Infrared synchrotron radiation spectroscopy and microspectroscopy: new tools for interdisciplinary applications

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Abstract Synchrotron radiation sources, whose number is steadily increasing, are undoubtedly the most powerful and brilliant sources in the X-ray range. Although the synchrotron emission covers with high brilliance also the infrared region, its use in this energy range has developed at a much slower rate. Nowadays, after a couple of decades of attempts, the aim of extending the unique performances of the synchrotron source to the infrared domain is achieved by several dedicated beamlines in different countries. With their high-brilliance, polarized and broad-band radiation one may perform experiments that are out of the range of conventional sources from the near-IR up to the far-IR range.

Keywords Infrared spectroscopy, Synchrotron radiation, Beamlines

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1 Introduction

Observations and studies of the interaction of e.m. radiation with matter, in the framework of the linear theory, have provided us with much of our knowledge of the world surrounding us. This is certainly true for the X-ray region of the radiation spectrum. This is also true since the nineteenth century,[1] for a non-ionizing radiation like infrared radiation. Actually, infrared spectroscopy probes the rotations and the vibrations of molecules (their “finger-print” spectral region), the low-energy excitations of solids (phonons, excitons, polarons, etc.), the forces between a surface and an adsorbate, and many other low-energy phenomena of basic importance for condensed matter physics, chemistry, biophysics, and materials science.

In the last few decades, important developments enabled one to improve the spectroscopic methods of the non-visible region, and particularly of the infrared region of the spectrum. Chemists discovered IR spectroscopy in the 60s of the last century and began to investigate ever more complex molecular structures. In the same years a giant step in the detection of infrared spectra was made with the introduction of Michelson interferometers coupled to computers able to perform in a short time Fourier-transforms. The physicist Gerhard Herzberg played a crucial role in the evolution of IR spectroscopy and was awarded with the 1971 Nobel Prize in Chemistry. The 70s witnessed a revolution that has continued ever since, as Fourier transform spectrometers became available to an ever-broader cross-section of the scientific community.

Until mid-eighties the only broad-band IR radiation sources available were those of the early experiments, namely globars or mercury lamps. The emittivity of a globar, which can be roughly approximated by that of a black body heated to 1500 or 2000 K, is peaked at $\lambda \approx 5$ μm, and decreases rapidly for $\lambda > 20$ μm, the crucial region of the far infrared where mercury lamp has slightly better performances. Moreover, just a small fraction of the power emitted by these sources on a 4π solid angle can be focused on the sample. Moreover, the spectra collected with conventional sources are affected by a poor signal-to-noise ratio whenever the experiment is made under non-standard conditions or on small samples.

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Today, a wide variety of spectroscopic methods and photon-scattering experiments are basic tools for research in physics, chemistry, biology and medicine. Modern spectroscopies and applications demand a high source stability, like in differential spectroscopy, or a large angle of incidence, as in surface science, or a small spot, as in infrared microspectroscopy and in experiments at high-pressure. Although the development of the techniques, of the sources and of the instrumentation allowed infrared spectroscopy to become one of the most applied characterization techniques in industry and in many technological processes, the demand of intense and brilliant sources oriented the research towards synchrotron radiation storage rings. Indeed, Fourier-transform spectroscopy requires a broad-band source. Synchrotron radiation sources not only fulfill these requirements, but also exhibit a high brilliance over a “white” spectrum, polarization properties and the absence of thermal fluctuations.

2 A short history

Nowadays infrared synchrotron radiation (IRSR) is growing at a fast rate and the increasing demand of new beamlines emerges in the most industrialized countries. However, although suggested for the first time in 1966[2] and then in the early 70’s[3] in the USA, the use of IRSR developed at a low rate. This has been mainly due to technical reasons associated with the difficulty to manufacture large optical elements capable both to collect a large solid angle and to withstand the power load of the synchrotron sources. Another reason has been to the spectacular development of SR in the UV and X-ray domain, because the lack of intense and brilliance sources in these energy ranges heavily engaged the scientific and budgetary effort of the research institutions in these decades.

The first attempts aimed at extending the use of the synchrotron source to the infrared date back to the seventies, when pioneering observations were made at Stoughton by Stevenson and coworkers[3] and at Orsay by Lagarde and coworkers.[4] However only at the beginning of the 80's, a port dedicated to the extraction of IRSR was built on the ring of Daresbury by Yarwood.[5] After several attempts, this project was paused for a few years. One of the young member of the original Daresbury team, Takao Nanba, coming back in Japan in 1985 started the construction on the UVSOR ring, one of the first synchrotron radiation dedicated rings, of the first IRSR beamline that later opened to users.[6,7] Almost contemporary measurements of the characteristics of synchrotron radiation in the infrared region have been investigated at BESSY using Fourier spectroscopy.[8] A couple of years later, in 1987, Gwyn Williams inaugurated the first infrared beamline in the USA, at the NSLS ring at Brookhaven.[9] This initiative triggered a rapid development of the IRSR in the USA and other beamlines were realized. The first IRSR European beamlines were installed and commissioned in the early 90's at Lund (Sweden) by Bengt Nelander on MAX,[10] at Orsay by Pascale Roy and coworkers on the SUPERACO ring[11] while at Daresbury the new IR group led by Michael Chesters[12] restarted the IRSR research using the available second generation synchrotron radiation SLS ring.

