thermoplastic materials this orientation anisotropy is intimately related to the crystallization behaviour. These fundamental aspects which are directly associated to important design parameters such as the mechanical performance or resistance, and others, and related to the chemical composition and distribution of phase domains, ultimately control the final properties of the polymeric product.

The modification of multiphase polymeric systems, by chemical or physical means, is one of a battery of strategies which can be used to incorporate specific tailor-made structures or morphologies, which can improve performance or generate value-added properties to materials for diverse applications. One of the most important parameters to control in multiphase polymeric systems is the organization of the different components and the interactions which take place between them. The rigorous characterization of the chemical and physical structure of these materials, on scales which vary between a few nanometers to various tens of microns, as a function of the type and degree of modification, is of paramount interest in our research. We have used vibrational microspectroscopy for many years in conjunction with other chemical and structural characterization techniques to obtain vital information. Synchrotron infrared microspectroscopy (SIRMS) can be successfully applied to many of these issues. Although there are relatively few studies on polymers in the literature, SIRMS has already allowed us to probe a number of scientifically and technologically interesting materials^{163,164}. We have studied polymorphic crystalline interphases in polypropylene / LCP-fiber composites^{166,167}, and obtained fundamental information on their nature as a function of temperature and shear. We have also made some measurements on micro-patterned polymeric membranes as biodegradable supports for skin therapy¹⁷⁴. Thus, we propose to study the structural, morphological, orientational and compositional parameters that condition solid-state properties of a range of multiphase polymeric materials, detailed below.

1. CRYSTALLINE SUPERSTRUCTURES AND INTERPHASES^{163,164,166,167} We wish to continue our work on the nature of lamellar organization in both transcrystalline and cylindrical crystalline morphologies in polyolefins. In this respect, it is necessary to consider the application of new sampling strategies optimized for synchrotron IR microspectroscopy in order to produce dichroic images of specific areas of the samples, Figure 2.8. The purity of the polarization characteristics of the synchrotron beam are an important issue, and the possibility to perform polarisation modulation experiments^{175,176} would be highly desirable for rapid, precise SIRMS imaging.

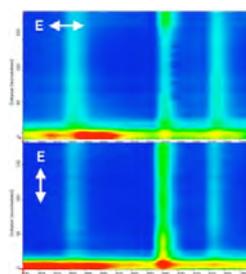


Fig.2.8. Natural positional dichroism with synchrotron radiation in the cylindrical beta-phase of an iPP

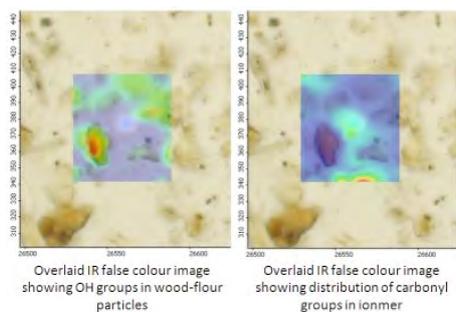
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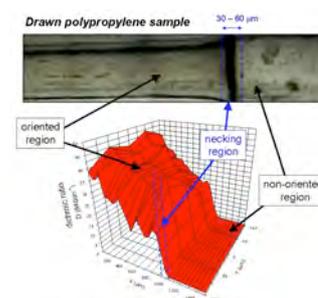
2. NANOSTRUCTURED POLYMER MATERIALS^{177,178} Modifying polymer properties and morphology via inclusion in nanostructures: Polymer-cyclodextrin inclusion compounds and the subsequent conformationally-tailored polymer chains released from the cyclodextrin channel can lead to new properties, and are especially interesting for nanostructuring polymer blends. We have developed a number of materials with different polymers. The study will involve the application of SIRMS to analyze both the conformational characteristics and the heterogeneity of nanostructured polymer micro-particles, with dimensions between 5 – 20 μm .

3. WOOD-BASED COMPOSITES The use of renewable sources in the development of new materials is of fundamental importance. Wood-flour, generated from wood-cuttings can be recycled as a filler in different polymer systems, however, its performance is compromised due to poor adhesion between the wood and the polymer. Compatibilization agents can be added in low concentrations to improve adhesion between specific components, and their efficiency depends on the nature of the interactions which take place, affecting a wide number of chemical and physical properties and driving the final morphology and ultimate performance of the materials^{179,180}. We aim to deepen our understanding of the distribution of compatibilization in order to design more effective coupling strategies as a function of the matrix polymer and the nature of the wood surface. We hope to be able to



demonstrate a close association between the compatibilizing agent and the wood-flour, and a gradient of distribution within the matrix.

4. ORIENTED POLYMERS, THEIR BLENDS AND NANOCOMPOSITES The measurement of chain orientation is essential for understanding the behaviour of anisotropic polymeric materials. In this respect, polarised infrared spectroscopy is a powerful, well-established tool for investigating polymer anisotropy, employing orientation parameters, $\langle P_{200} \rangle$ calculated from dichroic ratios. Although IR microspectroscopy has previously been used for this type of analysis, relatively large areas have been considered in order to obtain orientation information from optically thick moulded parts, drawn materials and microtomed sections¹⁸¹, and more recently infrared imaging microspectroscopy using a focal plane array detector in conjunction with an IR polariser provided fast large-area images of orientation profiles in microtomed injection-moulded samples¹⁸². As an example, in the Figure we show polarised IR microspectroscopy measurements made in our laboratory with a spatial aperture of 100 μm , demonstrating the high sensitivity observed in the dichroic ratios of a band characteristic of the polymer chain in the necking region of a drawn polypropylene film. To date, high spatial resolution data have not been reported. However, the study of the deformation behaviour with high spatial resolution in polymers has been successfully achieved using Raman spectroscopy and x-ray diffraction (XRD), including synchrotron microfocus methods¹⁸³. But, both techniques have limitations: x-ray only provides evidence from crystalline regions, and fluorescent or highly



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absorbing polymers are difficult to study by Raman. In contrast, synchrotron infrared microspectroscopy (SIRMS) allows one to obtain orientation data from both amorphous and crystalline regions in semicrystalline polymers. One of the key advantages of the IR method over other techniques is that information can be obtained simultaneously from different phases in multi-component systems. The conformational and orientational analysis during the early stages of drawing of well-characterised polymer matrices, such as polypropylene, poly(ethylene terephthalate), poly(ether ether ketone), etc., will allow us to determine highly localised orientation profiles in various samples with different drawing conditions (draw ratio, strain rate, draw temperature), and compare them with those obtained from polymer blends (microparticle domains) and nanocomposites prepared under the same conditions. This will provide us with information to understand more about the fundamental mechanisms of chain rearrangement, which take place when an elongational force is applied, and how the presence of other polymeric components or nanoreinforcements and their nature (fullerene, CNT, graphene, etc.), in terms of interfacial interactions, can affect these processes. Finally, the development of specialised micro-stretching apparatus for real-time high spatial resolution imaging of orientation in microscopic domains is of great interest.

5. IMAGING OF POLYMER – BIOMEDICAL INTERPHASES^{174,184} The association of polymer substrates and biomedical surfaces, such as skin or tissues, also depends fundamentally on the type of interaction which takes place. However, in order to dot the polymer with specific functionality in, for example, tissue therapy applications, the polymer surface needs to have a carefully designed microstructure which promotes the required cell-function in the presence of the polymer, which may even serve as a nutrient for cell growth in the case of biodegradable systems. Recently, our work has involved developing novel porous substrates as cell supports for tissue regeneration with cell-based therapies based on mesenchymal stem cells¹⁷⁴. We have had some very positive initial results in the characterisation of laser micro-patterned samples by SIRMS, demonstrating that the crystallinity of the polymer substrate can be modified at the pores, see Figure 2.9. We now wish probe substrates that have also been modified by plasma, and by chemical functionalisation, where the presence and distribution of active functional groups close to the pores is desirable. We expect a clear indication of the distribution of functionality around the pores, which is essential for tailored cell growth in a physiological environment. It would also be interesting to study the nature of cells adhered to the polymer surface.

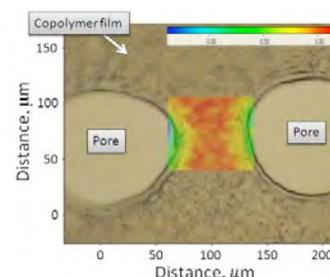


Fig.2.9. Crystallinity map of PHBHV pore structure

6. SELECTIVE PLASMA MODIFICATION OF MULTICOMPONENT SYSTEMS: The surface modification of polymers to improve properties such as adhesion, reactivity, surface selectivity, etc. is a powerful method for extending the application scope of both commodity and advanced polymeric systems. Different processes occurring on the surface can lead to a variation in the morphological profile. Depending on the type of chemical groups to be introduced, the plasma intensity and the nature of the radiation, the modification profile can vary between 1 nm to 10 μm . The use of such modified materials in multilayer, blends or composite systems has important implications in the development of controlled interfacial behaviour, and the design of polymer-polymer interphases. Angular microtomy is probably one of the required experimental preparative methods required; however, the combination of the high sensitivity of SIRMS and surface-selective IR reflection techniques, such as ATR imaging, will be of considerable interest.

7. PRESERVATION OF NATIONAL HERITAGE: MACROMOLECULAR SYSTEMS: *Degradation of ancient polymers:* Many important materials for national heritage are made from or supported on polymeric materials. A careful study of evidence for the degradation of these materials, related to their origin and environmental history can be key issues in their preservation. We have made some preliminary measurements on 19th Century photographic materials. Careful microtomy is essential in most cases with these delicate and often unique samples.

Team members: Dr. Gary Ellis, Prof. Carlos Marco Rocha, Prof. Marian Gómez, Dr. Zulima Martin, Gonzalo Santoro, Dr. Mohammed Naffakh, Dr. Horacio Salvagione, Dr. Ana Diez Pascual (ICTP)
Dr. Ignacio Jiménez, Madrid Materials Science Institute (ICMM)

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STUDY OF POLYMER COATINGS OBTAINED BY SPIN-COATING

Dr. Daniel Rueda

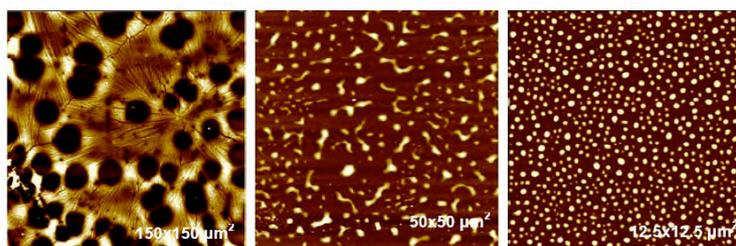
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The scientific and technological interest of polymer thin films is of great present time and with clear perspective of growth. The great size of macromolecules and intrinsic viscosity restricts the methods to follow to obtain polymer films in the rank of the nanometres. It is obtained successfully, nevertheless, by means of the use of diluted solutions in combination with the method of spin-coating. Within the study of polymer coatings ("polymer thin films") obtained by spin coating on silicon wafer is crucial the interaction polymer-substrate that will define the morphology of the polymer coating^{185,186}. On the one hand, the nature of the monomer unit and by another one the chemical nature of the surface of the substrate where they are going away to anchor the segments of polymer chains are the determinants of the structure and morphology of the interface substrate-polymer. It will determine the conformations of the polymer chain adhered to the substrate, which will as well determine the subsequent addition of chains and growth of the polymer coating.

We think that the application of the IR-spectroscopy with synchrotron light to explain the structure of the interface polymer-substrate is singular and of great potential. The dichroic character of vibration modes of polymer bonds will facilitate the knowledge of the space disposition of the chain segment respect to the substrate as well as the conformation of the chain. This molecular information, will allow clarifying two problems of great importance in the study of polymer thin films:

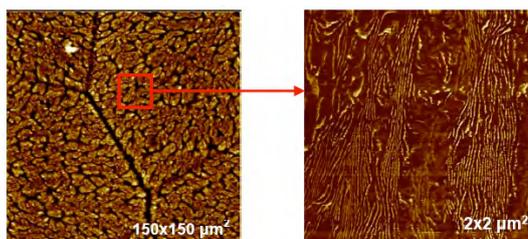
1. The underlying mechanisms and forces in the total or partial wetting of the substrate by polymer, which will guide to us, without a doubt, in the experimental conditions to explore for the attainment of homogenous and continuous polymer coatings.



AFM micrographs of poly-propylene adipate (PPA) thin films with thicknesses in the range of 10 – 100 nm, showing different degree of dewetting.

2. The crystallization of polymer in conditions of confinement¹⁸⁷. In particular, how it influences the interaction with the substrate in the preferential direction of the polymer chains, and as a result in the orientation and consequent nanostructuring of crystals¹⁸⁸.

Spherulitic morphology of a PPA thin film (thickness about 200 nm). The zoom shows lamellar crystals mainly organized edge-on with respect to the silicon substrate.



Team members:

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SYNCHROTRON FTIR IMAGING TO STUDY POLYMERIC MULTICOMPONENT SYSTEMS AT THE INTERFACIAL SCALE

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It is generally accepted that in multicomponent polymeric systems (blends and composites) the interphases play a crucial role in their final performance. However, there is not enough information available for a full understanding of the relation between the interphase and the final properties of these materials. Researchers in this field do not yet agree on the extension of the interphase^{189,190,191,192}. Perhaps the important question is that this region can be studied at different scales depending on the information required, going from a few nanometers to hundreds of microns. Besides, it is clear that one extraordinary way to understand the properties of interphases is to get chemical information from it non-destructively. Therefore, to take into account both aspects one would think about infrared microscopy increasing as much as possible the spatial resolution as to inspect chemically the nearest interfacial layer to each phase in the system. The use of FTIR imaging from synchrotron radiation might be the key to solve this problem because of the high brightness of this radiation which makes it possible to monitor processes occurring in the interphase at a spatial resolution of at least two micrometers in the high-frequency region of the IR spectrum.

Among other systems, those formed by modified epoxy thermosets should receive special attention due to the great deal of applications they have. In these materials, monitoring the cure process as well as different ageing phenomena at the interphases are essential for understanding their properties and performance¹⁹³. Different aspects can be considered in these studies: reactive components, stoichiometry, modifiers of properties, cure conditions, etc. In addition, making use of the medium range of the infrared a lot of information coming from the different components (IR bands) can be obtained at the interphase: i) chain interpenetration; ii) chemical reactions; iii) accessibility of small molecules such as water; iv) phase separations. Moreover, even information about the mechanisms of all those process can be obtained because, from IR spectra, specific interaction between functional groups can be analyzed.

There is a type of composite system which has not been deeply studied in terms of their morphology. These materials are those formed by reinforcement (particles, fibres, etc.) and a polymer blend acting as the matrix¹⁹⁴. In fact their morphologies at the interface are not very well known. It seems evident that a preferential adsorption of one of the matrix components must exist depending on the surface properties of the reinforcement. This preferential adsorption will influence, if one of the components is a thermocurable system, in the cure process and the final interfacial morphology. Both aspects must be very important in relation to the final properties of the composites. Due to this fact, monitoring the location relative to the reinforcement during the cure reaction, in order to follow the phase separation (if it exists), and the final morphology obtained should be investigated in order to understand the final performance of the material. Furthermore, chemical information must be the requirement with maximum spatial resolution because this is the only way to be sure about the distribution of all the components of the system in a relatively small region as can be an interphase.

Scientific Team: Dr. J. Gonzalez-Benito, Dr. Dania Olmos, Dr. Gustavo González-Gaitano, Dr. Pedro Remiro

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SAMS CHARACTERIZATION TO PROMOTE SURFACE POLYMERIZATION ON NANOSTRUCTURED SURFACES

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Self-assembled monolayers (SAM) have received increasing attention during the last decade because of the wide range of applications they can be used in, for instance in corrosion inhibition, molecular electronic devices, wettability or adhesion. In our research group we have been working with different kind of molecules to form the monolayer on several substrates, such as gold, copper or silicon wafers.

A method has been developed to enhance the nucleation step in a polymerization process through surface nanostructuring by self-assembly. For this purpose the monolayer orientation plays a very important role. The terminal group of the SAM acts as a nucleation site for the polymer deposition, indeed it has been demonstrated the importance of the molecule length for the correct formation of the SAM.

Besides, we have been investigating the effect of the monolayer as a corrosion inhibitor in metals. Previous results have confirmed that the assembling of a monolayer decrease the corrosion rate because of the insulating effect of this one. The alkyl chain prevents the electron transfer and serves as a barrier for corroding species, therefore retarding the dissolution of the metal.

The homogeneity and density of the monolayer is the key factor to achieve these properties. One technique used to study the degree of order in monolayers is PM-IRRAS, which gives a general overview about its packing. And that we have use to study the packing difference between C12 and C6 pyrrolyl alkane thiols and selenols on copper surfaces (Figure 1).

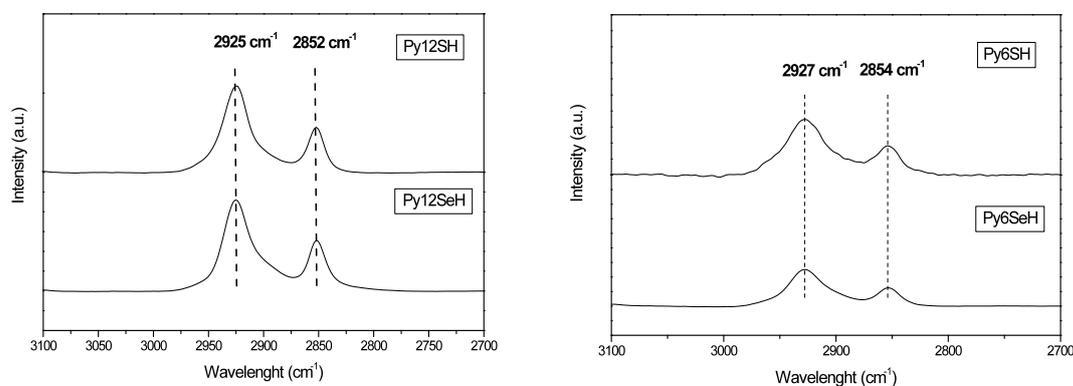


Figure 2.11. PM-IRRAS of 12-(N-pyrrolyl)dodecanethiol (Py12SH) and 12-(N-pyrrolyl)dodecaneselenol (Py12SeH) in the left picture, and 6-(N-pyrrolyl)hexanethiol (Py6SH) and 6-(N-pyrrolyl)hexaneselenol (Py6SeH) in the right picture.

Nevertheless, there is a lack of information when it is necessary a deeper study in the characterization specially in the role of the end group in the structuring of the SAM. Because of this MIRAS can offer us several advantages. The high resolution obtained with this light source could help us to a better analysis of the chain interactions, which lead to the ordering of the monolayer, to the investigation of possible gauche defects and to determine the orientation and importance of the SAM terminal group, among others.

Team Members:

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MOLECULAR CONFORMATIONS IN CONFINED MULTILAYERED POLYMER SYSTEMS

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Multilayered polymer systems are constituted by an alternate stacking of two immiscible polymers. The films are made up of thousands of thin layers, with layer thicknesses ranging from a few nanometers (nanolayered materials) up to several microns (microlayers). These multilayered materials are designed to combine the properties of the parent homopolymers, giving rise to a synergistic system with enhanced properties. The control of the end properties requires a deep understanding of fundamental physical phenomena under confined conditions.

A multiple co-extrusion process is employed to generate the starting multilayered materials. Multilayers can be composed of alternate layers of glassy materials or crystallizable ones. Preceding studies suggest that in multilayers of poly(ethylene terephthalate) (PET)/ polycarbonate (PC), the crystallization of PET from the glassy state is hindered for layer thicknesses below $1\ \mu\text{m}$ ¹⁹⁵. The final nanostructure of the crystallized material is envisaged to depend on the molecular conformations and short range packing of the starting glassy material that arise under specific processing conditions. The thickness of the individual layers should also play an important role on the development of different conformers. So far, all these inter-relationships have been little explored.

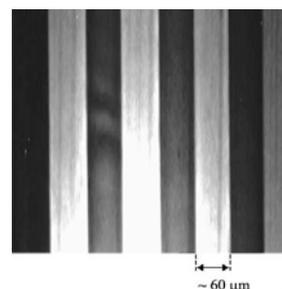


Figure 2.10. Optical micrograph of a micro-layered PET/PC

Synchrotron Radiation Micro-Infrared experiments would be extremely useful to examine the molecular conformations of the starting multilayered materials, and its evolution with temperature and time. IR has been successfully applied to study the deformed microstructure of glassy PET after cold-drawing¹⁹⁶. A conversion of gauche to trans conformers was observed in real time during the drawing process¹⁹⁶. For multilayered materials, mid-IR would allow to investigate the effect of both, processing and confinement (decreasing layer thickness), on the molecular conformations of the glassy state. IR dichroism will also be very helpful for these studies as orientational effects are envisaged. The relaxation of the stretched conformations in real time, as the temperature is raised above the glass transition temperature will be also of great interest, particularly for cold-crystallization studies.

REAL-TIME CRYSTALLIZATION OF NATURAL RUBBER NANOCOMPOSITES UNDER STRETCHING

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Polymer nanocomposites (PNCs) represent a new class of materials compared to conventional filled polymers, as they can possess enhanced properties through nanoscale reinforcement. A great deal of effort has been devoted to understanding the reinforcing mechanism of PNCs containing highly anisotropic nanofillers. On the other hand, vulcanized natural rubber under deformation has been the subject of intensive research interest^{197,198,199}. Several major topics in polymer science such as rubber elasticity theory and structure-property relationships in polymeric solids were initiated from this subject.

¹⁹⁵ F. J. Baltá Calleja, F. Ania, I. Puente Orench, E. Baer, A. Hiltner, T. Bernal, S. S. Funari. *Progr. Colloid Polym. Sci.* 2005, 130: 140-148

¹⁹⁶ C. Pellerin, M. Pézolet, P. R. Griffiths. *Macromolecules* 2006, 39: 6546-6551

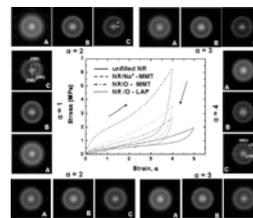
¹⁹⁷ S. Toki et al., New Insights into Structural Development in Natural Rubber during Uniaxial Deformation by In situ Synchrotron X-Ray Diffraction" *Macromolecules*, 35, 6578-6584 (2002)

¹⁹⁸ S. Trabelsi et al., Effective Local Deformation in Stretched Filled Rubber, *Macromolecules*, 36, 9093-9099 (2003)

¹⁹⁹ S. Toki et al., Molecular orientation and structural development in vulcanized polyisoprene rubbers during uniaxial deformation by in situ synchrotron X-ray diffraction *Polymer*, 44, 6003-6011 (2003)

The roles of molecular orientation and deformation-induced crystallization were found to be of particular importance because of their effect on the final mechanical properties²⁰⁰. Stress-induced crystallization of elastomers has been studied by different techniques: X-ray scattering, infrared spectroscopy, birefringence, electron microscopy, dilatometry, etc...

We aim to analyze the effect of the nanoparticles on induced crystallization of natural rubber under stretching by spatially resolved FT-IR reflection microspectroscopy with synchrotron radiation, in order to examine crystalline and orientational parameters from developing (real-time) and structured crystalline domains as a function of different processing parameters, such as the temperature, stretching rate and elongation, as well as localised aging and relaxation phenomena probed by conformational rearrangements.



Team members:

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CARACTERIZATION OF COMPOSITIONAL GRADIENTS WITH MICRON-SCALE RESOLUTION IN TAILORED BIOCOMPATIBLE POLYMERIC MATERIALS

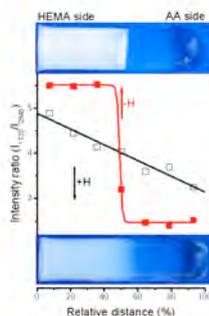
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Ordered and gradient polymeric materials are very attractive in coating and film technologies. We have recently done some work in this particular area^{201,202}, and we intend to continue with this research by preparing gradients

with variable sensitivity components such as NIPam (thermosensitive) or ionizable vinyl units (pH-sensitive). The gradient materials incorporating this type of components will exhibit gradient sensitivity, and may be very attractive as drug delivery systems, bio-actuators, etc. One of the major points of this work is to achieve a controlled gradient on a microscale, and it is therefore necessary to accurately characterise such microgradients. Resolved vibrational microspectroscopy may be the target technique for this, and synchrotron infrared microspectroscopy can provide fast and powerful complementary chemical information at similar resolution scales as those obtained by Raman microscopy. As example, some representative optical photographs of cylindrical gradients, together with the changes in the intensity ratio of Raman spectra (I_{1720}/I_{2945}) along the long axis of the cylinders are represented.



Team members:

Dr. Helmut Reinecke, Dr. Alberto Gallardo, Dr. Carlos Elvira, Dr. Rodrigo Navarro, Monica Pérez, Myriam Gómez and Diego Velasco.

²⁰⁰ J. Carretero-Gonzalez et al., Real time Crystallization of Organoclay Nanoparticles Filled Natural Rubber Under Stretching, *Macromolecules*, 41, 2295-2298 (2008)

²⁰¹ Reinecke H, Aguilar MR, Güven G, Piskin E and Gallardo A. A simple procedure to tailor the compositional gradient of copolymeric materials, *e-polymers* 2009, 020

²⁰² M.R. Aguilar, H. Reinecke, A. Gallardo, *In situ formation of hema-nipa compositional gradients during polymerization*, *J. Macromol. Sci.* 2009, A47, 000

THE STRUCTURE OF THE INTERFACIAL REGION IN POLYMER-BASED NANOCOMPOSITES: THE SURFACE-BONDED ORGANIC LAYER AND THE INTERFACIAL POLYMER

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In recent years we have prepared and characterised different types of silica and silicates modified with various alkoxy silanes under special conditions^{203,204}. In some cases these particles have been subsequently used to prepare nanocomposites with, for example polyethylene. The dielectric properties of different polyethylene-based nanocomposites have been studied and the structure of the interfacial region seems to play a major role on the dielectrical behaviour of these materials^{205,206}. We are interested in a deeper characterization both of the structure of the surface-bonded organic layer and on the structure of the interfacial polymer.

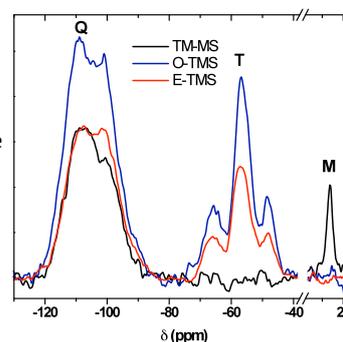


Figure 2.13. ²⁹Si CP/MAS NMR spectra for ethyl trimethoxysilane, octyl trimethoxysilane and trimethyl methoxysilane modified silica using p-toluenesulfonic acid. The figure shows the Q, T and M regions.

