APS
SYNCHROTRON INFRARED SPECTROSCOPY AT SOLEIL

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Outline

I-INTRODUCTION

I-1: Forewords:

Infrared spectroscopy covers a tremendous number of studies including for instance the characterisation of chemical content of material, the optical studies of solids or the pure vibrational and rotational molecular spectroscopy.

Fourier Transform Infrared spectroscopy (FTIR) is an easy-to-use and non destructive method which belongs to the main analytical techniques in chemistry, physics and biology. Although, the commercial IR spectrometers are equipped with conventional thermal (globar) sources providing power comparable to the IR radiation emitted from a synchrotron, the synchrotron IR light because of its brightness (100-1000 times greater)[1] has allowed important breakthroughs in two area : extension to the lowest energy range (Far infrared) and study of extremely small samples. Nowadays, extraction of infrared radiation is part of almost all developing programs in existing or planned facilities (see annex 1)

Despite the fact that the first observation of the emission of an infrared radiation from a storage ring has been made early [2], spectroscopic applications were made possible only in 1985 in gas phase, followed, five years later by the design of a far-IR beamline dedicated to surface studies at the NSLS[3]. The original emphasis was made in the so called far – infrared region (between 20 and 1000 microns). Nowadays, the far infrared region (and more recently the millimeter region) motivates several original fundamental spectroscopic studies.

Soon after (1993) it was realized that infrared microscopy would also benefit a lot from the high brightness of the synchrotron source[3]. Due to the broad application of such an analytical tool, the advantages brought about by the improved resolution *(factor of 10 approximately)*, have been rapidly exploited by various communities and the motivation for using this technique has continuously grown as manifested by the increasing demand for beamtime at the existing synchrotron IR microscopy stations.

In parallel to the experimental applications of synchrotron infrared spectroscopy, a constant effort aiming at providing a more accurate description of the observed infrared emission was pursued. At LURE, Wisconsin facility and at ANKA , another mechanism responsible for the IR emission was emphasized and worked out theoretically and experimentally[1] : Edge Radiation. This emission results from the longitudinal acceleration or deceleration of relativistic particles when leaving or entering a magnetic device (bending magnet, undulator, steering magnet...) and is of particular interest in the IR since photons are emitted in a much narrower cone than from a bending magnet. This mechanism has been studied experimentally and theoretically and it is now possible to predict its spatial and spectral distributions.

I-2: Synchrotron IR project at SOLEIL: the objective.

Far-IR spectroscopy and microscopy stations are both implemented at LURE, and have been operated since 1992 and 1998 respectively. The users community is well established, and has expressed motivation and needs for the continuation of their programs in a national synchrotron facility such as SOLEIL. To date, both beamlines are oversubscribed.

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[1] W. Duncan and G.P. Williams *Applied Optics* **22**(1983) 2914.

[2] P. Lagarde, *Infrared Physics* **18**(1978)395

[3] G.L. Carr, P. Dumas, C.J. Hirschmugl and G.P. Williams, “Infrared Programs at the National Synchrotron Light Source”, *Nuovo Cimento* **20D** 375 (1998)

[1] P. Roy, Y.-L. Mathis, J.-P. Marx, J. Michaut, B. Lagarde, A. Gerschel and P. Calvani, Il Nuovo Cimento 20D (4), (1998), 415 and references therein.

The construction of SOLEIL has attracted the interest of the already-existing IR users and future potential users and we believe that a synchrotron infrared project at SOLEIL is of paramount interest.

As said before, Infrared spectroscopy is part of almost all developing programs of Synchrotron facilities. At SOLEIL, the infrared beamlines and scientific programs proposed hereafter could be of outstanding quality if the location of the exit ports, equipments to be installed and developed are chosen with a particular care of their complementarities with other synchrotron-based techniques and of the scientific program in which they are included.

Far-IR and microscopic investigations share the same requirements for the optimum collection geometry of the IR photons emitted by the synchrotron source, and stability of this source. However, the interest and involvement of the various communities in the far-IR or in the microscopic applications being somehow different, the scientific case for the far-IR and microscopic projects will be presented separately.

This project concerns ***two IR stations*** at SOLEIL, one dedicated to far-IR spectroscopy, and one dedicated to IR microspectroscopy and imaging. These two beamlines will be internationally competitive, and will make possible state-of-the-art IR investigations for several (national and international) groups. This proposal is organised as follow : for both FIR spectroscopy and micro-spectroscopy, we, firstly, present the main scientific topics, pointing out the corresponding communities, the necessity to use IRSR with examples illustrating the scientific problems, then, we propose technical solutions for both extraction geometries (edge radiation and bending magnet), details of the transport optics and spectrometers.

II- FAR-IR SPECTROSCOPY

II- 1: Introduction:

The spectral domain of ***far infrared*** ($\lambda \cong$ 10-200 µm, or $\omega=1/\lambda \cong$ 50-1000 cm-1) remains one of the last borders in vibrational spectroscopy. It is an experimentally challenging domain due to the limited intensity of the "classical" thermal sources which is little over the emission of the room temperature blackbody of the optical elements. This difficulty can be overcome by the use of high brightness sources, which are equivalent to several thousands degree-blackbody. Apart from monochromatic laser (FEL, OPO), synchrotron is the only source presenting both a noticeable gain in brilliance and sufficient stability for feeding an interferometer.

The absorption in the far infrared corresponds to transitions from an initial state to a low energy final excited state. For isolated molecules, this excitation corresponds to rotational transitions, vibrational excitations of large molecules or roto-vibrational transitions. Their measurements at high resolution provide a better description and understanding of species or chemical reactions.

In the case of condensed matter, the intermolecular motions have characteristic resonant frequencies in the far-IR. The study of intra- and inter-molecular vibrations yields information on bonding properties in crystals, glasses, liquids and melts, thereby providing a microscopic description of thermochemical properties.

In solids, the infrared absorption, also referred to as optical studies, provides information on electronic and structural properties of condensed materials through the understanding of electronic excitations, such as crystal field, charge transfer and excited states of insulators, intraband transitions (Drude band or plasmon), and interband electronic transitions. It also allows studies of transitions evidenced in the phase diagram such as those occurring as the doping level, temperature, pressure or confining geometry are modified.

In surface and interface studies, adsorbates which are bonded to a substrate are characterized by adsorbate-substrate absorption bands in the 250-500 microns region (except for hydrogen, which is a light atom). As these vibrational motions have a very poor dynamic dipole moment (one of the atom involved in the motion is a substrate atom, almost " rigid"), detection and identification of such bands were precluded until the use of a synchrotron radiation source. Additionally, thanks to the strict proportionality of the IR radiated intensity with the current of the storage ring, unrivalled information have been obtained, which are of paramount importance for understanding reaction dynamics at surfaces (more particularly the large change of electronic properties of metallic substrates by adsorbates).

II-2- Scientific projects and related communities.

1. High resolution spectroscopy of isolated species

Molecular high energy resolution spectroscopy is currently used to study the nuclear movements of molecules, radicals, molecules of Van der Waals and molecular aggregates in the gas phase. For far infrared absorption in the gas phase, the molecular movements involved are rotations, vibrations or torsions and deformations of the "soft" molecules (ex: carbon chains).

In the next five years (2000-2005), a new generation of powerful satellite spectrometers for monitoring atmospheric changes on a global scale will be launched into orbit [i]. These instruments will provide large amounts of data that need to be correctly analyzed in order to understand and predict chemical and analytical processes in the earth atmosphere. For this purpose, reference data obtained from laboratory measurements are essential. However, fundamental data for infrared and far infrared molecular transitions are still limited. As an illustration, only 20 species have been identified in space in contrast with the 100 species observed from coupling radio measurements and observations. In the far infrared region, the lack of adequate laboratory equipment is even more striking. The coupling of a high-resolution spectrometer in a wide frequency domain with a high sensitivity thermoregulated absorption set-up is clearly needed.

Interferometry by Fourier transform at very high resolution is an essential tool to undertake these laboratory studies as its advantages (broad spectral field, multiplexing, high precision calibration in frequency and intensity etc…) make it an ideal spectroscopic technique. Fed by high brilliance synchrotron infrared radiation, the interferometer can then be coupled with a cell with multiple reflections of weak opening. The long path length allows to detect low absorbance bands without the need of increasing the pressure thus minimizing Doppler broadening.

The very high brightness of the synchrotron radiation allows to achieve absorption lengths of 100 meters. The association of these three elements (Synchrotron source, Interferometer and multiple path cell) constitutes an ensemble of very high detectivity. One can then extend measurements to absorption of species produced under low concentration such as van der Waals molecules produced in cooled cells and neutral or charged radical species created in the plasmas generated by electric discharges.

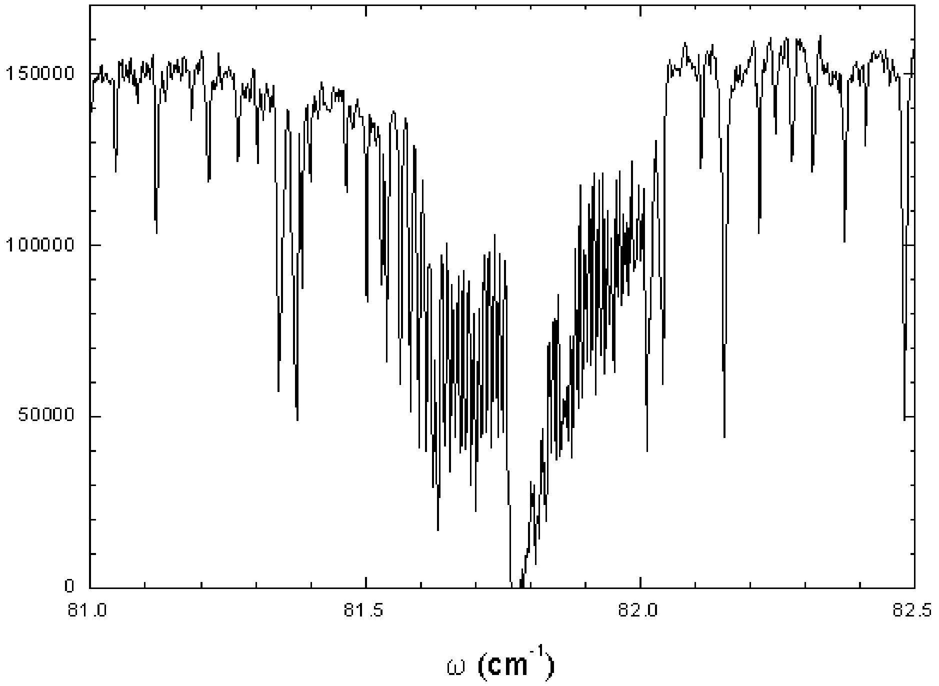
It is worth noticing that for this type of measurements, the low divergence of the synchrotron source is important at two levels: it allows the optimal use of the high resolution without the need for an iris (necessarily limiting the flux) and it permits a very efficient transport through the long path cell. In consequence, compared to the flux radiated by other continuum sources used in the far infrared, the use of synchrotron radiation reduces considerably times of recording for an equivalent signal-to-noise ratio.

The scientific communities interested by this project are as follows:

- experimental spectroscopists who seek spectral structures possibly produced by new molecular species.
- spectroscopists specialized in the analysis and interpretation of the spectra, and in the modelling of molecules.
- researchers working on ab-initio quantum chemistry calculations.
- physicochemists of the atmosphere
- astrophysicists who identify the spectral structures in the various astrophysical objects by using the results of laboratory work

An example :far infrared ro-vibrational structures of NO_2

A coupling of SR with far infrared interferometer has been realized for the first time on the Swedish Infrared facility by Nelander and co-workers. More recently, on the SIRLOIN beamline at LURE, a complete set-up for atmospheric studies has been developed. It comprises a high-resolution interferometer (Bomem DA8 3X, energy resolution: 1 μeV) and a thermoregulated multiple reflection cell. The path of 28 meters in the cell allows the measurements of gaseous samples at low pressures therefore avoiding the pressure broadening effects (displacements and broadening of absorption lines). The first spectra realized on NO_2 in the domain 40-150 cm^{-1} (5 - 20 meV) at a pressure of 1 mbar have well demonstrated the superior sensitivity allowed by the use of synchrotron radiation compared to the best IR conventional sources. The rotational structures are remarkably resolved particularly in the Q branch of NO_2.



Q branch of NO_2 measured in the far infrared range with a resolution of 0.004 cm^{-1} with a 28 m multiple reflection cell at 1 mbar pressure.

2 Microconfined Liquids and soft condensed matter

Another topic in the far infrared absorption technique calls upon the great diversity and the stability of the nanostructures in liquid matrix. Adjustable microtubules and spherical cavities with sizes between some nanometers and some micrometers can now be produced at will. One can accurately select the dimensions of these structures, and therefore the number and the nature of the molecules they contain. The use of chemically inert matrices, the fluorocarbons, allows to encapsulate biological objects together with a controlled quantity of hydration water. For this reason, it is particularly interesting for applications in pharmacology and cosmetology.

