Terahertz Microspectroscopy and Infrared Reflection-Absorption Spectroscopy Apparatuses at UVSOR-II

Shin-ichi Kimura*, Yoko Sakurai*, Eiken Nakamura* and Takafumi Mizuno†

*UVSOR Facility, Institute for Molecular Science, Okazaki 444-8585, Japan
†School of Physical Sciences, The Graduate University for Advanced Studies, Okazaki 444-8585, Japan

Abstract. We have recently constructed two specialized end stations, one is the terahertz microspectroscopy (THz-MS) and the other the infrared reflection-absorption spectroscopy (SR-IRAS). Both instruments have been tested using synchrotron radiation in the infrared and terahertz regions at UVSOR-II. The THz-MS station covers the wavenumber region of 15,000 $- 40$ cm^{-1} with the spatial resolution as same as the wavelength. This apparatus is a powerful tool for the electrodynamics on strongly correlated materials at low temperatures and under high pressures and also for the molecular vibration imaging of living cells. On the other hand, the SR-IRAS station covers the IR range down to 300 cm^{-1} with a high accuracy. The change of Al–N stretching and pyramidalization modes at 423 and 460 cm^{-1}, respectively, due to potassium doping in Alq$_3$ molecules on an Ag surface was observed.

Keywords: Infrared synchrotron radiation, terahertz microspectroscopy, infrared reflection-absorption spectroscopy
PACS: 41.60.Ap, 42.72.Ai, 78.30.-j, 78.68.+m

INTRODUCTION

The advantage of the infrared synchrotron radiation (IRSR) compared with other light sources is the high brilliance nature in the wide wavenumber region. Many infrared microspectroscopy systems in the middle infrared region are working in the world in order to use the high brilliance. It is well known that IRSR is useful not only for the middle infrared region but also for the far-infrared (terahertz, THz) region compared with thermal light sources such as globar and mercury lamps. In order to take advantage of this high brilliance feature in the THz region, the first IRSR beamline has been constructed at UVSOR, Institute for Molecular Science, Okazaki, Japan about two decades ago [1]. The beamline has provided a lot of activities in the solid state research domain in the THz region.

In 2003, UVSOR storage ring was upgraded to become a low emittance ring with new equipment, namely, six undulators on three long and three short straight sections [2]. The IRSR beamline was also reconstructed in order to take advantage of the higher flux using a large acceptance angle of 215(H) × 80(V) mrad^2 [3]. The name was also changed to BL6B(IR). To collect the SR from the long emission arc, a "magic mirror" with vertical angle focusing (firstly installed at SPring-8 BL43IR [4]) was employed for the first mirror. The mirror chamber was directly connected to the bending magnet chamber in order to collect a high photon flux. The beam line covers a very wide photon energy range of 0.4 meV – 3 eV (3.2 – 25,000 cm^{-1}) using a Michelson-type (Bruker 66v/S) and a Martin-Puplett-type (JASCO FARIS-1) rapid-scan interferometers. To use the high brilliant IRSR and the rapid-scan-type FTIR provides us the high accuracy of reflectivity measurements [5]. The high brilliance property of SR is useful for a microspectroscopy (MS) and for a reflection-absorption spectroscopy (IRAS) of adsorbed molecules on surfaces not only in the middle-IR region but also in the THz region. [6]. Then we recently constructed two end stations, MS and IRAS. In this paper, the MS and IRAS are depicted and some of our measurements are also reported.