The structural analysis of the surface-bonded organic layer can be made to a certain point^{203,204} by using solid-state NMR, both ²⁹Si (if the inorganic surface is silicon-based and then organic modifier is a silane) and ¹³C. As shown in Figure 2.13, this technique provides information on the type of linkages in which organic Si is involved (T region) and on the extent of the surface modification by evaluation of the (Q region). However, Cross Polarization experiments are usually performed because of the small amount of silanes incorporated and the results are by no means quantitative.

We have also studied the bulk conformational structure of the polyethylene nanocomposites²⁰⁷, though the approach is rough, and a technique allowing the specific measurement of the polymer at the interfaces is required.

Why MIRAS? For the study of the surface bonded organic layer and most especially of the interfacial polymer, infrared microspectroscopy seems the best option, as it can yield information on the conformational structure of the interfacial polymer and the surface-bonded organic layer and on specific interactions taking place at the interface. The structure of the interfaces is crucial for many properties and in particular, according to our results^{205,206} on the dielectric performance of polyethylene-based nanocomposites.

Team members: Prof. Julio Guzmán, Dr. Pilar Tiemblo, Dr. Nuria García, Dr. Mario Hoyos, Dr. Jose Manuel Gómez-Elvira

²⁰³ Use of p-toluenesulfonic acid for the controlled grafting of alkoxy silanes onto silanol containing surfaces: Preparation of tunable hydrophilic, hydrophobic, and super-hydrophobic silica García, N., Benito, E., Guzmán, J., Tiemblo, P. *Journal of the American Chemical Society* 129 (16), pp. 5052-5060 (2007)

²⁰⁴ Functionalization of SBA-15 by an acid-catalyzed approach: A surface characterization study García, N., Benito, E., Guzmán, J., Tiemblo, P., Morales, V., García, R.A. *Microporous and Mesoporous Materials* 106 (1-3), pp. 129-139 (2007)

²⁰⁵ Electrical strength in ramp voltage AC tests of LDPE and its nanocomposites with silica and fibrous and laminar silicates, Hoyos, M., García, N., Navarro, R., Dardano, A., Ratto, A., Guastavino, F., Tiemblo, P. *Journal of Polymer Science, Part B: Polymer Physics* 46 (13), pp. 1301-1311 (2008)

²⁰⁶ The development of electrical treeing in LDPE and its nanocomposites with spherical silica and fibrous and laminar silicates Tiemblo, P., Hoyos, M., Gómez-Elvira, J.M., Guzmán, J., García, N., Dardano, A., Guastavino, F. *Journal of Physics D: Applied Physics* 41 (12), art. no. 125208 (2008)

²⁰⁷ Evidence of a monoclinic-like amorphous phase in composites of LDPE with spherical, fibrous and laminar nanofillers as studied by infrared spectroscopy. Tiemblo, P., Guzmán, J., Serrano, R., Hoyos, M., García, N. *European Polymer Journal* 45 (1), pp. 30-39 (2009)

DETERMINATION OF POLYMER AND ADDITIVE CONCENTRATION GRADIENTS IN THIN FILMS AND POROUS MEMBRANES

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Synthetic polymers have achieved an outstanding importance as materials for the fabrication of semi-permeable membranes, particularly for treatment of water and gas separation. Both applications are nowadays of strategic importance. Polymer membranes for water filtration and purification are commonly prepared by the method of phase inversion, from polymer solutions which usually contain a mixture of polymers or polymers plus additives. Thus, an inhomogeneous distribution of the materials may define a concentration gradient, in such a way that the composition at the external surface of the membrane (flat or tubular) may be quite different from that of the inner surface. Furthermore, not only the chemical composition but also the microstructure and the cavities size distribution affect the performance of membranes. These facts make it important to be able to count on advanced analytical techniques in to accurately identify the composition of thin polymer layers at the external and inner surface because they work as separation layers in polymer membranes.

We are particularly interested in obtaining spatially resolved IR spectra of membrane surfaces, continuous and porous surfaces, of technical and experimental membranes as finished materials. The possibility to obtain spectral maps of various regions within cross sections of flat and tubular membranes would make it possible obtain the gradient of composition. A powerful technique such as synchrotron infrared microspectroscopy will be necessary as the overall thickness of some membranes is below 200 μm , see Figure 2.14.

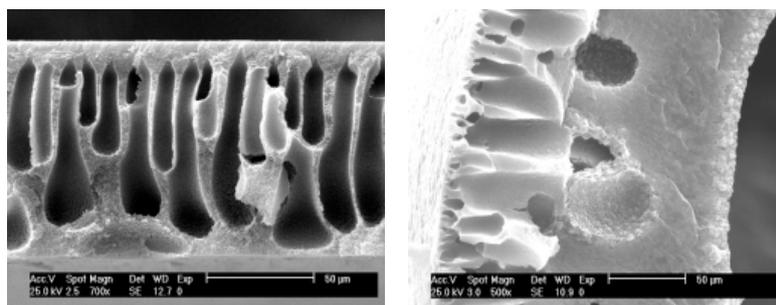


Fig.2.14. SEM images of flat and tubular membrane cross-sections. Scalebar = 50 μm

It would be also interesting to be able follow the loss of associated solvent and the development of molecular order in these materials upon applying thermal treatments. Gas membranes often require heating up to 400°C, so special heating cells in which microspectroscopy can be performed would be required.

To date, conventional FTIR with ATR, SEM and thermogravimetric Analysis have been used for the study of these phenomena. Although a great deal of information can be obtained by these traditional tools, the possibility of real-time registering of spectra, and the possibility of attaining IR spectra from very small areas, would greatly improve our capabilities for entirely following the complex phenomena of membrane formation, and for conveniently studying the relationship between chemical composition, concentration gradient, microstructure and behaviour of polymer membranes.

Team members:

Dr. Angel E. Lozano, Prof. José G. de la Campa, Prof. Javier de Abajo, Dr. Eva Maya, Dr. Dulce Muñoz, Dr. Mariola Calle + Ph.D. students.

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<http://www.ictp.csic.es/qm/paginaWEB.htm>

CHARACTERIZATION OF THE DISTRIBUTION OF CONDUCTING POLYMERS ON CARBON MATERIALS (CARBON FIBRES AND CARBON NANOTUBES)

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Porous carbon/conducting polymers composites seem to be very interesting materials to be used as electrodes for supercapacitors, because they take the advantage from both, the double layer mechanism provided by porous carbon materials and the pseudo-capacitive contribution from conducting polymers. From our research on the preparation and characterization of porous carbon/conducting polymers composites, we conclude that the final performance of the composites as supercapacitors depends on the properties of the starting porous material and also on the polymerization process²⁰⁸. We have used activated carbon fibres (ACF) as porous carbon and polyaniline (PANI) as conducting polymer. In order to understand the effect of the different properties and preparation methods and to optimize the composite performance in this application, the characterization of these materials by a position resolved technique, sensitive to both the porous texture and the polymer, is very interesting. μ SAXS has been successfully used by our research group to characterize the porosity of ACF across the fibre diameter^{209,210,211,212}.

Figure 2.12 includes the scattering curves obtained by μ SAXS corresponding to the measurements at the centre of the fibre for a commercial ACF (A20) and two ACF/PANI composites prepared using the sample A20, one prepared by a chemical method (A20_C) and another one prepared by an electrochemical method (A20_E). It is seen that the intensity decreases for the samples ACF/PANI composites compared to the starting ACF (sample A20) in the scattering region corresponding to micropores. This decrease of scattering intensity for the ACF/PANI composites can indicate that the deposition of polyaniline takes place inside the microporosity existing in the starting ACF, although no spectroscopic evidence of the polymer formed is obtained.

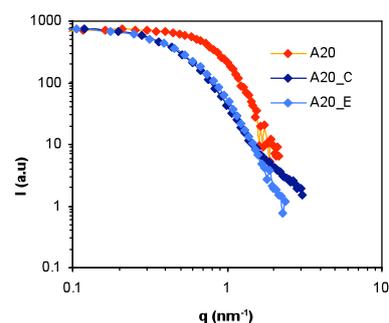


Fig. 2.12

Additionally, it would be very interesting to perform IR experiments with a high time resolution to follow the polymerization mechanism upon the different polymerization processes and at a given fibre position, as well as across the fibre direction. This kind of study could be applied to other systems.

Team members: Dr. Diego Cazorla-Amorós, Dr. Dolores Lozano-Castelló, Dr. Francisco Montilla, Dr. Emilia Morallón. Web page: <http://www.ua.es/electro/en/portada.htm>

Team members:

Dr. Diego Cazorla-Amorós, Dr. Dolores Lozano-Castelló, Dr. Francisco Montilla,
Dr. Emilia Morallón. Web page: <http://www.ua.es/electro/en/portada.htm>

²⁰⁸ Bleda-Martinez MJ, Morallon E, Cazorla-Amorós D. *Electrochim. Acta* 2007; 52: 4962-4968

²⁰⁹ Lozano-Castelló D, Raymundo-Piñero E, Cazorla-Amorós D, Linares-Solano A, Müller M, Riekkel C. *Carbon* 2002; 40: 2727-2735

²¹⁰ Lozano-Castelló D, Raymundo-Piñero E, Cazorla-Amorós D, Linares-Solano A, Müller M, Riekkel C. *Studies in Surface Science and Catalysis* 2002; 144: 51-58

²¹¹ Lozano-Castelló D, Cazorla-Amorós D, Linares-Solano. *Chemical Engineering Technology* 2003; 26: 852-857

²¹² Lozano-Castelló D, Maciá-Agulló JA, Cazorla-Amorós D, Linares-Solano A, Müller M, Burghammer M, Riekkel C. *Carbon* 2006; 44: 1121-1129

IN SITU CHARACTERIZATION OF THIN POLYMER FILMS ON ELECTRODE SURFACES

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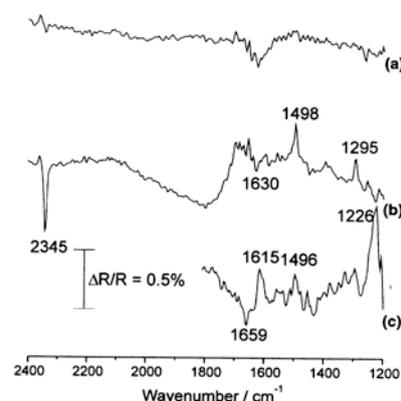
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The oxidation of aniline on metal substrates has received considerable attention in recent years, largely because the polymerisation product of the electrochemical reaction (polyaniline) has promising applications in a variety of technological fields, such as electrochromic devices, sensors, charge storage systems, or protection against corrosion. In order to obtain the most suitable material for each particular use, the physical, optical, chemical or electrochemical properties of the polymer have to be modified. In general, the insertion of some ionizable groups in the polymer backbone such as the carboxylic and sulfonic among others resulted in modified polyaniline structures with better processability and pH dependence.

The preparation of thin films of conducting polymers can be done by electrochemical polymerization²¹³. The characterization of the oxidation mechanism of the monomer and the structural characterization of the polymer films on the electrode surface are subjects of great interest. Then, the use of in situ spectroscopic techniques (IR, Raman, etc.) coupled to the electrochemical technique is very useful for this characterization.

The Figure shows, as an example, the spectra obtained for a Pt electrode in 1 M HClO₄ + 5x10⁻³ M m-aminophenol solution. The potential was stepped to higher values, taking 100 interferograms at each step (i.e. about 50 s). The availability of an IR technique with a high time resolution would allow us to deepen into the polymer mechanism.



Team members:

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2.4.2 Expressions of Interest

STRUCTURAL CHANGES INDUCED BY TEMPERATURE IN POLYCARBONATES AND POLYPROPYLENES

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Characterization of structural changes in polycarbonates and polypropylenes induced by temperature. Effect of modified nanofillers. Interphases and degradation in biomaterials.

CHARACTERISATION OF POLYMER BLENDS AND NANOCOMPOSITES

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Characterisation of polymer blends and nanocomposites, and imaging of diffusion processes in films and fibres.

EVALUATION OF HETEROGENEITIES AND INTERPHASES IN MULTICOMPONENT POLYMER-BASED MATERIALS

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²¹³ F. Cases, F. Huerta, R. Lapuente, C. Quijada, E. Morallón y J.L.Vázquez. J. Electroanal. Chem., 529 (2002)59-65; H.J. Salavagione, J. Arias, P. Garcés, E. Morallón, C. Barbero y J.L.Vázquez. J. Electroanal. Chem., 565/2 (2004) 375-383; N. Boutaleb, A. Benyoucef, H.J. Salavagione, M. Belbachir y E. Morallón. European Polym. J. 42 (2006) 733-739; F. Montilla, I. Pastor, C.R. Mateo, E. Morallón y R. Mallavia. J. Phys. Chem. B, 110(12) (2006) 5914-5919; C. Sanchís, H.J. Salavagione, J. Arias-Pardilla y E. Morallón. Electrochim. Acta 52 (2007) 2978-2986

2.5 Archeology, Archeometry and Cultural Heritage

Knowledge of the materials that constitute objects of cultural heritage is very important to be able to extract information about the techniques used in their manufacture, the origin of the materials used, the commercial trade that allowed these products to be obtained, and their use by their owners. Solid and reliable non-destructive analytical techniques must be exploited in order to obtain high-quality information from often minute and difficult samples, frequently unique, priceless and/or irreplaceable. Advanced characterisation techniques based on synchrotron radiation^{214,215}, and in particular Synchrotron Infrared Microspectroscopy (SIRMS) have made in recent years a considerable impact in this area. Some of the most spectacular SIRMS results are related to archaeological discoveries, studying materials such as the ancient frescos²¹⁶ or the skin of mummies²¹⁷, and have provided great insight into aspects of the way of life hundreds and thousands²¹⁸ of years ago. As well as providing new details from diverse materials, SIRMS can furnish valuable information about the best techniques for conservation and, if necessary, the most suitable methodologies for restoration.

This research area is very important in Spain, which has a particularly rich archaeological, anthropological, architectural and cultural heritage, distributed throughout the Iberian peninsula, and numerous scientific cases have been presented.

2.5.1 Scientific Cases

ANALYSIS OF HETEROGENEOUS AND COMPLEX MICROMETRIC MIXTURES OF ANCIENT PAINTING MATERIALS

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The technical quality of ancient paintings and their state of conservation is directly related to the nature of the pigments and binding media used in their elaboration. The compatibility among all the products is important as they are not inert but react with one another and/or with the environment. Such processes take place over a long time period. These phenomena are especially important because apart from the direct reaction among pigments and binding media when they are mixed, all chemical reactions taking place are heavily affected by kinetic factors (dissolution, diffusion, solid state reactions and aging processes). As all these processes influence the state of conservation of the art works, the knowledge of the final products is essential in order to be able to propose appropriate advice on necessary restoration procedures.

²¹⁴ D. Creagh, Synchrotron Radiation and its Use in Art, Archaeometry, and Cultural Heritage Studies, in Physical Techniques in the Study of Art, Archaeology and Cultural Heritage, D. Bradley, D. Creagh (Eds.), Vol. 2, Elsevier, 2007, pp. 1-95

²¹⁵ L. Bertrand, Synchrotron Imaging for Archaeology, Art History, Conservation, and Palaeontology, In Physical Techniques in the Study of Art, Archaeology and Cultural Heritage, Volume 2 (2007), pp. 97-114. Bradley, D and D. Creagh (Eds). Elsevier.

²¹⁶ Donatella Barilaro, Vincenza Crupi, Domenico Majolino, Germana Barone and Rosina Ponterio, A detailed spectroscopic study of an Italian fresco, , Journal of Applied Physics 97 (2005) 044907

²¹⁷ Cotte, M., et al., *Studying skin of an Egyptian mummy by infrared microscopy*. Vibrational Spectroscopy, 2005. 38(1-2): p. 159-167

²¹⁸ Cotte, M., et al., *New insight on ancient cosmetic preparation by synchrotron-based infrared microscopy*. Analytica Chimica Acta, 2005. 553(1-2): p. 105-110

The identification of impurities, reagents, reaction compounds and aged binders is of high interest in determining the stability of the painting and in reversing ageing or alteration processes. Moreover, the determination of impurities and reagents may give us information on the preparation procedures of the pigments used. This is interesting in itself from the technological and historical points of view which are often related to other fields such as glass, ceramic or dyes industries, ancient or modern.

SR-FT-IR microspectroscopy has allowed us to isolate and identify the different compounds from very small samples^{219,220,221}. The painting layers are made up of a complex and heterogeneous mixture of substances. These inorganic and organic pigments and binders, reaction compounds and alteration compounds from submillimetric layers; typical painting layers thickness between 20 to 100 μm , see Figure 2.15.



Fig.2.15. Cross section from paint sample that shows the layered structure and their heterogeneous mixtures.

Also, the use of SR-FT-IR microspectroscopy with a bolometer detector allows far-infrared to be reached and thus expand the possibilities of this technique in the study of ancient paintings. The high intensity and high brilliance of synchrotron radiation in the far infrared is necessary to make these measurements.

Team members: Dr. Salvador Butí and Dr. Nati Salvadó (Dept. Chemical Engineering, EPSEVG)
Dr. Trinitat Pradell (Dept. Physics and Nuclear Engineering, ESAB), Technical University of Catalonia.

INFRARED SPECTROSCOPIC DIAGNOSTIC OF CULTURAL HERITAGE OBJECTS USING IR SYNCHROTRON RADIATION

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Over the last years and within the framework of the CSIC *Thematic Network on Cultural Heritage*²²², our group has been involved in the application of IR and Raman spectroscopic techniques for characterization of materials of interest in Cultural Heritage objects, such as pigments and binders^{223,224,225}, lead comes of historical windows²²⁶ and others. Vibrational spectroscopic techniques have been also employed by us to follow the effect of different conservation treatments applied to stones, such as for example laser cleaning²²⁷ or water repellents and

²¹⁹ N. Salvadó, S. Butí, M. Tobin, E. Pantos, T. Pradell (2005) : Advantages of the use of SR-FTIR microspectroscopy: Applications to Cultural Heritage. *Analytical Chemistry* 77(11) 3444-3451

²²⁰ N. Salvadó, S. Butí, E. Pantos, F. Bahrami, A. Labrador, T. Pradell (2008): The use of combined Synchrotron Radiation micro FT-IR and XRD for the characterization of Romanesque wall paintings. *Appl. Phys. A* 90, 2008, 67–73

²²¹ N. Salvadó, S. Butí, J. Nicholson, A. Labrador, H. Emerich and T. Pradell; Identification of reaction compounds in micrometric layers from 15th century Gothic paintings using combined SR-XRD and SR-FT-IR (*in revision in Talanta* 2009)

²²² <http://www.rtpnc.csic.es/>

²²³ M. Castillejo, M. Martín, M. Ouja, D. Silva, R. Torres, C. Domingo, J.V. García-Ramos, S. Sánchez-Cortés, "Spectroscopic Analysis of Pigments and Binding Media of Polychromes by the Combination of Optical Laser-based and Vibrational Techniques, *Applied Spect.* 55 (8), 992-998 (2001)

²²⁴ M. Castillejo, M. Martín, M. Ouja, E. Rebollar, C. Domingo, J.V. García-Ramos, S. Sánchez-Cortés, "Effect of wavelength on the laser cleaning of polychromes on wood", *J. Cult. Herit.*, 4, 243-249 (2003)

²²⁵ A. Kaminska, M. Sawczak, M. Oujja, C. Domingo, M. Castillejo and G. Sliwinski, "Pigment identification of a XIV/XV c. wooden crucifix by means of the Raman spectroscopic technique", *J. Raman Spectrosc.* 37,1125–1130 (2006)

²²⁶ M. García-Heras, M.A. Villegas, J.M.A. Caen, C. Domingo, J.V. García-Ramos, "Patination of historical stained windows lead comes from different European locations", *Microchemical Journal* 83, 81-90 (2006)

²²⁷ P. Pouli, C. Fotakis, B. Hermosín, C. Sáiz-Jiménez, C. Domingo, M. Oujja, M. Castillejo, "The laser induced discoloration of stonework; a comparative study on its origins and remedies, *Spectrochim. Acta A* 71, 932-945 (2008)

consolidant products²²⁸. The availability of micro-FTIR spectroscopy employing IR synchrotron radiation will enlarge very much our capabilities in the diagnosis of Cultural Heritage objects, as well as the capabilities of other Research Groups involved in the above mentioned CSIC Thematic Network.

In particular, the possibility of Synchrotron-based Micro-Imaging techniques, so interesting in the biological and medical field²²⁹, will allow the chemical mapping of special Artworks, where the knowledge of the distribution of materials is a very important data.

Our group at the “Instituto de Estructura de la Materia, CSIC”, as well as the CSIC Thematic Network will clearly benefit from the implementation of an IR beamline at the ALBA Synchrotron.

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Dr. Sagrario Martínez-Ramírez (IETcc-CSIC)
Dr. Marta Castillejo (Institute of Chemical Physics “Rocasolano”, CSIC)

HISTORIC AND MODERN COATINGS FOR STONE MATERIALS FROM ARCHITECTURAL HERITAGE

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Protective historical patinas have received a great amount of study, with whole conferences dedicated to them. The fact that they are the result of mixing both inorganic (lime, gypsum, natural pigments) and organic (milk, eggs, etc.) compounds make patinas materials that suffer both mineral and chemical transformations with time. We are highly involved in studying various aspects of the protection and conservation of stone materials, and our work in this specific field ranges from the fundamental characterization of historical materials used for stone conservation^{230,231,232,233} to the analysis of effective conservation techniques of recent protective and consolidant products (current synthetic, organic and inorganic products)^{234,235,236,237,238}, and even the decay these products can cause to the stone²³⁴.

²²⁸ C. Domingo, M. Álvarez de Buergo, R. Fort, S. Sánchez-Cortés, J.V. García-Ramos, M. García-Heras, “Possibilities of the molecular Infrared and Raman spectroscopies to monitor the polymerization process of water repellents and consolidants in treated stones”, *Progress in Org. Coat.* 63, 5-12 (2008)

²²⁹ C.Conti, P. Ferraris, M. Garavaglia, E. Giorgini, C. Rubini, S. Sabbatini, G. Tosi, “Microimaging FTIR of Head and Neck Tumors. IV”, *Microsc. Res. Tech.* 72, 67–75 (2009) and references therein.

²³⁰ Vazquez-Calvo, C., Alvarez de Buergo, M., Fort. R., Varas, M.J. Characterization of patinas by means of microscopic techniques. *Materials Characterization* 58, 1119–1132 (2007)

²³¹ Vazquez-Calvo, C, Gomez Tubio, B., Alvarez de Buergo, M., Ortega Feliu, I., Fort. R., Respalda, M.A. The use of a portable energy dispersive X-ray fluorescence spectrometer for the characterization of patinas from the architectural heritage of the Iberian Peninsula. *X-Ray Spectrometry* 37, 4, 2008, 399-409

²³² Vazquez-Calvo, C., Alvarez de Buergo, M., Fort. R. Overview of recent knowledge of patinas on stone monuments: the Spanish experience. In: *Building Stone Decay: from Diagnosis to Conservation*. R. Prikrýl & B. Smith (eds). The Geological Society of London. Special Publications 271, 295-307 (2007)

²³³ Alvarez de Buergo, M., Fort. R. Protective patinas applied on stony façades of historical buildings in the past. *Construction & Building Materials*, 17/2, 83-89 (2003)

²³⁴ Varas, M.J., Alvarez de Buergo, M., Fort. R. : The influence of past protective treatments on the deterioration of historic stone façades: a case study. *Studies in Conservation* 52, 110-125 (2007)

²³⁵ Fort. R., Alvarez de Buergo, M. Basic methodology for evaluating and selecting water-proofing treatments applied to carbonatic materials. *Progress in Organic Coatings*, 43/4, 258-266 (2001)

²³⁶ Gomez-Heras, M., Alvarez de Buergo, M., Fort. R., Rebollar, E., Oujia, M., Castillejo, M. : Laser removal of water repellent treatments on limestone. *Applied Surface Science*, 219/3-4, 290-299 (2003)

Our group applies a wide range of analytical techniques we have used to study patinas, including polarized light microscopy (transmitted light), fluorescence microscopy, SEM+EDS, XRD, FTIR, ICP-MS, LIBS, and XRF. Some examples are shown in the Figure of data obtained from patinas studied by us in the laboratory. Given the versatility and rich information available from infrared spectroscopy, we would like to generate complementary data via high spatial resolution synchrotron infrared microspectroscopy (SIRMS), initially applied to patinas designed by us in the laboratory in order to calibrate the possibilities of the technique.

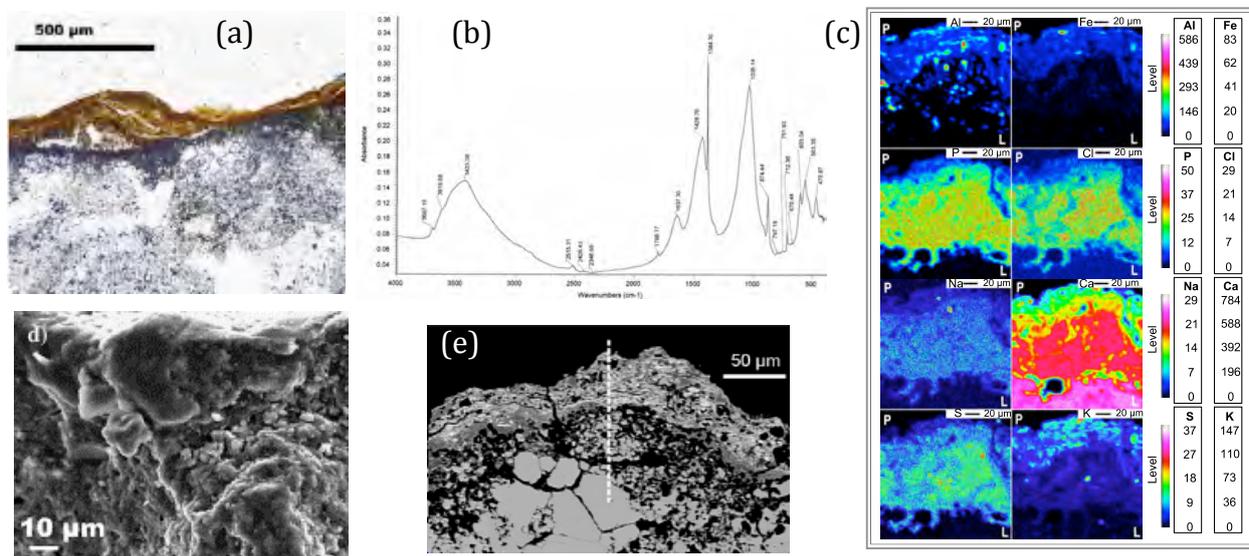


Fig.2.18 Various studies on patinas (a) optical microscopy, (b) FTIR, (c) microprobe, (d) (e) SEM.

These patinas have been deeply studied by our group, see Figure 2.18, within a National research project²³⁹ an on-going doctoral thesis²⁴⁰, and a recent patent²⁴¹.

Team members:

Dr. Mónica Álvarez de Buergo, Dr. Rafael Fort González, Carmen Vázquez-Calvo, Dr. Paula López-Arce, Dr. M^a José Varas.