The infrared synchrotron radiation is particularly well adapted to the study of these microstructures and the characterization of molecular interactions in confined phases of the matter. While exploiting the diversity of compounds and their dimensions of containment one can separate the study of the connections at the matrix-compounds interfaces and that of the interactions between molecules. Examples of inclusion concern biomolecules in solution, pure liquids in particular water in its various states or solutions.

For these studies, synchrotron radiation constitutes the only source allowing a continuous sweep in all frequency area of the spectrum,. One can thus measure in only one experiment the modifications induced by a change of local state as reflected on several molecular mechanisms. For example, in the case of an aqueous solution, the effect of a change in dimension or in composition manifest itself in three areas of the spectrum: in the far infrared one measures the connectivity in the network of hydrogen bonds, the intermediate region is the domain of librations responsible for the rupture and the renewal of these connections, the mid infrared is the range where the forces of attachment of OH bonding to the walls of the cavity or the intramolecular vibrations of dissolved molecules can all be accessed.

The access to the physics and chemistry of the aqueous environment around biomolecules, polymers, ionic structures or hydrophobic structures will be largely facilitated by confinement out of neutral matrix. This aqueous environment allows to increase the signal-to-noise ratio made up by the specific absorption of the aqueous solutions (for example protein solution) compared with the considerable absorption of interstitial water, embedding the spectrum of the components in solution. Other supramolecular structures lend themselves particularly well to the study of ligand-substrate interactions and to that of the dynamics of the molecules included inside the cages.

Community of scientists who applied for beamtime on SIRLOIN and showed interest in *the development of application of FIR studies for soft condensed matter*

- **M. P. Krafft**, *Institut Charles Sadron, Strasbourg.*
- **Eric Prouzet, E. Boissière**, *Laboratoire des Matériaux et Procédés Membranaires, Montpellier*
- **Alain Mermet,** *ESRF, Grenoble*
- **Alain Gerschel**, *Laboratoire de Chimie-Physique, Bât 350, Orsay*
- **C. Bourgaux,** *LURE*
- **H. Remita**, *Laboratoire de Chimie-Physique, Bât 350, Orsay*

3-Optical Properties of Material

The scientific objective of this set of themes is the study of the optical properties of materials under well-controlled temperature and pressure conditions. One example concerns the non-conventional crystals such as the high critical temperature superconductors (HTCS) and the organic superconductors of low dimensionality. For these studies, the synchrotron radiation is particularly well adapted since the single crystal samples are usually quite small.

Measurements by reflectivity and transmission in a broad field of the infrared give information about the crystal structure of the material through the phonons and other reticular excitations, about the electronic excitations coupled with the crystal lattice (in the mid infrared), or, at higher energy, about pure electronic excitations (in the near infrared and visible). Particular attention will be paid to the modifications of these bands occurring through phase transitions induced by changes in pressure and temperature.

The study of materials at ultrahigh pressure is currently experiencing an unprecedented surge of breakthroughs that were deemed inconceivable only a few years ago. With the development of ultra-high pressure diamond cell technique, it is now possible to reach pressures equivalent to the Earth's core (i.e. 300 Gpa or 3 Mbar). Studying the effect of pressure on materials is essential for a range of problems spanning condensed matter physics and chemistry, Earth and planetary science, material science and technology. Different techniques are currently used for high pressure studies; in particular, infrared optical spectroscopy provides information on pressure-induced changes in electronic excitations, including crystal field, charge transfer, excitonic spectra of insulators and semiconductors, interband and intraband transitions in metals, and novel phase transitions such as pressure-induced metallization. Infrared spectroscopy can also provide information on low-energy collectives excitation, such as phonon modes.

An example of system studied with far infrared synchrotron radiation concerns the $Bi_2Sr_2CuO_6$ (BSCO) cuprate with Tc=20 K. There, the low number of carriers has allowed one to resolve the spectral contributions that are shielded by the Drude absorption in other systems with higher Tc. In this system, the low energy optical conductivity shows a huge incoherent component at finite frequency which softens with decreasing temperature. This component has been resolved for the first time (See Figure) revealing a sharp, normal Drude contribution[2], with most of spectral weight located below 50 cm-1. These results question the well-established model of the "anomalous Drude" response in high-Tc superconductors.

Optical conductivity of BSCO at various temperatures. It shows a conventional sharp Drude term, well separated by a deep minimum around 80 cm-1 from a huge polaron-like peak. The inset reports the behavior of the infrared spectral weight, of which about 50% condensates at zero frequency below Tc.

Synchrotron infrared spectroscopy has emerged as an important new tool in the porto folio of high-pressure techniques. The technique has been shown to be especially relevant in the far-infrared region, where the brightness of the synchrotron light is more intense than conventional black bodies. There, the intense flux of synchrotron beam increases the brightness of the collimated beam by 2 to 3 orders of magnitude over conventional globar source. At the moment, only the Spring-8 IR beamline and the NSLS (USA) beamlines are equipped with anvil cells for high-pressure infrared studies, while in Europe such a facility is still lacking.

- **P. Calvani, S. Lupi, A. Nucara,** *Dipartimento di fisica, Università La SapienzaP.le Aldo Moro, 2, 00185 ROMA, Italie*

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[2] *«Evidence of two species of carriers from the far infrared reflectivity of Bi2Sr2CuO6 "* . S. Lupi, P.Roy, P. Calvani and M. Capizzi,. *Phys. Rev. B. 62 (18), 12418. (2000).*

- **H. Lemée Cailleau**, *Groupe Matiere Condensee et Materiau, UMR C.N.R.S. 6626, Universite de Rennes, batiment 11a - campus de Beaulieu35042 Rennes cedex France*
- **S. Klimine, Marina N. Popova**, *Institute of Spectroscopy, Russian Academy of Sciences, 142092 Troitsk, Moscow region*
- **Prof. Dr. Alois Loidl**, *Experimentalphysik V, Institut für Physik, Universität Augsburg*
- **H. Szarc,** *Laboratoire de Chimie-Phsique, Orsay*
- **J.L. Sauvageol, Jean-Louis Bantignies,** *Groupe de Dynamique des Phases Condensées CC026, UMR 5581 C.N.R.S. - Universite Montpellier II, 34095 Montpellier, cedex 5, France*
- **Professor Gordon Davies**, *Head of Department, Physics Department, King's College London, Strand, London WC2R 2LS.*
- **Alain Michalowicz, Jacques Moscovici,** *Groupe de Physique des Milieux Denses (GPMD), Departement de physique - UFR de Sciences et Technologie, Universite Paris XII-Val de Marne, 61, Avenue du General de Gaulle, 94010 Creteil cedex - France*

4. Time resolved Studies

In addition to the use of the pulsed structure of the SR for pump-probe studies, time resolved studies can be achieved through the use of "step-scan" interferometry. This mode of operation allows to obtain time resolved infrared absorption spectra by reconstructing the interferogram and gives access to time resolution in the domain 10 nsec – 1msec. It is noteworthy that it requires a « resetting » of the time scale by a laser pulse of excitation or an electronic trigger pulse. Applications may concern solid state excitations, photochemically induced processes or electrochemical surface reconstruction… At the moment, however, only applications to biomolecules functional studies have been considered. This kind of measurements is the direct extension of the « encapsulated liquid» theme. It aims at understanding the role of the water in the transmission of information between biological objects and more particularly up to what point does the transitory water supply networks intervene in the transport of protons and the functionality of proteins, through the collective dynamics of these systems. Our experimental approach is based on the infrared transmission in a very broad spectral range.

The study of biomolecules in their functional medium, often including 70 % of water or more, is difficult because of the very intense aqueous signal, masking far weaker contributions from the protein signal. This difficulty can be circumvented by encapsulating water nanodroplets in a non-aqueous liquid matrix by means of micellar systems, in which the biological macromolecules are inserted. The specificity of the experimental device on synchrotron radiation , is the simultaneous access to bands specific to the intramolecular vibrations (bands of frequencies, ω>800 cm-1) and the intermolecular vibrations (bands of frequencies, ω<1200 cm-1).

5. Heterogeneous Catalysis

IR spectroscopy of adsorbed molecules is a powerful technique for the investigation of catalytic active sites (typically a metal M) at the surface of oxide[3] or zeolitic materials [4]. This

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

[4] A. Zecchina, C. Otero Arean, Chem. Soc. Rev., 25 (1996) 187.

technique is based on the study of the perturbation induced by the active sites to the stretching and bending modes of the adsorbed molecules . Such modes occurs typically in the mid-IR region, where conventional instrument (lab-scale) are very efficient. Conversely, nothing, or very few, is known up to now on the perturbation of the M-support stretching frequency induced by the adsorption process. This is due to the fact that such modes occur in the far-IR region, where the laboratory sources have a negligible power. It is thus evident that the use of the synchrotron radiation could open this new frontier to the scientific investigation.
The comprehension of catalytic reactions greatly benefits from establishing correlations between the adsorption characteristics of catalyst and their activity. The realization of reactional cells constitutes an essential step aiming at defining catalyst under experimental conditions close to those which are associated to the catalytic act. The materials are thus placed at high temperature (300°C-500°C), under reactional atmosphere and possibly under pressure (1-40B). It is also often necessary to reproduce as closely as possible the constraints of the catalysis reaction when applying the techniques of analysis.

In addition to the development of the adapted reactional cell, the realization of these experiments requires the distribution of reactive gases at the entry. This installation includes a set of gas lines (H2, N2+O2, CO, NO, H2S, Ar) equipped with a mass regulation system, a mixing stage and the reactional cell itself with its pressure and temperature control. The setting of the control cells, of the gas flows and of the temperature should be computer controlled. The gases used will be selected in order to reach the concentrations fixed by the catalytic conditions. Finally, the presence of a gas extractor on this line is essential if one wants to ensure the security of the assembly.

Community of scientists who manifested interest in the development of application of FIR studies of heterogenous catalysis during the may 2001 workshop :

- **D. Bazin**,*LURE - UMR 0130*
- **X. Carrier, G. Constentin, C. Louis, P. Massiani, C. Thomas,** *Laboratoire de réactivité de surface - UMR 7609*
- **F. Studer,** *CRISMAT, UMR 6508*
- **F. Garin,** *ECPM-LERCSI-UMR7515*
- **C. Especel, L. Pirault-Roy, M. Guerin** *LACCO, UMR 6503*
- **P. Gilson, F. Mauge, J. Leglise**, *LCS, UMR 6506*
- **Khodakov, A. Griboval, C. Lamonier, E. Payen**, *Laboratoire de Catalyse de Lille, UPRESA 8010.*
- **C. Lamberti, A. Zecchina**' Dipartimento di Ingegneria Chimica e Scienza dei Materiali, Politecnico di Torino, Corso Duca degli Abruzzi 24, I-10126 Torino, Italy

II-3- Experimental technique and environment

The experimental station generally consists in a commercial IR interferometer fed with synchrotron radiation through the emission port. The interferometer level of pumping imposes sometimes a second window on this port. It is completed with one or several beamsplitter(s) and detector(s) adapted to the energy domain. It also includes various set-ups allowing the conditioning of the investigated sample (temperature, pressure, and orientation relative to the polarization of the incident light) and to the type of measurements (microscopy, transmission,

ellipsometry, reflectivity, etc.). A commercial Michelson interferometer as compared to grating spectrometers is ideally adapted for its use on a synbchrotron IR source. We cite briefly its main advantages: the possibility of measuring a large domain of frequency by a scan of the mobile mirror (multiplex), the fact that the resolution is limited by the displacement of the mobile mirror and does not impose a small slit (the Jacquinot advantage), the fact that the absolute energy absorption structures can be determined with a precision only limited by a laser bandwidth superimposed on the beam trajectory (the Connes advantage).
For the scientific projects cited above two instruments will be necessary : a high resolution FTIR (Bruker, model 120 HR) allowing energy resolution of 0.2 micro eV ($2\ 10^{-3}$ cm^{-1}) and a lower resolution allowing time resolved (step scan) measurement. The SR beamline will feed either one or the other of these spectroscopic ensembles used respectively for molecular studies (gas phase) and condensed matter measurements as for these, the natural width of the structure do not justify the high resolution.

II-4- Cost and staff:

1. Budget

The budget, reported hereafter, is estimated. It takes into account the fact that the SIRLOIN Bis beamline has been developed to incorporate a number of costly elements able to be transferred on Soleil. (See Annex 6) These include controls (3 x 46 kEuros), step scan spectroscopic station (53 kEuros), detectors (2 x 30 kEuros).

Basic costs of transport beamline:

Optics and new components for the IR beamline transfer	**230 kEuros**

Major expenses posts

High-resolution FTIR spectrometer	**382 kEuros**

The spectrometer includes 4 detectors (2 bolometers, InSb, Cu:Ge or B:Si,) and 3 beamsplitters (CaF_2, KBr, Mylar).