What are the main reasons of success of the infrared synchrotron radiation in these last years? Actually, in the infrared region, energy of the electron beam (for E>0.5 GeV) does not affect the synchrotron radiation spectral distribution, while intensity is proportional to the current circulating in a storage ring. As a consequence almost all rings are equivalent in term of infrared emission and current and stability, which both increased significantly in these last years, represent the qualifying parameters. To summarize, an ideal infrared source to be used for spectroscopy and micro-spectroscopy is a low emittance, stable low energy storage ring with high current (>1 A) possibly working in topping up mode. Starting from these consideration, when in the early nineties in Frascati a new project for a low energy, high current collider was approved, we proposed the construction of SINBAD, a dedicated IRSR beamline.[13] At Frascati, the previous synchrotron radiation source operational at 1.5 GeV, ADONE, was dismantled in 1994, for leaving place to the new collider DAΦNE. Designed to work with high current (> 1 A) and at low energy (0.51 GeV), it was and is an ideal source of infrared radiation. The optical layout of SINBAD (Synchrotron INfrared Beamline At DAΦNE) was calculated applying for the first time the ray-tracing simulation techniques, typical of the UV and X-ray range, to the infrared domain.[14] The Istituto Nazionale di Fisica Nucleare started the construction of SINBAD in 1997. The experimental apparatus, including a Michelson interferometer suitably modified for high-vacuum operation (1.33 mPa), an infrared microscope, high-pressure cells, and several detectors, is the result of the cooperation between the Laboratori Nazionali di Frascati and the Department of Physics of University La Sapienza that funded and installed the instrumentations.

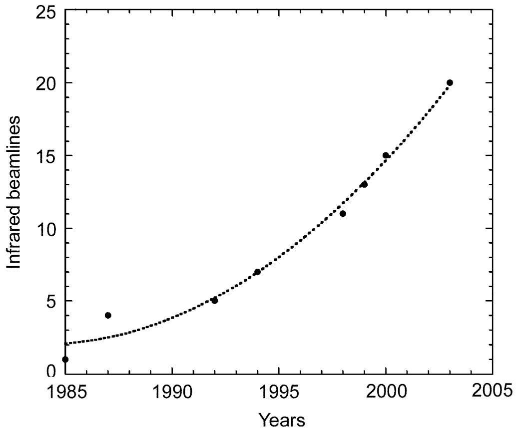

Fig.1 Evolution with time of the number of infrared beamlines in the world. The beamlines in commissioning or in construction are included.

All around the world other IR beamlines come later and nowadays there are more than fifteen dedicated IRSR beamlines in the world (see Fig.1). Most of them have been installed in the USA (up to six at Brookhaven, in addition to those of Berkeley and Stoughton), in a context of growing interest of industrial users for infrared microscopy. In spite of the pioneering experiments made in France, Britain and Germany in the seventies, in Europe the development of IRSR has proceeded at a slower rate. However, in order to fill the gap with USA and Japan in this field, in 1995 the European Union has funded a network coordinated by the Department of Physics of University La Sapienza. The network was aimed at providing a forum for the European groups involved in the realization and the exploitation of IRSR sources. This initiative has greatly helped to realize the infrared beamline at Frascati and to better exploit those of Orsay and Daresbury. Moreover, the network has organized the first international meetings in this field (University of Rome III in 1995; LNF-INFN Frascati in 1996 and LURE-Orsay in 1997) and has published the first book entirely devoted to IRSR.[15] In the last years several other meetings and workshops devoted to IRSR and its applications were organized in the USA.[16]

3 Characteristic properties of infrared synchrotron radiation emission

The infrared region of the electromagnetic spectrum is a very wide region that covers at least three orders of magnitude from 10 up to 10000 cm^{-1}. In this region intense sources are available for the experimentalist, e.g. globar to cover the mid-IR energy region or Hg lamp for the far-IR domain. However, stability and brilliance are the main limitations of these sources, so that modern storage rings may offer unique opportunities for experiments that require brilliance, intense beam for time resolved spectroscopy and/or polarized beam up to the far-IR domain.