STUDY OF HYDROXYL GROUPS AND MOLECULAR WATER BY SPATIALLY RESOLVED FTIR IN NOMINALLY NON-HYDROUS MARBLE AND LIMESTONE ROCKS: APLICATIONS TO THE SPANISH ARQUITECTURAL HERITAGE WEATHERING

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Spanish Architectural Heritage is largely built with limestone and marble, i.e., CaCO₃ or (Ca,Mg)CO₃. These compounds are nominally anhydrous, but always contain hydroxyl groups or molecular water in interfaces. In addition, these carbonated rocks are bonded with the classic *opus caementitium* or Roman mortar which also is a

²³⁷ Alvarez de Buergo, M., Fort, R., Gomez-Heras, M. : Contributions of Scanning Electron Microscopy to the Assessment of the Effectiveness of Stone Conservation Treatments. *Scanning*, 26/1: 41-47 (2004)

²³⁸ Domingo, C., Alvarez de Buergo, M., Sánchez-Cortés, S., Fort, R. & García-Ramos, J.V., Gomez-Heras, M. Possibilities of monitoring the polymerization process of silicon-based water repellents and consolidants in stones through Infrared and Raman spectroscopy. *Progress in Organic Coatings* 63, 5-12 (2008)

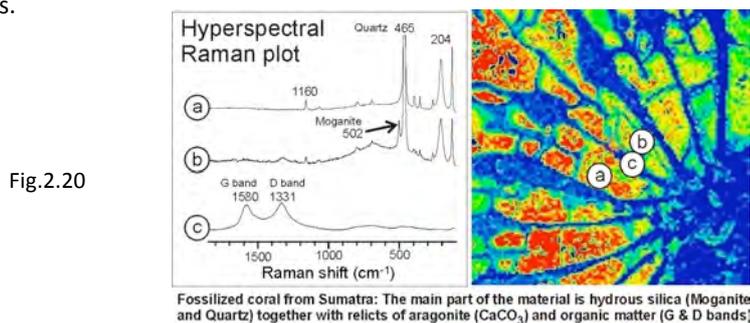
²³⁹ “Diseño de pátinas de protección en materiales pétreos del patrimonio arquitectónico”, BIA 2003-04073, 2004-2006

²⁴⁰ “Técnica tradicional de protección y embellecimiento de la piedra en el patrimonio arquitectónico: pátinas históricas en la Península Ibérica” by María del Carmen Vázquez Calvo

²⁴¹ “Procedimiento de preparación de patinas o películas para superficies pétreas y sus aplicaciones”, Invention nº P200702293, CSIC 2007

CaCO₃ cement, silica sand and pozzolanic hydrous silicates. Obviously, all mechanisms linked with the OH and H₂O groups are crucial studying the alteration mechanisms of this important heritage^{242,243}. In addition, we are also involved in studies on historical minerals of our National Museum of Natural History in which the exact definition of OH & H₂O groups are also crucial to be characterized.

We propose perform laboratory driven experiments on sliced special carbonated materials such as Strontianite (ZnCO₃) from Strontian (UK), pure white marble from Macael (Almeria), smithsonite (SrCO₃) from Picos de Europa (Santander), fibrous aragonite from Toral de los Vados, Ermida, Carmenes, etc (Spain), looking for these hydrous inter-fibre molecules which may enclose interesting data on genesis or alteration mechanisms. Our initial explorations using cathodoluminescence (CL), thermoluminescence^{244,245} (TL), photoluminescence²⁴⁶ (PL), radioluminescence²⁴⁷ (RL) and ionoluminescence²⁴⁸ (IBL) and Raman microspectroscopy, see Figure 2.20, point to the necessity of work under cryogenic conditions on spatially resolved systems to clarify doubts and some defect-emission linkages.



We are looking for improved spectra of high quanta quality together with spatially resolved resolution, and applied to those spectra bands linked with OH and H₂O molecules in nominally non-hydrous minerals. We are confident that MIRAS could offer us some advanced measurements.

Team members: Prof. Javier García Guinea and Dr. Elena Crespo Feo

INVESTIGATION OF PICTORIAL LAYERS IN WALL-PAINTINGS FROM THE SOUTH OF SPAIN BY MEANS OF SYNCHROTRON RADIATION BASED INFRARED SPECTROSCOPY

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²⁴² Cardenes V., Garcia-Guinea J., Monterroso C. & de la Horra R. (2008) Protocol for assessing the effectiveness of protective coatings for roofing slate. MATERIALES DE CONSTRUCCION 58, 263-279

²⁴³ Fernandez-Cortes, A; Calaforra, JM; Garcia-Guinea, J (2006) The Pulpi gigantic geode (Almeria, Spain): geology, metal pollution, microclimatology, and conservation. ENVIRONMENTAL GEOLOGY. 50, 707--716

²⁴⁴ Correcher V, Garcia-Guinea, J, Bustillo M.A., Garcia R. (2008) Study of the thermoluminescence emission of a natural alpha-cristobalite. RADIATION EFFECTS & DEFECTS IN SOLIDS. Accepted Manuscript Ref. Nr. SSD-01-07

²⁴⁵ Correcher, V; Gomez-Ros, JM; Garcia-Guinea, J; Martin, PL; Delgado, A (2006) Thermal stability of the thermoluminescence trap structure of bentonite. RADIATION PROTECTION DOSIMETRY. 119, 176--179

²⁴⁶ Sanchez-Munoz, L; Garcia-Guinea, J; Sanz, J; Correcher, V; Delgado, A (2006) Ultraviolet luminescence from defect complexes in the twin boundaries of K-feldspar. CHEMISTRY OF MATERIALS. 18, 3336--3342

²⁴⁷ Garcia-Guinea, J., Sanchez-Moral S., Correcher V., Sánchez-Muñoz, L Cuezva, S. Cremades A., Benavente D. and Galan J.M. (2007) Phosphor plasters of CaSO₄:Dy on the courtyard wall of Djehuty's tomb (Luxor, Egypt) RADIATION MEASUREMENTS Volume 43, Issues 2-6, February-June 2008, Pages 849-853

²⁴⁸ García-Guinea, J., Correcher, V. Sanchez-Muñoz, L. Lopez-Arce, P., Townsend P.D. and Hole D.E. (2007) Radiation damage of variscite in historic crafts: Solarization, decolouration, structural changes and spectra from ionoluminescence. RADIATION PHYSICS AND CHEMISTRY, 77(1), 18-22.

The research into cultural heritage involves the investigation of both the original techniques and materials and those employed during past restorations, as well as possible degradation processes²⁴⁹ from the generation of the object to the present day. All of these studies must be undertaken with the utmost view to preserving the cultural heritage. In fact, such studies are decisive for the selection and adequate planning of conservation methods. The analysis of small and/or heterogeneous samples, such as paintings and corrosion products, requires the smallest probe and the highest spectral resolution possible. As an example, we show two optical microscopy images of patina samples found in the church of Saint Paul, in Ubeda, Spain, Figure 2.19.

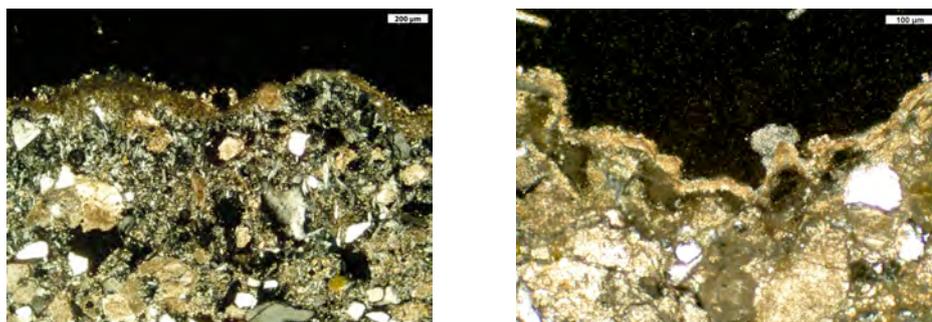


Fig.2.19. Patinas from Saint Paul's church. Cross-polarised light. (a) Thin and discontinuous patina covering an ornamental element (northern façade), (b) Irregular patina covering a weathered supporting ashlar on the western façade.

The study of these samples by Raman microscopy was difficult due to the high fluorescence background, while ATR-FTIR was very useful in providing information about the presence of oxalate in the samples. However, by this technique was not possible to obtain information about the distribution of the compounds along the sample. In this sense, SR-FT-IR would be a powerful analytical technique for the characterization of these materials²⁵⁰. The layered structure of paint samples formed by a complex mixture of compounds and the presence of minor compounds makes it necessary to perform analyses at the microscopic level^{251,252}. The high analytical sensitivity and high spatial resolution of synchrotron radiation-based techniques, in particular SR-FT-IR, would allow the identification of complex mixtures of compounds that constitute the different layers of ancient paintings. SR-FT-IR has 100 to 1000 greater brightness than conventional IR sources and gives a high spectral signal to noise at diffraction-limited spatial resolution. Furthermore, the micro size (better than 10×10µm for FT-IR) of the beam enables one to obtain detailed compositional profiles from the different chromatic and preparation layers. Of particular importance, is the possibility of obtaining two-dimensional chemical maps that can provide information about the execution techniques of the paintings by distinguishing between preparation layers and pictorial layers. Degradation patterns would also be identified with the aid of these 2D-maps.

On the other hand, the examination of the far infrared region (FIR) is very significant when examining inorganic pigments^{253,254}. Synchrotron FTIR can provide higher signal-to-noise ratio spectra compared with conventional FTIR with a global light source.

²⁴⁹ Weathering of gilding decorations investigated by SR: Development and distribution of calcium oxalates in the case of Sant Benet de Bages (Barcelona, Spain), A. Lluveras, S. Boularand, J. Roque, M. Cotte, P. Giraldez and M. Vendrell-Saz, *Applied Physics A: Materials Science and Processing*, (2008) 90, 23-33

²⁵⁰ Advantages of the use of SR-FT-IR microspectroscopy: Applications to cultural heritage, N. Salvado, S. Buti, M. J. Tobin, E. Pantos, A. J. N. W. Prag and T. Pradell, *Analytical Chemistry*, (2005) 77, 3444-3451

²⁵¹ Synchrotron-based X-ray spectromicroscopy used for the study of an atypical micrometric pigment in 16th century paintings, M. Cotte, E. Welcomme, V. A. Sole, M. Salome, M. Menu, P. Walter and J. Susini, *Analytical Chemistry*, (2007) 79, 6988-6994

²⁵² The use of combined synchrotron radiation micro FT-IR and XRD for the characterization of Romanesque wall paintings, N. Salvado, S. Buti, E. Pantos, F. Bahrami, A. Labrador and T. Pradell, *Applied Physics A: Materials Science and Processing*, (2008) 90, 67-73

²⁵³ Analyses of a green copper pigment used in a thirteenth-century wall painting, E. Bidaud, E. Halwax, E. Pantos and B. Sipek, *Studies in Conservation*, (2008) 53, 81-92

²⁵⁴ Far infrared and Raman spectroscopy analysis of inorganic pigments, E. Kendix, G. Moscardi, R. Mazzeo, P. Baraldi, S. Prati, E. Joseph and S. Capelli, *Journal of Raman Spectroscopy*, (2008) 39, 1104-1112

MIRAS OF PREHISTORIC ROCK PAINTINGS

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A key point in the study of prehistoric rock paintings is to achieve the absolute dating of these works of art. According to our experience^{255,256,257,258,259,260,261} most of the pictographs are made using inorganic pigments. Therefore, radiocarbon AMS ¹⁴C dating is not possible. The detection of organic binders would solve this problem. Although many efforts have been made, this is still a challenge for the spectroscopic techniques at laboratory level. We hope that MIRAS could help us to find possible binders in the paints used by the prehistoric artists. We have detected a clay mineral, illite, used as binder in a white paint by SEM/EDX²⁵⁸, Fig. 2.16, but we have been unable to detect the organic binder.

The distribution of the materials present in the painting panels, i.e. their microstratigraphy, is fundamental in order to detect superposition of pictographs, degradation processes and to proceed for possible dating based on layers of calcium oxalate accretions related with the paintings^{256,257,258,259,261}. We have used optical microscopy with polarized light and Raman microscopy to study multi-layer cross sections of prehistoric paintings^{255,256,257,258,259}, Fig. 2.17. MIRAS microstratigraphic studies, with no problem associated to fluorescence radiation, and higher sensitivity and spatial resolution than conventional infrared microspectroscopy to trace compounds, would provide more detailed information on the materials present and their microstratigraphic distribution.

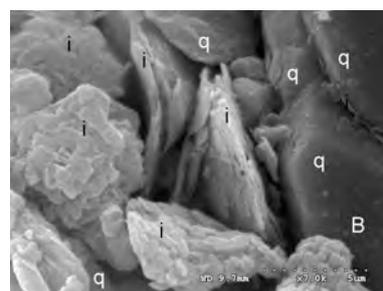


Fig. 2.16

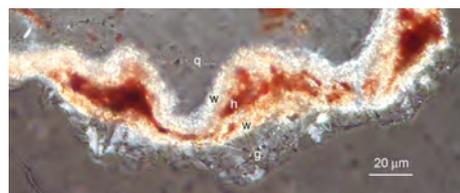


Fig. 2.17

Team members: Dr. Antonio Hernanz and Dr. Jose M. Gavira-Vallejo, Dept. Ciencias y Técnicas Físicoquímicas (UNED)
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CHARACTERISATION OF COMPOUNDS IN COMPLEX MATRICES USING SR-FTIR SPECTROSCOPY AND APPLIED TO SAMPLES COMING FROM THE ARTISTIC AND CULTURAL HERITAGE

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The Scientific Technical Services of the University of Barcelona have an FTIR laboratory with some equipment and accessories that gives support to many research groups of the University, as well as to other research groups of

²⁵⁵ Hernanz, A.; Mas, M.; Gavilán, B.; Hernández B. *J.Raman Spectrosc.* 37, 492-497 (2006)

²⁵⁶ Hernanz, A.; Gavira-Vallejo, J.M.; Ruiz-López, J.F. *J.Raman Spectrosc.* 37, 1054-1072 (2006)

²⁵⁷ Hernanz, A.; Gavira-Vallejo, J.M.; Ruiz-López, J.F. *J.Optoelect Adv.Mat.* 9, 512-521 (2007)

²⁵⁸ Hernanz, A.; Gavira-Vallejo, J.M.; Ruiz-López, J.F.; Edwards, H.G.M. *J.Raman Spectrosc.* 39, 972-984 (2008)

²⁵⁹ Ruiz, J.F.; Mas, M.; Hernanz, A.; Rowe, M.W.; Steelman, K.L.; Gavira, J.M. *Int.Newsllett,RockArt (INORA)*, 46, 1-5 (2006)

²⁶⁰ Hernanz, A.; Bratu, I.; Marutoiu, O.F.; Marutoiu, C.; Gavira-Vallejo, J.M.; Edwards, H.G.M. *Anal. Bioanal.Chem.* 392, 263-268 (2008)

²⁶¹ Gavira-Vallejo, J.M.; Hernanz, A.; Ruiz-López, J.F. *Memoria. La Historia de Cerca*, 10, 51-54 (2008)

public centres and private users. One of the accessories chosen for many applications during the last years has been the FTIR microscope, as more and more users are interested in the analysis of tiny samples.

Some of the requests we have had, are from people belonging to the conservation and restoration of cultural heritage field. Samples are very small, they can not be destroyed at all and people requesting this kind of analysis need normally scientific support for interpretation purposes, see Figure 2.21.

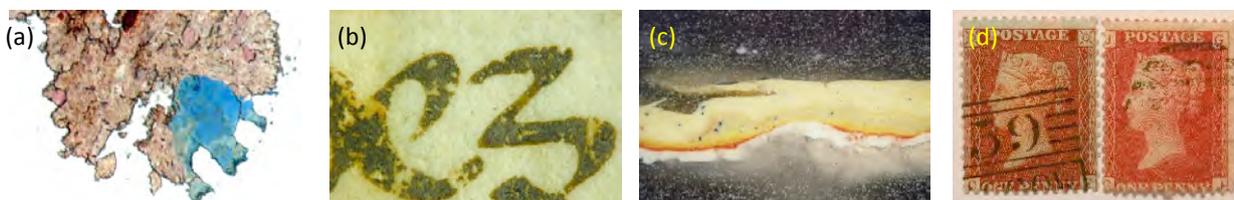


Fig.2.21 Some examples of samples for FTIR microspectroscopic analysis

Some of the cases we have in hand are the following: The study of thin layers of varnishes over old films, which can include dyes mixed with the celluloid, Figure 2.21a; The study of possible dyes over hairs found in mummies and graves from prehistoric ages; Migration of iron galls inks over paper and parchment in ancient documents from archives and museums^{262,263}, Figure 2.21b; Determination of some degradation products such as oxalate salts; Analysis of thin surfaces of ivory pieces which change their colour after some time in darkness. Possible change of protein component; and the analysis of cross-sections from paintings and prints^{264,265}, Figure 2.21c.

Another field that requires the work with small samples and non-destructive techniques are forensic science applications²⁶⁶, which includes analysis of forgeries^{267,268} (Figure 2.21d) drugs, fibres, cosmetics, etc in all kind of matrices.

In many cases spatial resolution is a handicap for resolving these determinations. Matrices are normally a problem when compounds to be identified are mixed with them (papers, polymers, wood, paints, gems, minerals...) It is generally necessary some physical or chemical extraction of the substances from their matrices. Therefore manipulation and preparation of extraction methodologies requires time and pieces of samples to be destroyed for analytical optimization. Moreover, most of the samples do not show a clear physical separation between matrix and sample to be analyzed.

The use of a Synchrotron IR beam with mapping or imaging accessories, would allow to us to distinguish between matrix, particles of interest and interface areas, in order to obtain a clear spectrum of the selected bands for each substance and therefore to characterize these substances imbedded in the matrix. Imaging or mapping microscope coupled to the synchrotron light, would solve in a very fast way, characterization of small samples in complex matrices. Moreover, interface changes and degradation products produced in those substances could be easily detected.

²⁶² Fourier transform infrared spectroscopy applied to the characterisation of 17th-20th century calcographic and xylographic inks, M.T. Romero and N.Ferrer, *Mikrochim. Acta* 131,237-245 (1999)

²⁶³ Characterisation by FTIR Spectroscopy of Ink Components in Ancient Manuscripts, N.Ferrer and M.Carme Sistach, *Restaurator*, 2005, 105-117

²⁶⁴ Colored inks analysis and differentiation: A first step in artistic contemporary prints discrimination, A.Vila; N. Ferrer; JF García., *Analytica Chimica Acta*. 588 (2007) pp. 96-107

²⁶⁵ Chemical composition of contemporary black printing inks based on infrared spectroscopy: Basic information for the characterization and discrimination of artistic prints. A.Vila; N. Ferrer; JF García., *Analytica Chimica Acta*. 591 (2007) pp. 97-105

²⁶⁶ Núria Ferrer, *Forensic Science Applications of Infrared Spectroscopy. Vibrational, Rotational and Raman Spectroscopies. Encyclopedia of Spectroscopy and Spectrometry* (p.603-615), Academic Press Ltd. 2000 Ed. John C. Lindon, George E. Tranter and John L. Holmes

²⁶⁷ Fourier transform infrared spectroscopy applied to ink characterization of one-penny postage stamps printed 1841-1880, N. Ferrer and A. Vila, *Analytica Chimica Acta* 550 (2006)161-166

²⁶⁸ Development of a fast and non-destructive procedure for characterizing and distinguishing original and fake euro notes, A.Vila, N.Ferrer, J.Mantecón, D.Bretón and J.F.García, *Analytica Chimica Acta* 559 (2006)257-263

2.5.2 Expressions of Interest

CHEMICAL ALTERATIONS ON THE SURFACE OF NEANDERTHAL BONES

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Analysis of dental enamel, determination of age rings, etc.

SPECTROSCOPIC STUDIES ON CULTURAL HERITAGE PIGMENTS

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2.6 Surface Science and Catalysis

The study of, or at, surfaces or interfaces is fundamental for many areas of science, from biology to solid-state physics and catalysis. SIRMS is making significant inroads into studies in these areas^{269,270}, since IR spectroscopy can offer valuable and detailed information. In the area of heterogeneous catalysis, for example, the study of adsorbed molecules is important for the investigation of catalytic active sites, typically metallic, at the surface of oxide²⁷¹ or zeolitic²⁷² materials, and is based on the study of the perturbation induced by the active sites to the stretching and bending modes of the adsorbed molecules, which occur typically in the mid-IR region. Clearly it is also important to add that information on the metal-support stretching frequency lies in the far-IR region. Several studies on catalytic processes have been reported in the literature. It is often necessary to reproduce as closely as possible the constraints of the catalytic reaction when analysing the process, and this can require special sample environments, such as reaction cells with capabilities for high temperature (up to 600°C), defined gas atmosphere, and sometimes pressure (up to 50 Bar).

The study of surfaces is widespread amongst the synchrotron IR community, and many examples can be found, including quality control and contaminant identification for the microelectronics industry, diverse areas related to surface corrosion¹³³, including metals such as steels^{273,274}, aluminum and its alloys²⁷⁵, and solid-state and semiconducting materials^{276,277,278}, self-assembled monolayers²⁷⁹, and nanoelectronic devices²⁸⁰.

A number of new areas now are emerging within the Spanish scientific community.

²⁶⁹ Hirschmugl, C.J., *Frontiers in infrared spectroscopy at surfaces and interfaces*. Surface Science, 2002. 500(1-3): p. PII S0039-6028(01)01523-0

²⁷⁰ Hoi-Ying N. Holman,, Karl Nieman,, Darwin L. Sorensen, Charles D. Miller,, Michael C. Martin,, Thomas Borch,, Wayne R. McKinney, and, Ronald C. Sims, Catalysis of PAH Biodegradation by Humic Acid Shown in Synchrotron Infrared Studies, *Environmental Science & Technology* 2002 36 (6), 1276-1280

²⁷¹ A. Zecchina, D. Scarano, S. Bordiga, G. Spoto and C. Lamberti, *Adv. Catal.*, 46 (2001) 265-398.

²⁷² A. Zecchina, C. Otero Arean, *Chem. Soc. Rev.*, 25 (1996) 187.

²⁷³ Eng, C.W., et al., *Uranium association with corroding carbon steel surfaces*. Surface and Interface Analysis, 2003. 35(6): p. 525-535

²⁷⁴ Eng, C.W., et al., *Spectroscopic study of decontaminated corroded carbon steel surfaces*. Surface and Interface Analysis, 2004. 36(12): p. 1516-1522

²⁷⁵ Chidambaram, D., et al., *Studies on the repassivation behavior of aluminum and aluminum alloy exposed to chromate solutions*. Surface and Interface Analysis, 2003. 35(2): p. 226-230

²⁷⁶ Falcaro, P., et al., *Highly ordered "defect-free" self-assembled hybrid films with a tetragonal mesostructure*. Journal of the American Chemical Society, 2005. 127(11): p. 3838-3846

²⁷⁷ Carini, G.A., et al., *Material quality characterization of CdZnTe substrates for HgCdTe epitaxy*. Journal of Electronic Materials, 2006. 35(6): p. 1495-1502

²⁷⁸ Lee, J.S., et al., *Electric-pulse-induced local conducting area and joule heating effect in VO₂/Al₂O₃ films*. Infrared Physics & Technology, 2008. 51(5): p. 443-445

²⁷⁹ F. Bensebaa, P.L'Ecuyer, K. Faid, CH. Py, T.J. Tauge, R.S. Jackson Grazing angle microspectroscopy of micropatterned self-assembled monolayers. *Applied Surface Science* 243 (2005) 238-244

²⁸⁰ Tony Jun Huang, Amar Flood, Chih-Wei Chu, Seogshin Kang, Tzung-Fang Guo, Tohru Yamamoto, Hsian-Rong Tseng, Bi-Dan Yu, Yang Yang, J. Fraser Stoddart, Chih-Ming Ho, *In situ Infrared Spectroscopic Studies of Molecular Behavior in Nanoelectronic Devices IEEE-NANO 2003, San Francisco, USA, 12-14 Aug. 2003, Vol. 2, pp. 698 – 701*

2.6.1 Scientific Cases

STUDY OF CATALYST BEHAVIOUR UNDER REACTION CONDITIONS

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Our interest in using synchrotron infrared radiation is for studying the behaviour of catalysts under reaction conditions (operating spectroscopy). In this sense we are interested in the interaction of molecules with the catalyst surface and their evolution under reaction conditions. For this purpose special catalytic cells will be developed and adapted to the infrared compartment (or microscope).

There are two main subjects of interest; (1) the *in-situ* behaviour of transition metal mixed oxides in catalytic reactions in the frequency range of 4000-600 cm⁻¹, and (2) the *in-situ* behaviour of single crystal metal surfaces in oxidation reactions. In the latter case studies under grazing incidence radiation are necessary, as well as measurements in the mid (4000-600 cm⁻¹) and low frequency (600-100cm⁻¹) regions.

(1) *In-situ* catalytic study of transition metal mixed oxides: The Mo- or W-based bronze systems are interesting materials showing redox and acid properties. Their catalytic properties have been tested in several reactions such as the amm(oxidation) of propane to acrylonitrile an acrylic acid²⁸¹, and other acid catalysed reactions²⁸². Their micro porosity (formed by 7 and 5 member rings of 4-5Å) should play an enhanced factor in some of these cases. Previous *in-situ* IR studies by using conventional global IR light have shown interesting results in the determination of reaction intermediate species²⁸³, however due to the low surface area of the samples a low signal intensity has been obtained in most cases. In this sense the use of synchrotron radiation would enhanced the signal to noise ratio. On the other hand polarization dependent experiments could be of interest in order to define crystal face dependent catalysis (crystal sizes of the Mo- or W-based systems are in the order of 5 μm²⁸⁴), and define reactivity confined in the catalyst channels.

(2) *In-situ* catalytic study of single crystal metal surfaces: The reactivity of single crystal metal surfaces in several oxidation and or hydrogenation reactions is of great interest from a fundamental point of view. In this case grazing incidence radiation is necessary (IRRAS). The main porpoise is the study of the formation of metal- oxygen and/or metal-carbon species, their nature and their reactivity toward reactant molecules. This type of studies requires measurements in the far IR region (600-100 cm⁻¹), which are not able to be performed with conventional global IR sources. Thus the need of synchrotron radiation is of essential importance in this case. For this type of experiments a UHV chamber dedicated to synchrotron IR surface studies would be interesting, connected to another UHV chamber for sample preparation and cleaning.

(3) Study of the adsorbate-substrate interaction in the far-infrared region by grazing incidence radiation of gold nanoparticles functionalized with several ligands for biomedical applications.