Cabin for IR stations (with fluids, water, air conditioner, gas evacuation …)	**46 kEuros**
Sample apparatus	**228 kEuros**

Specialized 'sample cells' are required in combination with the FIR line. These may include: transfer optics for high-pressure (diamond anvil) and absorption experiments; long-path temperature controlled gas cell (e.g. 4 m long with absorption paths of 200 m); a long-path electric-discharge cell for molecular ions and free radicals (about 1-2 m long); and a supersonic jet expansion apparatus. The latter requires large vacuum pumps (Roots booster/mechanical backing).

2- Staff:

Such a far-IR beamline requires **three** permanent scientists (or preferably two scientists and one engineer), one post doc and one PhD student.

III- INFRARED MICROSPECTROMETRY AND IMAGING:

III-1: Introduction.

Infrared microscopy has benefited a lot from the high brightness of the synchrotron source[6],[7]. The lateral resolution, which is achievable, has become diffraction- limited (half of the probing wavelength in a confocal configuration) [8]. This analytical technique is mainly used in the mid-IR region (2.5 to 50 microns), which is the domain where almost all of the internal motions of individual molecular groups show resonant frequencies. It is used for identification of compounds, as each molecule has its own vibrational spectrum (vibrational "fingerprint"). Thanks to its improved lateral resolution (about one order of magnitude) synchrotron IR microscopy has became an important application field, in microspectrometry and in chemically-selective imaging technique, opening up new investigations, for example in Geology, Cellular Biology Forensic science and Environment.[9],[10]

III-2: Scientific projects.

1*: Geological applications :*

Several studies carried out during the last decades have demonstrated that most of the rock formation and successive transformations in the earth evolution involve a broad variety of fluids (silicate magma, water solution, gas/hydrocarbon mixture, etc…). For instance, the identification of organic matter included in fluid inclusions inside a mineral phase is of prime importance for petroleum exploration. FTIR is known as having the best detection limit for all the relevant fluids [11]. One example of fluid identification by synchrotron IR microscopy is shown on Fig. III-1

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[6] GL Carr, JA Reffner, GP Williams. Performance of an infrared microspectrometer at the NSLS. *Rev. Sci. Instr.* **66**(1995)1490.

[7] J.L. Bantignies, G.L. Carr, P. Dumas, L.M. Miller, G.P. Williams, "Applications of Infrared Microspectroscopy to Geology, Biology, and Cosmetics", *Synchrotron Radiation News*, **11 (4)**, 31-36 (1998).

[8] G.L. Carr. "Resolution limits for infrared microspectroscopy explored with synchrotron radiation." *Rev. Sci. Instr.*, **72**, 1613-1619 (2001).

[9] L.M. Miller, P. Dumas, N. Jamin, J.L. Teillaud, J.L. Bantignies, G.L. Carr, "Applications of synchrotron infrared microspectroscopy to the study of biological cells and tissues," *Amer. Inst. Phys. Conf. Proc.*, **165**: 75-76, 2000.

[10] L.M. Miller, G.L. Carr, M. Jackson, G.P. Williams, P. Dumas, "The impact of infrared synchrotron radiation on biology: Past, present, and future," *Synchrotron Radiation News*, **13**: 31-37, 2000

[11] N. Guilhaumou, P. Dumas, G.L.Carr and G.P.Williams, "Synchrotron Infrared Microspectrometry applied to Petrography in micron scale range: Fluid chemical analysis and mapping". *Applied Spectroscopy* **52** 1029 (1998).

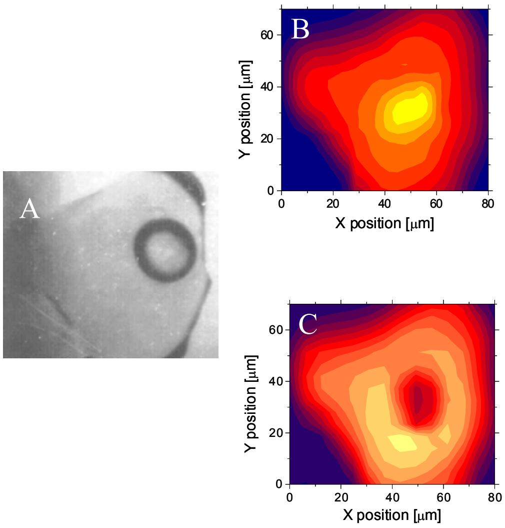

Fig III-1:A- Optical image of a fluid inclusion in a calcite sample from Tunisia. B- chemical image of CO2, with is obviously contained into the visible bubble within the inclusion C: chemical image of the aliphatic (CH_2) chains, the fluid constituent of the inclusion. From ref 11.

The Earth's deep interior may contain up to four times the amount of water present today in the hydrosphere. These estimates have been made by measuring the water content either of the mantle xenoliths that reach the surface, or of the lavas emitted at mid-oceanic ridges. Both methods yield similar values ranging from 100 to 500 ppm by weight of H_2O in the Earth's upper mantle (30 to 670 km depth), but do not allow to determine whether this amount of water can be totally stored in the nominally anhydrous mantle phases (olivines, pyroxenes, garnets and their high-pressure polymorphs) or if some water is free or accumulated in special hydrous phases like the DHMS (dense hydrous magnesium silicates). To determine the importance of nominally anhydrous minerals as water reservoirs in the mantle, numerous studies have been undertaken to measure the solubility of water. If true, the evolution and dynamics of the whole mantle would be affected by the presence of water in the transition zone as this part of the mantle plays a central role in the mantle dynamics and water strongly modifies the physical and chemical properties of rocks. For instance, the presence of water dissolved in olivine increases consequently the creep rate; it enhances the electrical conductivity of olivine and could also reduce significantly the seismic wave velocities. Deeper investigations in petrography during the last decades have demonstrated that most of the rock formations and their successive transformations in earth evolution are dealing with any kind of fluid, whether the fluid is a silicate magma, a water solution, and/or a mixture of gas and hydrocarbon. The volatile species are more or less involved in all chemical reactions concerning mineral crystallization and transformations. Some like CO_2 and H_2O appeared recently noticeable in the mechanism of magmatic transformations during the mantelic evolution. The identification of the organic matter included in fluid inclusions inside mineral is of prime importance for petroleum exploration. The search for life in extraterrestrial materials is directly linked with search of water and organic molecules in meteorites. FTIR is known as having the best detection limit for all these fluid characterizations. Therefore, it appears challenging for petrologists to detect and analyse very locally within representative minerals the chemical composition of the fluids at each step of the evolution at a few micron scale range with a non-destructive method.

This has led to numerous investigations and an increase demand of beamtime at the MIRAGE beamline, at LURE, from:

- *MNHN, . Laboratoire de Minéralogie. C.N.R.S., ESA 7058, 61 rue Buffon 75005,Paris, France* : **N. Guilhaumou, and N. Sauter**
- *Lab. de Sciences de la Terre, UMR 5570 CNRS-UCB Lyon1-ENS Lyon* : **I. Daniel, E. Chamoroo-Perez, Ph. Gillet, B. Reynard**
- *Lab. de Physique des Milieux Condensés, UMR 7602 CNRS-PVI :* **J.C. Chervin, Ph. Pruzan, B. Cany**
- *Laboratoire Mécanismes de transfert en Géologie, UMR 5563, Equipe de Minéralogie, CNRS - Université Paul Sabatier 31000 Toulouse, France* : **J. Ingrin**
- *Laboratoire de Géosciences Marines CNRS, Institut de Physique du Globe de Paris* : **P. Philippot**
- *Laboratoire Pierre Sue,CEN Saclay :* **H. Bureau**

2- Studies of interstellar durst particles :

Much of what we know about the interstellar medium and other stars comes from spectroscopy. Infrared spectroscopy generally provides identification of *solid compounds* and *minerals* in the dust. Recently, the Infrared Space Observatory (ISO) has greatly expanded the infrared spectroscopy of interstellar and circumstellar regions. Features are seen in emission from hot regions, or, absorption in cold regions illuminated from behind by a continuum source. To associate a specific absorption feature with a particular compound or mineral the infrared signature must have been measured in the laboratory for comparison.

Interstellar grains occur in molecular clouds in interstellar space. These interstellar grains generally show broad 10 and 20 μm absorption features that suggest a disordered silicate. Interstellar grains also show several features near 3 μm consistent with C-H stretching vibrations in aliphatic hydrocarbon. Thus, the dominant type of interstellar grain is thought to be a glassy silicate coated with organic matter. *Circumstellar grains* occur in clouds surrounding other stars. A variety of grains, including crystalline silicate, glassy silicate, oxides, and other phases, many yet unidentified, occur in the circumstellar environment.

Since the mid-1970s NASA has recovered interplanetary dust particles (IDPs), fragments from comets and asteroids, from the Earth's stratosphere. These small (~5 to 25 μm) IDPs decelerate from interplanetary velocity (>11 km/sec) in the Earth's upper atmosphere, generally without significant heating. These particles are similar in composition and mineralogy to primitive meteorites, but many IDPs have high volatile element contents, very unequilibrated mineralogy, and spots of high D/H. Many of the IDPs are very primitive, having experienced minimal thermal and aqueous alteration. Thus they are good candidates for the preservation of interstellar grains.

A comprehensive project to characterize the components of IDPs, meteorites and terrestrial minerals, has begun in 1999 in an effort to identify the compounds and minerals in interstellar and circumstellar grains. The IDPs, which are believed to be fragments of comets and asteroids, consist of micron to sub-micron aggregates of different minerals and compounds. Because of the small size of these individual subunits, the high intensity of synchrotron-based FTIR is required to obtain spectra of the subunits of the IDPs. [12]

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[12] P. I. Raynal, E. Quirico, J. Borg, D. Deboffle, P. Dumas, L. d 'Hendecourt, J. -P. Bibring and Y. Langevin - "Synchrotron infrared microscopy of micron-sized extraterrestrial grains"
Planetary and Space Science, **48**(12-14) 2000, 1329-1339

The Institut Astrophysique Spatiale (Orsay) is strongly involved in the synchrotron infrared activity, at LURE. It owns the IR microscope, and accordingly, 30% of beamtime is allocated to such studies.

Involvement :

- *Institut d'Astrophysique Spatiale – Bât 121 – 91405 Orsay Cedex*: **Eric Quirico, Pierre-Ivan Raynal, Karine Demyk, Janet Borg and Louis d'Hendecourt**

3- *Long term projects in Astrophysics and in Geology:*

The users of these communities have identified the following directions along which they are willing to pursue or initiate studies:

- Asteroids and Cosmic –originated particles are been collected in space, and will be transported to Earth within two years. A rich collection of small samples will need to have access to IR microscopic beamlines (not only), in order to be identified (structural and chemical composition).
- The StarDust 2007 expedition is actually collecting particles from comet tails, which will be available for analysis in 2007. Prior to this collection, efforts have been suggested to be enforced in order to identify " laboratory samples " which can mimic the structure and composition of the expected composition of this collection.
- Extraterrestrial dust particles have characteristic infrared emission spectra.. The results from the Infrared Space Observatory (ISO) have raised several questions about the evolution of the structure and chemical composition of silicate dust. In particular, the ISO-SWS spectra (2-45 μm) of evolved oxygen-rich stars exhibit emission bands at wavelength > 20 μm due to lattice vibration in crystalline silicates. However, none of these bands has yet been detected in the Interstellar Medium (ISM). The observed ISM silicate bands at ~ 9.8 and ~18 μm are broad and structureless indicating that the silicates in the ISM are amorphous. The absence of the crystalline silicate bands in the ISM spectra seems to indicate that crystalline silicates disappeared in the ISM. Infrared microanalysis has been very successful at LURE, but they need to be completed by infrared microscopic studies in the region of 50 microns. This will be made possible at SOLEIL (see below)
- Inclusions in various rocks from the Deep Earth must be studied, to address satisfactorily several problems of the Deep Earth Composition.
- To figure out the protonation scheme of various rocks in the Deep Earth, high pressure studies (up to 100 Gpa) have been initiated at LURE, and the community has expressed a strong need for their continuation at SOLEIL. High-pressure diamond anvil cells have been adapted for IR microscopic studies.

4- *Biologically relevant studies:*

Biological samples have been examined with IR microscopes equipped with conventional IR sources for nearly 20 years. Although conventional IR microspectroscopy has proven extremely valuable for resolving the chemical components in biological samples, the low brightness of the internal source (globar) has been the limiting factor in the achievable lateral resolution (typically > 15 μm). This constrains the analysis of biological specimens to the tissue level only. Individual biological cells are typically 5-30 μm in diameter, making them too small to probe with a conventional IR source.

Thus for a typical biological specimen, the diffraction-limited spatial resolution for primary lipid (C-H stretch), protein (amide I), and nucleic acid (P-O stretch) absorption features is approximately 3, 6, and 12 μm, respectively. The improvement in spatial resolution achieved by using a synchrotron IR source has only been realized recently, and applications to biological systems are still in their infancy.