Among the several properties of the synchrotron radiation emission, which hold true also for the IR domain, we may underline: brilliance, collimation, stability, polarization and time structure. In addition, synchrotron radiation is a continuous source so that all wavelengths are available for experiments in the entire IR domain.

3.1 Brilliance

The brilliance is the photon flux density (photons/s/mA/mrad horizontal 0.1% bandwidth) taking into account the electron beam divergence, the opening radiation angle and the electron beam source size (flux/mrad vertical/mm^2). The gain in brilliance of infrared synchrotron radiation with respect to a conventional source may attain two orders of magnitude or more. For a bending magnet source this quantity is a function of the wavelength λ and varies with the angle of acceptance.[17] This latter is determined by the dimension of the exit port placed in front of the magnet. In turn, this selects the arc of electron trajectory that contributes to the emission. At long wavelengths the brilliance gain is of 10^3 or even more, a performance which can be overcome only by a monochromatic source like a free-electron laser. If we consider the loss of the beamline that transmit under vacuum the radiation to the sample, e.g., the reflectivity and the transmission of the diamond window, of the mirrors, the absorption from the residual gas, and other geometrical constraints that limit the optical transmittance of the beamline, an actual reduction of one order of magnitude of the gain compared to a conventional source, once measured at the sample position, appears realistic. However one easily obtains, in the far infrared, a gain that ranges from 10 to 100 for samples smaller than 1 mm in diameter (see Fig.2).

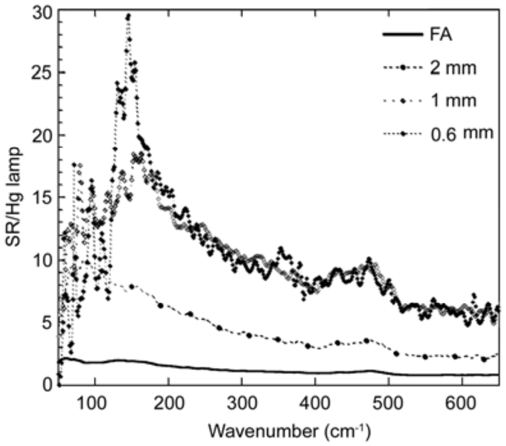

Fig.2 Intensity ratio between the IRSR source and the Hg lamp in the far-IR for the SINBAD beamline at DAFNE, as measured in the sample compartment of the interferometer for different pinholes from full aperture (FA) down to 0.6 mm in diameter.

3.2 Collimation

The complicated behavior of the brilliance is due to the combined effect of the horizontal and vertical collection angle and of the natural divergence $\theta_{\rm nat}$ of the synchrotron radiation. In the infrared domain this latter is much larger than in the UV or X region and depends on the photon wavelength λ through the relation:

$$\theta_{\rm nat} = 1.66\ (\lambda/\rho)^{1/3}$$

where ρ is the radius of curvature of the electron trajectory.[18] The equation shows that the divergence is already larger than 10 mrad for λ = 1 μm and that it increases significantly from the near-IR to the far-IR. This implies the use of focusing optics of large size and of a complex optical layout for transferring the infrared beam from the exit port to the experimental area usually located at several meters from the magnet.

3.3 Stability

Another remarkable advantage of IRSR with respect to thermal sources, whose intensity varies at random, is that the power delivered is intrinsically stable in time, and for energy of electrons E>0.5 GeV directly proportional to the current circulating in the beam. After correcting for the decrease of this latter, which can be monitored in real time, IRSR provides the spectroscopists with an absolute radiation source. This is of basic importance, for instance, in differential spectroscopy.

On the other hand, the IRSR spot at the sample may fluctuate if spatial instabilities of the electron beam are important. Actually beam fluctuations are important in the IR region where the source size is not diffraction limited[14] and this value depends on some parameters of the storage ring and in particular on energy of the ring. However, fluctuations may be amplified by the optical system and may produce serious problems in several applications such as microspectroscopy. At the NSLS of Brookhaven, this problem has been solved by a feedback that automatically corrects the electron orbit by acting on the electromagnetic fields along the ring. An alternative to reflecting optics, in particular in the far IR region, to minimize these effects is represented by cylindrical waveguides that can easily replace complicated optical layouts. Polarization properties are lost, however the multiple reflections along the pipe makes the infrared beam intrinsically stable against small displacements of the source, while the transmittance is comparable with that of standard mirror-optics beamlines.[19]

3.4 Polarization

It is well known that SR is linearly polarized in the orbital plane, while above and below it is elliptically polarized. When observed at a particular angle over the orbit, the radiation is circularly polarized. Since the early pioneering works in the visible region,[20] several investigations performed both in the VUV and X-ray regions fully confirmed these predictions. The polarization properties of infrared synchrotron radiation are very promising for applications, in particular in the far-IR region. By placing a slit on the exit port in principle one can then select the desired degree of polarization and the flux. When dealing with polarization, one may define three polarization rates, two of which are the most important: the normal linear polarization rate (P_1) and the circular polarization rate (P_3) defined in term of the linear and circular photon fluxes. As it can be recognized in Fig. 3, for the case of SINBAD, the first observations indicate that >80% circularly polarized light can be obtained by a slit that selects 50% of the total flux available. A few interesting applications have been already explored successfully, like the extension to the infrared of studies of circular dichroism in magnetic materials,[21] but many other can be figured out for such intense and brilliant sources.