Team members: Dr. P. Concepción (1,2&3), Dr. J.M. López Nieto (1), Dr. A. Corma (2), Dr. P. Botella (3)

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IN-SITU SPECTROSCOPIC STUDIES ON SOLID-LIQUID INTERFACES CONCERNING THE GROWTH OF THIN FILMS OVER METALLIC ELECTRODES

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There is an important amount of work done on the characterization of copper anodization mechanisms. In alkaline medium, as the potential is swept from hydrogen evolution through oxidation, it is known that at potentials negative with respect to p-type Cu₂O formation, an adsorbed submonolayer of hydroxide organizes onto the surface. The formation of this hydroxide layer has been regarded as necessary to the further oxide growth. The electrochemical studies show evidence of previous processes to OH-adsorption, related with adatom/adion formation and surface reconstruction. Recent investigations lead us to consider that water structuring over the electrode may play an important role in these phenomena. After OH-adsorption, certain Cu⁺-dissolution takes place, and it is supposed that Cu₂O formation would occur by a mixed mechanism that involves both heterogeneous nucleation as well as Cu-OH dehydration.

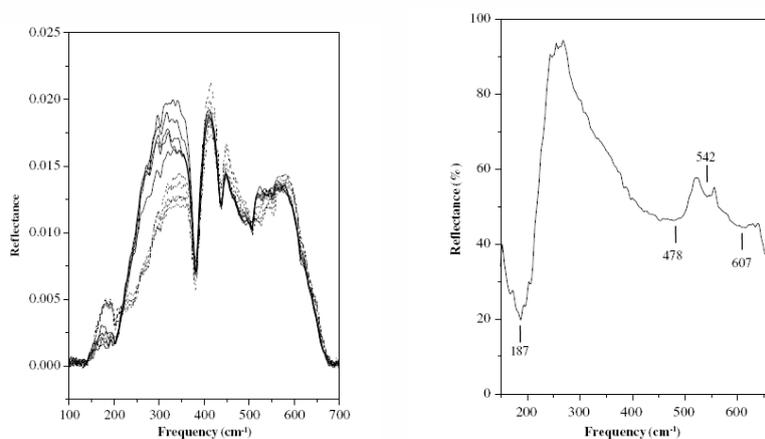


Fig.2.22. (a) Single channel reflectances at -1.1 V (broken lines) and 0 V (solid lines); (b) *In situ* far-IR spectrum of a Cu microelectrode at 0 V obtained with a grazing angle objective.

The use of synchrotron IR light would be of primary importance to study the water structure over the electrode as well as the OH-adsorption, Cu⁺-dissolution and Cu₂O formation. From the work of Melendres et al.²⁸⁵ the possibility to assess the Cu anodization and identify Cu₂O and CuO has been demonstrated, see Figure 2.22. Our intention is to extend these studies to other electrode-electrolyte interfaces such as metallic oxides, chalcogenides and biological-inorganic systems.

IN SITU AND OPERANDO STUDIES ON CERIA-SUPPORTED VANADIUM OXIDE CATALYSTS

Dr. Miguel A. Bañares

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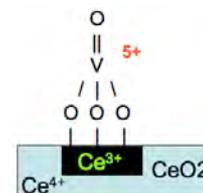
banares@icp.csic.es

Ceria-supported vanadium oxide catalysts exhibit important changes, mainly related to the interaction between ceria support and the supported oxide phase, which is a molecularly dispersed vanadium oxide. We have done studies based on *in situ* Raman spectroscopy during the oxidative dehydrogenation reaction of ethane to ethylene with simultaneous online activity measurements (*operando* Raman-GC), and during temperature-programmed

²⁸⁵ F. Hahn, Y.-L. Mathis, A. Bonnefont, F. Maillard, C. A. Melendres, *In situ* synchrotron far-infrared spectromicroscopy of a copper electrode at grazing incidence angle, *Synchrotron Rad.* (2007). 14, 446-448

treatments, such as reduction (*in situ* TPR-Raman), and calcination (*in situ* TPO-Raman)^{286,287}; these confirm that the formation of CeVO₄ (Raman bands at 843, 775 and 260 cm⁻¹) demands high temperatures, and that this solid-state reaction is promoted by vanadia loading.

In supported oxide catalysts, vanadium species remain molecularly dispersed, as surface isolated VO_x, with a terminal oxygen (vanadyl group, V=O), characterized by a Raman band at 1023 cm⁻¹ and three V-O-Ce bridging oxygens, **which are not observable by Raman spectroscopy, but are IR active**. The Raman analyses confirm that dispersed VO_x species, and not the commonly proposed bulk V₂O₅ phase, reacts with ceria support (Raman band at 460 cm⁻¹) forming CeVO₄.²⁸⁷

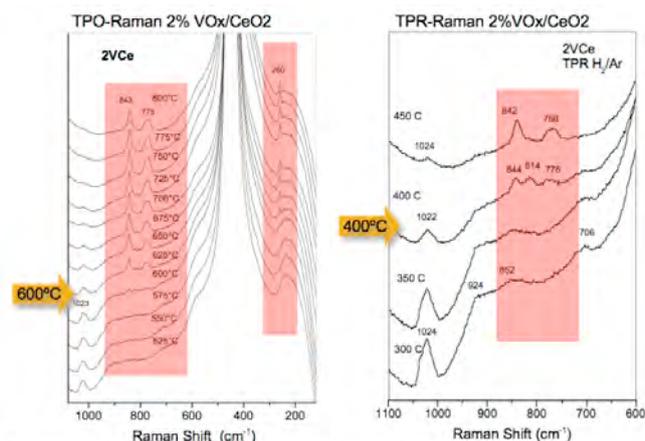


Structure of vanadium oxide species dispersed on ceria^{287,288}.

Preliminary *in situ* XAS and *in situ* EPR analyses²⁸⁸ confirm that vanadium is present as V⁵⁺ and promoted the reduction of cerium sites to Ce³⁺ at the interface between cerium and vanadium oxides. *In situ* TPR- and TPO-Raman studies²⁸⁶ confirm that a reducing environment facilitates in 200 °C the solid-state reaction between surface vanadia and ceria to form CeVO₄, constituted by Ce³⁺ and V⁵⁺ cations. This is critical to understand at a molecular scale the structure-activity relationships in supported oxide catalysts. Typically, the redox cycle operates at the supported oxide (i.e., vanadium). However, the redox cycle appears to operate on the cation of the support (cerium) for ceria-supported vanadia.

Structural Raman information and simultaneous Arrhenius plots in the Raman-GC studies suggest that the V-O-Ce bond must be invoked as the active site^{287,289}, and not the terminal V=O bond, as commonly believed. The redox cycle appears connected to cerium sites. Thus, redox cycle during the oxidative dehydrogenation of ethane to ethylene would trigger the formation of CeVO₄.²⁸⁷

However, there is no direct evidence. This could be drawn from *in situ* and *operando* MIRAS analyses of the V-O-Ce bond during reaction.



Representative Raman spectra during *in situ* TPO-Raman (left panel) and *in situ* TPR-Raman (right panel) of 2% V⁵⁺/CeO₂, during heating in synthetic air and during reduction in 10% H₂/He, respectively.

We propose a study that combines Raman and IR analyses to tackle the actual nature of the active site in V⁵⁺/CeO₂ catalysts. IR MIRAS provides complementary molecular information, essentially on the V-O-Ce bond and surface hydrocarbon species, which combined with simultaneous Raman determinations would allow nailing the actual nature of the active site in ceria-supported vanadium oxide catalysts. Such a work would comprise analyses of the structures of vanadium and cerium phase during heating in air (*in situ* TPO), in reducing environment (*in situ* TPR) and during reaction with simultaneous activity/selectivity analysis (*operando* Raman-MIRAS).

Team members:

Prof. Miguel A. Bañares, Dr. Vanesa Calvino Casilda, Dr. Anna Elzbieta Lewandowska, Ricardo Lopez Medina, Elizabeth Rojas Garcia, Ewelina Joanna Mikolajska, Manuel Garcia Casado

²⁸⁶ MV. Martínez-Huerta, G. Deo, JLG Fierro, and Miguel A. Bañares “Changes in Ceria-Supported Vanadium Oxide Catalysts during the Oxidative Dehydrogenation of Ethane and Temperature-Programmed Treatments” *Journal of Physical Chemistry C* 111 (2007) 18708-18714;

²⁸⁷ MV. Martínez-Huerta, G. Deo, JLG Fierro, IE Wachs, and Miguel A. Bañares “Operando Raman-GC Study on the Structure-Activity Relationships in V⁵⁺/CeO₂ Catalyst for Ethane Oxidative Dehydrogenation: The Formation of CeVO₄” *Journal of Physical Chemistry C* 112 (2008) 11441–11447,

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ADSORPTION OF CHOLESTERIC LIQUID-CRYSTAL POLIMERS ON METALIC SUBSTRATES

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Cholesteric liquid-crystal polymers (CLCP), synthesized in our lab, when dispersed in solution, self-organize on metal surfaces (Ag, Au), either on colloidal spheres or on thin films²⁹⁰. Their helical macromolecules, shown in Figure 2.23, open and are adsorbed onto the metallic surface by π -stacking of the aromatic rings extended parallel to the interface, with their aliphatic lateral chains perpendicularly directed towards the solution, as shown schematically in Figure 2.24.



Fig 2.23. Helicoidal molecule of PTODBME.

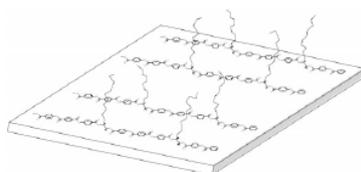


Fig. 2.24. Adsorption of PTODBME on a thin Ag lamina.

This capability of CLCP to self-assemble on metal surfaces, allows us to design functionalized interfaces which are provisioned with chemical and physical properties of interest for molecular recognition experiments. Together with their novel opto-electronic properties, it opens interesting possibilities in the field of nanotechnology, as optoelectronic liquid-crystal devices. To date we have obtained spectroscopic information from silver and gold nanoaggregates at a spatial resolution in the order of a few microns using Raman microspectroscopy, Figure 2.25. It is of considerable interest to apply synchrotron IR microspectroscopy in the reflection mode to complement the spectroscopic data from these microdomains.

Finally, we have recently prepared by *spin coating* CLCP on Pt/ TiO₂ / SiO₂ / Si(001) and Si(111), substrates respectively. It would be of great interest to study these materials by Synchrotron based – FTIR microspectroscopy, and correlate the spectroscopic information with other microscopy images.

Team members: Dr. Mercedes Pérez Méndez, Javier Sanguino Otero
Dr. Paloma Tejedor, Madrid Institute of Materials, ICMM (CSIC)

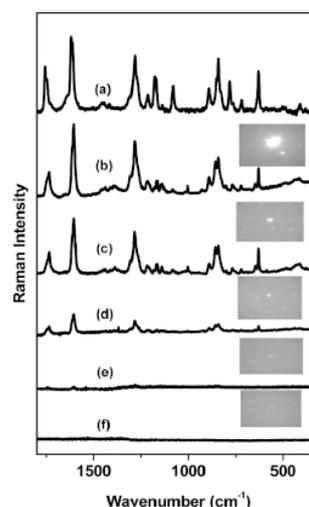


Fig. 2.25. (a) Micro-Raman of CLCP in solid state; (b)-(e) micro-SERS spectra of CLCP immobilized on Ag nanoaggregates with different nanoparticle concentration; and (f) non- aggregated particles.

2.6.2 Expressions of Interest (* Expression of Interest presented at the miras.2008 workshop)

STUDY OF THE ORIENTATION OF BIOMOLECULES ON SURFACES

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CHARACTERISATION OF ORGANIC MOLECULES ADSORBED ON SURFACES*

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²⁹⁰ S. Sánchez-Cortés, R. Marsal-Berenguel, M. Pérez-Méndez, "Adsorption of a Cholesteric Liquid-crystal Polyester on Silver and Gold Nanoparticles and Films Studied by Surface-Enhanced Raman Scattering", *Applied Spectroscopy* 2004 Vol. 58 N° 5, pp 562 – 569

2.7 Instrumental Developments and Sampling Methodologies

Over recent years, there has been considerable growth in the knowledge pool in the area of synchrotron IR radiation, and much effort is currently being dedicated to the development of specialised instrumentation and techniques to take advantage of the unique nature of synchrotron sources. Further, in IR microspectroscopy and imaging there have been important advances in recent years in instrumentation and detector technology, etc. However, the use of a synchrotron source for IR microspectroscopy opens up whole new areas where the approaches adapted from conventional techniques are not wholly adequate. Thus, there are many opportunities for the improvement of existing technologies and development of new strategies specifically adapted to the synchrotron. Some of these areas are discussed below, along with some scientific cases.

2.7.1 IR spectroscopy under high pressure

The combination of high pressure techniques with synchrotron radiation has been very fruitful and has led to edge-breaking results in fields like geophysics²⁹¹, planetary models²⁹² or materials science²⁹³. On the other hand, high pressure techniques have also been fruitful when combined with FTIR spectroscopy in order to deal with problems like lattice dynamics (polar phonons)^{294,295,296}, polymerisation and reactivity of simple gas phases^{297,298}, protein aggregation²⁹⁹, etc. A practical reason for this is the fact that diamond anvil cells are fully compatible with standard FTIR microscopes^{300,301}. However, FTIR spectroscopy at very high pressure becomes difficult with conventional IR sources due to the small size of the high pressure region in megabar diamond anvil cells, sometimes well below 100 μm . These difficulties can be overcome in IR synchrotron sources owing to the smaller focus size and larger photon intensity.

Synchrotron IR microspectroscopy (SIRMS) is ideally suited to matching the geometrical requirements of diamond anvil cells, allowing both point microscopy and mapping of, for example, microcrystals with typical crystal sizes up to 10 x 10 μm , such that different crystals

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may be examined separately. The extended spectral range and linear polarization are supplementary advantages for IR spectroscopy experiments under high pressure.

Many examples of high-pressure SIRMS can be found in the literature, and the team of R. Hemley at the NSLS, Brookhaven National laboratory have been especially prolific in this area³⁰².

2.7.1.1. Scientific Case

IR SPECTROSCOPY UNDER HIGH PRESSURE AT MIRAS

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The High Pressure Group of the University of Valencia is currently involved in the implementation of a FTIR spectrometer especially designed to perform experiments in diamond anvil cells, in the framework of the MALTA-Consolider project³⁰³. On the basis of the previous considerations, the group strongly supports a FTIR beamline at ALBA, and intends to develop the following research lines:

1) Lattice dynamics of materials under high pressure. Many materials of interest in our research field belong to centro-symmetric groups and the full characterization of their lattice dynamics under pressure requires the combination of Raman and IR spectroscopies. These materials can be included in two families i) materials of technological interest like p-type transparent conductors with delafossite structure, scintillators with schelite or wolframite structure, some super-hard materials, etc.³⁰⁴ and ii) materials of geophysical interest like magnesiowustites, perovskites and spinels.

2) High-spin-low-spin transitions under high pressure in materials of geophysical interest. Some of the materials studied by the group, like the high pressure phases of rock-salt (Zn, TM)O alloys with metal are related to ferropericlase/magnesiowustite, in which high-spin-low-spin transition have been shown to have implications in the mantle heat transport³⁰⁵.

3) Metallization of materials under high pressure. This is also of interest in material science, and geophysics (rock-salt and spinel phases). Transport measurements under pressure will be combined with FTIR microspectroscopy³⁰⁶.

4) Reactivity and catalysis under high pressure. This subject is an important part of the MALTA-Consolider project³⁰³. We intend to investigate the catalytical properties of minerals on abiotic organic synthesis by means of FTIR spectroscopy under extreme conditions³⁰⁷.

Team members:

Dr. Alfredo Segura García del Río, Dr. Chantal Ferrer Roca, Dr. Domingo Martínez García, Dr. Juan Fco. Sanchez Royo, Dr. Julio Pellicer Porres, Dr. Daniel Errandonea, Raúl Lacomba Perales, Javier Ruiz Fuertes.

³⁰² <http://www.bnl.gov/u2a/publications/index.html>

³⁰³ <http://www.malta-consolider.com/>

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³⁰⁷ G.W. Luther GW, "Activation of diatomic and triatomic molecules for the synthesis of organic compounds: Metal catalysis at the subseafloor biosphere", *Subseafloor Biosphere At Mid-Ocean Ranges, Geophysical Monograph Series* 144, 191(2004)

2.7.2 Near-field SIRMS

There is considerable current interest, particularly from the nanomaterials and nanotechnologies communities in overcoming the limits set on spatial resolution by diffraction effects in IR microscopy by applying near-field conditions for the delivery and/ or detection of radiation.

It is well known that the advances in SFM now allow one to measure surface topography at spatial resolutions in the 5 – 20 nm range, and a number of sophisticated techniques are available to obtain specific chemical and structural information³⁰⁸. Using near-field techniques, a number of high spatial resolution spectroscopic and imaging methods have already been developed. For example, with near-field optical microscopy in the infrared region between 1 – 10 μm , combined with a free-electron laser, a spatial contrast of between $\lambda/6$ - $\lambda/40$ has been observed³⁰⁹. Near-field Raman imaging has also been developed combining Raman microscopy and AFM, and 50 nm spatial resolution can be achieved with specially enhanced tips^{310,311}. Infrared imaging with 100 nm spatial resolution has been reported from polymer blends combining near-field microscopy with AFM, using aperture-less scattering tips irradiated with an IR laser^{312,313}. With this type of arrangement, a spatial resolution of 17 nm ($\lambda/600$) was previously reported from a Au – Si grating³¹⁴. Finally, using a novel probe infrared spectra of polymer films have been obtained in an AFM at a spatial resolution of around 100 nm, by detecting photothermally induced temperature fluctuations at the sample surface using a miniature wire resistance thermometer^{315,316}.

A synchrotron source has the considerable advantage of broadband operation over the whole IR spectral region, compared to laser sources, but achieving the maximum possible brightness is vital for success. The ultimately desired spatial resolution in, for example, biomedical applications is <100 nm, and in nanocomposites it would be interesting to be able to achieve <50 nm. Broadband near-field synchrotron IR measurements have been demonstrated with an apertureless nanoscopic thermal probe³¹⁷, and more recently data has been published from both the fingerprint³¹⁸ and terahertz regions^{319,320}.

There is some interest in Spain in combining near-field approaches with a synchrotron beam, and it will be of great advantage to involve key laboratories in the Madrid and Barcelona areas specialized in scanning probe technology and force microscopies, as well as employing innovative approaches based on surface-enhanced phenomena.

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³²⁰ Schade, U., et al., *THz near-field imaging of biological tissues employing synchrotron radiation*. *Ultrafast Phenomena in Semiconductors and Nanostructure Materials IX*, 2005. 5725: p. 46-52

2.7.2.1 Scientific Case

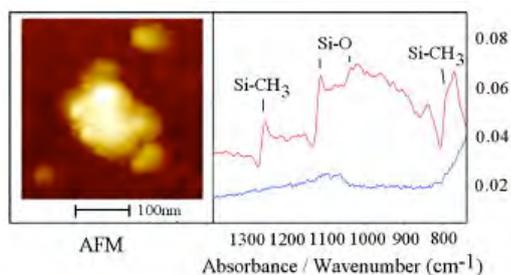
NEAR FIELD SURFACE-ENHANCED INFRARED ABSORPTION (SEIRA) USING IR SYNCHROTRON RADIATION

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The combination of high brightness broadband IR radiation provided by a synchrotron, with confocal microscopic techniques offers the possibility of reaching diffraction limited spatial resolution in the infrared region. On the other hand, the Surface-Enhanced Infrared Absorption (SEIRA) technique that our group has successfully implemented in Spain^{321,322,323,324,325,326,327} allows one to increase the sensitivity of IR spectroscopy in up to 2-3 orders of magnitude. The conjunction of these techniques in ALBA will provide the capabilities of performing Near-Field Surface Enhanced Infrared Absorption (SEIRA)³²⁸. As can be seen in the Figure (Fig. 4 from reference³²⁸), the SEIRA spectrum of a silicon film coated with 60 nm gold nanoparticles is obtained from an enhanced region of about 200 nm, well below the mid-infrared diffraction limit of around 10 microns.



Our "Surface Spectroscopy and Surface Plasmon Photonics" group of the "Instituto de Estructura de la Materia, CSIC", is very interested in implementing this type of Near-field SEIRA experiments, with a view to improve both the characteristics of SEIRA substrates to be used in Surface-Enhanced Spectroscopy based chemosensors, and the development of powerful synchrotron IR based nm scale probes.

Team members:

Prof. Concepción Domingo and Dr. Santiago Sánchez-Cortés, Dr. José Antonio Sánchez-Gil, Prof. José Vicente García-Ramos

³²¹ S. Sánchez-Cortés, C. Domingo, J.V. García-Ramos, J.A. Aznárez, "Surface-Enhanced vibrational study (SEIR and SERS) of dithiocarbamate pesticides on gold films", *Langmuir*, 17, 1157-1162 (2001)

³²² E.A. Carrasco, M. Campos-Vallete, P. Leyton, G. Diaz, R.E. Clavijo, J.V. García-Ramos, N. Inostroza, C. Domingo, S. Sánchez-Cortés, R. Koch, "Study of the interaction of pollutant nitro polycyclic aromatic hydrocarbons with different metallic surfaced by surface-enhanced vibrational spectroscopy (SERS and SEIR)", *J. Phys. Chem. A*, 107 (45), 9611-9619, (2003)

³²³ C. Domingo, J.V. García-Ramos, S. Sánchez-Cortés, J.A. Aznárez, "Surface-enhanced infrared absorption of DMIP on gold-germanium substrates coated by self-assembled monolayers", *J. Mol. Struct.* 661-662, 419-427 (2003) (Número especial dedicado al Prof. B. Schrader)

³²⁴ R. F. Aroca, D. J. Ross, and C. Domingo, *Appl. Spectrosc.* 58, 324A (2004) (Focal Point Article)

³²⁵ Leyton, C. Domingo, S. Sanchez-Cortes, M. Campos-Vallette, J. V. Garcia-Ramos, "Surface Enhanced Vibrational (IR and Raman) Spectroscopy in the Design of Chemosensors Based on Ester Functionalized p-tert-Butylcalix[4]arene Hosts", *Langmuir* 21, 11814-11820 (2005)

³²⁶ P. Leyton, C. Domingo, S. Sanchez-Cortes, M. Campos-Vallette, G. Díaz F., J.V. Garcia-Ramos, "Reflection-Absorption IR and Surface-enhanced IR of Tetracarboethoxy t-butyl-calix[4]arene, a Host Molecule with Potential Applications in Sensor Devices", *Vib. Spectrosc.* 43, 358-365 (2007)

³²⁷ C. Domingo, S. Sánchez-Cortés, J.V. García-Ramos, V. Resta, J. Gonzalo, "Pulsed Laser deposited Au nanoparticles as substrates for Surface Enhanced Vibrational Spectroscopy", *J. Phys. Chem. C*, 111, 8149-8152 (2007)

³²⁸ Mark S. Anderson, "Nearfield surface enhanced spectroscopy using targeted nanoparticle deposition", *Appl. Phys. Lett.* 92, 123101 (2008)

2.7.3 Terahertz spectroscopy

There are exciting new developments for spectroscopic imaging in the “Terahertz Gap” using coherent synchrotron radiation (CSR) in the far-IR. Although CSR in the far-IR was first detected at LINAC-based sources, broadband coherent enhancement of FIR synchrotron radiation was observed at the Jefferson Laboratory (USA) free electron laser for sub-picosecond electron bunches. At several electron storage rings fluctuating bursts of coherent FIR radiation have been observed but which are not suitable for FIR spectroscopy. However, for the first time, steady state, coherent FIR radiation from an electron storage ring was achieved at BESSY, Germany. At BESSY the bunch length and shape is manipulated to be comparable to the wavelength of the radiation by tuning the storage ring optics into a dedicated *low alpha* mode³²⁹, where alpha, α , is the momentum compaction factor describing the orbit length variation with beam energy. The electron bunches behave like large, single macro-particles and the emitted electromagnetic waves from each electron of the bunch add up coherently, leading to a spectacular increase in the radiation power, see Figure 2.26.

At BESSY³³⁰, a power increase of up to 10^5 compared to the normal, incoherent synchrotron radiation in the range of $10\text{--}60\text{ cm}^{-1}$ ($0.3\text{--}1.8\text{ THz}$) has been recorded. The brilliance of a CSR source is ideally suited for spectroscopic applications with a very low optical throughput, e.g. for the spectroscopic investigation of samples with sample areas in the range of the diffraction limit.

Most 3rd generation synchrotrons now develop THz programmes: notably BESSY and ANKA (Germany), ALS³³¹, J. Lab and NSLS (USA), Elettra (Italy), UVSOR (Japan), amongst others. The implementation of THz microspectroscopy may be of interest to prospective Spanish users, since it can provide opportunities in several interesting fields. Current THz science application areas range from the study of protein motions and dynamics, biological and medical imaging^{320,332}, to security screening (detection of bioagents & explosives), solid-state physics and superconductivity^{333,334,335}, astronomy, planetary science, mineralogy, etc.

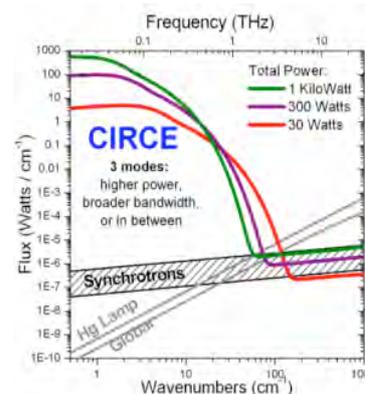


Fig.2.26 Flux at CIRCE.
Courtesy of M.Martin (ALS)

³²⁹ H. Wiedemann, *Particle Accelerator Physics* (Springer-Verlag, Berlin, 1993), Chap. 8.1.2.

³³⁰ M. Abo-Bakr, J. Feikes, K. Holldack, P. Kuske, W. B. Peatman, U. Schade, and G. Wüstefeld, H.-W. Hübers, Brilliant, Coherent Far-Infrared (THz) Synchrotron Radiation, *Phys. Rev. Lett.*, 2003, 90, 1-4

³³¹ CIRCE at ALS is a projected \$20M programme for a dedicated THz radiation facility.

³³² U. Schade et al., THz near-field imaging of biological tissues employing synchrotron radiation *Proc. SPIE Vol. 5725* 46 (2005).

³³³ E.J. Singley, M. Abo-Bakr, D.N. Basov, J. Feikes, K. Holldack, H.-W. Hübers, P. Kuske, M.C. Martin, W.B. Peatman, U. Schade, G. Wüstefeld, *New scientific opportunities with intense coherent THz synchrotron radiation: Measuring the Josephson plasma resonance in Bi2Sr2CaCu2O8*, *Phys. Rev. B* 69, 092512 (2004).

³³⁴ M. Ortolani, P. Calvani, S. Lupi, U. Schade, A. Perla, M. Fujita, K. Yamada, *Effects of Superconductivity and Charge Order on the sub-Terahertz reflectivity of La1.875Ba0.125-ySryCuO4*, *Phys. Rev. B* 73, 184508 (2006).