The high spatial resolution of a synchrotron IR source permits the chemical mapping of single living cells for the first time. Individual mouse hybridoma B cells have been examined during necrosis and also the end phases of mitosis [14]. In these experiments, a cytospin was used to deposit cells onto BaF_2 disks. This technique does not kill the cells, but rather removes excess solution while keeping them hydrated, which suspends their activity for several hours. Infrared maps are collected during this time by automated scanning of the sample on a precision X-Y,micro stage. After >8 hours, the cells dehydrate and die. On Fig III-2 are reported the infrared maps of the proteins (nucleus) and of the lipids during the cell division

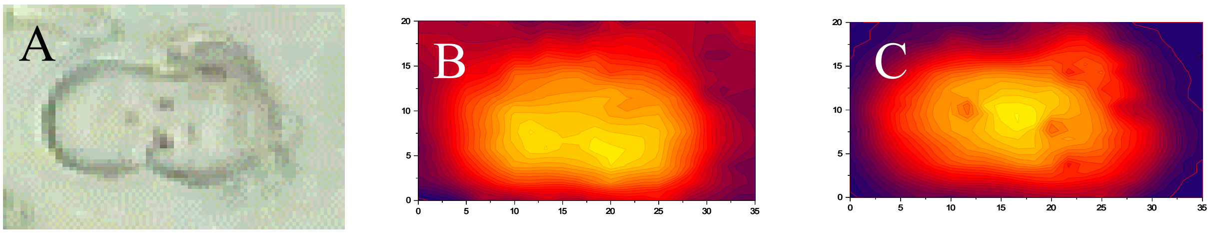

Fig III-2: A: optical image of a cell undergoing division (size 25x 15 μm) B: Chemical image of the protein distribution. One can note the formation of the two nuclei C: Chemical image of the lipids distribution: they are playing an important role during the construction of the inter-membrane wall. From ref 11

In another study, similar cells were examined during the process of apoptosis (i.e. programmed cell death), where a single cell was probed in 50:50 D_2O/H_2O solution for several hours while apoptosis progressed [15] Evidence of protein aggregation and degradation was clearly observed in the frequency of the Amide I band (protein secondary structure finger print)

With the ability to probe smaller and smaller areas with the synchrotron IR microscope, new techniques are currently being applied to aid in sample visualization with fluorescence microscopy and probed with the IR microscope. Once identified, the IR microscope can be used to analyse the chemical environment in and around that region of interest. It should be noted that fluorescent labels are generally present in extremely low (i.e.nanomolar) concentrations, so they do not interfere with the IR technique; they are used exclusively for visualizing a region of interest.

Studies of biological relevance have a tremendous prospect. From cellular biology, at single cell level, to high contrast study in tissues, this field will emulate new studies, and necessitate nearby facilities and equipment for biological manipulations. Currently, infrared

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[14] Jamin, N., Dumas, P., Moncuit, J., Fridman, W. H., Teillaud, J. L., Carr, G. L. & Williams, G. P. (1998). Highly resolved chemical imaging of living cells by using synchrotron infrared microspectrometry. *Proc Natl Acad Sci U S A* **95**(9), 4837-40.

[15] J.L. Teillaud, N. Jamin, L. Miller, J. Montcuit, P. Dumas and G.P. Williams to be published.

investigations at LURE, on tumoral human lymphocytes irradiated with γ doses between 2 and 60 Gy, have shown changes in the ARN and secondary structure of the proteins [16].

The study of human tissues (such as skin and hair) is a topic of paramount importance not only for medical application, but also for cosmetic purpose. Synchrotron IR microscopy is currently exploited at LURE, for the study of human hair composition and structure. It has been shown that fatty acids are, unexpectedly, highly localised in the central part of human hair [17](Fig. III-3)

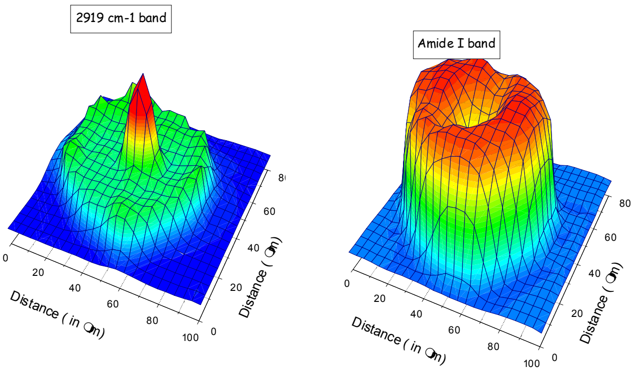

Fig III-3: Chemical mappings of lipids (left) and proteins (right) across a human hair cut. While the protein concentration displays a dip at the location of the medulla, the lipids are highly localized in this medulla . From Ref 17

Studies of human skin and hair is currently carried out, at the MIRAGE beamline (LURE) with industrial partners.(*Laboratoire de Biologie Végétale Yves Rocher, Issy les Moulineaux , Sanofi-Synthélabo Recherche, Montpellier, Yves Saint Laurent Beauté, Neuilly sur Seine* , *L'OREAL Recherche, Aulnay sous Bois*)
Several studies are undertaken to identify tumoral tissues and cells, using synchrotron IR microscopy. This has potential application in diagnosis of such a disease. To illustrate the spectroscopic signature of such a disease, fig. III-4 shows the IR spectra, recorded inside the nucleus , of a healthy and tumoral cell.

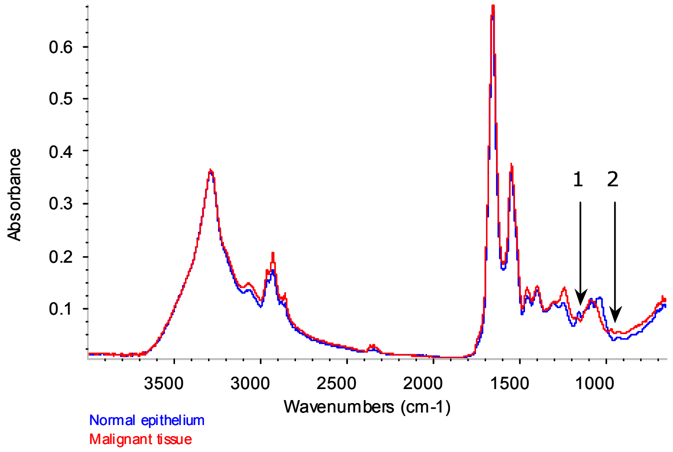

Fig III-4: Normal(healthy) cell (blue) compared to a tumoral cell (red). Marked differences (labelled 1,2) can be seen in C-O and C-O-P phosphorylated proteins and nucleic acids (unpublished)

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[16] N. Gault, J.L. Lefaix, J.L. Poncy and P. Dumas "Infrared microspectroscopic studies of radiation-induced apoptosis of human lymphocytes " submitted

[17] L. Kreplak , F. Briki , Y. Duvault, J. Doucet , C. Merigoux , F. Leroy , J.L. Lévêque, L. Miller , G.L. Carr ,G.P. Williams and **P. Dumas** "Profiling lipids across Caucasian and Afro-American hair transverse cuts, using synchrotron infrared microspectrometry" *International journal of Cosmetics Science.* 23 1-6 (2001).

In addition, it has been recently shown that IR microscopy could be used as a diagnostic tool in the case of Alzheimer disease; it will be utilized as such in the future.

Moreover, combined fluorescence analysis as sample visualization benefits from the use of fluorescence illumination. Fluorescent compounds absorb and subsequently light at wavelengths longer than the absorbed wavelength. Primary (natural) fluorescence is known to occur in plant cell walls, wool, as well as many pharmaceutical products. Secondary fluorescence arises from the use of fluorescent dyes or fluorochromes to illuminate samples that do not exhibit native fluorescence. The dyes are typically bound to the compounds of interest. For example, immunofluorescence, where fluorochrome labels are attached to specific antibodies, has become a widespread and powerful technique in cell biology for visualizing targeted antigens. Moreover, since fluorescent labels are present at a much lower concentration (~10^{-9} M) than conventional stains (~10^{-4} M), they do not interfere with the IR imaging, while allowing a much more accurate correlation of IR images and target proteins. To date, combining fluorescence microscopy and infrared micro-spectroscopy has required analyses with two separate microscopes. This procedure requires somehow marking the fluorescent regions of interest and picturing the corresponding image before transferring the sample to the infrared microscope. The optical design (finite tube length) of earlier infrared microscopes did not allow the ready insertion of accessory optics, such as optical components for fluorescence microscopy. Fluorescence assisted IR microscope are made commercially available nowadays.

Involvement:

- *CEA – DSV – DRR Laboratoire de Radiotoxicologie, BP. 12, F 91680 Bruyères le Châtel :* **J.L. Lefaix, J.L. Poncy, N. Gault**
- *Département de biologie, Université d'Evry-Val d'Essonne, Boulevard F.Mitterand, 91125 Evry* : **N. Jamin**
- *Laboratoire de RMN biologique, ICSN-CNRS, 91190 Gif sur Yvette* **: B. Gillet, S. de la Porte**
- *Institut National de la Santé et de la Recherche Médicale, Unite INSERM 255, Laboratoire de Biotechnologie des Anticorps, Institut Curie, F75248 Paris cedex 05* : **J.L. Teillaud, J. Montcuit, W.H. Fridman**
- Unité INSERM 539, CHU Nantes : **M.F. de la Cochetière**
- *LURE* **: J. Doucet, F. Briki, L. Kreplak, C. Merigoux, I. Ascone, R. Fourme**
- *Laboratoire de recherche des musées de France,UMR 171 du CNRS,C2RMF 6, rue des Pyramides,75041 Paris Cedex 01* : **Philippe Walter**
- *Laboratoire de Biologie Végétale Yves Rocher, Issy les Moulineaux :* **S. Marull, C. Fromageot,**
- *Sanofi-Synthélabo Recherche, Montpellier:* **A. Barbier**
- *YSL Beauté, Neuilly sur Seine* : **M. Lebel , J.M. Baret**
- *L'OREAL Recherche, Aulnay sous Bois* : **Y. Duvault, J.C. Garson and F. Leroy**
- L'OREAL Recherche- Direction Communication : Clichy : **J.L. Lévêque.**
-

5 : Material science.

In the microelectronic field, components are continuously miniaturised and the control of surface contaminant is a major problem with a difficult identification by visual inspection. Contaminants localisation can be obtained by UV light or polarized light (for refringent material) and simultaneously identified chemically by infrared microscopy. The origin of the contamination in the manufacturing process can be found afterwards. Small defects in wafer can be localized, for example defect formed by O_2 in silicon gives an absorption feature near 1100 cm-1. The study of corrosion and coatings on various materials are domains where chemical imaging using infrared microscopy shows its usefulness.
Study of polymer films and compounds is probably the field which has most benefited from IR spectroscopic study using laboratory source. Indeed, synchrotron infrared studies will be very beneficial for such studies, as already highlighted by several studies performed at the MIRAGE beamline.

Involvement:

- *Laboratoire de Spectrométrie Infrarouge et Raman, Université Lille*: C. Depecker , **P. Dhamelincourt**
- *Laboratoire de Photochimie Moléculaire et Macromoléculaire, Aubière*: **J.L. Gardette**
- *LTVP-ENSAM 151 Bd de L'Hopital 75013 PARIS* : **B. Fayolle, J. Verdu.**
- *DSM/DRECAM/LSI/LPI CEA SACLAY* **: N. Betz**
- *Dipto de Fisica e Ingenieria, Instituto de Ciencia y Tecnologia de Polimeros ,Madrid*: **G. Ellis**
- *Saint Gobain Recherche, Aubervilliers:* **Y. Richenlow, H. Arribart**

III-3: Experimental technique and environment

1/ Instrument:

Confocal infrared microscopy will be achieved with commercial instruments. New microscope operates with infinity corrected objectives, making the technique readily confocal, with higher output signal. Additionally, the microscope will be equipped with fluorescence lamp, to assist the biological and geological studies. This is also commercially available. Moreover, for rapid switching between frequency range analysis, two detectors will be housed inside the detector compartment of the microscope, and the rapid switching will be ensured by a computer-controlled mirror.
The objective stage of the microscope will be modified in order to feed a laser beam, and collect the induced–fluorescence, especially in the case of high pressure experiments (the internal pressure is measured indirectly from the position of the fluorescence band of a ruby located inside the diamond anvil cell).
The sample stage will also be improved by introducing extra-fine motion control, for reflectivity and grazing incidence measurements.
The spectrometer bench, which is associated with the microscope, must have the ability of rapid exchange of beam splitter, especially in the case of the low frequency studies of extraterrestrial particles, and the comparison of their absorption spectra with that of the emission spectra collected by ISO.

2- Accessories and added capabilities:

To fully use the potentialities offered by the use of synchrotron–powered IR, several accessories have to be provided to users.