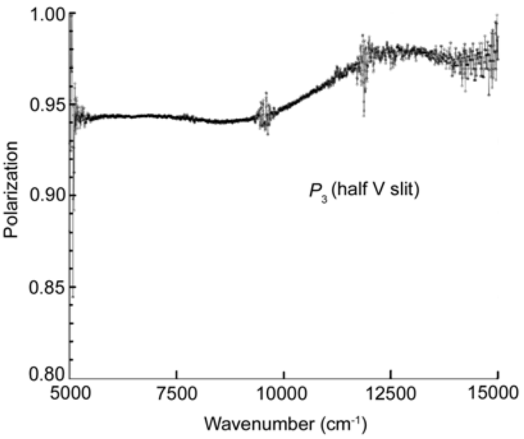

Fig.3 Circular polarization of the SINBAD radiation in the mid and near IR. With half slit open an intense flux is available for the experiments, with a circular polarization fraction P_3>90%.

3.5 Pulsed structure

Another feature of relevance to experiments in the IR domain is the pulsed structure of IRSR. Electrons in storage rings travel in *bunches* that have lengths on the order of 1 to 10 cm or more. When *bunches* are bended by a magnetic field e.g., in a bending magnet or in a wiggler, they radiate producing short pulses of light from tens of picoseconds up to about 1 ns depending on the ring and its mode of operation. These light pulses are suitable to investigate time-dependent phenomena in different systems on a nanosecond time scale.[22,23] Even if IR lasers can produce shorter pulses at much higher power levels, only IRSR exhibits a continuum spectral output in the entire IR domain and a high stability. IRSR can then be used for pump-probe experiments using standard FTIR spectroscopic techniques. Actually, using Fourier transform spectroscopy and photovoltaic detectors in the mid-IR regions, a time resolution better than 0.1 μs can be achieved. This property will be extended to the far infrared when fast detectors are available. Indeed, the typical cut-off frequency of a liquid-helium-cooled bolometer is presently 300 Hz, even if much faster detectors based on superconducting devices are being developed.

4 Sources and beamlines

The most common sources of IRSR are bending magnets. Nonetheless one beamline, at Orsay, has been designed to extract radiation from a wiggler device. Moreover, charges entering and exiting a magnet of an electron storage ring emit edge radiation at wavelengths long compared to the critical wavelength of ordinary synchrotron radiation.[24] The far-field edge radiation is emitted along the straight section axis in a hollow cone with its maximum at an angle $\theta \approx 1/\gamma$, where γ is the relativistic mass factor. This radiation, equivalent to transition radiation, may be used as a bright infrared (IR) source. Several IR beamlines are utilizing or are planned to utilize edge radiation.[25-27]

In the case of a bending magnet, the considerable size of the source and the large intrinsic divergence of IRSR require an optical layout including large aspherical mirrors that transfer and focus the beam to the entrance pupil of an interferometer. The standard extraction system of IRSR from the bending magnet of a storage ring is based on a flat mirror, placed in front of the port at 45° with respect to the electron orbit, that deflects the radiation cone on a focusing mirror, often an ellipsoid. In this way a large solid angle can be collected, such as 90×90 mrad at Brookhaven (U4IR port) or 20×45 mrad at SINBAD. If the electron beam energy E is high (>1 GeV), the thermal load on the first optical elements cannot be neglected. Indeed the power density associated to the “hard” X-ray radiation in the central region of the extraction mirror, is consistent and the mirror has to be cooled. The first mirror has even to be partially shielded by an absorber when the beam energy is high or the distance from the source is short. The second mirror, typically an ellipsoid, focuses the radiation on a window that isolates the ultra-high-vacuum section of the beamline, connected to the ring, from the remaining part. The first beamlines were equipped with natural diamonds, 2 cm^2 or more in size. Cutting such windows was difficult and expensive. Nowadays, the availability of large synthetic diamond films makes the use of diamond much simpler. Diamond is chosen for its excellent hardness and chemical stability, and for its "flat" transmittance in the whole infrared domain (except for an absorption band at ~2000 cm^{-1}, e.g. ~5 μm). Moreover, synthetic diamond can be grown with a wedging angle of the order of 1° or more, in order to suppress multiple reflections and brazed on standard CF flanges.[28] After the diamond window (DW) the pipe is kept in a lower vacuum regime, for reducing the infrared absorption from air (both water vapor and carbon dioxide are strong IR absorbers due to their permanent dipole moments) and a suitable optical system transfers the radiation to the interferometer.