³³⁵ M. Ortolani, S. Lupi, L. Baldassarre, P. Calvani, U. Schade, Y. Takano, M. Nagao, T. Takenouchi, H. Kwarada, *Low-energy electrodynamics of superconducting diamond cond-mat/0602150*, *Physical Review Letters*, 2006.

2.7.3.1 Expression of Interest

MOLECULES OF INTEREST IN ATMOSPHERIC AND ASTROPHYSICAL PROCESSES OR IN COMBUSTION MEDIA

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IR / THz spectroscopy at high spectral resolution of species of interest due to their participation in atmospheric or astrophysical processes, or in combustion media, to support remote diagnosis techniques. The parameters of interest are frequency and intensity of absorption, energy of the implied levels, broadening coefficients and pressure induced shifts and their dependence on pressure, rotational energy transfer rates due to inelastic collisions. A high resolution FTIR spectrometer (like the Bruker IFS125HR) would be required. This type of research would be similar to that performed at AILES (SOLEIL).

2.7.4 Far-IR spectromicroscopy

Many inorganic, mineral, and semiconductor materials have low energy vibrational modes or crystal lattice phonon modes that are not typically accessible in the mid-infrared. Additionally, when these samples are of minute dimensions or are extremely heterogeneous, a microscopic analysis technique required to collect spectra of the sample or its component domains. The large far-IR flux of the synchrotron source, in combination with its brightness advantage, makes it possible to perform long wavelength examinations on such minute or heterogeneous samples.

A FTIR instrument was upgraded at NSLS with a custom-built Si beamsplitter and an external Si bolometer detector, and Far-IR microspectroscopy has been demonstrated, extending the long wavelength spectral range of a conventional IR microscope to below 50 cm^{-1} ($200\text{ }\mu\text{m}$), while still maintaining its performance in the mid-IR³³⁶. An example from GaAs is given in Figure 2.27. A dedicated beamline is now available at Brookhaven³³⁷.

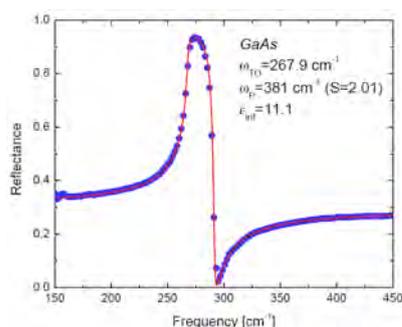


Fig. 2.27. Far-IR microspectroscopy reflectance spectrum of GaAs, and single oscillator fit. Courtesy of L. Carr (NSLS)

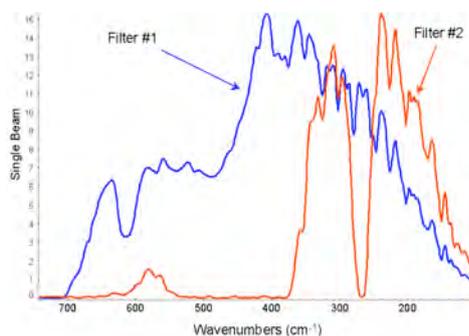


Fig. 2.28. First data from far-IR reflection microspectroscopy at SOLEIL. Courtesy of P. Dumas (SOLEIL)

³³⁶ Miller LM, Smith GD, Carr GL, Synchrotron-based biological microspectroscopy: From the mid-infrared through the far-infrared regimes, *Journal of Biological Physics*, 29, 219-230 (2003)

³³⁷ <http://infrared.nsls.bnl.gov/u10a/default.htm>

Very recently an similar far-IR microspectroscopy arrangement has been built and is currently under testing on the SMIS-2 beamline in SOLEIL³³⁸, and very good low frequency performance has already been demonstrated in the reflectance mode, see Figure 2.28. This philosophy can be adapted at ALBA to access microscopic samples with low frequency modes.

It is worthy to mention that some scientific cases and expressions of interest received are explicitly related to spectroscopy in the far infrared region. Although this work is not strictly pertinent to the miras² microspectroscopy proposal, especially where ultra-high vacuum apparatus is required along with the subsequent space and technical demands, we feel that the far-IR interests should be noted, with a view to pondering in the future the implementation of an IR beamline dedicated to and optimised for the far-IR region. In the meantime, advanced synchrotron far-IR beamlines can be found at various European synchrotron facilities, eg. BESSY (Germany), SOLEIL (France), Max-Lab (Sweden), DAFNE (Italy), etc.

As well as the example shown below, scientific cases which refer to far-IR spectroscopy and microspectroscopy measurements can also be found in Section 2.5 and 2.6

2.7.4.1 Scientific Case

BIOMOLECULES ON SURFACES AND THE STUDY OF MINERALS

Dr. Eva Mateo-Martí

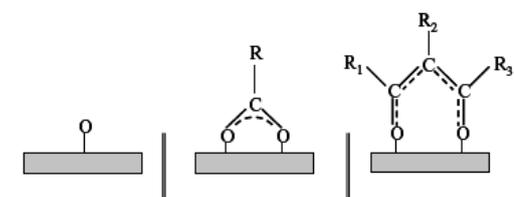
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Infrared spectroscopy has become one of the most versatile techniques for probing the organic/metal interface, however, it is remarkable that this success is largely restricted to the spectral region $>800\text{ cm}^{-1}$. The Far-IR information can be principally useful; especially in monitoring characteristic molecule-metal stretching vibrations in the low frequency region to identify which of the various functional groups are involved in anchoring the molecule to the surface. However, little direct experimental information exists about the adsorbate-metal bonding mode, and the synchrotron Far-IR experiments could be designed to close this gap.

A detailed chemical analysis of the adsorbed organic species may be made, at sub-monolayer sensitivity to the low frequency region using high brilliance synchrotron radiation sources.

Fig.2.29. Summary of the $\nu_{\text{Cu-O}}$ vibrational frequencies observed for the atomic species, the OCO unit and the OCCCO³³⁹ unit.



O/Cu(110)	389 cm^{-1}	Formate/Cu(110)	378 cm^{-1}	MAA/Cu(110)	285 cm^{-1}
		Formate/Cu(100)	378 cm^{-1}	AA/Cu(110)	304 cm^{-1}
		TA/Cu(110)	378 cm^{-1}		

Relevant bands of mineral structure are in the far-infrared region, therefore it would be relevant to generate a far-infrared data base of minerals in order to make a comparison with space mission data, and data obtained from minute particles or dust grains. As an example spectra from Mars measured in the region from 100 to 360 cm^{-1} were obtained during three different observation periods from NASA's Kuiper Airborne Observatory.

³³⁸ <http://www.synchrotron-soleil.fr/Recherche/LignesLumiere/SMIS>

³³⁹ V. Humblot, C.J.A. Bingham, D. Le-Roux, E. Mateo-Martí, A. Mc.Nutt, T.S. Nunney, M. Ortega-Lorenzo, A.J. Roberts, J. Williams, M. Surman and R. Raval, "Synchrotron Far-IR RAIRS studies of complex molecules on Cu(110)". Surface Science 537 (2003) 253-264

2.7.5 Time-resolved IR microspectroscopy

Time-resolved spectroscopy is one of the most solicited experimental approaches by users and potential users. Several possibilities now exist to be able to measure ultra-fast processes (from the sub-ns range), fast processes (microseconds) to longer processes of minutes and even hours, and can be developed at a synchrotron IR beamline. Several time-resolved studies microspectroscopy studies of diverse systems have been published in the literature^{340,341,342}.

A feature of synchrotron radiation is that it is pulsed. The electrons do not form a continuous distribution around the synchrotron orbit, but rather travel in 'bunches'. Depending on the design of the storage ring, these bunches can be between 1 – 10 cm long, and they only radiate when they pass through a bending magnet, resulting short pulses of light in the range of tens to hundreds of picoseconds. These pulses can be used to probe systems exhibiting time-dependent phenomena on a sub-nanosecond time scale. Although other methods (e.g., mode-locked lasers) are capable of producing even shorter pulses, none can rival large spectral range of the synchrotron source and allow the use of high-performance FTIR spectrometers.

The combination of short, sub-nanosecond pulse time-structure and the wide spectral range not found in any other pulsed infrared source, provides an very powerful base for time-resolved spectroscopy using the pump-probe technique^{343,344,345}. In this a short duration excitation is applied to the system (the pump), after which the system begins to relax back toward equilibrium, and the aim is to follow the relaxation as a function of time. This can be achieved by monitoring the pump stimulus with another pulse that spectroscopically probes the system at a particular instant of time relative to the pump. Time-resolution is achieved by the probe pulse, thus the detector does not necessarily require a fast response. This has an important effect on the signal:noise ratio, as the pump-probe method allows low bandwidth detection to be used with signal levels comparable to those obtained from by conventional sources. In addition to the use of the pulsed structure of synchrotron radiation for pump-probe studies, time resolved studies can be also be obtained by using "step-scan" interferometry. In this mode of operation, time resolved infrared absorption spectra can be obtained by reconstructing the interferogram, giving access to time resolution in the 10 nsec – 1 msec domain, useful for many processes such as solid-state excitations, photochemically induced processes, electrochemical reactions at surfaces, and biochemical processes.

³⁴⁰ X Chen, Z Shao, N Marinkovic, L Miller, P Zhou, M Chance, Conformation Transition Kinetics of Regenerated Bombyx Mori Silk Fibroin Membrane Monitored by Time-resolved FTIR Spectroscopy, *Biophys. Chem.*, 89, 25-34 (2001).

³⁴¹ R Lobo, J LaVeigne, D Reitze, D Tanner, Z Barber, E Jacques, P Bosland, M Burns, G Carr, Photoinduced Time-Resolved Electrodynamics of Superconducting Metals and Alloys, *Phys. Rev. B: Condens. Matter*, 72, 024510 (2005).

³⁴² Lobo RPSM, LaVeigne JD, Reitze DH, et al., Photoinduced time-resolved electrodynamics of superconducting metals and alloys, *PHYSICAL REVIEW B* 2005, 72, 024510

³⁴³ Carr L, Lobo RPSM, Hirschmugl CJ, et al. Accelerator-Based Infrared Sources And Applications Proceedings of the Society of Photo-Optical Instrumentation Engineers (SPIE) Volume: 3153 Pages: 80-86 Published: 1997

³⁴⁴ Carr GL, High-resolution microspectroscopy and sub-nanosecond time-resolved spectroscopy with the synchrotron infrared source, *Vibrat. Spectrosc.* 1999, 19, 53-60

³⁴⁵ Lobo RPSM, LaVeigne JD, Reitze DH, et al., Subnanosecond, time-resolved, broadband infrared spectroscopy using synchrotron radiation, *Rev. Sci. Instrum.*, 73, 1-10 (2002)

2.7.6 Special experimental environments

Many potential users have interests in specific sampling environments, or the possibility to apply some type of perturbation to the sample and measure its response. Temperature and pressure cell, reaction cells, humidity cells, flow cells, etc. can all be adapted to the IR microspectroscopy laboratory with relative ease, and some are already commercially available.

Controlled pressure environments

The requirements for high pressure microspectroscopy have been detailed in Section 2.7.1

Controlled Temperature and Humidity Environments

Many areas require a careful control of temperature, whose limits depend on the nature of the samples. Often, especially in the case of biological and some polymer samples, the humidity must also be known and carefully regulated. The temperatures to be considered should range from cryogenic (cells are available for reflectance and transmission measurements down to 10 K) to high temperatures (up to 800°C may be required for catalyst research). Controlled heating apparatus are commercially available that provide precise control and measurement of the sample temperature, precise control of heating and cooling rates, and the possibility of developing ramps for dynamic experiments with specific and reproducible thermal history during the microscopic measurements, and can be incorporated into the instruments software to synchronize data measurements with temperature/humidity measurements, either by in house computer interfacing, or from the instrument manufacturers.

Dynamic processes

The adaptation of micro flow-mixer cells³⁴⁶ and micro-channel confinement³⁴⁷ techniques to the synchrotron infrared microspectroscopy environment opens up many opportunities in diverse scientific areas, including organic chemistry reactions, enzymatic processes, drug delivery, polymerization, cell-pharmaceutical response analysis, gas diffusion, degradation, etc.

Lab-on-a-chip microfluidic imaging has already been demonstrated with ATR-FTIR imaging microspectroscopy^{348,349}, Figure 2.30. However, the higher sensitivity and spatial resolution

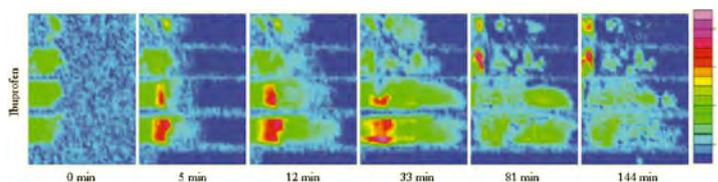


Fig. 2.30 FTIR images of the distribution of ibuprofen during its dissolution in water, from reference³⁴⁸.

with the synchrotron source allows quite sophisticated microsystems to be designed and imaged, which contemplate picogram sampling volumes this eliminating many of the problems derived from water absorption.

³⁴⁶ N Marinkovic, A Adzic, M Sullivan, K Kovacs, L Miller, D Rousseau, S Yeh, M Chance, Design and Implementation of a Rapid-Mixer Flow Cell for Time-Resolved Infrared Microspectroscopy, *Rev. Sci. Instrum.*, 71, 4057-4060 (2000).

³⁴⁷ N.F. Boussein, L.S. Hirst, Y. Li, C.R. Safinya, Z. Abu Samah, N. McDonald, R. Pynn, "Ordering of filamentous proteins and associated molecules through confinement in micro-channels," *Appl. Phys. Lett.* 85, 5775 (2004)

³⁴⁸ K. L. Andrew Chan and Sergei G. Kazarian, ATR-FTIR spectroscopic imaging with expanded field of view to study formulations and dissolution, *Lab Chip*, 2006, 6, 864-870

³⁴⁹ Sergei G. Kazarian, Enhancing high-throughput technology and microfluidics with FTIR spectroscopic imaging, *Analytical and Bioanalytical Chemistry*, 2007, 388, 529-532

An example of possible experiments include cell culture analysis, where a huge impact on the understanding of cellular mechanics, rapid screening of drug targets, the development of absorption-distribution-metabolism-excretion models for toxicology, are but a few of the future potential areas. In Figure 2.31, optical trapping (A) and AC dielectrophoresis were employed to precisely position neural cells inside microfluidic systems for further study and manipulation⁵⁶. The “T” arrangement and the linear array of cells can be clearly observed (scale bars = 50 μm).

Clearly this type of experimental approach also provides access to time-resolved imaging, generating information not only on reaction dynamics, but also on reaction kinetics and interphase structure development in steady-state systems.

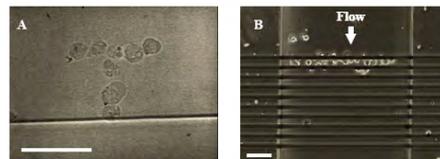


Fig.2.31 Neural cell trapping⁵⁶

Other specialised sampling cells which may be considered are photochemical cells, electrochemical cells, reaction cells, stretching apparatus, etc. commented in some of the scientific cases.

2.7.7 Combined techniques

The combination of synchrotron IR microspectroscopy with other techniques is highly desirable. Multiple technique endstations are being developed at various synchrotrons, such as at the ID13³⁵⁰ beamline at ESRF, where synchrotron x-ray microfocus and Raman microscopy can be performed *in situ* on the same sample. Raman and infrared microspectroscopy have been combined in the same instrument by various manufacturers and there is some interest to combine SIRMS and Raman for simultaneous measurements (at least one scientific case mentions this). Raman microspectroscopy is also used at some synchrotrons as an offline tool³⁵¹, and careful correlation between the sampling position in both the IR and Raman measurements can be made using specifically designed sample holders. Also, reactors, pressure cells and stretching apparatus can generally be used on the Raman system without limitations, offering a valuable additional characterization tool.

The combination of other synchrotron based techniques is another option, such as the combination synchrotron IR with a UV/VUV/XUV source and beamline in order perform “two-colour” pump-probe experiments³⁵² combining these two wavelengths. Of course this type of arrangement, with this and other techniques, will depend on the geometrical and space limitations.

Finally, special consideration in the design of sample holders to be used at different beamlines is a useful and affordable way to combine different techniques at the synchrotron, and is a philosophy already applied at other synchrotrons (eg. ESRF, SOLEIL).

³⁵⁰ <http://www.esrf.eu/UsersAndScience/Experiments/SCMatter/ID13/>

³⁵¹ The SMIS beamline at SOLEIL now offers a Raman microspectroscopy option to its users.

³⁵² Nahon, Laurent; Renault, Eric; Couprie, Marie-Emmanuelle; Nutarelli, Daniele; Garzella, David; Billardon, Michel; Carr, G. Lawrence; Williams, Gwyn P.; Dumas, Paul, Two-color experiments combining the UV storage ring free-electron laser and the SA5 IR beamline at Super-ACO, Proc. SPIE 1999, Vol. 3775, p. 145-154, Accelerator-based Sources of Infrared and Spectroscopic Applications, G. Lawrence Carr; Paul Dumas; Eds.

2.8 Other Areas

A few expressions of interest were received related to other areas, which are detailed below:

WATER CONTENT IN CERAMIC MATERIALS AND REACTIVITY IN METALLIC OXIDES*

Dr. Inmaculada Colera Garzón

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STUDY OF THE REACTION OF SYNTHETIC HYDROXYAPATITE WITH DIFFERENT OXIDES*

Dr. Begoña Savioni Cardiel

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NEAR- AND MID-INFRARED CHARACTERIZATION OF SILICON MICROSPHERES

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ANALYSIS AND CHARACTERIZATION OF MICROSTRUCTURED LINEAR AND NON-LINEAR LASER MATERIALS

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* Expressions of Interest presented at miras.2008 workshop

3. The MIRAS beamline

The aim of the proposal is to construct a state-of-the-art synchrotron infrared microspectroscopy facility at ALBA with the capacity to address the present and future requirements of the scientific community, not only in Spain but also in Europe as a whole.

3.1 Requirements

Current projections suggest that there will be demand for two modes of operation on such a beamline. Firstly a single point “confocal scanning” microspectrometer such as is installed on the many existing IR beamlines world-wide, to provide the highest spatial resolution for the investigation of small and complex samples. Secondly, a multi-pixel line-scanning FTIR imaging system would be included. This system would allow the “imaging” of larger area samples at slightly lower spatial resolution.

The confocal scanning system will deliver a beam of approximately 1000x the brightness of a conventional infrared source into a diffraction limited spot of 1-6 μm diameter. The design of the beamline optimises performance in the mid-IR range but will give significantly enhanced performance, compared to a conventional source, in both the far-IR and mid-IR regions. Commercial FTIR microscope and imaging systems will be installed, which conventionally operate between 600 cm^{-1} and 4,000 cm^{-1} , but this can be readily extended to 100 cm^{-1} to 10,000 cm^{-1} by including a number of beam-splitter and detector options. Development of detectors in the defence and commercial sectors is very competitive, and is expected to lead to continual improvements in instrument performance. Ultimately it is possible that optimised single point measurement and optimised imaging will be combined in a single instrument, however, at present this is not the case so it is prudent to plan for a capability to illuminate more than one instrument.

The instruments under consideration are generally fitted with motorized sample stages, autofocus systems, and motorized apertures. Similarly, steering mirrors in the optical transfer system delivering light to the infrared microscopes will be motorised and under remote control. The ability to control many aspects of the microscope set-up via software, including focus, aperture size and sample selection, will make the beamline amenable to remote access and control. We shall aim to develop operating protocols which allow users to control some of the simpler experiments from their home laboratory. Operation of the infrared systems will be via dedicated software provided by the manufacturer. Our experience is that users are happy with this approach, and are often experienced in operating the software on arrival at the synchrotron, having used similar systems in their own laboratories.

A wide range of sample environments and sample handling facilities must be provided on the beamline, reflecting the diverse range of the infrared user community. Sample environments required include high pressure (to 90GPa), high and low temperature (800 K to 4 K), and controlled humidity. Gas and liquid flow-cells will also be required, both for biological experiments at near ambient conditions and for *in-situ* work on heterogeneous catalysts at moderate pressures up to 1 MPa. Provision will also be made for micro-ATR (attenuated total reflection) measurements with the appropriate objectives, grazing-angle microscopy, and a side port accessory will be included for the examination of large or bulky objects.

The SIRMS end-stations should be located within an enclosed, temperature-controlled environment in a dedicated suite of laboratories which provide adequate support facilities including a basic workshop and tools section for the direct maintenance of the beamline, a preparation lab with ancillary equipment for sample preparation, and a controlled user area which includes off-line facilities for monitoring experiments and data analysis, which will need the provision of computer stations or data points for use with personal lap top computers for up to six people in a comfortable environment. In addition it will be necessary to develop rapid and convenient protocols for presenting images and spectra to collaborators at remote sites whilst the users have beam time, in order to maximise the efficiency of beamline use.

4. Beamline Specification

4.1 Sources and Extraction of IR radiation

A number of options for achieving acceptable extraction angles for IR operation have been considered. Several constraints were faced: steric and geometrical constraints, floor space availability, available straight sections, etc. After extensive discussions with the team from CELLS, the recommendation is for the employment of a modified dipole vessel which will allow collection angles of **43 mrad** (horizontal) x **25.17 mrad** (vertical) be adopted. The IR radiation will be collected using a horizontal geometry, by means of positioning the extraction mirror inside the dipole vessel, employing a similar system to that used at the Australian Synchrotron^{353,354}.

Initial Wavefront

In order to assess the beamline's performance with this geometry, a calculation of the initial wavefront has been carried out using SRW³⁵⁵ for two prototypical wavelengths in the mid-IR and far-IR, which are displayed in Fig. 4.1

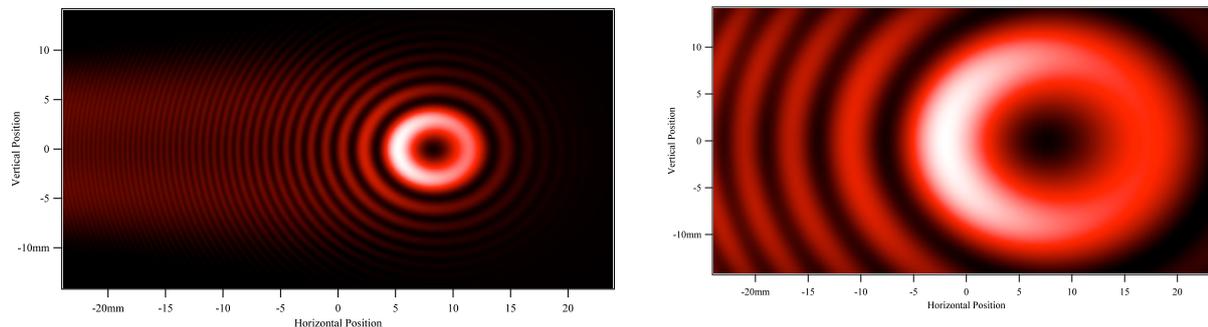


Fig.4.1. (Left) Initial wavefront at 10 microns (1000 cm^{-1}) and (right) Initial wavefront at 100 microns (100 cm^{-1})

Such an extraction would make the IR beamline at ALBA highly competitive at the International level. Figure 4.2 reports the calculated flux in the mid- to far-IR range, in comparison with that reported for the most recent infrared beamlines at SOLEIL (France), DIAMOND (UK) and Australian Synchrotron.

³⁵³ Creagh, D., et al., *An infrared beamline at the Australian synchrotron*. Synchrotron Radiation Instrumentation, Pts 1 and 2, 2007. 879: p. 615-618

³⁵⁴ Creagh, D., J. McKinlay, and P. Dumas, *The design of the infrared beamline at the Australian Synchrotron*. Radiation Physics and Chemistry, 2006. 75(11): p. 1995-1999.

³⁵⁵ Chubar, O., et al., *Simulation and optimization of synchrotron infrared micro-spectroscopic beamlines using wave optics computation: ESRF and SOLEIL's cases*. Synchrotron Radiation Instrumentation, Pts 1 and 2, 2007. 879: p. 607-610.

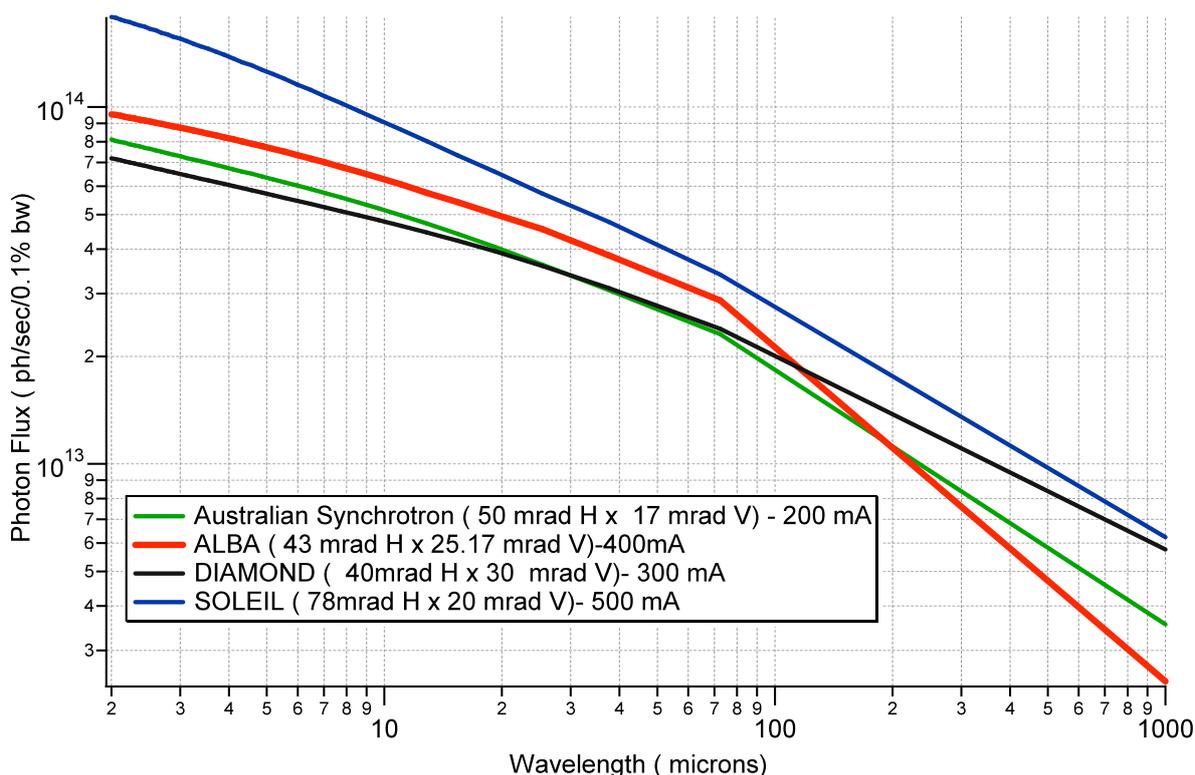


Fig. 4.2. Calculated flux at ALBA (red line), considering the proposed extraction of 45 mrad (H) x 25.17 mrad (V), and its comparison with SOLEIL (blue), DIAMOND (black), and Australian Synchrotron (green)

This demonstrates that the adopted extraction geometry is well suited to the efficient collection of the emitted IR radiation over the complete frequency domain. It is important to point out that the slightly lower flux in the very far-IR region is due to the limitation in the vertical size of the aperture. This only becomes significant at frequencies below 50 cm⁻¹ (200 μm), and consequently is a limitation for possible studies in this frequency region. In the context of the current proposal it is clear that the 25 mrad vertical acceptance angle provides a very acceptable collection efficiency in the range above 20 μm (500 cm⁻¹), but compromises very slightly the performance on moving further towards the Far-IR.