- ✓ High pressure cell, and fluorescence measurement capability (Ar laser, monochromator …)
- ✓ Specific cells for in-situ studies (temperature variation, fluid circulation).
- ✓ Environment: incubator, centrifugator, cryo-microtome
- ✓ Micro-ATR objective: some analysis on cut samples are precluded (especially for precious samples, antique particles or object). The use of a micro-ATR objective allows to probe the near-surface region of an object (evanescent wave –based micro-spectroscopy)
- ✓ Grazing incidence objective: This objective allows detecting monolayers adsorbed on metallic substrate, within few microns square area. Important applications can be achieved in small metallic surfaces, and electronic components
- ✓ Heating and cooling devices, for in-situ study of time-evolved events (polymer, catalysis etc..)
- ✓ Special cell for recirculating the liquid media: this may be crucial for following the chemical composition and structural changes of single cell in biology.
- ✓ Sample preparation is crucial in IR microscopy studies. Users do not have access to special equipment such as cryo-microtomes (preparation of thin samples slices about few microns thick). It is important to have an access to such equipment, (it can, however, be shared with other beamlines).
- ✓ Culture and collection of living cells is crucial for their rapid analysis, and the follow up of their transformation. A dedicated hood for biology, equipped with one incubator and biological-specific handle tools (micropipettes etc..) is essential near the microscope room.
- ✓ A nearby optical microscope, equipped with a CCD camera, phase contrast capability, is important to locate samples prior to their analysis with the IR microscope.
- ✓ 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 microscope)
- ✓ Modification of existing IR microscope for simultaneous fluorescence determination of the high pressure (ruby fluorescence) without motion of the sample.
- ✓ Modified sample stage, to add extra motion for fine alignment, especially for reflection experiments on small particles, and polarization studies (rotation of the sample)
- ✓ Access to a preparation laboratory, with high pressure cell components and dedicated techniques for sample loading
- ✓ Possibility of complementing their IR study with X-ray microscopic study on the same particle (which needs to develop adaptable sample holders for micro-analytical tools at SOLEIL)

3-Electronics, computers and detectors:

A computer room is highly desirable for the infrared community. Data analysis cannot be made “at home” due to the licensed software associated with all spectrometers. Moreover, data storage is important in infrared, and we would need to have access to large data storage (several Gbytes). Moreover, imaging analysis capability will be developed at SOLEIL (they are currently under development at LURE). These analyses would require large access to computers for the users (IR data analysis is much more time demanding that IR acquisition time).

Infrared microspectrometry has been made user-friendly with the advent of new instruments and software controls. Automated stage allows acquisition of mappings without the constant help and assistance of a beamline scientist. The analysis are much more stringent, and requires more expertise and help in the interpretation.
Two permanent scientists (or one permanent and one associated scientist), one engineer, and one technician (shared with the second IR beamline) are requested.

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[i] Proceedings of the 1st European symposium on Atmospheric measurements from space, Vol 1 and 2, ESA earth sciences Division, ESTEC, Noordwijk.

IV- IR-BEAMLINES AT SOLEIL: THE OPTICAL PROJECT.

The radiation produced classically in bending magnets presents various advantages over conventional sources of infrared such as mercury lamps and Globar. Its first asset over globar consists in providing a flux of photons extending down to the far infrared and submillimeter ranges in a limited cone, as opposed to the laboratory source emitting in all space. For this reason, the SR can be considered as a source being approximately 100 times brighter than black body at 1200K . In the longer wavelength range, however, the emission exceeds the standard dimensions of the ring vacuum chambers. Extraction of far infrared from classical bending magnet is therefore very challenging especially in the third generation sources.

In addition to the emission resulting from the transversal deflection in bending magnets or undulators, longitudinal acceleration induces a strongly collimated emission of light mostly concentrated in the lower energy range, known as the edge radiation. The spatial distribution of edge radiation forms a cylindrically symmetric hollow cone and is peaked at smaller angles. Collecting far infrared from edges of bending magnet is therefore more tractable in the third generation sources.

In the following section, we describe the two types of sources, with their characteristics in the mid- and far-IR frequency range. This leads to conclude that the edge radiation-based beamline is well suited for both the microspectroscopy and the far infrared spectroscopy, while only microscopy can accommodate for a bending magnet port, without important modifications of the vacuum chambers. We stress that Edge radiation beamline is our priority to fulfil the needs for this joined Infrared Project (far-IR and microscopy).

IV-1: The source.

This section is directed towards the source characterization, e.g. calculation of the number of photons per unit of time (sec), and per unit of radiative surface and solid angle emitted at the synchrotron storage ring within a well-defined percent of the energy bandwidth (bw, usually 1%).

In the following, we have calculated the performances (in terms of flux and brightness) for infrared photons emitted from two types of source: bending magnet and edge radiation, considering the existing constraints in the machine design and the possible modification of the vacuum chambers and hexapoles.

At this point, there is an important parameter characterizing the SR-source: the natural divergence. This quantity basically describes the spatial distribution of synchrotron radiation as a function of the photon-energy or wavelength. The natural divergence is quite small for small wavelengths, but becomes much larger at higher wavelengths (far-IR region) , introducing important constraints in the collection optics. In the IR region, the natural divergence is very well approximated by the expression:

$$\sigma_n = 0.511\left(\frac{\lambda}{\lambda_c}\right)^{0.33}\frac{10^{-3}}{E(GeV)}$$

where E is the synchrotron energy and λ_c the critical wavelength. The edge source natural divergence has been evaluated by two times the angle of maximum emission as described further.

Fig IV-1 shows the natural divergence at SOLEIL, versus the wavelengths, together with the optimum angle for collecting the maximum intensity in the case of edge radiation [⊗]

[⊗] The optimum collection angle for the edge radiation has been calculated, using the formula $2\xi_{ER} = 4\sqrt{\frac{\omega}{d}}$, where d is the distance from the source (2.3 meters at SOLEIL)

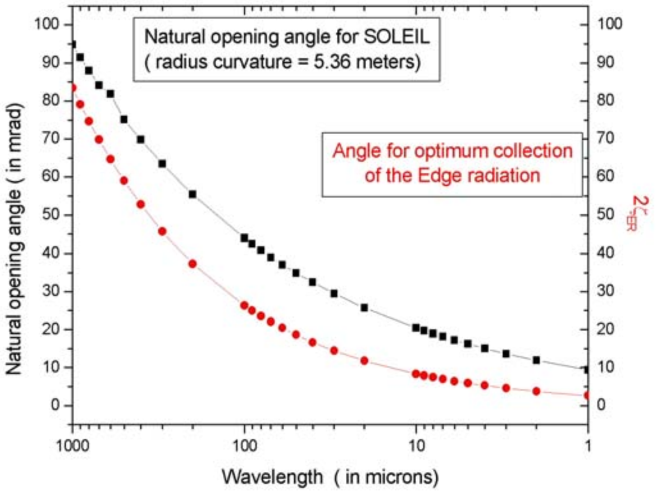

Fig IV-1: Natural divergence and angle for optimum intensity of Edge Radiation versus the wavelength, at SOLEIL.

This natural divergence angle introduces severe constraints in beamline design when one tries to optimise the collection of long wavelength photons using a bending magnet source. It can be seen, on Fig IV-1 ,that the edge radiation provides a better solution to collect long therefore discuss, in turn, bending magnet and edge radiation as IR sources, and their performances for both far-IR and microscopic beamlines.

1/ Bending magnet:

One possible extraction port for such a purpose has been identified as 1° port on bending magnets of cells C01, C02 and C03 of Soleil .
In order to carry out calculations of the flux and brightness expected for such geometry, we used a comprehensive program based on the calculations published in ref.1. The program can calculate the total flux output and the maximum brightness using radiation natural opening angle. An etendue can be entered and the signal calculated. The intrinsic horizontal and vertical source size are entered, and the source sizes due to projection and diffraction are calculated. Bessel function of order 1/3 are calculated for light polarized perpendicular to the orbit plane, and of order 2/3 for light polarized parallel to the orbit plane. The brightness is then the ratio of the emitted flux by the emittance.
For the following calculation, we choose an etendue of 1 mm^2. There are three scenarios for extracting the beam:

1- A geometry defined by the crotch which must be redesigned for larger apertures: Θ_H= 50 mrad and Θ_V = 10 mrad
2- Modifying hexapole H6 (increasing its opening slit from 20 to 26 mm), delivering Θ_H= 50 mrad and Θ_V = 13 mrad
3- Modifying both the vacuum chamber , and the hexapole H6 up to 35 mm , giving Θ_H= 50 mrad and Θ_V = 17 mrad.

We have calculated the flux and brightness for these three cases, and compared with the calculations carried out for two best competitive IR microscopic beamlines: NSLS (beamline U10B)[18] and ALS (beamline BL1.4.3)[19].

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[18] G.L. Carr, O. Merlo, M. Munsli, S. Pringerand, S.C. Ho *SPIE* **3775**(1999) 22.
[19] Michael C. Martin and Wayne R. McKinney" The First Synchrotron Infrared Beamlines at the Advanced Light Source: Microspectroscopy and Fast Timing", *Proceed. Mater. Res. Soc.*, **524**, 11 (1998).

The parameters that have been entered into the calculations are reported on Table IV-1:

Facility	Energy (GeV)	Collection geometry (HxV) mrad	Radius of curvature (meters)	Intrinsic source size (HxV) microns
SOLEIL	2.75	50x10 , 50x13 and 50x17	5.36	53x37
ALS (BL1.4.3)	1.9	40x10	4.9	70x50
NSLS (U10B)	0.8	40x40	1.91	900x300

Fig IV-2 and IV-3 display the calculated flux and brightness respectively at SOLEIL, for the three conditions, and for an electron beam of 400 mA, together with the values calculated for ALS (current 400 mA) and NSLS (current 1000 mA).

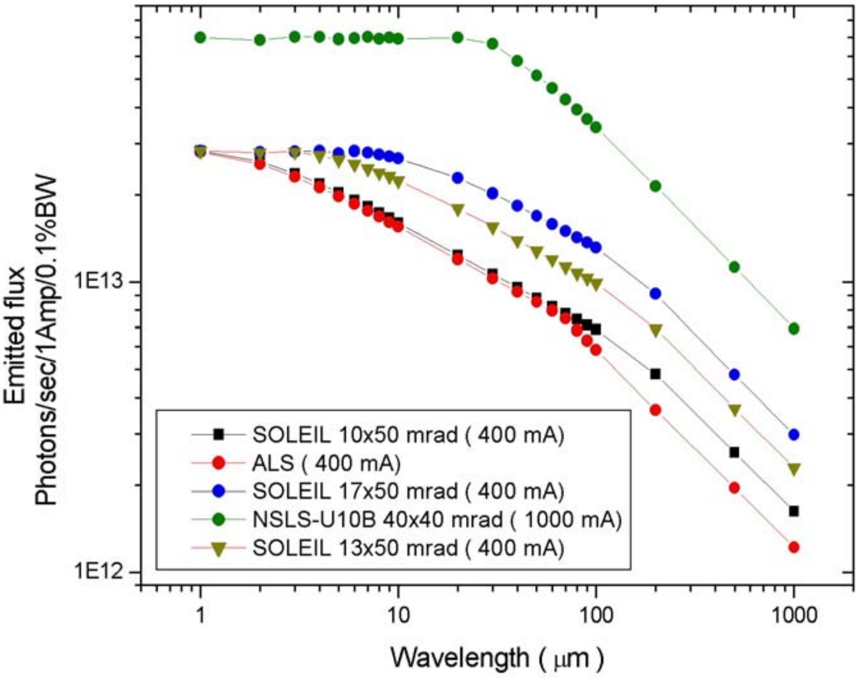


Fig.IV-2: Emitted flux for bending magnet source on 1° beamline ports at SOLEIL (I=400 mA), compared to U10B beamline at NSLS and BL1.4.3 beamline at ALS

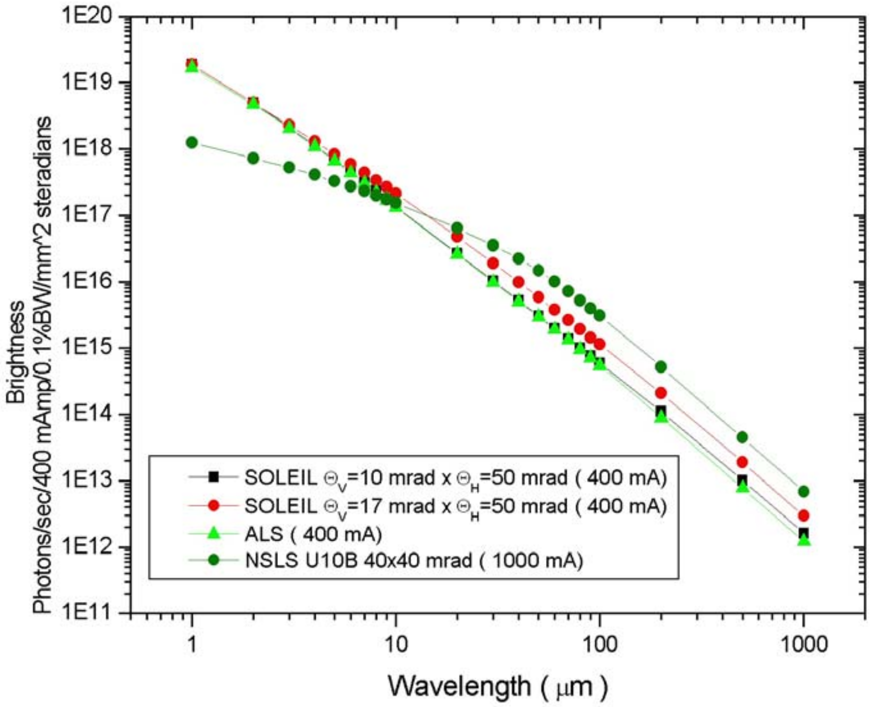


Fig.IV-3: Brightness for bending magnet source on 1° beamline ports at SOLEIL (I=400 mA), compared with that of the NSLS and ALS.

