Recent applications and current trends in analytical chemistry using synchrotron-based Fourier-transform infrared microspectroscopy

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Synchrotron radiation based Fourier-transform infrared (SR-FTIR) microspectroscopy is an emerging technique, which is increasingly employed in analytical sciences. This technique combines FTIR spectroscopy (namely specific identification of molecular groups within a variety of environments: organic/inorganic, crystallized/amorphous, solid/liquid/gas) with high brightness, and therefore small spot size and faster acquisition of high-quality spectral imaging data from a synchrotron light source.

In this article, we review several recent applications of SR-FTIR that have led to much of the improved analytical capabilities. Performing analytical science at large-scale facilities allows one to access state-of-the-art equipment and capabilities, receive expert assistance from the facility staff, and have the possibility of combining SR-FTIR microscopy with other synchrotron-based X-ray microimaging techniques.

Keywords: Cultural heritage; Earth science; Fourier-transform infrared (FTIR); High pressure; Microspectroscopy; Polymer science; Space science; Synchrotron; X-ray; Vibrational linear dichroism

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1. Introduction

The aim of this article is to discuss the new capabilities provided by synchrotron infrared (IR) beam-lines in the field of analytical chemistry. We illustrate with recent examples of applications in the fields of CH, space science, Earth science, biology, high pressure, and polymer science with vibrational linear dichroism. It was predicted years ago [1] that the IR emission from a synchrotron radiation (SR) source has potentially higher brilliance compared to a thermal source. However, it took more than a decade of development to harness the advantages of such sources. Modern IR spectroscopy uses the interference pattern of an IR beam split into two beams having a variable path-length difference (FTIR interferometry), typically sampled 10–100 times/ms, so the stability of the source on such a

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scale is of the utmost importance. Today, most SR facilities offer a port dedicated to IR spectroscopy and spectro-microscopy (Table 1). The high electron-beam stability of modern third-generation machines and the use of optical beam-stabilizing techniques [2] provide the required source stability for high-quality FTIR spectroscopy. The synchrotron source offers brightness (or brilliance or spectral radiance) 2–3 orders of magnitude higher than a thermal (laboratory-based) IR source [3,4], a high degree of polarization, as well as light pulses in the 2–10 ps time scale [5]. They are thoroughly exploited in the far-IR (FIR)/THz, and mid-IR (MIR) regions. In the long-wavelength domain, both flux and brightness exceed those of the thermal source [6].

The most rapidly expanding application of the synchrotron IR source is microspectroscopy on individual sample spots, as well as for chemical imaging. The principal advantages of the method are enhanced lateral resolution (typically at or very close to the diffraction limit [7,8] combined with superior signal-to-noise ratio obtained without resorting to prohibitively long acquisition times. These advantages have been widely exploited in synchrotron facilities worldwide. Numerous achievements in a variety of scientific disciplines (e.g., soft matter [9,10], geology [11–13], biology [14–23], environmental science [24,25]) have been reported. The increasing demand for beam time, as well the potential for impact in fields such as analytical chemistry, has triggered the construction of more synchrotron IR beam lines worldwide (Table 1).

IR-microscopy imaging makes use of the rich, unique spectroscopic absorption features found in the MIR spectral region for chemical identification to form images based on these absorption bands. However, there is increasing interest in extending the spectral range to lower frequencies. This trend is motivated by developments in coherent THz spectroscopy and imaging [26] as well as by the need of the space-sciences community to identify complex minerals found in interplanetary dust particles [27]. The broad spectral coverage and high brightness of SR reaches well into the FIR, to below 1 THz and coherent SR has the potential to be an exciting powerful THz source [28,29].

Basic work has been done at BESSY II [30] to make this coherent broadband THz source accessible to spectroscopic applications at storage rings for not only conventional spectroscopic techniques [31–34] but also near-field spectral imaging on biological samples in the THz range [35,36]. The purpose of this review article is to illustrate how synchrotron IR emission has advanced IR microspectroscopy and imaging in analytical

Table 1. Facilities that plan (P) or operate (O) mid-IR beam-lines. List: http://infrared.als.lbl.gov/content/web-links/45-srir

Facility	Location	Beamline	URL
ALBA	Barcelona, Spain	1 P	www.cells.es/Beamlines/SECOND-PHASE/MIRAS/
ALS	Berkeley, USA	2 O, 1 P	infrared.als.lbl.gov/
ANKA	Karlsruhe, Germany	2 O	ankaweb.fzk.de/website.php?page=instrumentation_beam&id=1
Australian Synchrotron	Melbourne Australia	1 O	www.synchrotron.org.au/index.php/ aussyncbeamlines/infrared-micro/beamline-team
BESSY II	Berlin, Germany	1 O	www.helmholtz-berlin.de/
CAMD	Baton Rouge, USA	1 O	www.camd.lsu.edu/pdf/NIMA-IR.pdf
CLS	Saskatoon, Canada	2 O	www.lightsource.ca/experimental/midir.php
DAFNE	Frascati, Italy	1 O	www.lnf.infn.it/
Diamond	Oxfordshire, UK	1 O	www.diamond.ac.uk/Home/Beamlines/B22.html
Elettra	Trieste, Italy	1 O	www.elettra.trieste.it/experiments/beamlines/sissi/
ESRF	Grenoble, France	1 O	not accessible as general User instrument
INDUS-1	Indore, India	1 P	www.cat.ernet.in/index.html
Jlab	Newport News, USA	1 O	www.jlab.org/FEL/terahertz/
MAX-lab	Lund, Sweden	1 O	www.maxlab.lu.se/beamlines/bl73/
Metrology LS	Berlin, Germany	2 O	www.ptb.de/mls/
NSLS	Brookhaven, USA	6 O	infrared.nsls.bnl.gov/
NSRL	Hefei, China	1 O	www.nsrl.ustc.edu.cn/EN/
NSRRC	Hsinchu, Taiwan	1 O	www.nsrrc.org.tw/lifensrrc/bl14a1.htm
SESAME	Allan, Jordan	1 P	www.sesame.org.jo/About/Beam.aspx
Siam PS Photon Source	Nakhon Ratchasima Thailand	1 P	www.slri.or.th/new_eng/index.php?option=com_content &task=view&id=52&Itemid=89
SLS	Villigen, Switzerland	1 O	sls.web.psi.ch/view.php/beamlines/ir/index.html
SOLEIL	Gif-sur-Yvette France	2 O	www.synchrotron-soleil.fr/portal/page/portal/ Recherche/LignesLumiere/SMIS
SPring-8	Hyogo, Japan	1 O	infrared43.spring8.or.jp
SRC	Madison, USA	2 O	www.src.wisc.edu/facility/complist.htm
SSLS	Singapore	1 O	ssls.uus.edu.sg/facility/facility.htm
SSRF	Shanghai, China	1 P	ssrf.sinap.ac.cn/english/
UVSOR	Okazaki, Japan	1 O	www.uvsor.ims.ac.jp/inforuvsor/beamlines.pdf