Extraction mechanism and dipole chamber

For the extraction of the beam from the “crotch” region of the dipole chamber, an extraction mechanism analogous to that adopted at the Australian Synchrotron IR beamline is suggested. In Fig. 4.3 photographs of the extraction mirror, and the dipole vessel are shown, providing insight to the positioning and geometry of the extraction mirror.

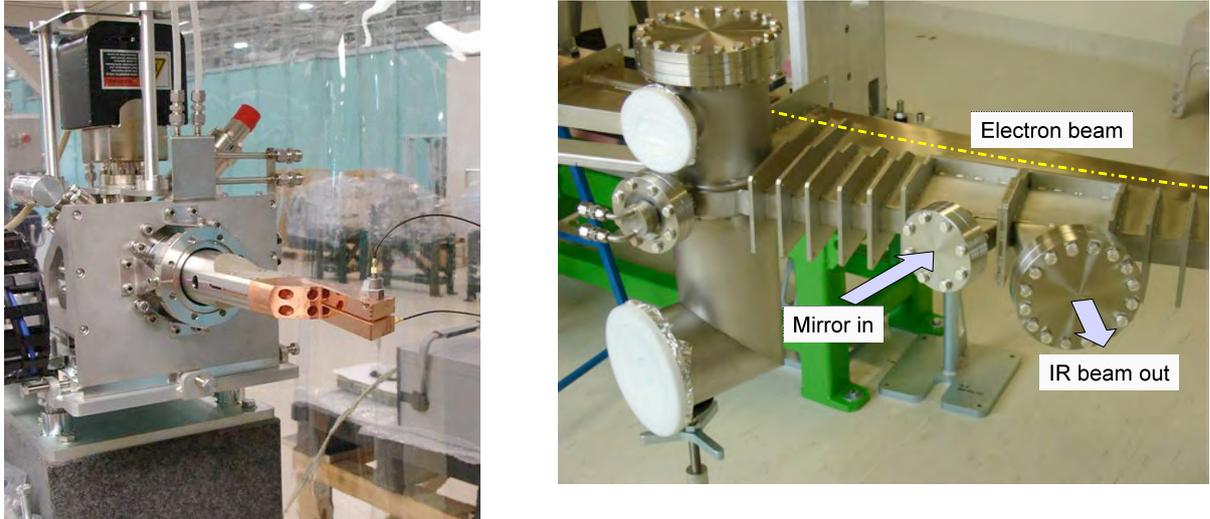


Fig. 4.3. Extraction mirror at the Australian Synchrotron, and modified dipole chamber

Working in conjunction with the team at CELLS, a modified dipole chamber design has been developed for the IR beamline at ALBA, and this is shown in Figure 4.4. Precise details of the modified dipole chamber are available, if required.

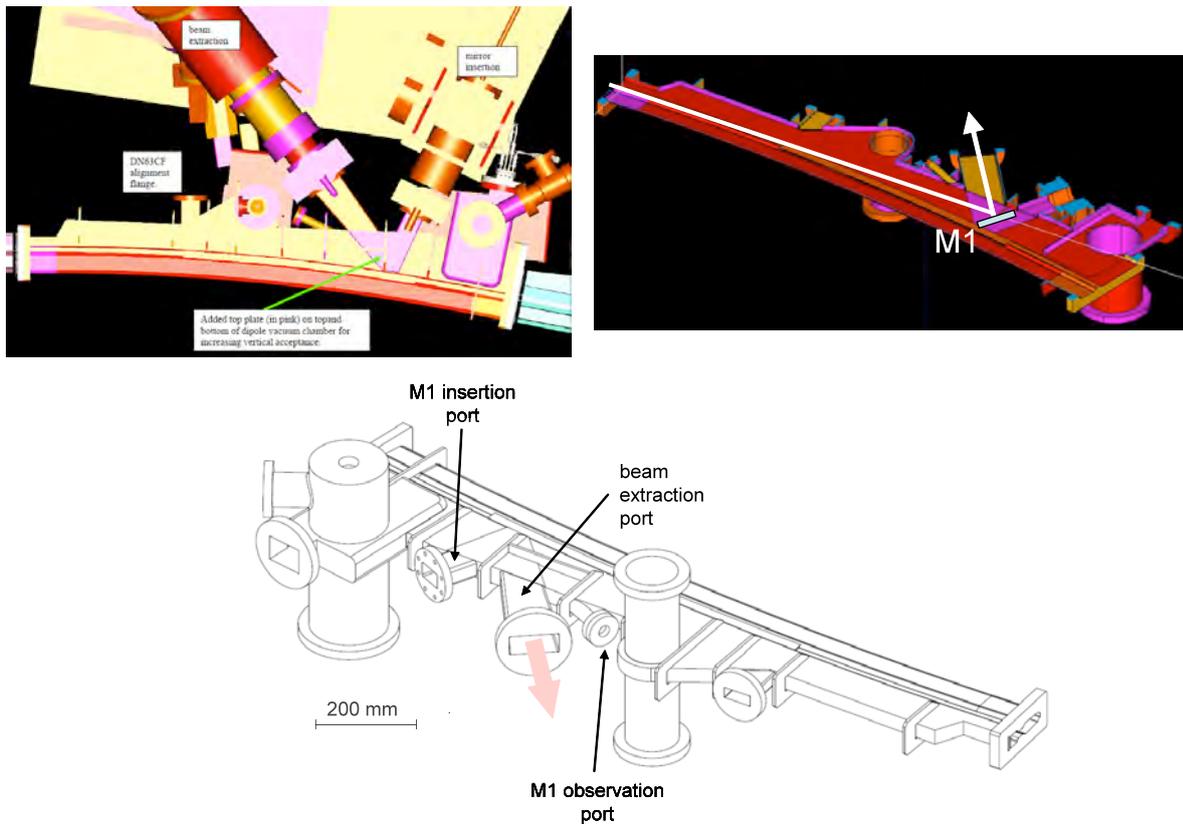


Fig.4.4. Design of modified dipole chamber for IR beamline on ALBA

Thus, the beam will be extracted in the horizontal plane by a plane mirror situated directly inside the dipole vessel (denominated **M1**). This mirror has a central slot of around 2mm height to avoid overheating of the mirror element by the intense X-ray and UV beam. The projected heat load distribution on the first mirror is very high, as is shown in Figure 4.5. The mirror slot will subtend an angle of approx. 2 mrad, thus avoiding all of the heat load on the first M1 mirror. An example of such a mirror design was already shown in Figure 4.3, for the Australian Synchrotron, and is being very successfully employed in other synchrotrons worldwide, eg. SOLEIL.

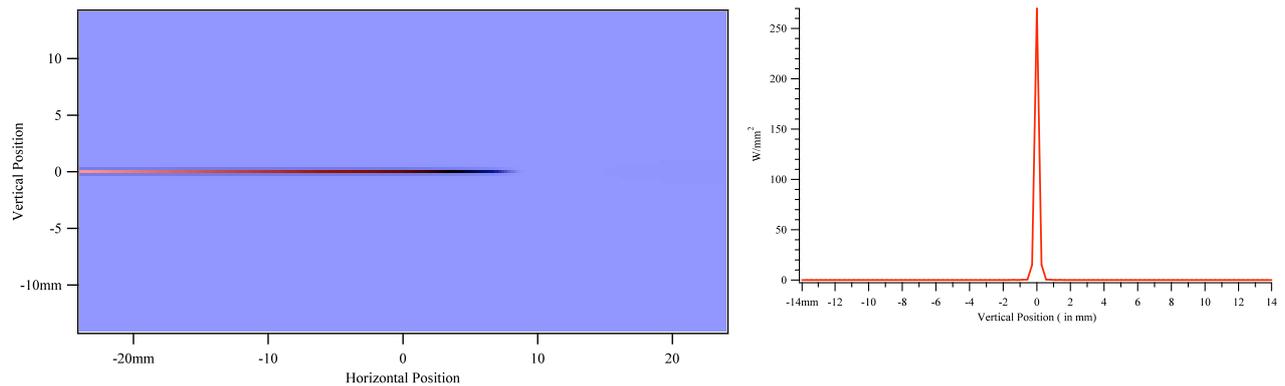


Fig.4.5. Heat power distribution, and peak power at position -23 mm. This calculation has been made for a M1 mirror located at 1.1 m from the source

Further, an added advantage in the design is the placement of a series of thermal sensors (thermocouples) close to the edges of the slot in **M1**. These will be highly sensitive to shifts in the electron beam orbit, and will allow for precise control of the steering of the electron beam, thus ensuring that the hard radiation passes through the slot and avoids damaging the mirror.

4.2 Transfer optics

Proposed optical layout

In the design of the extraction and transfer optics, two possible placements on the storage ring have been considered, and preliminary designs are currently available for both. With respect to the present proposal we have chosen to present only one of the options for simplicity in communicating the conceptual design. This option refers to the placement of the IR beamline at Bending Magnet 31 of the ALBA storage ring.

Figure 4.6 shows a proposed optical schematic for the transfer optics with dimensions in mm.

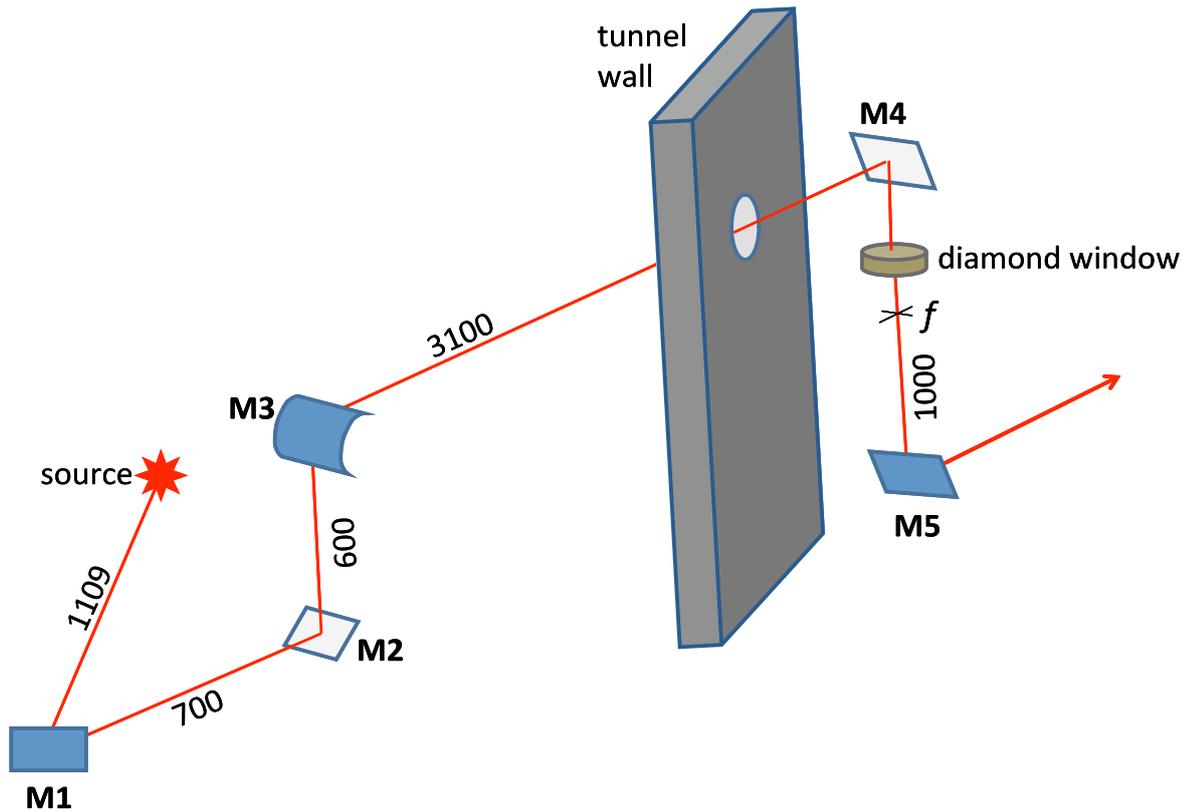


Fig. 4.6. Extraction optics scheme from source to experimental area

As mentioned previously, the slotted mirror **M1** placed at 1109 mm from the source extracts the beam. A second flat mirror **M2**, situated at 1200 mm from **M1**, in the same horizontal plane will direct the extracted radiation vertically, to an elliptical mirror **M3**. The beam will be directed directly outwards, through a hole in the tunnel wall to the radioprotection area. The flat mirror **M4**, will direct the beam downwards through a CVD diamond window, with the focal point of the beam just past this window. The positioning of the focus outside the diamond window will greatly facilitate the metrology and alignment of the beamline. The radiation protection area and beam propagation to the instruments will be discussed in the next section.

One of our objectives in the design of the extraction optics is to minimize the introduction of aberrations into the beam in order to maintain the maximum purity of the characteristics of the synchrotron wavefront as it propagates through the optical train. For this reason we have adopted $f/1$ optics with a symmetrical design. We regard this as essential in order to obtain homogeneous illumination character at the sample focus³⁵⁶, and maintain to the maximum the unique polarization characteristics of the synchrotron beam.

Beamline propagation simulation

The beamline optics have been simulated using SRW³⁵⁵ (by wavefront propagation using Fourier optics) and Ray tracing (employing Ray³⁵⁷), and the footprints of the wavefront at each

³⁵⁶ We have corrected for the horizontal extraction angle (19.31°) outside the radioprotection area.

³⁵⁷ RAY. The BESSY Ray Tracing Program. v.24.3 Franz Schaefers.

element are illustrated in Figure 4.7. It should be noted that Rays does not account for the edge radiation (ER), and in this case we considered pure BM emission along the whole horizontal fan. However, the two approaches are complementary, and serve to confirm the parameter values introduced into the SRW simulations.

Wavelength= 10 μm (= 1000 cm^{-1})

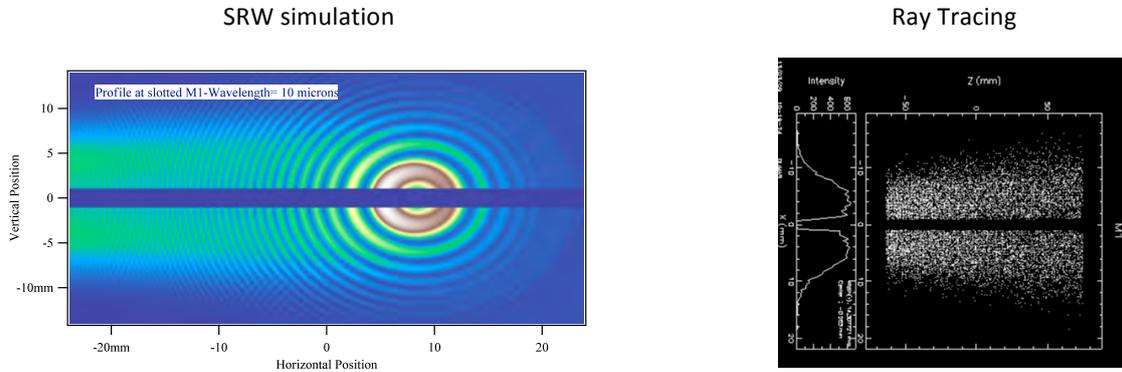


Fig. 4.7a. At the first slotted M1 mirror

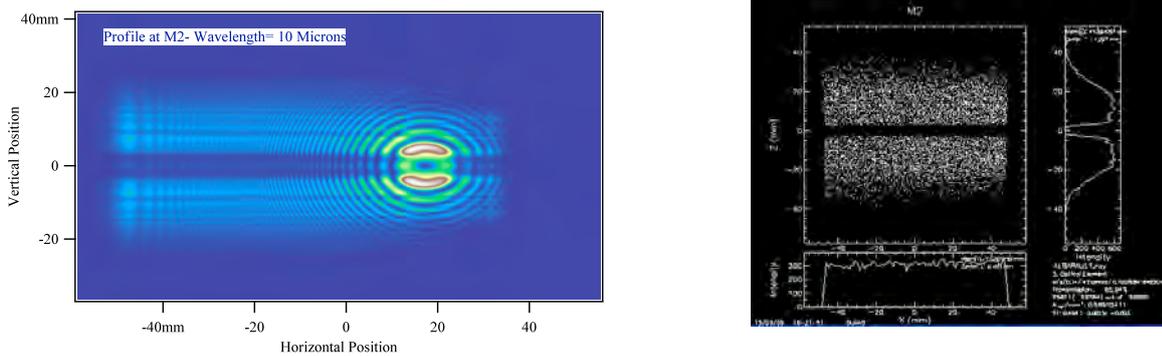


Fig. 4.7b. At the second (flat) mirror M2

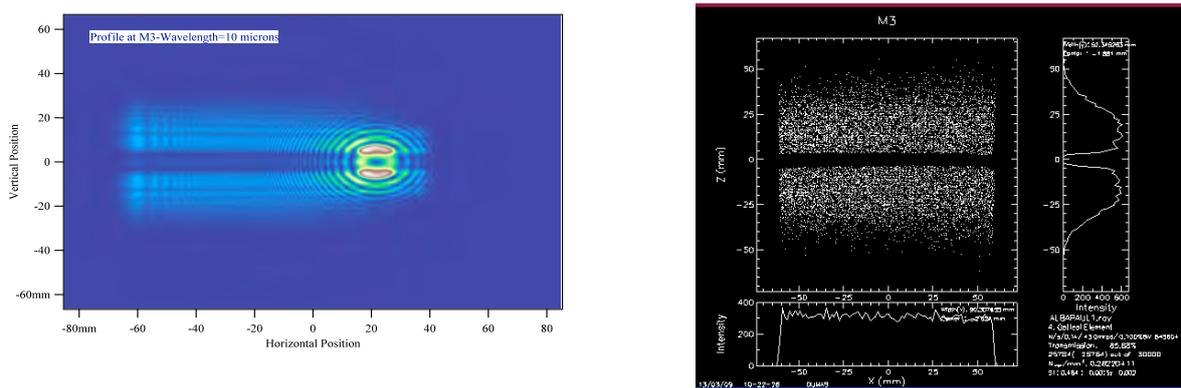


Fig. 4.7c. At the third elliptical mirror M3

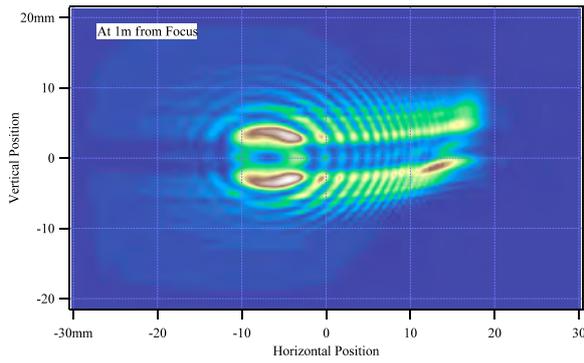


Fig. 4.7g. At 1 meter from the first focus point

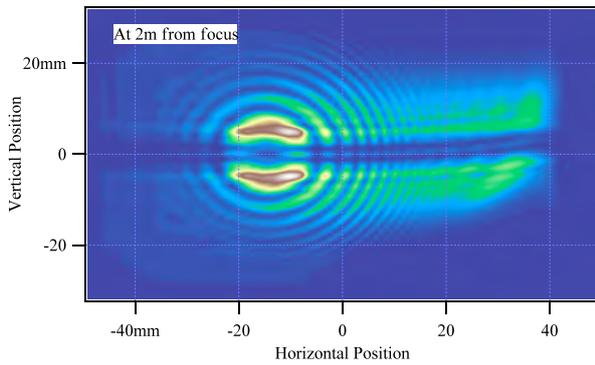
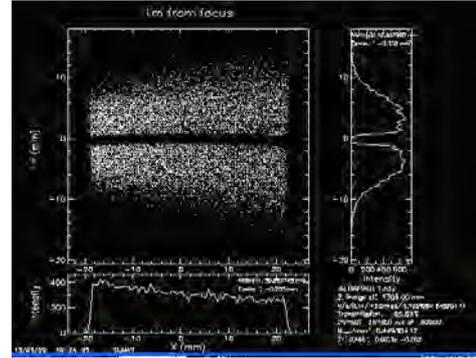
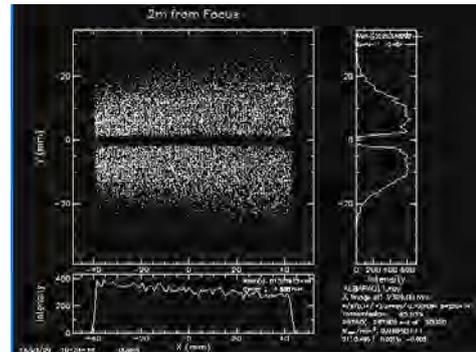


Fig. 4.7h. At 2 meters from the first focus point



The SRW and Rays approaches are very consistent, with SRW providing the most appropriate wavefront simulation as it accounts for both the edge and the continuous field radiation.

We have also simulated with SRW, the initial wavefront propagation of a prototypical far infrared wavelength, 100 μm to demonstrate that the proposed extraction geometry and optical set up is also well suited for the collection and utilization of far-infrared, Figure 4.8. Several scientific cases mentioning the exploitation of the far-IR region can be found in Sections 2.5, 2.6 and 2.7.4.

Wavelength= 100 μm (= 100 cm^{-1})

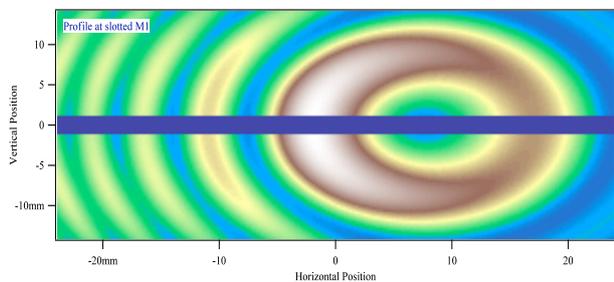


Fig. 4.8a. At the first slotted M1 mirror

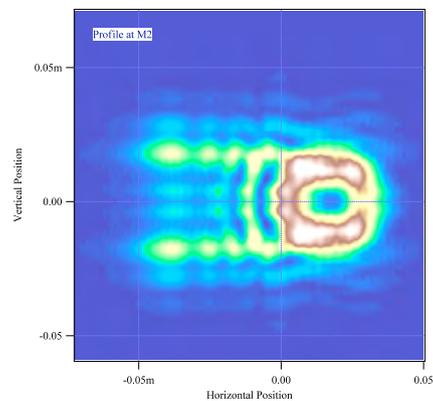


Fig. 4.8b. At the second (flat) mirror M2

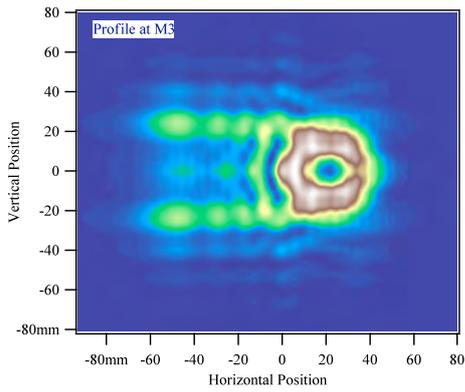


Fig. 4.8c. At the third elliptical mirror M3

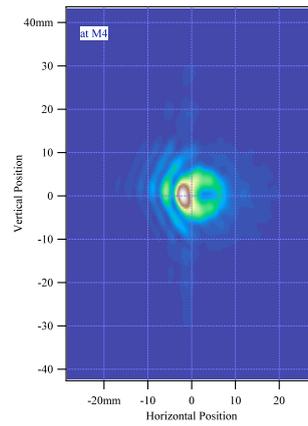


Fig. 4.8d. At the fourth (flat) mirror M4

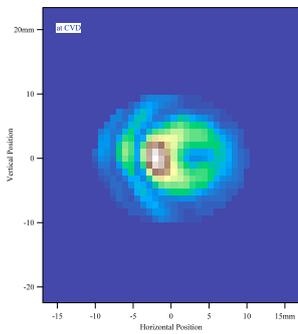


Fig. 4.8e. At the CVD diamond window, located 10 cm upstream of the focus point

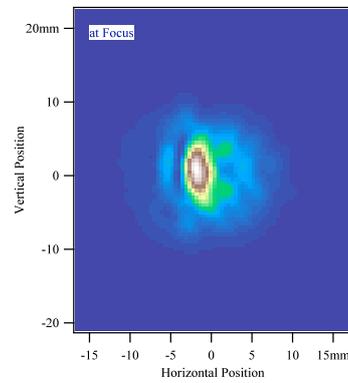


Fig. 4.8f. At the first focusing point, outside the tunnel wall

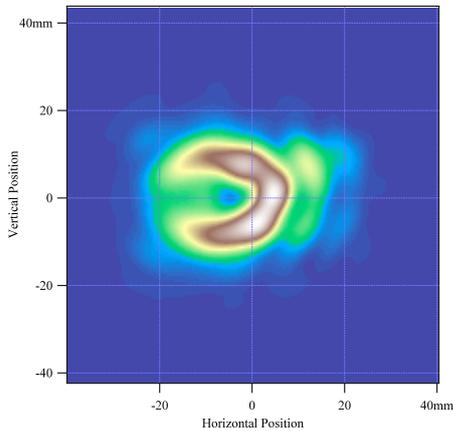


Fig. 4.8g. At 1 meter from the first focus point

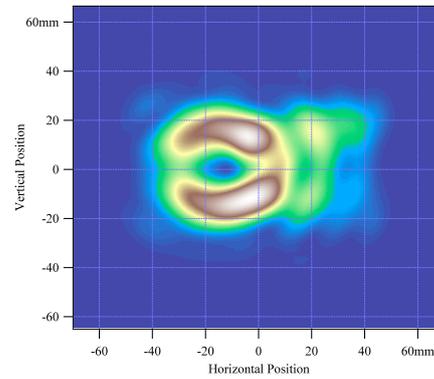


Fig. 4.8h. At 2 meters from the first focus point

In order to obtain a sufficient beam size before splitting, the simulation indicates that it is preferable to separate the beam in two separate branches at a position two meters after the primary focus. This permits a very flexible optical design: after the focus, at one meter away from it, one flat mirror will direct the beam horizontally outside the radioprotection hutch. Therefore, in the restricted access area, two stepper motors will allow an easy alignment of the beam in case of slight misalignment during the various phases of construction and instrument alignments.