At Frascati, the optical system of the SINBAD beamline transfers the radiation, after the first focus, as a plane wave to a second focus located at the entrance pupil of a Michelson interferometer, the same detection device that one uses with conventional sources. In the case of SINBAD even if the radiation source is an arc of several cm along the electron trajectory, its image on the pupil (Fig.4) has a size of a few mm^2 even at the longest wavelengths. The whole optical layout of SINBAD, one of the longest beamlines due to the constraints of the DAΦNE hall, is shown in Fig.5. As already mentioned, bending magnets are not the only sources of infrared radiation. Interesting infrared sources are also the edge of a magnet, where the field experiences rapidly drops to zero, and a wiggler or an undulator. Unlike for a uniform dipole (as in Fig.4), due to coherence effects different emission patterns can be associated with each source. As an example, both the edge effect and the wiggler emission contribute to the radiation collected by the SIRLOIN beamline of LURE, at Orsay.[11] Its peculiar extraction system has indeed provided the first evidence for the infrared emission from the edge of a bending magnet.[25] For $\lambda >> d / \gamma^2$, where d is the length required to deflect an electron through an angle of order $1/\gamma$, the edge radiation may be even brighter than that emitted from the uniform magnetic field region.[26,28] Similar effects are found at both edges of an undulator.[29] The first beamline designed by R.A. Bosch to exploit the edge effect is operational at the Aladdin storage ring of Stoughton (USA), as well as the one at ANKA, in Karlsruhe.[27] For all beamlines where the exit port views only a central portion of the magnet, the edge effect is negligible and the intensity can be reliably calculated by use of ray tracing simulation of the electron source. As an example, in Fig.6 the ratio $I_{SR}(\omega)/I_{BB}(\omega)$ of the SR intensity with respect to a black body (BB) is plotted vs. d, and compared with the corresponding calculations of the Actual Brilliance Ratio reported for SINBAD in Ref.19. All data are normalized to a beam current of 1 A under the assumption that the intensity is linear with the current. Therein, BB is a Hg lamp for $\lambda = 100$ μm and a globar for $\lambda = 2$ μm. As one can see, at 100 μm $I_{SR}(\omega)/I_{BB}(\omega) \approx 2$ for full aperture (~ 4 mm) and approaches a maximum value of 20 for $d = 1$ mm. The experimental data are even higher than theory. However the agreement is quite satisfactory. The deviations observed in the far infrared for the smallest apertures can be attributed to diffraction effects, which cannot be taken into account by ray-tracing calculations.

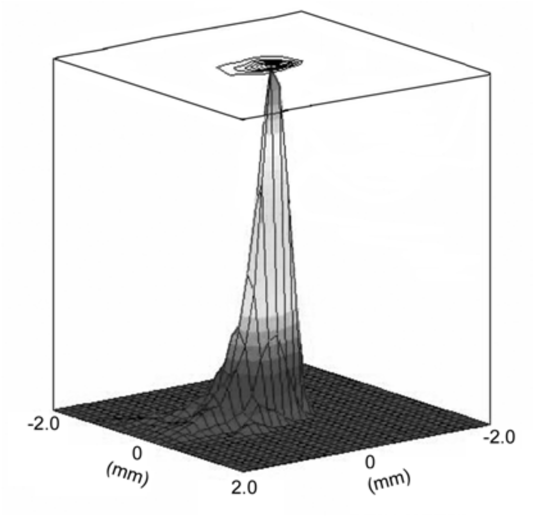

Fig.4 Intensity distribution at the last focus of SINBAD, placed at the entrance of the interferometer, as obtained by ray-tracing simulation. One may remark the small size of the image of the bending-magnet source.

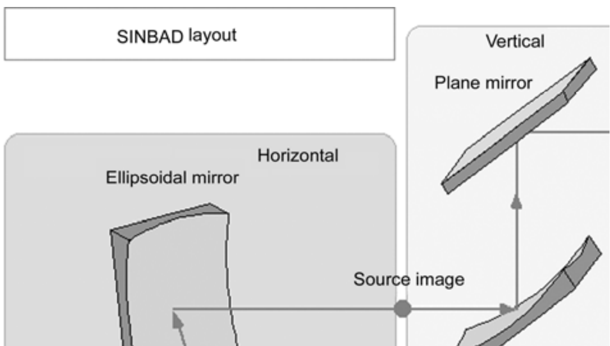

Fig.5 Optical layout of SINBAD, the infrared beamline installed at Laboratori Nazionali di Frascati of the INFN.