Considering that most of the infrared studies in microscopy focus on the 2.5- 20 microns wavelength region, the collection geometry of HxV= 50x10 mrad, achieved on 1° beamline port, with standard apertures after redesigning the crotch is well adapted for synchrotron IR microscopy, making the performances at SOLEIL internationally competitive.

However, it is important to note that this geometry is not appropriate for a competitive far-IR beamline. Therefore, the need for an alternative source, namely edge radiation, is developed hereafter.

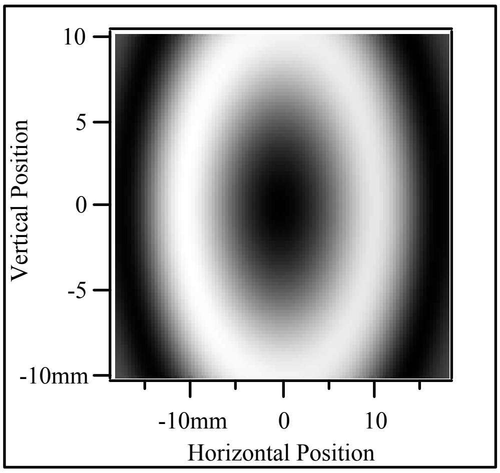
It is important to note that IR microscopy can accommodate either bending magnet or edge radiation.

2/ Edge Radiation:

In addition to the emission resulting from the transversal deflection in bending magnets or undulators, longitudinal acceleration can produce a strongly collimated emission of light mostly concentrated in the lower energy range.

The so-called Edge Radiation (ER) is the result of a sudden change of the longitudinal velocity when charged particles enter or exit a magnetic element. This emission has been theoretically studied and it is now possible to predict both spectral and spatial distribution with excellent accuracy (Notice that a computer code is freely available for the valuation of the distribution of infrared flux from various magnetic field devices. [i]

The spatial distribution of edge radiation as calculated by this software is presented on the figure above. It forms a cylindrically symmetric hollow cone and is radially polarized, the angle of maximum emission opens up for increasing wavelength. At λ, the cone peaks at an angle $\theta=(\lambda/R)^{1/2}$, with respect to the straight section axis. Numerical evaluations based on an integration of such spatial distribution are presented further.



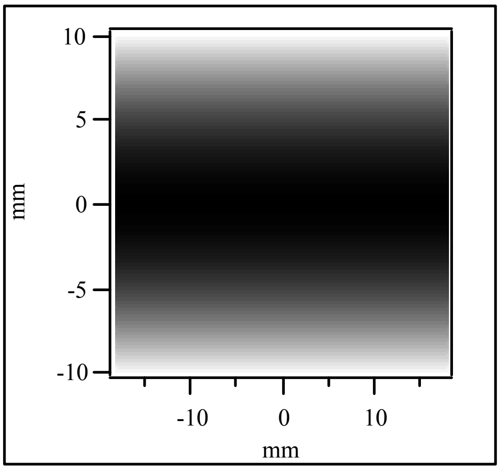


Fig 2

Fig 1 Intensity distribution at 100 microns for a dipole (left) and an edge measured at 2.3 m from the source point. The dipole presents a uniform distribution in the horizontal plane, the edge presents a cylindrical distribution.

An experimental confirmation of this spatial distribution was provided recently on the Edge based beamline at the Anka facility and in described in Annex 4.

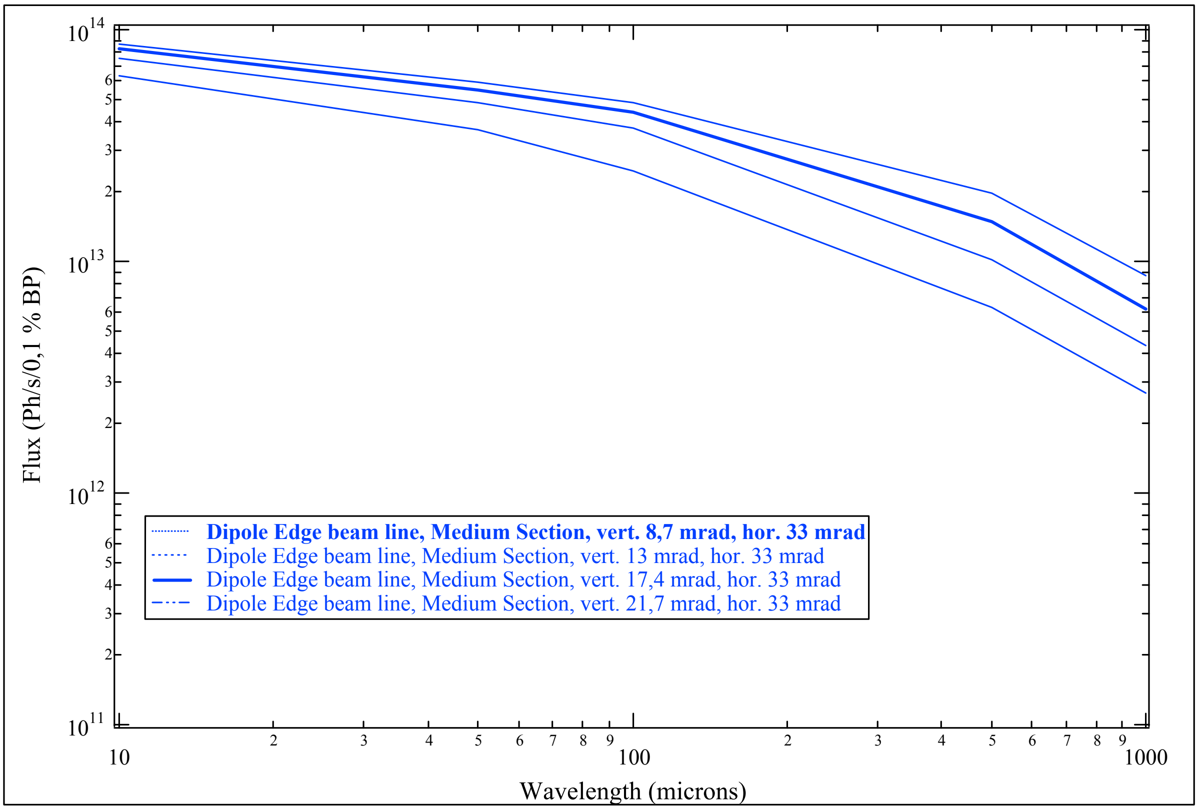
Using SRW, the flux collected in various solid angles are presented for the edge emission resulting from a bending magnet collected downstream of a straight section (See figure 2). The various solid angles correspond to various levels of modifications of the vacuum chambers and hexapoles.

For the first and second cases, both the slit in the dipole chamber and the hexapole H6 spacing are increased respectively at 9 mm and 30 mm, allowing collection angles of: Θv (up to) 13 mrad and Θh= 33 mrad for the edge and of Θ_H= 50 mrad and Θ_v = 10 mrad for the dipole.

For the third and fourth case the crotch and the hexapole H6 spacing are increased respectively at 12 mm and 40 mm, allowing collection angles of: Θv (up to) 17 mrad and Θh= 33 mrad

This set of curves illustrates the need for large collection angle and suggest clearly that the edge emission is better adapted for the far infrared range. It should also be noticed that, when collected downstream from a straight section, interference between the edges at the upstream and downstream ends of a straight section of length L causes the change in slope between 100 and 1000 cm-1. This interference is certainly over-estimated in the SRW software, which is based on the assumption of two sources interfering freely in space before being both limited by the collecting optics. The real situation would be better described by a largely masked upstream source (with emission greatly limited by the narrow wall of the vacuum chamber) interacting with the well collected downstream source As this can not be taken into account with the current version of the SRW software, the calculations of brilliance cannot be made.

Another advantage(s) of edge emission lies in its intrinsic energy-limited range of emission, minimizing the heating of the optics caused by the higher energy part of the radiation. Thanks to this limited power, one may not need to mask the central zone of the extraction mirror in contrast with the constant field emission where either a slot or a mask is mandatory to handle the power load.



IV-2 Beam transport and collection optics

1. Far Infrared beamline

A far infrared beamline can be subdivided into four parts: - extracting optics which together with the port will set the collected angle, - the transport line under UHV which ends with a window, - the transport line under secondary vacuum, - the spectroscopic station.

The extracting optics are composed of a mirror whose size and position allow the collection of a solid angle as large as possible of either the emission from the constant field region and / or the emission from the edge of a bending magnet. Alternatively the edge emission may be collected together with an important contribution from the constant field region of the downstream dipole. A major challenge with the extraction optics is the very high heat load caused by the higher energy part of the spectrum. As mentioned previously, the edge allows a minimization of the heating but on higher energy machines, getting rid of this heat is mandatory. Although the full characterisation of this optics is not been fully made yet, we recommend to reproduce the solution developed at the ANKA facility: an extracting mirror made from a 7mm thick Beryllium block placed on a cooled copper block. As, Be is transparent to x-rays it allows again to minimize the portion of heat load on the mirror. Between the two materials (Be and Cu), a sheet of indium provides a good thermal exchange with the water-cooled copper block. Alternative options have been chosen in other facilities: the mirror presents either a slit in the middle allowing most of the high energy photons (emitted in smaller angles) to pass through or a mask in front of the small angle region. Both solutions imply a masking of the small angle and therefore losses of intensity that may be important in the mid infrared region.

The second part of an IRSR beamline includes a set of mirrors allowing the transport and the focusing of the beam onto a window separating the UHV ring vacuum from the secondary vacuum. This window which clearly needs to be transparent in the infrared is generally wedged to avoid multiple reflections and their associated multiple images that are especially detrimental in combination with Interferometry techniques. In most new beamlines, this window is made of CVD diamond. Refocusing optics can be made of elliptic, cylindrical or spherical mirrors.

The third part of the beamline starts after the window and is again composed of an ensemble of mirrors whose function is to transport the beam to the spectroscopic station. By placing two identical mirrors on both parts of the focus point, one minimizes the degradation of the image caused by the use of off-axis reflections.

2- Infrared microscopy beamline:

On mid infrared beamline for spectromicroscopy the beam is usually, first reflected by a water-cooled mirror and focused, using an approximate f: 1 ellipsoid or off axis spherical/toroidal mirror, onto a UHV compatible diamond window. Compared to an X-ray beam, this transport is more " flexible", in terms of steric constraints inside the tunnel. Beam can be deviated towards the top, and get around components such as magnets etc… The proper design for extraction will be made after a thorough consideration of the space availability around the front end.

Up to the diamond window, several UHV pumps and valves are set, as usually installed in all other front ends. After the diamond window, the beam should be collimated in order to be transported to the spectrometer, generally located several tens of meters away. Off axis spherical, and a pair of cylindrical mirrors, will be used. Each of them will be finely tuneable by computer controlled step motors, to compensate for any drift of the orbit between injections. The transport of the beam from the diamond window to the spectrometer requires a rough vacuum, in order to avoid adsorption of the beam by the ambient water and CO_2. Two two-axis tip/tilt mirrors, which direct the beam onto the interferometer, equipped with position optical sensors, will serve as active feedback for reducing noise from beam motion. (ALS 1999 Activity Report pp. 78-79).