The scheme proposed is given in Figure 4.9.

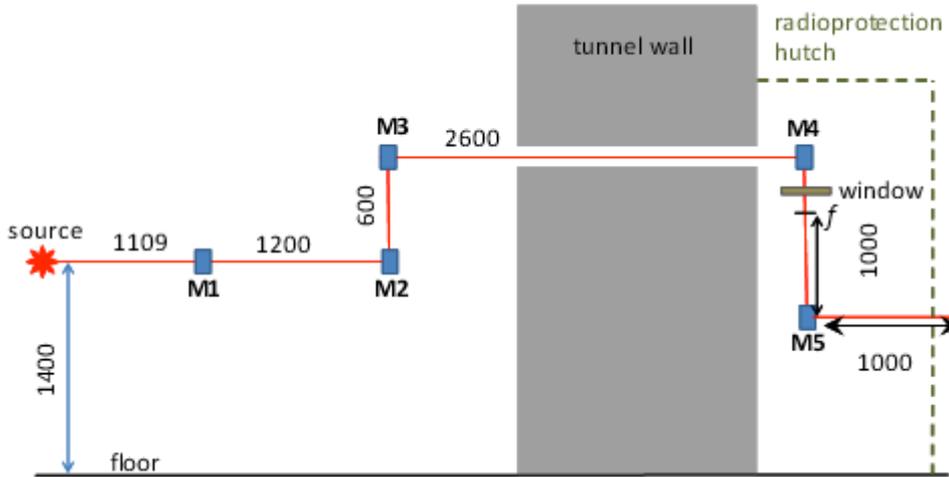


Fig. 4.9. Vertical section of the optical design. The splitting of the beam will occur right outside the tunnel wall

Radioprotection hutch

The radioprotection hutch will be designed to accommodate the mechanics , and supports for M4 mirror, the CVD diamond windows and the M5 mirror. One chicane will be necessary to introduce the compressed air for opening and closing the gate valves, ion pump power supply, gauge readings and cables for step-motor motions of M4 and M5.

One access door will be necessary, but the control of access could be given to the control room, restricting user-access to this area as generally implemented at other beamlines. An example of such a radioprotection hutch at SOLEIL is shown in Figure 4.10.

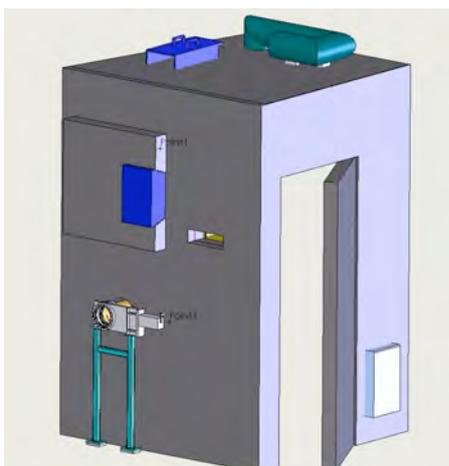


Fig.4.10. Example of a radioprotection hutch (SOLEIL)

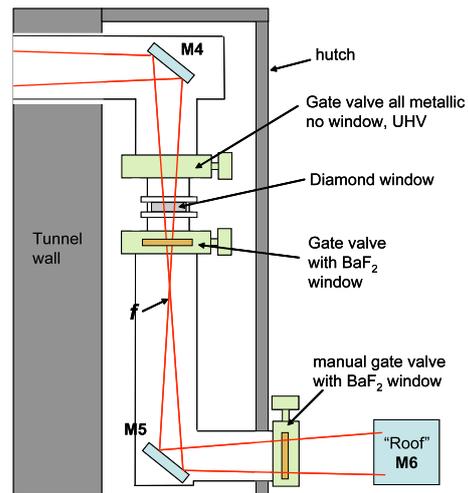


Figure 4.11. Proposed optical design in hutch at ALBA

In Figure 4.11 a proposed optical design inside the radioprotection hutch is shown. It includes two gate valves on either side of the CVD diamond window, and another window valve downstream. In this arrangement we can avoid breaking the diamond window as it will never suffer a different pressure on either side, and a fast gate valve is not required.

4.3 Experimental Area

A possible layout is reported in Figure 4.12 below.

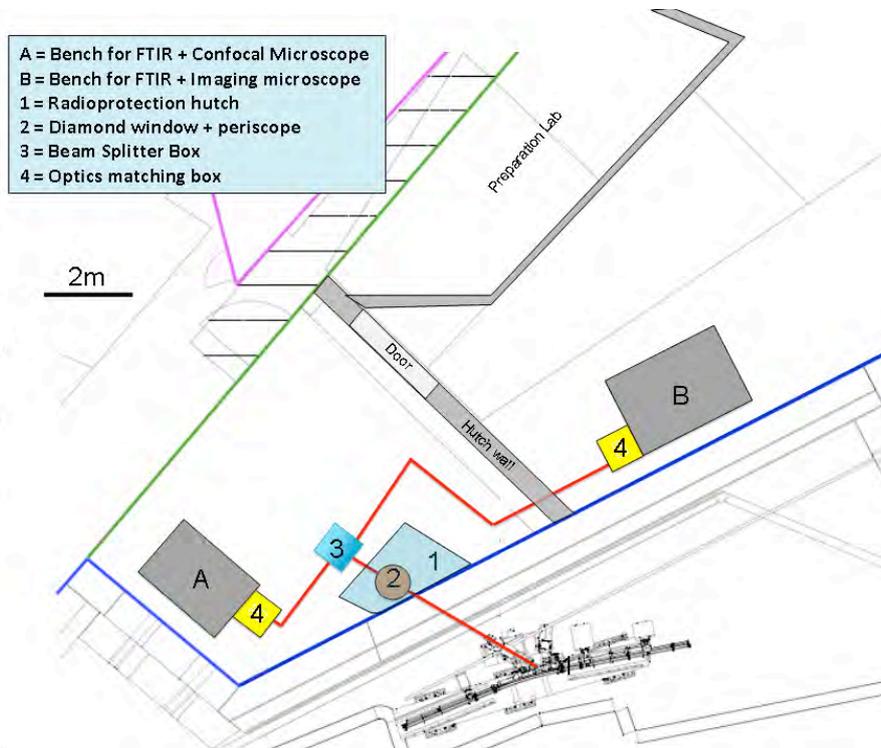


Fig.4.12 Possible beamline and experimental area layout

As suggested above, a “roof” mirror will be placed immediately outside the radioprotection wall. This is designed to split the beam into two separate paths, one propagating the bending magnet emission, and one mainly the edge radiation emission. Both beams will be directed towards two independent spectrometers, Figure 4.13.

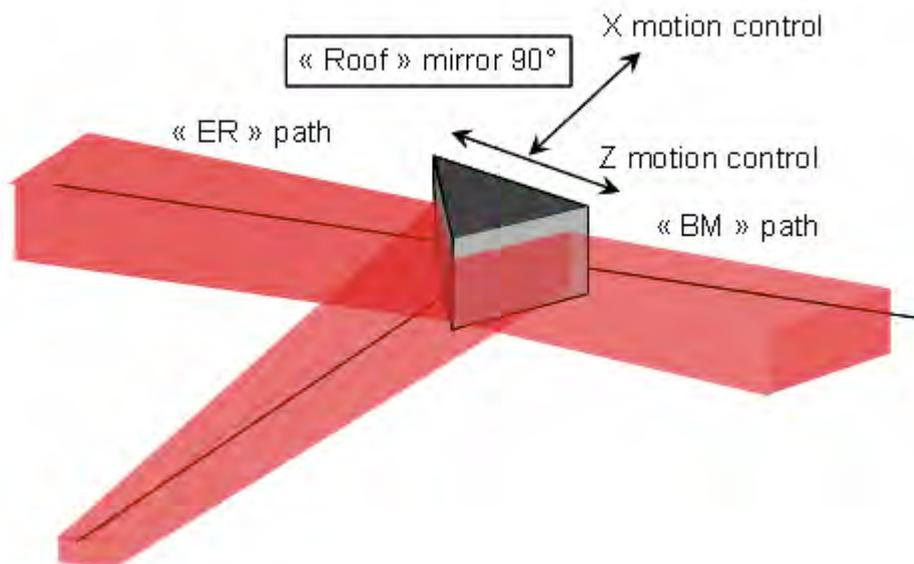


Fig. 4.13. “Roof” mirror , with x and z motions , to split the beam into two opposite direction outside the radioprotection wall

Branch beam propagation

We have simulated both the size and position of the mirror to separate, with almost equal flux, the two branches. The two branches and corresponding mirror sizes appropriate for such a splitting design are shown in Figure 4.14.

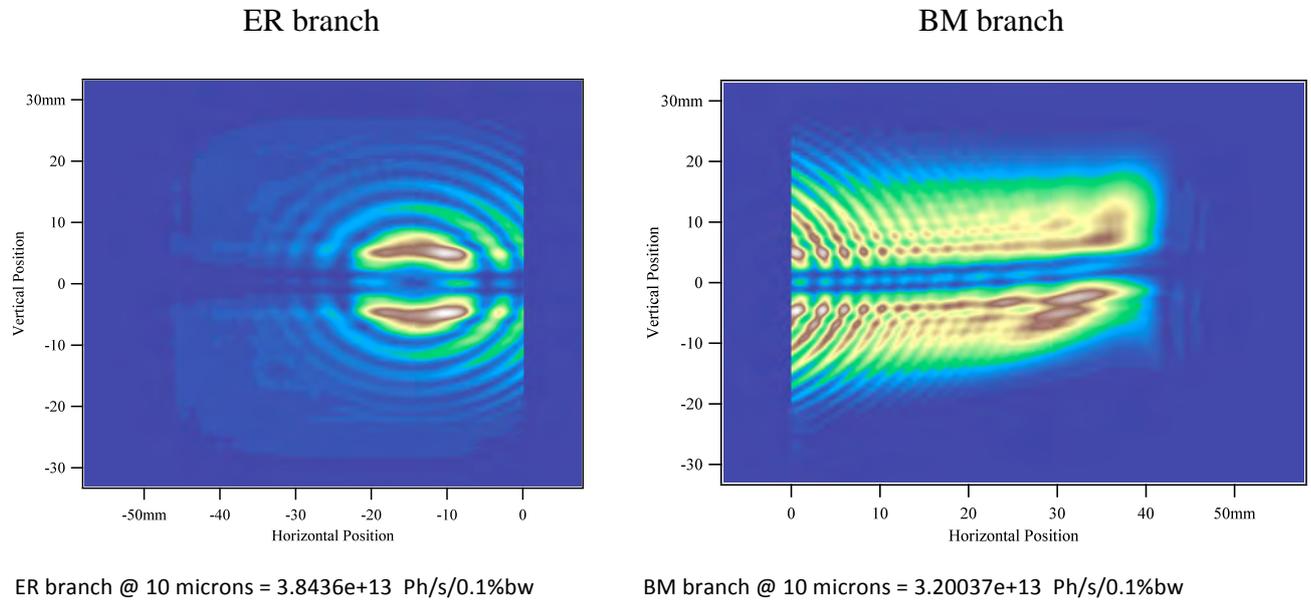


Fig. 4.14a. At the position of the “roof” mirror

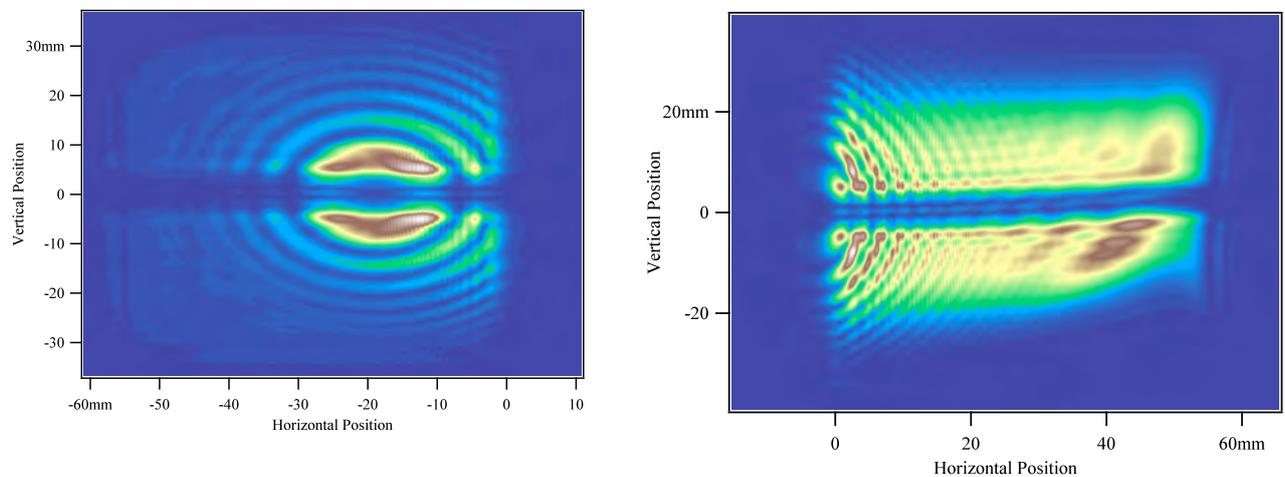


Fig. 4.14b. At a position 60 cm away from the splitting mirror

End-station Optical Coupling

The coupling with the spectrometers depends of several parameters:

- precise location of the spectrometer
- type of interferometer, and microscope

Once these parameters are fixed, the two branches will be collimated and transported to the instruments, accounting for the accurate size of the entrance beam into the instrument, for a full and efficient optical matching with the focusing optics of the microscopes.

Final optical coupling to the spectrometers will be achieved using specially designed mirror boxes, similar to those used at SMIS in SOLEIL, see Figure 4.15. Here a great flexibility can be achieved and the beam-waist of the collimated beam optimised to the Jacquinot-stop aperture using various mirror combinations, depending on the experiment type and spectral range required (microfocus, imaging, high resolution, etc.)

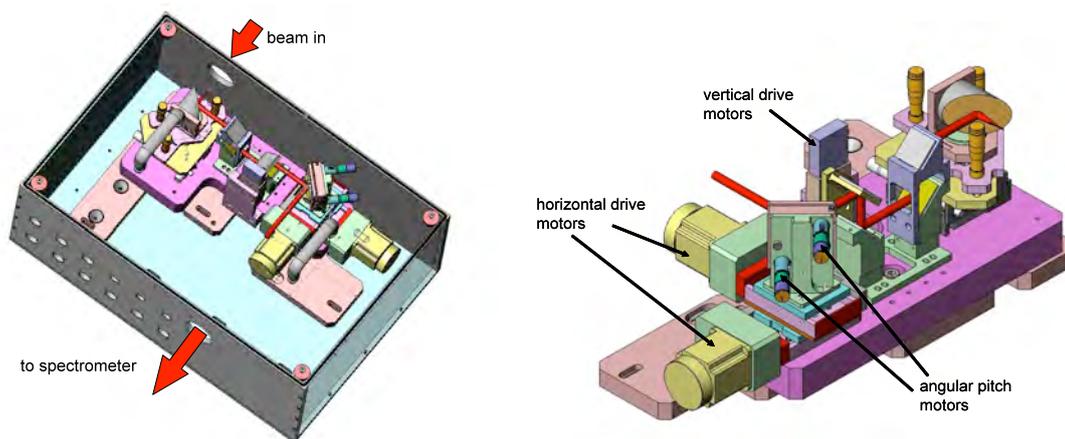


Fig. 4.15 Mirror box design at SMIS beamline, SOLEIL. Courtesy of P. Dumas.

The shape of the ER branch is almost square, and most probably a pair of slightly-off-axis spherical mirrors would be our first choice for aperture matching optimization. For the BM branch, the rectangular shape of the beam will require some correction to match to the almost circular entrance pupil of the spectrometer. Therefore, our first choice would be to use for a pair of cylindrical mirrors to round the beam before entering the spectrometer. Such calculations and optimizations will be easily performed, once the precise occupation of the ground floor space is established.

Microscopes, Accessories and Laboratory Facilities

At the experimental station two commercial FTIR interferometer/microscope set-ups are proposed. The use of off-the-shelf instrumentation for the experimental station is currently the standard option in the construction of synchrotron IR microspectroscopy beamlines. The microscope on branch “A” should be optimised for confocal measurements. The microscope on branch “B” will be available for imaging spectroscopy, and may have slightly lower lateral resolution performance. However, by employing an evacuated FTIR instrument, this will offer broad spectral range microspectroscopy, down to the far-IR.

The accessories and facilities required to suit users needs are detailed below:

- Microscopy accessories
 - Micro-ATR objective. The use of a micro-ATR objective allows to probe the near-surface region of an object

- Grazing incidence angle objective: This objective allows detecting monolayers adsorbed on metallic substrates, within few microns square area. Important applications can be achieved in small metallic surfaces, and electronic components
- Automated switching between broad band detectors in the mid-IR, and thermal detector for infrared studies in the 20-50 microns region (possible in modern IR microscopes)
- Nearby optical microscopy, equipped with a CCD camera, phase contrast capability, is important to locate samples prior to their analysis with the IR microscope.
- Modified sample stage, to add extra motion for fine alignment, especially for reflection experiments on small particles, and polarization studies (rotation of the sample)
- Adaptable sample holders to use with other microscopy techniques, eg X-ray microscopic studies on the same sample
- Special Cells
 - High pressure diamond anvil cell
 - Temperature cell and heating and cooling devices, for in-situ study of time-evolved events
 - Special flow cells for re-circulating liquid media. Microfluidics cells.
- Laboratory facilities
 - Access to a preparation laboratory. Sample preparation is crucial in IR microscopy studies. Users may require access to special equipment such as cryo-microtomes, hot-pressing apparatus, etc. It is important to have an access to such equipment, even if it is shared with other beamlines.
 - A dedicated hood for biology, equipped with one incubator and biological-specific handling tools (micropipettes etc.) is essential nearby.
 - A computer room is highly desirable. Data analysis cannot be made “at home” due to the licensed software associated with all spectrometers. Moreover, data storage is important in infrared, access to large data storage is required.

4.4 Estimated costs

The following table summarises the approximate costing for constructing and equipping a MIRAS beamline at ALBA.

BEAMLINE OPTICS AND RELATED ISSUES	
EXTRACTION MECHANISM	
UHV, mechanics, gate valves, control	~ 200 k€
M1 (including mirror mounting)	~ 10 k€
M2 (including mirror mounting)	~ 2 k€
M3 (including mirror mounting)	~ 6 k€
RADIOPROTECTION HUTCH	
UHV outside tunnel (mechanics, supports, pumps)	~ 30 k€
Hutch	~ 70 k€
CVD window	~ 10 k€
M4 + M5 (including mirror mounting)	~ 4 k€
TRANSFER OPTICS	
1x "roof" mirror	~ 4 k€
Splitter box	~ 5 k€
2x matching mirror box	~ 5 k€
Metalwork & Mirror Mounts	~ 50 k€
Electrical installation, computing, fluids	~ 120 k€
SUBTOTAL	~ 516 k€
EXPERIMENTAL AREA AND FACILITIES	
SPECTROMETERS	
FTIR "A"	~ 60 k€
MICROSCOPE "A"	~ 100 k€
FTIR "B"	~ 80 k€
MICROSCOPE "B"	~ 120 k€
OPTICAL TABLES	~ 20 k€
ACCESSORIES	
Bolometer FarIR	~ 15 k€
Liq. He Cryostat	~ 15 k€
Anvil Pressure Cell	~ 15 k€
Temperature Cell	~ 10 k€
Humidity cell	~ 5 k€
Flow cells (microfluidics)	~ 5 k€
LABORATORY	
Tools	~ 15 k€
Furniture	~ 150 k€
Safety equipment / areas	~ 15 k€
Optical microscopes	~ 10 k€
Air conditioning system	~ 10 k€
Analysis hardware	~ 6 k€
Analysis software (licenses)	~ 10 k€
SUBTOTAL	~ 661 k€
TOTAL ESTIMATED COST	1,177 k€

5. Concluding remarks

The development of an IR microspectroscopy programme at ALBA will be a very important research infrastructure for the Spanish scientific community. It has the particular advantage in that the possible applications for high resolution IR microspectroscopy and imaging span all of the key scientific areas of research currently underway in Spain. This proposal has presented only the tip of the iceberg of the potential users, as many research groups are not yet aware of the possibilities that SIRMS (or MIRAS) can offer them.

We are confident that the conceptual design of the beamline presented here will serve the needs of the scientists reflected in this proposal, and will provide a strong framework to take onboard the research demands of future users, and those of industrial concerns that have already manifested interest in the initiative.

Gary Ellis
Madrid, March 2009

Appendix I. IR beamlines worldwide

Synchrotron facility	IR Beamline	E (Gev)	I (mA)	Magnetic field (T)	Bending radius (m)	Collecting angle H x V (mrad)	(1) BM (2) ER+BM
ALS	1.4.3 5.4	1.5 1.9	400	1.27 5.0	4.9 6.1	40X10	(1)
ANKA	IR1	2.5	300	1.5	5.559	45X15	(2)
Australian	IR	3.0	200	1.3	5	58X17	(2)
BESSYII	IRIS	1.9	100	9.38	4.361	60 X 30	(2)
CLS	mid-IR 01B1-1	2.9	300	1.354	7.14	58X58	(1)
CAMD	IR	1.3- 1.5	300- 150	1.48	2.928	50X50	(1)
Indus-1 Indus-2	IR-Beam	0.45 2.5	100 300	1.5 1.502	1.0 --	50X30	(1)
Diamond	B22	3	(300- 500) mA	1.4	7.151	50X30	(2)
DELTA	BL-2	1.5	120	5	3.35	14X8 mm	(1)
(ELETTRA	BL 9.1	2-2.4	140- 320	1.2-1.45	5.5	70X25	(1)
ESRF	ID21	6.03	200	0.857	23.366	8.5x18	ER
NSLS	U2A	2.800	300	1.36	6.875	45X45	(1)
NSLS	U10B	--	--	--	--	40X40	(1)
NSLS	U12IR	--	--	--	--	90X90	(1)
NSLS	U2B	--	--	--	--	45X45	(1)
NSLS	U4IR	--	--	--	--	90X90	(1)
NSLS	U10A	--	--	--	--	40X40	(1)
SRC		1	190		2.083	60X60	ER
UVSOR	BL6A1	0.75-1	100- 500	1.14	2.2	60X80	(1)
SPring8	BL43IR	8	100	0.679	39.3	36.5X12.5	(1)
NSRRC	BL14A1	1.5	240	-	3.495	70X30	(1)
MAXLAB	73	-	280	1.4675	1.59	60X100	(1)
Daφne	SINBAD	0.51	5.2A	1.2	1.4	50X50	(1)
SLS	X01DC	2.4 2.7	400	1.45 1.57	5.71	61X39	(1)
SSLS	ISMI	0.7	300	4.5	0.519	100X18.8	ER
SRRC	BL14A	1.3- 1.5	240	1.2407	3.495	60X90	(1)
SOLEIL	SMIS	2.75	500	1.71	5.360	78X20	(2)

Appendix II. Statistics from miras.2008

MIRAS 2008 Workshop

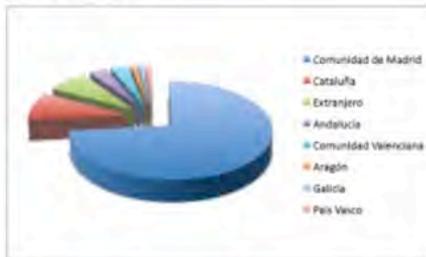
The miras.2008 Workshop was celebrated in Madrid on the 14th - 15th of April 2008, to introduce the technique and its current applications, and demonstrate the future possibilities of an IR beamline in ALBA to diverse groups of the Spanish scientific community from Universities, CSIC (Spanish Scientific Research Council), Institutions and Companies. The workshop presented 8 invited lectures by international experts from the USA, France, Germany, United Kingdom and Spain. As a consequence, various research groups in Spain have already expressed their intention to exploit the technique in their future research. Some statistics from the workshop are presented below.



Profile of the 100 attendees at miras.2008



Laboratory type



Geographical origin

Appendix III

FORMULARIO DE EXPRESIÓN DE INTERÉS*

Datos personales.....

Nombre:

Apellidos:

e-mail:

Grupo / Departamento:

Institución:

Teléfono de contacto:

Datos relacionados con su especialidad e interés en MIRAS.....