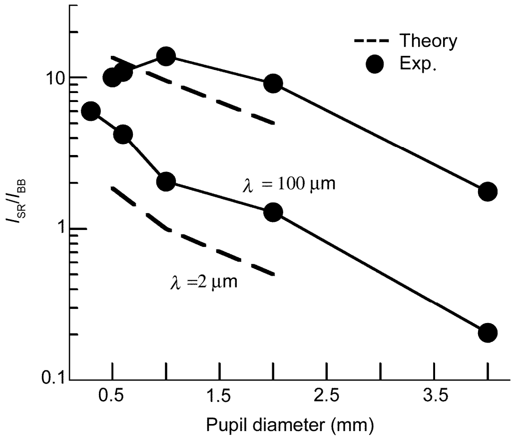

Fig.6 The ratio between the intensity of SR and that of the black body (BB) is reported vs. the diameter of an aperture at the sample position, both in the far and the mid infrared. In the former case BB is an Hg lamp, in the latter case a globar. The solid lines are guides to the eye. The dashed lines give the Actual Brilliance Ratio between SR (at 1 A) and BB, as calculated for SINBAD.[19]

About coherence properties of infrared synchrotron radiation, energetic electron bunches in storage rings produce the emission of incoherent synchrotron radiation, however they should also produce a roughly comparable power output of coherent radio-frequency radiation.[30] Preliminary experiments did not show evidence of coherent enhancement of the synchrotron radiation emission in the long-wavelength infrared domain for bunch lengths of about 30 cm.[31] Additional investigations were necessary, on modern synchrotron sources with shorter bunch length, to observe coherence effects in the infrared region. Recently Carr and coworkers reported observation of coherent synchrotron radiation from the NLSL VUV ring and partially characterized this emission. Multiparticle coherent emission occured in the very far infrared from bunched electrons, peaked near a wavelength of 7 mm, much shorter than the nominal electron bunch length, indicating the presence of a density modulation within the bunch.[32] More recently at BESSY II, coherent emission generated by a controlled, steady-state process was observed in the 1-0.3 mm wavelength range.[33]

5 Spectroscopy with infrared synchrotron radiation

The unique features of IRSR allow the spectroscopists to collect higher quality data in a number of experiments usually performed with conventional sources. In a few cases, IRSR has opened to routinely infrared spectroscopy new fields of application, where too severe experimental conditions prevented the use of standard sources.

5.1 Physics and chemistry of surfaces

One of the earliest applications of IRSR has been the study of molecular adsorbates on metallic surfaces. The observation of their vibrational lines and of the shifts with respect to those of isolated molecules provides information on the molecule-surface interaction, on the eventual ordering of the adsorbate, on the amount of stress on molecular bonds. Such results are also of great interest for applied research, for instance in electrochemistry. As one is interested in monitoring the intramolecular vibrations of molecules that are generally aligned orthogonally to the surface, the electric field of the infrared radiation should also be perpendicular to the surface. This implies that the angle of incidence should be as large as possible. Performing such experiments at grazing incidence with a conventional source, when moreover the adsorbate is a monolayer, is a very hard task. By use of IRSR one has: i) the high brilliance necessary to get a small and intense spot on the sample even at grazing angles; ii) the high stability needed to perform differential spectroscopy. One may thus obtain excellent signal-to-noise levels even in such severe conditions. As an example Fig.7 shows the far infrared absorption from a half-monolayer of CO adsorbed on copper.[34]

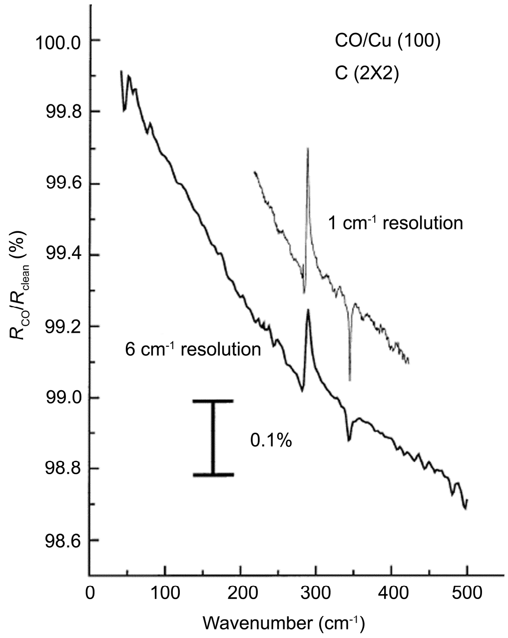

Fig.7 The change in reflectance of a Cu(100) single-crystal surface induced by the adsorption of 0.5 monolayers of CO, as measured at the U4IR beamline at NSLS at grazing incidence and shown for two different resolutions (from Ref. 34). The negative peak (with respect to the broad reflectivity background) monitors the carbon-metal vibrational mode, the positive peak corresponds to the hindered rotational mode.