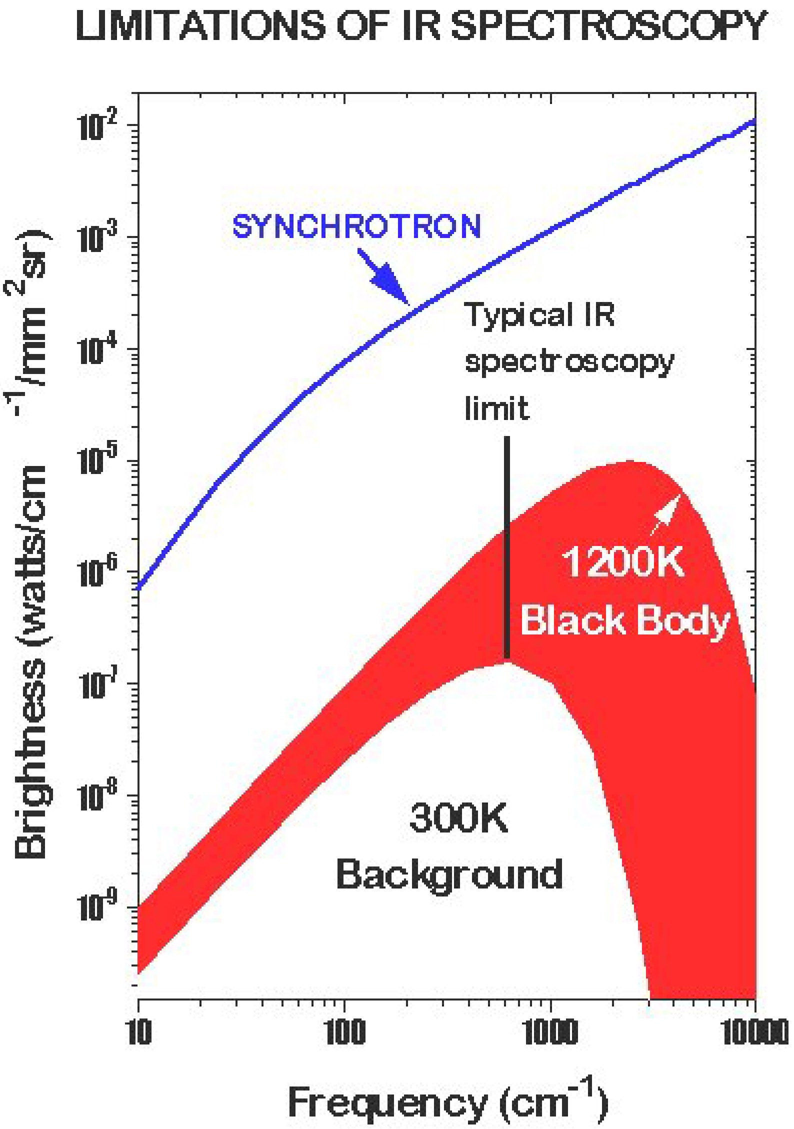
Annex 1

Synchrotron Infrared beamlines: updated July 2001

Synchrotron facility	*Energy (GeV)*	*Operating*	*Under construction or planned*	*Extraction*	*Collecting geometry (vertical x horizontal) mrad total*	*Scientific Programme*
SRC- Daresbury (England)	2	1	1	B M	60x60	Far-IR Microscopy
ALS-Berkeley(USA)	1.5-1.9	1	3	B M	10 x 40	Far-IR Microscopy
SurfII-NIST- Gathebourg (USA)	0.28	1		B M	70x70	Microscopy
NSLS-Brookhaven(USA)	0.8	6		B M	U2A(40x40) U2B(40x40) U4IR(90x90) U10A(40x40) U10B(40x40) U12IR(90x90)	Time resolved Millimeter region Microscopy Far-IR
Aladin-SRS-Wisconsin (USA)	0.8-1	1		Edge Radiation		Microscopy Far-IR (foreseen)
Max-Lab I and II(Sweden)	1.5	1	1	B M	60x100	Far-IR , Microscopy
UVSOR (Japan)	0.75-1	2		B M	60x80	Far-IR
SINBAD-Dafne-(Italy)	0.51		1	B M	50x50	Microscopy Far-IR
SRRC (Taiwan)	1.3-1.5		1	B M	60x90	Microscopy Far-IR
NSRL (China)	0.8		1	B M	-	-
Bessy II (Germany)	1.7		1	B M	30 x 60	Microscopy Far-IR
Spring-8 (Japan)	8	1		B M	15x 36.5	Far-IR
Saskatoon (Canada)	2.5-2.9		3	B M	58x58	Microscopy Far-IR
ANKA (Germany)	2.5	1		D E	10x30	Microscopy Far-IR
LURE (France)	0.8	2		B M and D E	18x45	Microscopy Far-IR
SLS (Switzerland)	2.1		1	B M	10x30	Microscopy Far-IR
DELTA (Dormund)	1.5		1	-	-	-
HELIOS-1 (Jlab-FEL-USA)			1	-	-	Microscopy
HELIOS-2 (Singapore)			1			
Elettra (Italy)	2		1	-	-	Microscopy Far-IR
Campinas (Brazil)	2		1	-	-	-
SAGA (Japan)			1	B M	-	Spectroscopy and microscopy- Mid-IR
Elettra (Italy)			1	Bending Magnet	-	Spectroscopy and microscopy- Mid-IR

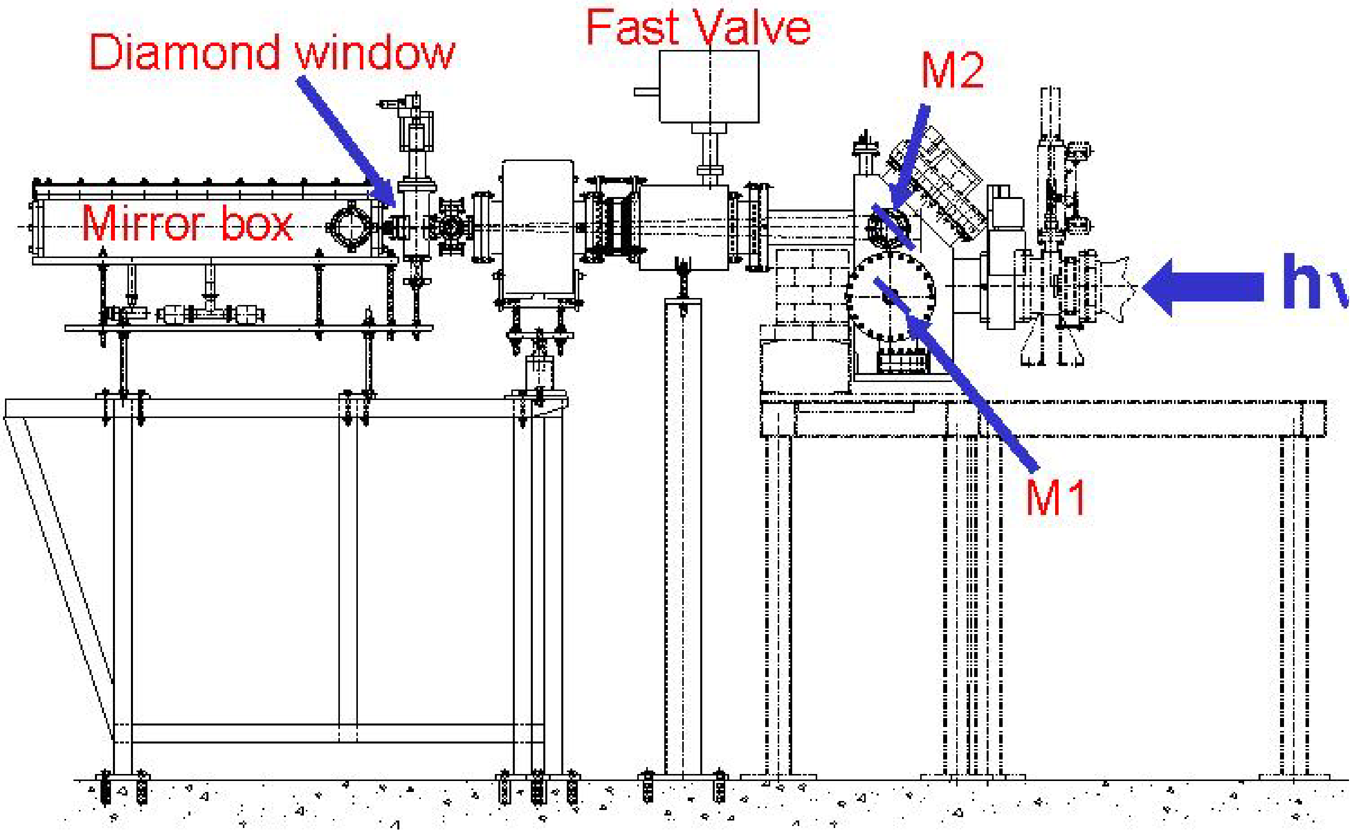
Annex 2

Comparison of synchrotron radiation and conventional source, over the infrared region



Annex 3

Schematic of a typical beamline transport



Annex 4

Measurements and calculations of synchrotron Infrared emission

Measurements of edge and constant field synchrotron Infrared emission

Measurements of edge and constant field synchrotron Infrared emission

The infrared beamline of the 2.5 GeV Anka facility (responsible: Y.L. Mathis) exploits both the edge emission together with a significant contribution from the constant field emission (collection angle: 15 mrad in the vertical direction and 30 mrad of horizontal angle.
An experimental comparison of the intensity and spatial distribution of both types of sources was performed recently. The Figure 1 is a photograph obtained with an infrared camera sensitive to the mid infrared (7-14 microns). On this picture, one recognize clearly the typical cylindrical distribution caused by the edge source next to the uniform intensity originating from the constant field source. Figure 2 is the result of the integration in the vertical directions of the pixels included in the rectangle. These measurements confirm clearly the advantage of edge source in terms of flux and show that the interference pattern is clearly not fully destructive as the central shaded zone is less pronounced that the predictions.

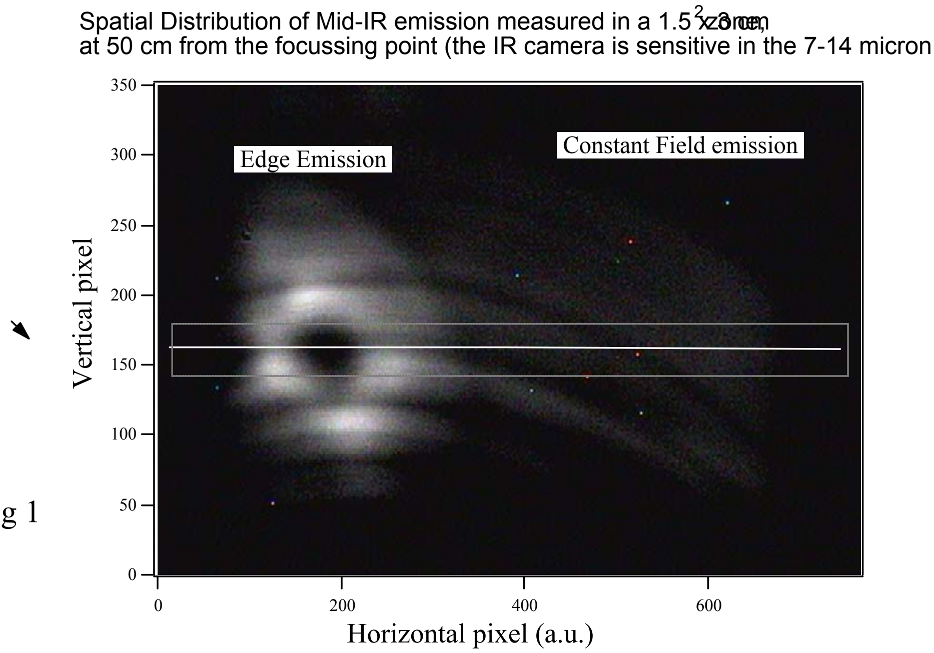
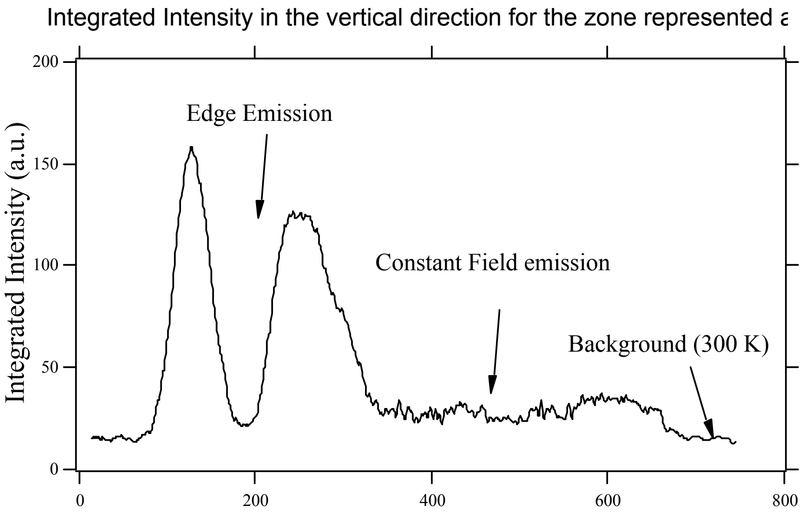