Área(s) de especialidad Por favor seleccionar uno o más opciones de de la lista

Alimentos, Agricultura
 Análisis Forense
 Análisis Tecnológico e Industrial
 Arqueología, Arquimetría, Patrimonio Cultural
 Biología, Biomateriales, Biomedicina
 Geología, Geoquímica, Geofísica
 Materiales Cerámicos, Vidrio
 Materiales Poliméricos
 Superficies, Electroquímica, Catálisis
 Otro(s) - por favor especificar a continuación

Indicar de las siguientes opciones todos los tipos de experimento que le puede interesar

<input type="checkbox"/> Mid-IR	<input type="checkbox"/> Far-IR	<input type="checkbox"/> Terahertz
<input type="checkbox"/> Tiempo-real	<input type="checkbox"/> Alta resolución	<input type="checkbox"/> Presión / Temperatura
<input type="checkbox"/> Microscopía	<input type="checkbox"/> Transmisión	<input type="checkbox"/> Reflexión

Appendix IV: Contributors to the Scientific Case

The Scientific Case leaders underlined and persons who presented Expressions of Interest are marked with an asterisk*. It should be noted that some Departments with numerous research groups have presented more than one case. Please note, no specific order has been established for the contributors (except alphabetical order of Research Centres/Departments)

From the CSIC

Institute of Agrochemistry and Food Technology (IATA)

- **Novel Materials and Nanotechnology Lab.**

Dr. Jose Maria Lagarón

Dr. Maria Jose Ocio

Dr. Amparo López-Rubio

Dr. Carla Soler Pro

Institute of Catálisis and Petroleum Chemistry (ICP)

- **Catalytic Spectroscopy Laboratory**

Prof. Miguel A. Bañares

Dr. Vanesa Calvino Casilda

Dr. Anna Elzbieta Lewandowska

Ricardo López Medina

Elizabeth Rojas García

Ewelina Joanna Mikolajska

Manuel García Casado

Institute of Chemical Physics “Rocasolano”

Dr. Marta Castillejo

Institute of Construction Science “Eduardo Torroja” (IETcc)

- **Dept. of Synthesis, Characterization and Recycling of Materials**

Prof. A. Palomo

Dr. Ana Fernández-Jiménez

Dr. Inés García Lodeiro

Dr. Ana Belén Cabrera

Dr. Sagrario Martínez Ramírez

Cristina Ruiz-Santa-Quiteria

M^a José Sanchez Herrero

M^a Cruz Alonso Alonso*

Institute of Industrial Fermentations (IFI)

- **Dept. of Food Characterization. Advanced Analytical and Extraction Techniques group.**

Dr. Elena Ibáñez Ezequiel

Prof. Alejandro Cifuentes Gallego

Dr. Carolina Simó Ruiz

Dr. Virginia García-Cañas

Dr. Miguel Herrero Calleja

Dr. José Bernal del Nozal

Dr. José Antonio Mendiola

Dr. M^a Dolores del Castillo Bilbao

Dr. Javier Moreno Andujar
Dr. Miryam Amigo-Benavent
Dr. Jose Manuel Silván Jimenez

Institute of Polymer Science & Technology (ICTP)

- **Dept. of Biomaterials**

Dr. Alberto Gallardo
Dr. Helmut Reinecke
Dr. Carlos Elvira
Dr. Rodrigo Navarro
Mónica Pérez
Myriam Gómez
Diego Velasco

- **Dept. of Chemistry and Properties of Polymeric Materials**

Dr. Jose Manuel Gómez-Elvira

- **Dept. of Elastomer Science & Technology**

Dr. Miguel Angel Lopez-Manchado
Dr. Miguel Arroyo Ramos
Dr. Raquel Verdejo
Javier Carretero-González
Marianella Hernández Santana

- **Dept. of Macromolecular Chemistry. Polycondensation and Polymeric Membranes group**

Prof. Javier de Abajo González
Prof. José G. de la Campa
Dr. Ángel E. Lozano
Dr. Eva Maya
Dr. Dulce Muñoz
Dr. Mariola Calle

- **Dept. of Physical Chemistry**

Prof. Julio Guzmán
Dr. Pilar Tiemblo
Dr. Nuria García
Dr. Mario Hoyos
Dr. Leoncio Garrido
Prof. Rosario Benavente*
Dr. M^a Luisa Cerrada*

- **Dept. of Polymer Physics & Engineering**

Prof. Carlos Marco Rocha
Prof. Marian Gómez Rodríguez
Dr. Gary Ellis
Dr. Zulima Martín
Gonzalo Santoro Domingo
Dr. Mohammed Naffakh
Dr. Horacio Salvagione
Dr. Ana Diez Pascual
Dr. Mercedes Pérez Méndez
Javier Sanguino Otero

Institute of Structure of Matter (IEM)

- **Dept. of Macromolecular Physics (4 groups)**

Prof. Tiberio Ezquerro Sanz
Dr. Daniel Rueda Bravo
Dr. Esperanza Cagiao Escotado
Dr. Mari Cruz García Gutiérrez
Dr. Amelia Linares Do Santos
Dr. Aurora Nogales Ruiz
Dr. Alejandro Sanz Parras
Jaime Javier Hernández Rueda
José Carlos Canalda
Dr. Araceli Flores
Dr. Fernando Ania García
Prof. Concepción Domingo
Dr. Santiago Sánchez-Cortés
Dr. José Antonio Sánchez-Gil
Prof. José Vicente García Ramos
Dr. Sagrario Martínez-Ramírez
Dr. Marta Castillejo
Dr. José Luis Domenech

Materials Science Institute of Madrid (ICMM)

- **Dept. of Ferroelectric Materials**
Dr. Paloma Tejedor
- **Dept. of Porous Materials & Intercalation Compounds**
Prof. Eduardo Ruiz-Hitzky
Dr. Pilar Aranda
Dr. Margarita Darder
Francisco Fernández
Bernd Wicklein
- **Dept. of Surface Physics & Engineering**
Dr. Ignacio Jiménez Guerrero

National Centre for Metallurgy Research (CENIM)

- **Dept. of Materials Engineering**
Dr. Belén Chico González*
- **Dept. of Primary Metallurgy and Recycling**
Dr. Félix A. López Gómez
Prof. Dr. Francisco José Alguacil
Dr. Aurora López Delgado
Dr. Manuel Alonso Gámez
Dr. Isabel Padilla
Dr. Hanan Tayibi

National Institute of Aerospace Technology (INTA)

- **Astrobiology Centre**
Dr. Eva Mateo-Martí*

Spanish National Museum of Natural Sciences (MNCN)

Prof. Javier García Guinea
Dr. Elena Crespo Feo

Universities

Autonomous University of Barcelona (UAB)

- **Centre for Biophysics Studies**
Dr. Esteve Padros*
Dr. Josep Cladera*
- **Dept. of Animal & Plant Biology and Ecology**
Dr. Josep Girbal Lladó
- **Dept. of Applied Research in Historical Culture Group (GRAPAC)**
Dr. M. Eulàlia Subirà de Galdàcano*
- **Institute of Biotechnology and Biomedicine**
Dr. Salvador Ventura Zamora*

Autonomous University of Madrid (UAM)

- **Dept. of Biology. Plant Physiology Laboratory**
Dr. Luis Eduardo Hernández Rodríguez*
- **Dept. of Biology of Reproduction**
Dr. Jaime Gosálvez Berenguer*
- **Dept. of Food Science**
Dr. F. Javier Señoráns
Dr. Guillermo Reglero
Dr. Diana Martín
Dr. Carlos Torres
Dr. Tiziana Fornari
Dr. Susana Santoyo
Dr. Laura Jaime
Dr. Luis Vázquez
Dr. Pilar Luna
Dr. Mónica Rodríguez
- **Dept. of Materials Physics**
Antonio Benayas Hernández*

Carlos III University of Madrid (UC3M)

- **Dept. of Physics**
Dr. Inmaculada Colera Garzón*
Dr. Begoña Savioni Cardiel*
- **Dept. of Science and Technology of Materials & Chemical Engineering**
Dr. J. González-Benito
Dr. Dania Olmos
Dr. Gustavo González-Gaitano
Dr. Pedro Remiro

Keele University, UK

- **Institute for Science and Technology in Medicine**
Dr. Josep Sulé-Suso
Dr. Y. Yang

J.K. Pijanka

National University of Distance Education (UNED)

- **Dept. of Science and Physical Chemistry Techniques**
Dr. Antonio Hernanz
Dr. Jose M. Gavira-Vallejo
Dr. Santiago Martín Fernández
- **Department of Analytical Science**
Dr. Egor Gavrilenko
- **Department of Mathematical Physics and Fluids**
Dr. Santiago Martín Fernández

Ramon Llull University

- **Institute of Chemistry Sarriá (IQS) – Materials Engineering Group**
Prof. Salvador Borrós
Dr. Nuria Agullo
Dr. Carles Colominas
Dr. Albert Balfagón
Eng. José Luis Yagüe

Technical University of Catalonia

- **Dept. of Construction Materials (ETSECCPB)**
Dr. Lucía Fernández Carrasco
- **Dept. of Chemical Engineering (EPSEVG)**
Dr. Nativitat Salvadó
Dr. Salvador Butí
- **Dept. of Physics & Nuclear Engineering (ESAB)**
Dr. Trinitat Pradell

Technical University of Madrid

- **Dept. of Industrial Chemistry and Environmental Engineering**
Dr. Joaquín Martínez Urreaga*

Universtiy of Alicante

- **Electrocatalysis and Polymer Electrochemistry Group**
Dr. Emilia Morrallón
Dr. Diego Cazorla-Amorós
Dr. Dolores Lozano-Castelló
Dr. Francisco Montilla

Universtiy of Barcelona

- **Dept. of Physical Chemisrty**
Dr. Felipe Caballero-Briones
Dr. Fausto Sanz
- **Scientific Technical Services**
Dr. Nuria Ferrer

Universtiy of Castilla-La Mancha

- **Department of History**
Dr. Juan F. Ruiz-López

University Complutense of Madrid

- **Dept. of Materials Physics**
Dr. Oscar Rodríguez de la Fuente*

University of Jaen

- **Dept. of Physical and Analytical Chemistry**
Dr. María José Ayora Cañada*
Dr. Ana Domínguez Vidal*

Universtiy of Riems (France)

- **Dept. of Pharmacy**
Dr. Ganesh D. Sockalingum

Universtiy of Valencia

- **Materials Science Institute (2 groups)**
Prof. Alfredo Segura García del Río
Dr. Chantal Ferrer Roca
Dr. Domingo Martínez García
Dr. Juan Fco. Sanchez Royo
Dr. Julio Pellicer Porres
Dr. Daniel Errandonea
Raúl Lacomba Perales
Javier Ruiz Fuertes
Dr. Sonia Murcia Mascaros*
Dr. Clodoald Roldán García*

Mixed Centres CSIC-University & Others

Biophysics Unit (UBF-CSIC) – University of the Basque Country (UPV-EHU)

Dr. José Luís Rodríguez Arrondo*

Institute of Chemical Technology (ITP-CSIC) – Technical University of Valencia (UPV)

Dr. Pablo Botella Asunción
Dr. Patricia Concepción Heydon
Dr. J. M. López Nieto
Dr. A Corma

Institute of Economic Geology (IGE-CSIC) – University Complutense of Madrid (UCM)

- **Petrology Applied to the Conservation of Heritage Group**
Dr. Mónica Álvarez de Buergo
Dr. Rafael Fort González
Dr. Paula López-Arce
Dr. M^ª José Varas
Carmen Vázquez-Calvo

Materials Science Institute of Madrid (ICMM-CSIC) – Technical University of Valencia (UPV)

- **Dept. of Optic, Magnetic and Transport Properties**
Dr. Roberto Fellenosa Esteve*

National Energy, Environmental and Technological Research Centre (CEEMAT), Madrid

Dr. Catalina Gascó
Dr. Nuria Navarro

Technical Centre for Conservation of Heritage (CETEC-Patrimoni)

Dr. José Luis Prada
Montserrat Pugés
Rosa M^a Rocabayera
Manel Iglesias

Appendix V: Institutes and Research Centres in the area of Food and Agricultural Science

CSIC

- CENTRO DE CIENCIAS MEDIOAMBIENTALES (CCMA) - www.ccma.csic.es
- CENTRO DE EDAFOLOGÍA Y BIOLOGÍA APLICADA DEL SEGURA (CEBAS) - www.cebas.csic.es
- ESTACIÓN EXPERIMENTAL AULA DEI (EAD) - www.eead.csic.es
- ESTACIÓN EXPERIMENTAL DEL ZAIDÍN (EEZ) - www.eez.csic.es
- ESTACIÓN EXPERIMENTAL LA MAYORA (EELM) - www.eelm.csic.es
- INSTITUTO DE AGRICULTURA SOSTENIBLE (IAS) - www.ias.csic.es
- INSTITUTO DE AGROBIOTECNOLOGÍA (IDAB) - www.agrobiotecnologia.es
- INSTITUTO DE AGROQUÍMICA Y TECNOLOGÍA DE ALIMENTOS (IATA) - www.iata.csic.es
- INSTITUTO DE CIENCIA Y TECNOLOGÍA DE ALIMENTOS Y NUTRICIÓN (ICTAN)
- INSTITUTO DE CIENCIAS AGRARIAS (ICA) - www.ccma.csic.es
- INSTITUTO DE CIENCIAS DE LA VID Y EL VINO (ICVV) - www.icvv.es
- INSTITUTO DE FERMENTACIONES INDUSTRIALES (IFI) - www.ifi.csic.es
- INSTITUTO DE GANADERÍA DE MONTAÑA (IGM) - www.eae.csic.es
- INSTITUTO DE INVESTIGACIONES AGROBIOLÓGICAS DE GALICIA (IIAG) - www.iiag.csic.es
- INSTITUTO DE INVESTIGACIÓN EN CIENCIAS DE ALIMENTACIÓN (CIAL)
- INSTITUTO DE INVESTIGACIONES MARINAS (IIM) - www.iim.csic.es
- INSTITUTO DE LA GRASA (IG) - www.ig.csic.es
- INSTITUTO DE PRODUCTOS LÁCTEOS DE ASTURIAS (IPLA) - www.ipla.csic.es
- INSTITUTO DE PRODUCTOS NATURALES Y AGROBIOLOGÍA (IPNA) - www.ipna.csic.es
- INSTITUTO DE RECURSOS NATURALES Y AGROBIOLOGÍA DE SALAMANCA (IRNASA) - www.irnasa.csic.es
- INSTITUTO DE RECURSOS NATURALES Y AGROBIOLOGÍA SEVILLA (IRNAS) - www.irnase.csic.es
- INSTITUTO DEL FRÍO (IF) - www.if.csic.es
- MISIÓN BIOLÓGICA DE GALICIA (MBG) - www.mbg.csic.es

ASSOCIATED UNITS IN THE CSIC

- ESTACIÓN FITOPATOLÓGICA DE AREEIRO - www.efa-dip.org
- GRUPO DE ANÁLISIS Y CARACT. DE ALIMENTOS GRASOS
- GRUPO DE CEREALES DE ALTO VALOR AÑADIDO - CAVA
- GRUPO DE CIENCIA Y TEC. DE ALIMENTOS
- GRUPO DE CONSERVACIÓN Y SEGURIDAD DE ALIMENTOS
- GRUPO DE EDAFOLOGÍA Y ORDENACIÓN DEL TERRITORIO
- GRUPO DE ENTOMOLOGÍA APLICADA
- GRUPO DE GENÉTICA DE VIRUS DE PLANTAS
- GRUPO DE GESTIÓN SOSTENIBLE DE RECURSOS SUELO AGUA
- GRUPO DE HORTICULTURA SOSTENIBLE EN ZONAS ÁRIDAS
- GRUPO DE INTERACCIÓN PLANTA-MICROORGANISMO
- GRUPO DE INVESTIGACIÓN EN MICROBIOLOGÍA
- GRUPO DE MICROBIOLOGÍA Y PATOLOGÍA VEGETAL
- GRUPO DE NUEVOS PROC. EN TECNOL. DE ALIMENTOS
- GRUPO DE NUTRICIÓN Y SALUD GASTROINTESTINAL
- GRUPO DE QUÍMICA DEL ESTADO SÓLIDO
- GRUPO DE SISTEMÁTICA MOLECULAR
- GRUPO DE SOSTENIB. DE CULTIVOS GENÉTICAMENTE MODIFICADOS
- GRUPO INTERREL. INSECTO PATÓGENO-PLANTA Y AG.BIOCONTROL
- GRUPO S. INTEGR. PRODUC. AGRÍCOLA EXT.EN ZONAS MEDITERRANEAS
- GRUPO SEÑALIZACIÓN MOLEC. Y SIST. ANTIOXIDANTES EN PLANTAS
- LABORATORIO DE ENTOMOLOGÍA

- INSTO. DE INGENIERÍA DE ALIMENTOS PARA EL DESARROLLO (IAD)
- SECCIÓN DE BIOLOGÍA VEGETAL
- UNIDAD DE SUELOS Y RIEGOS

SOME UNIVERSITY DEPARTMENTS / GROUPS

- DPTO. QUÍMICA AGRÍCOLA, FACULTAD DE CIENCIAS – UNIVERSIDAD AUTONOMA DE MADRID (UAM) - www.uam.es/departamentos/ciencias/qagri
- DPTO. DE PRODUCCIÓN VEGETAL Y TECNOLOGÍA AGRARIA – UNIVERSIDAD DE CASTILLA LA MANCHA (UCLM) - www.uclm.es/dep/pvyta
- DPTO. PRODUCCIÓN AGRARIA – UNIVERSIDAD PÚBLICA DE NAVARRA (UNAVARRA) – <http://cms.unavarra.es/pagr>
- DPTO. INGENIERÍA Y CIENCIAS AGRARIAS – UNIVERSIDAD DE LEÓN (UNILEON) - www.unileon.es/index.php?nodoID=579

APPENDIX VI: Letters of Support

9th March 2009

TO WHOM IT MAY CONCERN

Dear Sir / Madam,

MIRAS

This letter is to express our interest and support for the **miras²** initiative to construct an Infrared Microspectroscopy beamline at the new Spanish Synchrotron ALBA in Cerdanyola del Vallès.

The access to such a versatile and powerful technique in Spain will be beneficial to both academic and industrial researchers alike, and will be particularly interesting for the study of advanced composite materials.

Yours sincerely,



Angeles Sánchez-Blázquez
Composite Technology Spain
Materials and Processes
Airbus España

Burgos, a 13 de Marzo de 2009

D. Francisco Javier Martínez Moral, Director de Investigación de la Empresa Grupo Antolin Ingeniería S.A., (perteneciente a GRUPO ANTOLIN), conoce la propuesta del ICTP (CSIC) de Madrid para la construcción de una línea de microespectroscopía IR con radiación sincrotrón en el nuevo sincrotrón ALBA de Barcelona.

D. Francisco Javier Martínez Moral, en nombre del GRUPO ANTOLIN manifiesta que la construcción de una herramienta tan versátil será algo muy positivo para la investigación española en muchos campos, entre los que se encuentran los materiales poliméricos o cerámicos con nanopartículas como carga, para conseguir nanocompuestos con nuevas funcionalidades, campos en los que Grupo Antolin está trabajando.

Por tanto considera que se trata de una propuesta del mayor interés

Y para que conste a los efectos oportunos, envía este escrito.

Firmado,



GRUPO ANTOLIN
INGENIERÍA S.A.
C/El Estrecho, s/n. 09001 BURGOS
TEL: 945 24 10 00 - ESPAÑA

Francisco Javier Martínez Moral
Director de Investigación
Grupo Antolin Ingeniería S.A.

Dr. Gary Ellis
Dpto. Física e Ingeniería
Instituto de Ciencia y Tecnología de Polímeros
CSIC, C/ Juan de la Cierva 3
28006 MADRID

TO WHOM IT MAY CONCERN

CIDAUT (Research and Development Center in Transport & Energy) is a R+D+I Foundation with thirteen industrial partners. The principal objective of CIDAUT is to nurture the competitiveness and the industrial development of companies in the automotive sector, enabling them to develop new products and processes. The Foundation promotes scientific investigation, technological development and innovation applicable to industry in general and to the transport and energy sectors in particular.

The development of advanced technologies for characterization is fundamental for applied materials research. In this respect, the access to powerful techniques associated with the use of synchrotron radiation can contribute significantly to the advancement of scientific knowledge in this area.

The development of a synchrotron infrared microspectroscopy (SIRMS) beamline at the Spanish Synchrotron ALBA, as outlined in the **miras²** initiative, will be an important advance providing a powerful and versatile characterization tool for groups in Spain with research interests related to the transport and energy sectors, and indeed to other diverse areas of materials, chemical and physical sciences.

Thus, on behalf of CIDAUT I wish to express my support for the **miras²** proposal.

Yours sincerely

Fundación
cidaut
Investigación y Desarrollo en Transporte y Energía
Juan Carlos Merino
Manager



Dow Chemical Ibérica, S.L
Apartado. 196
43080 Tarragona
España
Tel: +34 977 55 94 06
Fax: +34 977 55 94 05

TO WHOM IT MAY CONCERN

The Dow Chemical Company as a global manufacturing leader for polyethylene and material science innovations strongly supports the development of new materials as one of the main pillars of product competitiveness. Our R&D Departments have collaborated for several years with Universities and the Centro Superior de Investigaciones Científicas (CSIC) in the study of fundamental aspects of polymer science. In this respect, the availability of powerful characterization tools has proven essential in many projects.

In relation with the previous, I have been made aware through Doctor Gary Ellis of the Instituto de Ciencias y Tecnología de Polímeros, of the objectives and plans of work of their **miras²** proposal, which is centered on building a Synchrotron Infrared Microspectroscopy (SIRMS) beamline at the ALBA Synchrotron facility, near Barcelona.

I would like to express my support to this project since I consider SIRMS to be a very powerful technique to resolve fundamental and applied aspects in polymeric materials science, an area where Dow Chemical is particularly interested on.

Felip Vidiella
R&D Director
Europe, Middle East & Africa Plastics TS&D
The Dow Chemical Company

Tarragona, March, 10th 2009



10th March 2009

TO WHOM IT MAY CONCERN

Dear Sir / Madam,

This letter is to express our support for the **MIRAS²** proposal which will be presented to the SAC in March 2009.

For many years Repsol maintains a close interaction with academic research groups both in Universities and the C.S.I.C. through Research Projects and Contracts, for the study of fundamental aspects of chemical sciences in the development of a diverse range of materials. We are aware that the access to advanced characterization techniques is a key issue and, in this respect, the **MIRAS²** proposal for the development of a beamline dedicated to Infrared Microspectroscopy at the ALBA Synchrotron in Barcelona is of great interest.

The availability of an IR Microspectroscopy beamline will undoubtedly be valuable for academic and industrial research programmes in Spain.

Yours sincerely,

A handwritten signature in black ink, appearing to read "Begoña Peña", enclosed within a large, loopy, hand-drawn oval.

PhD. Begoña Peña Garcia
Technology Portfolio Manager
Repsol S.A.

Instituto de Ciencia y Tecnología de Polímeros
Juan de la Cierva,3
28006 Madrid
España

Attn. Dr. Gary Ellis

March 12th, 2009

TO WHOM IT MAY CONCERN

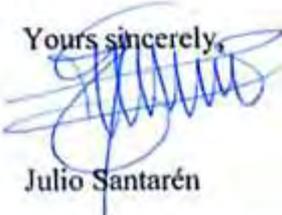
Dear Sir / Madam,

Our Company, TOLSA Group, has extracted clay minerals and researched, developed and manufactured products for domestic and industrial consumption for more than half a century. TOLSA is the world leader in the production of sepiolite, and has over 50 different applications in many industrial sectors, and through continuous development offers innovative solutions to customer needs. In this respect, the research work at TOLSA is developed together with other research groups from the world's most prestigious universities and research centres.

We have been made aware of the proposal for the development of a synchrotron infrared microspectroscopy (SIRMS) laboratory at the new Spanish Synchrotron facility, ALBA. This powerful technique is already making an important impact in many areas of research such as minerals, geology, environmental science and polymer science, all of which are important in our industrial field.

Thus we wish to express our interest in, and support for, the success of the MIRAS project, as it will provide an important characterization technique to research groups from diverse areas in Spain.

Yours sincerely,

A handwritten signature in blue ink, appearing to read 'Julio Santarén', is written over a blue circular stamp.

Julio Santarén

Group Process Development
& Applied Research Manager



**G E P****GRUPO ESPECIALIZADO DE POLIMEROS
RSQ, RSF** Juan de la Cierva .- 3.- 28002 Madrid

TO WHOM IT MAY CONCERN

Dear Sir / Madam,

As President of the Specialized Group of Polymers (GEP) of the Spanish Royal Society of Chemistry and the Spanish Royal Society of Physics, I am writing to express the support of the GEP to the creation of a beamline in the Spanish Synchrotron ALBA in Barcelona.

This beamline should be dedicated to a Synchrotron Infrared Microspectroscopy, SIRMS (or "MIRAS" in Spanish) facility which will provide an important and powerful technique for the characterization of a wide range of materials related to the polymeric area. Vibrational microspectroscopy, both IR and Raman, has been for many years fundamental in the characterization of polymeric materials, and the access to high spatial resolution at a synchrotron will certainly be very useful and necessary for the scientific activities carried out by many of the research groups in the Spanish Polymer Group.

If you require any complementary information regarding this letter of support, please do not hesitate to contact me at the e-mail: perena@ictp.csic.es

Yours sincerely,



José M. Perena

Research Professor of the CSIC

President of the Spanish Polymer Group

www.gpolimeros.org



COMITÉ DE ESPECTROSCOPIA
Sociedad Española de Óptica
Serrano, 121. 28006-Madrid

TO WHOM IT MAY CONCERNS

Infrared (IR) spectroscopy is one of the most employed characterisation techniques due to its versatility, and its combination with microscopy employing a synchrotron as the source of IR radiation, provides an extremely powerful tool with wide application possibilities. In recent years, growth of the Synchrotron Infrared Microspectroscopy (SIRMS or, in Spanish, MIRAS) technique has been spectacular precisely due to its great success in diverse fields, ranging many areas of interest.

A proposal for a new *beamline* for Phase II of ALBA (an ultimate generation synchrotron source, in Cerdanyola del Vallès, near Barcelona) is being prepared in the Institute of Polymer Science and Technology, under the coordination of **Dr. Gary Ellis** of the Department of Polymer Physics & Engineering for SIRMS measurements. This proposal has obtained a large support by means of almost 60 expressions of interest from groups working in different knowledge areas (Polymer Materials, Archeology and Cultural Heritage, Biology, Medicine, Surface Science, Catalysis, Electrochemistry, Ceramic Materials, etc.).

As the President of the Spanish Committee of Spectroscopy of the Spanish Optics Society I give my strongest support to this proposal and wish a great success in the opening of this new beamline devoted to MIRAS.

Dr. Santiago Sánchez Cortés
President of the Spanish Committee of Spectroscopy



MINISTERIO
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CONSEJO SUPERIOR
DE INVESTIGACIONES
CIENTÍFICAS

INSTITUTO DE RECURSOS
NATURALES Y
AGROBIOLOGIA DE
SEVILLA

12th March, 2009

TO WHOM IT MAY CONCERN

The CSIC Thematic Network of Cultural Heritage (RTPHC) is a reference organization for the diagnosis and studies on the conservation of Spanish Cultural Heritage, with activities which are grouped in five areas: Archeology and Architectural Heritage, Biology, Chemistry and Materials Science, Geology and Physics. At present the network consists of over 30 research groups from different CSIC Institutes.

Many of the research topics rely on sophisticated characterization techniques in order to obtain fundamental information on the objects and materials under study, and in recent years the advancements in accelerator-based techniques have provided important and breakthrough information in the area of cultural heritage.

In particular, synchrotron infrared microspectroscopy (SIRMS) has become an essential tool, and I wish to support the **MIRAS** proposal for the development of a beamline dedicated to this technique in the ALBA Spanish Synchrotron, near Barcelona, as it is of great interest to several Spanish groups already involved in its exploitation.

Yours sincerely

Prof. Cesáreo Sáiz Jiménez
Coordinator RTPHC
www.rtphc.csic.es

CORREO ELECTRÓNICO:

saiz@irnase.csic.es

AVDA. REINA MERCEDES,10
41012 SEVILLA
TELÉFONO: 95 4624711
FAX: 95 4624002



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CONSEJO SUPERIOR
DE INVESTIGACIONES
CIENTÍFICAS

INSTITUTO DE CIENCIA Y
TECNOLOGÍA DE POLÍMEROS



March 11th 2009

TO WHOM IT MAY CONCERN

As Director of the Institute of Polymer Science and Technology (ICTP) of the Spanish Scientific Research Council Agency (CSIC), I would like to express the support of the Institute to establish a beamline dedicated to Infrared Microspectroscopy at the new Spanish Synchrotron ALBA in Cerdanyola del Vallès, near Barcelona, which is due to be inaugurated this year.

The **miras²** proposal for building a synchrotron infrared microspectroscopy (MIRAS) facility in Spain is of significant interest to the materials science community in general, and particularly for polymeric materials research, as will extend the potential of the already important characterization techniques based on vibrational microspectroscopy to the polymer community. We consider that access to MIRAS will be very useful for the scientific activities carried out in our Institute, and is eagerly awaited by members who are already exploiting its advantages for their research.

If you require any complimentary information, please do not hesitate to contact me at the address indicated below.

Yours sincerely


Paula Bosch
Director ICTP *



C/ Juan de la Cierva, 3
28006 Madrid ESPAÑA
Telf. 91 562 29 00
Fax: 91 564 48 53