5.2 High-pressure studies in diamond anvil cells

Infrared spectroscopy by use of the synchrotron source is presently considered as a powerful tool for investigating the properties of matter at high pressure. The high brilliance of IRSR is needed for obtaining appreciable results in diamond anvil cells, where the size of the windows is of the order of 400 μm or smaller. The gain in sensitivity with respect to conventional sources may reach three orders of magnitude when using a Fourier transform interferometer, five orders when using a grating monochromator. Pioneering measurements by Nanba made at Okasaki (Japan) in the eighties, at pressures on the order of 10 GPa make the IR beamline at UVSOR as one of the first facilities where IRSR experiments with high pressure cells were performed.[35] Nowadays, infrared spectra at pressures even higher than 200 GPa are collected at Brookhaven by use of infrared microscopes.[36] Among the basic results obtained by this technique one may cite the determination of the phase diagram of solid hydrogen up to 200 GPa, by Hemley and collaborators. Spectra obtained for the first time with IRSR have excluded any metallization of hydrogen up to those pressures, imposing entirely new theoretical models for this system.[36] Recent results (see Fig.8) obtained at SINBAD address the possibility to perform experiments also on solid state systems under high pressure in the far-IR domain.

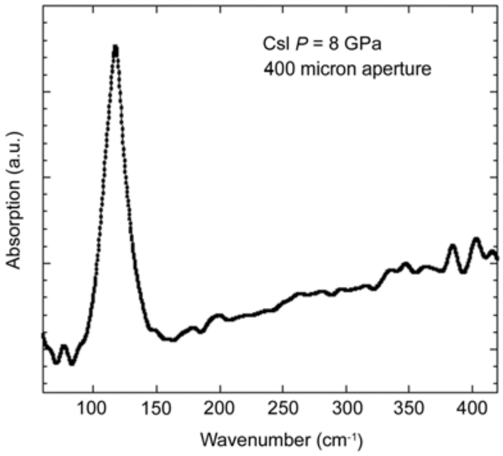

Fig.8 Far-IR absorption spectra at the resolution of 8 cm^{-1} of a diamond anvil cell containing a CsI powder at a pressure of 8 GPa at SINBAD. The peak is due to the CsI tranverse optical phonon, much better resolved and shifted towards higher frequencies with respect to zero pressure. The cell window diameter is ~400 μm.

5.3 Microspectroscopy

Infrared micro-spectroscopy is a unique technique that combines microscopy and spectroscopy for purposes of microanalysis. Spatial resolution, within a microscopic field of view, is the goal of the modern infrared micro-spectroscopy applied to condensed matter physics, materials science, biophysics and now to medicine.

IR-microscopy is a micro-analytical and imaging technique, which achieves contrast via the intra-molecular vibrational modes. The method is the same used in X-ray microscopy where contrast is achieved by recording spectra before and after the absorption edges of an element contained in the specimen. The gain in brilliance of IRSR with respect to black bodies is remarkable at shorter wavelengths, where an infrared microscope can work without experiencing major diffraction problems. The use of infrared microscopes coupled to synchrotron radiation sources has started recently, but has rapidly met with outstanding success. Indeed, the high brilliance of this source allows one to reduce the instrument's apertures to define geometrical areas of a few microns in the mid-IR region, e.g., at the diffraction limit, with good S/N.[37]

Fig.9 shows a spectrum taken on the inner part of the cross-section of a polymer laminate, commonly used as packaging material. The sheet comes out from the industrial process in form of a sandwich, where the recipe of the 10 μm-thick filling is unknown. The spectrum of such a thin inner layer, if taken by a microscope using a conventional source (Fig.9 – upper panel) does not help to solve the problem due to its poor contrast. The IRSR spectrum obtained by the group of Chesters at Daresbury (Fig.9 – lower panel) shows instead the "fingerprints" of the filling, which identify it as an ethylene/vinylacetate copolymer.[38]