Spatial Distribution of Mid-IR emission measured in a 1.5 x 3 cm^2 zone, at 50 cm from the focussing point (the IR camera is sensitive in the 7-14 micron

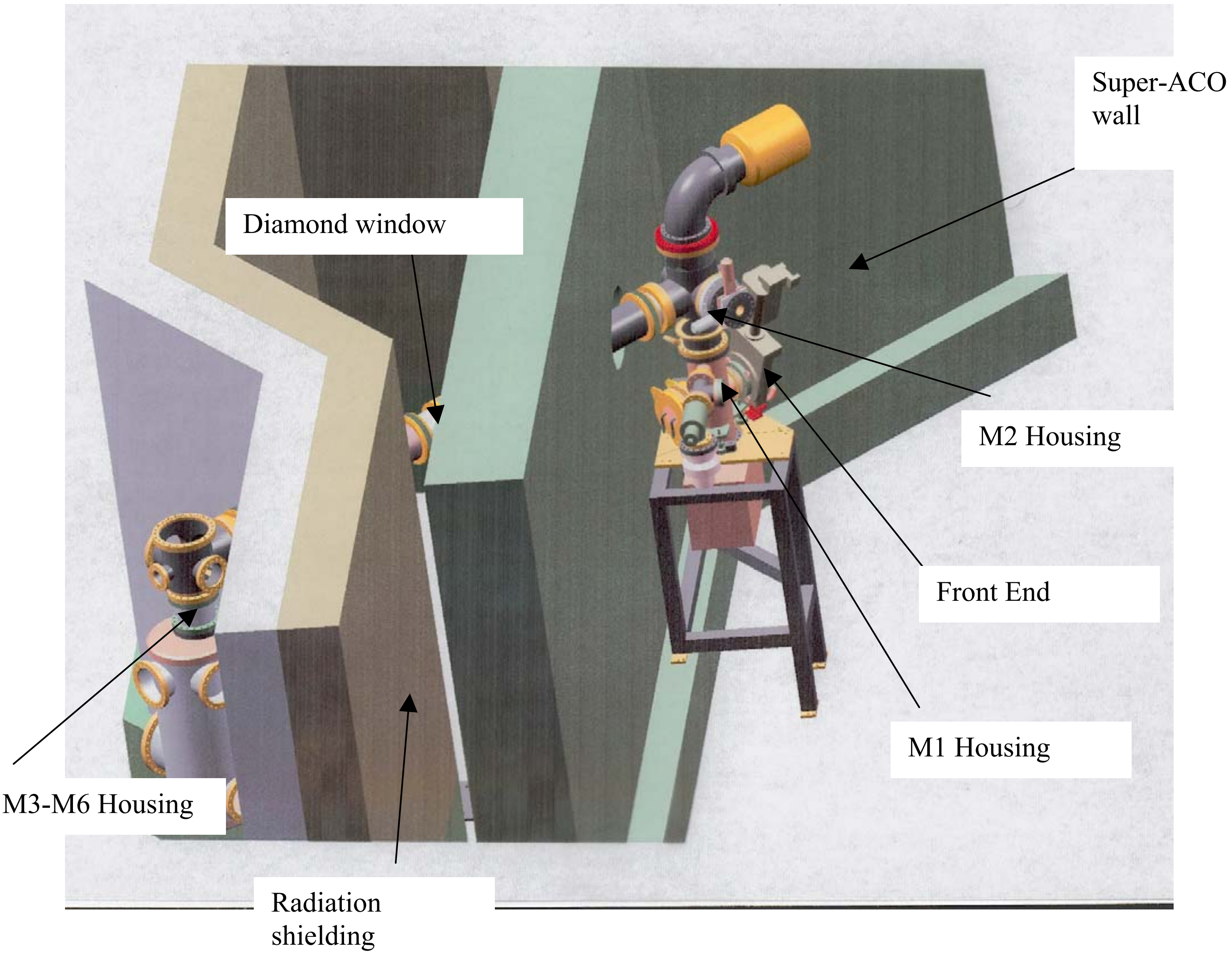
Fig 1


Integrated Intensity in the vertical direction for the zone represented a

An experimental confirmation of this spatial distribution was provided recently on the Edge based beamline at the Anka facility (responsible: Y.L. Mathis). This beamline is installed on a 2.5 GeV and allows the extraction of both the edge emission together with a significant contribution from the constant field emission. Figure 2 is a photograph obtained with an infrared camera sensitive to the mid infrared (7-14 microns). On this picture, one recognize clearly the typical cylindrical distribution caused by the edge source next to the uniform intensity originating from the constant field source. Figure 2b is the result of the integration in the vertical directions of the pixels as represented by the rectangle. In brief, these measurements confirm clearly the advantage of edge source in terms of flux and show that the interference pattern is clearly not fully destructive as the central shaded zone is less pronounced that the predictions.

Annex 5

The SU-1 Sirloin II beamline



The layout of the far infrared beamline under development at LURE is reproduced here. The source is the dipole edge SU1. The radiation extracted from the straight section is limited by the entrance slot to a solid angle of 14 (vert.) x 42 (hor.) mrads. It is collected upward by the plane extraction mirror 1. Then, a toroidal M2 focuses the radiation onto the natural diamond window recuperated from SIRLOIN, this 10 mm useful diameter; window separates the UHV part of the beamline from the high-vacuum part. Mirror 3 is another toroidal mirror, while mirrors 4 and 5 are flat mirrors bringing the beam close to the interferometer. Mirror M6 is a paraboloid, which focuses the beam on the entrance pupil of the interferometer. All these mirrors will be placed in vacuum chambers and will be aligned using high precision translator as described in annex 8.
The design of a far infrared beamline at SOLEIL has to be made, but it seems likely that many of these elements can be used.

Annexe 6:

References related to synchrotron Far IR spectroscopy

Synchrotron Radiation sources :

"Spectral distribution of infrared synchrotron radiation by an insertion device and its edges: A comparison between experimental and simulated spectra".
P. Roy, M. Cestelli, O. Marcouillé, A. Paolone, P. Giura, Y.-L. Mathis and A. Gerschel, *Phys. Rev. Lett. 84 (2000), 483.*

"New higher brilliance sources of infrared synchrotron radiation"
P. Roy, Y.-L. Mathis, A. Paolone, P. Giura, B. Tremblay, A. Nucara, S. Lupi, P. Calvani, and A. Gerschel*, in " Infrared Synchrotron Radiation" , Editeur: P. Calvani and P. Roy, Nuovo Cimento Press (1998), 415.*

"Magnetic field discontinuity as a new brighter source of infrared synchrotron radiation"
Y.-L. Mathis, P. Roy, B. Tremblay, A. Nucara, S. Lupi, P. Calvani, and A. Gerschel*, Phys. Rev. Lett. (1998), 80(3).*

" New higher brilliance sources of infrared synchrotron radiation: toward an edge radiation undulator "
P. Roy, O. Marcouille, A. Paolone , P. Giura and A. Gerschel*, Proceedings of the 12th International Conference on Fourier Transform Spectroscopy, ", Waseda University Enterprise Press (WUP), (2000).*

Far Infrared spectroscopic studies:

«Evidence of two species of carriers from the far infrared reflectivity of Bi2Sr2CuO6 "
. S. Lupi, P.Roy, P. Calvani and M. Capizzi,. *Phys. Rev. B. 62 (18), 12418. (2000).*

Dependence of Water Dynamics upon Confinement Size,
J.B. Brubach, A. Gerschel, V. Stradler, M.P. Kraft and P. Roy*, J. Phys. Chem. B, 105, 430 (2001).*

« Infrared investigation of water encapsulated in non ionic reverse micelles »
J.-B. Brubach, A. Mermet, A. Filabozzi, P. Colavita, A. Gerschel and P.Roy*, Journal de Physique VI, 10, (2000), Pr7-215.*

"Submillimeter and Infrared Spectroscopy on La0.85Sr0.15MnO3",
Paolone A., P. Roy, A. Pimenov , G. Rousse, A.A. Mukhin *Eur. Phys. J. B 16, 245, (2000).*

« The Complete Infrared Phonon Spectrum of pure and doped LaMnO3",
Paolone A. , P. Roy, A. Pimenov , A. Loidl, O. Melnikov, A. Y. Shapiro. *Phys. Rev. B 61, 11255 (2000).*

"Energy with increasing doping in Nd2-xCexCuO4-y"
S. Lupi, P. Maselli, M. Capizzi, P. Calvani, P. Giura and P. Roy, *" Collapse of the Polaron, Phys. Rev. Lett, 83 (23)(1999) 4852.*
" Infrared Spectroscopy Investigation of the charge ordering transition in LiMn2O4".

A. Paolone , P. Roy, G. Rousse, *Solid State Comm 111 (1999) 453.*

« The near infrared spectrum of Solid Silane”
Nucara, P. Calvani, S. Lupi and P. Roy, J. Chem. Phys., 107 (17), (1997), 6562.

« Synchrotron radiation used for Far Infrared Studies”,
Roy , Y.-L. Mathis, S. Lupi, B. Tremblay, A. Nucara, A. Tadjeddine and A. Gerschel, *Ferroelectrics 176, (1996), 261.*

“Polaron bands in the far and mid-infrared Spectra of e-doped cuprates”, in Polarons and bipolarons in High Tc Superconductors and related materials Calvani, S. Lupi, Roy P., M. Capizzi, P. Maselli, A. Paolone, W. Sadowski and S.W. Cheong, P. Dore, G. Paleologo, G. Balestrino, M. Marinelli, E. Milani, H. Berger, *edited by K. E. Salje et al, Cambridge University Press, (1995), 133*

“Cation-carbon stretching Vibration of Adducts formed upon CO adsorption on Alkaline zeolites”
C. Otero Arean, G. Turnes Palomino, A. Zecchina, G. Spoto, S. Bordiga and P. Roy, *Phys. Chem. & Chem. Phys., 1 (1999), 4139.*

References related to synchrotron IR microscopy

“Profiling lipids across Caucasian and Afro-American hair transverse cuts, using synchrotron infrared microspectrometry”
L. Kreplak , F. Briki , Y. Duvault, J. Doucet, C. Merigoux , F. Leroy , J.L. Lévêque, L. Miller , G.L. Carr ,G.P. Williams and P. Dumas. *International journal of Cosmetics Science.* 23 1-6 (2001).

“The Impact of Infrared Synchrotron Radiation in Biology: Past, Present and Future“
L.M. Miller, G.L. Carr, M. Jackson, P. Dumas and G.P. Williams
Synchrotron radiation News vol. 13, (5) (2000) 31-38.

“Synchrotron infrared microscopy of micron-sized extraterrestrial grains”
P. I. Raynal, E. Quirico, J. Borg, D. Deboffle, **P. Dumas**, L. d 'Hendecourt, J. -P. Bibring and Y. Langevin *Planetary and Space Science,* Volume 48, Issues 12-14, October 2000, Pages 1329-1339

« Chemical Applications of Synchrotron Radiation"
P. Dumas and G.P. Williams in “ Chemical Applications of Synchrotron Radiation” Advanced Series in Physical Chemistry Vol 12 (2001) World Scientific

“Enhancing the lateral resolution in infrared microspectrometry by using synchrotron radiation: applications and perspectives”
Paul Dumas , G. L Carr and Gwyn P. Williams Analysis,28(1) (2000)pp 68-74

“Optical design and performance of the IR microscope beamline at SUPERACO-France”
F.Polack, R. Mercier, L.Nahon, C.Armellin, J.P. Marx, M.Tanguy, M.E.Couprie, P.Dumas, SPIE, Eds : P.Dumas and G.L. Carr Vol.3575 (1999) 13.

“Two-color experiments combining the UV storage ring free-electron laser and the SA5-IR beamline at Super-ACO”
L.Nahon, E.Renault, M.E.Couprie, D.Nutarelli, D.Garzella, M.Billardon, G.L.Carr, G.P.Williams, and P. Dumas SPIE, Eds : P.Dumas and G.L. Carr Vol.3575 (1999) 145.

"Synchrotron Infrared Microspectrometry applied to Petrography in micrometer-scale range: fluid chemical analysis and mapping"
N. Guilhaumou, P.Dumas, G.L. Carr and G.P. Williams
Applied Spectr. 52(8)(1998) 1029.

" Highly resolved chemical imaging of living cells by using synchrotron infrared microspectrometry "
N.Jamin, P. Dumas, J. Moncuit, W.-H. Fridman, J.L. Teillaud, G.L.Carr, and G.P. Williams
Proceedings of the National Academy of SciencesVol. 95, Issue 9, 4837-4840, April 28, 1998

" Applications of Infrared Microspectroscopy to Geology, Biology, and Cosmetics"
J.-L. Bantignies , G. L. Carr, P. Dumas, L. Miller and G. P. Williams
Synchrotron radiation News 11(4) (1998) 31.

[ii] Computer code by O. Chubar and P. Ellaume : www.esrf.fr/machine/support/ids/Public/Codes/SRW/srwindex.html