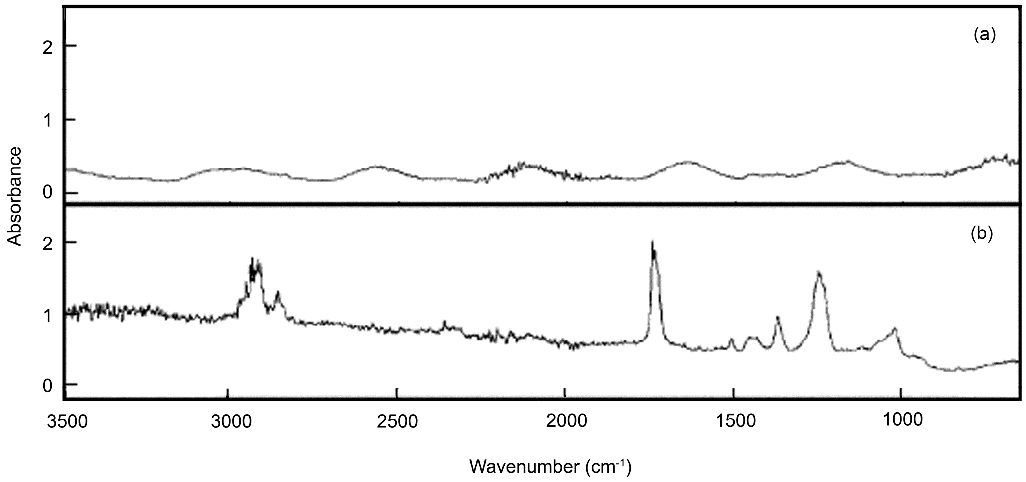

Fig.9 Infrared microspectrum of the central section (10 μm thick) of a polyethylene sheet with a conventional source (a) and with the Daresbury synchrotron source (b) (from Ref.38).

Other potential applications of the infrared microspectroscopy by synchrotron radiation concern geophysical researches such as the study of minerals, e.g. complex systems typically inhomogeneous. In these systems, for example, the visible-light objective of the microscope may select in a rock sample an area that contains a small fluid inclusion. After switching the microscope to the infrared, one may collect the spectrum of the inclusion. With IR the spectrum displays the fingerprint of an oil thus providing detailed information on its composition and quality.[39] The possibility of exploiting that rock as an oil source can then be evaluated on a sound basis. Recently a collaboration between University La Sapienza and the SERC of Daresbury performed infrared spectromicroscopy on meteoritic fragments collected by the Italian expedition to the Antarctic. These samples are strongly inhomogeneous and show insulating zones made of different silicates, a few tens of microns in size, embedded into a metallic matrix. By use of the IRSR microscope detailed spectra of those silicates have been collected, and characteristic lineshifts with respect to the laboratory spectra of the same substances have been recorded. These data will provide exhaustive information on the composition of the meteorite and on the conditions under which it was formed.[40]

However, other important applications are emerging in the biological researches. Indeed, Fourier transform-infrared micro-spectroscopy using synchrotron radiation may collect data with high resolution on the scale of 10~100 seconds up to area of a few microns opening a new scenario: infrared spectroscopy of entire cells and tissue. In this field, IR spectroscopy has important advantages compared to other techniques: the use of non-ionizing radiation and the almost negligible damage to samples under analysis. While in light microscopy, image contrast is achieved with stains or fluorescent materials, with IR the use of chemical reagents or stains is not necessary. Image contrast is simply produced from intrinsic IR absorption bands. The spectrum of a single red blood cell with and without carbon monoxide was reported in 1988 using a microscope connected to a conventional FTIR spectrometer.[41]

The IR spectrum of a biological system exhibits characteristic absorption bands (characteristic molecular vibrations) that appear at different positions with different relative intensities. Each spectral difference reflects a potential structural difference in the system. Therefore, vibrational spectroscopy allows defining sets of IR marker absorption bands of the various conformations. In Fig. 10 we show a typical IR spectrum of a biological specimen. This kind of spectrum that covers a wide spectral range can be recorded with spatial resolution using an IR microscope by averaging data from a reasonable number of scans. The arrows indicate, in the NIR and mid-IR ranges, the main IR bands that can be used to recognize and distinguish different samples and materials.[42] For instance, the amide I profile (1600~1700 cm^{-1}) can help to identify either the protein configuration or changes occurring in tissue.[43] Even if the infrared spectroscopy of whole cells needs major improvements in order to achieve full reliability, it represents a new challenging research field. In the near future it will certainly be able to detect pathologies or diseases within human cells.[44]

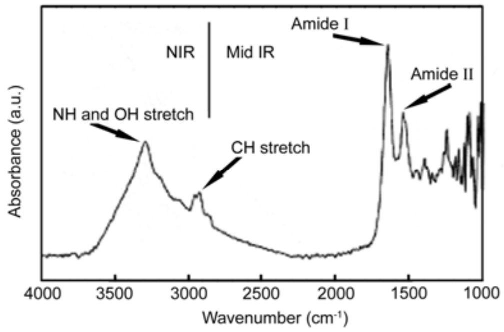

Fig.10 Infrared spectrum of a biological specimen recorded through a microscope. The arrows indicate the main IR bands that can be used to recognize and distinguish different specimens or changes in a biological system.

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