TERAHERTZ MICROSPECTROSCOPY STATION

IRSR is a powerful tool for microspectroscopy and imaging not only in the IR but also in the THz regions because of its high brilliance. Almost all IRSR beamlines in the world provide commercial IR microscopes end stations that are easy to use. Since the Schwarzschild mirrors in commercial IR microscopes are small, the microscope is available only in the mid-IR region, *i.e.*, it is not suitable for the THz region. However, we install a new microscope in order
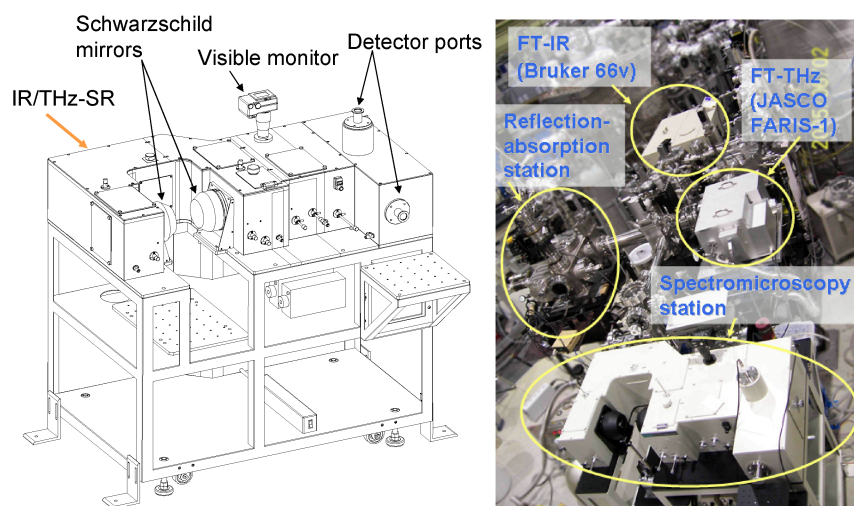
FIGURE 1. Schematic figure of terahertz microspectroscopy apparatus at UVSOR-II and the photo of the IR-THz beamline (BL6B) at UVSOR-II.

to cover the IR region down to the THz region as shown in Fig. 1. Some of the main features are ; 1) Large working distance because some specific experiments (at very low temperatures, under high pressures, a near-field spectroscopy, etc.) are planned. 2) We need to cover the THz region because quasiparticle states of correlated materials and finger print vibration mode of proteins appear only in this spectral range. In order to achieve these goals, we use a large-size Schwarzschild mirrors (Diameter = 140 mm, NA = 0.5, working distance = 106 mm, magnification = ×8) to reduce the diffraction effect in the THz region.

After installation of the THz microscope, we checked the spatial resolution in the different wavenumber ranges covered by the different FTIR beam splitters (Fig. 2). The spatial resolution was recorded by using the Bruker 66v/S interferometer and the transmission configuration. In the wavenumber region above 500 cm^{-1}, the globar lamp gives a good contrast. However, the use of UVSOR-II gives 10^2 times larger intensity and about 10 times smaller beam size. If 500 μm diameter pinhole is installed at another focus position of the Schwarzschild mirror, the width reaches the diffraction limit. In the wavenumber region below 600 cm^{-1}, in which the mylar 6 μm beam splitter is used, a good beam profile was observed with UVSOR-II in contrast with the very weak peak given by a globar lamp. In addition, the case of the mylar 23 μm beam splitter covering the lower wavenumber region below 200 cm^{-1} shows the good contrast and intensity in the peak image. The cut-off wavenumber for UVSOR-II is 40 cm^{-1} (150 cm^{-1} in the case of SPring-8 IR beamline [7]). This indicates that the THz microscope using UVSOR-II is a very efficient tool for microspectroscopy both in the IR and THz regions. This instrument is used for the electrodynamics on strongly correlated materials at low temperatures and under high pressures and also for the molecular vibration imaging of living cells.

INFRARED REFLECTION-ABSORPTION SPECTROSCOPY STATION

IRAS is a powerful technique for investigation of surfaces and interfaces. The IR spectrum below 1000 cm^{-1} of THz region contains important information about vibrational modes of adsorbed molecules and also of heavy atoms on surfaces. However, it is difficult to obtain the IRAS spectrum in this region using a typical laboratorial system with a globar source. IRSR enables the recording of such information in the THz region. That's why we have constructed as IRAS system using SR (SR-IRAS) at UVSOR-II.

Figure 3(a) shows the top view of the schematic drawing of the SR-IRAS apparatus. This device includes a UHV chamber with metal and organic evaporators, a focusing optical system and a detector. The horizontally polarized IRSR illuminates the off-axis parabolic mirror (M1, the focal length and the diameter are 152.4 and 50.8 mm, respectively.). The beam is focused on the sample surface with a reflectivity angle of 80 degree relative to the surface normal. The reflected light is collected by the second off-axis mirror (M2, f = 152.4 mm) and guided to the third off-axis mirror (M3, f = 101.6 mm) and then focused on the detector. The UHV chamber is separated from the low vacuum focusing
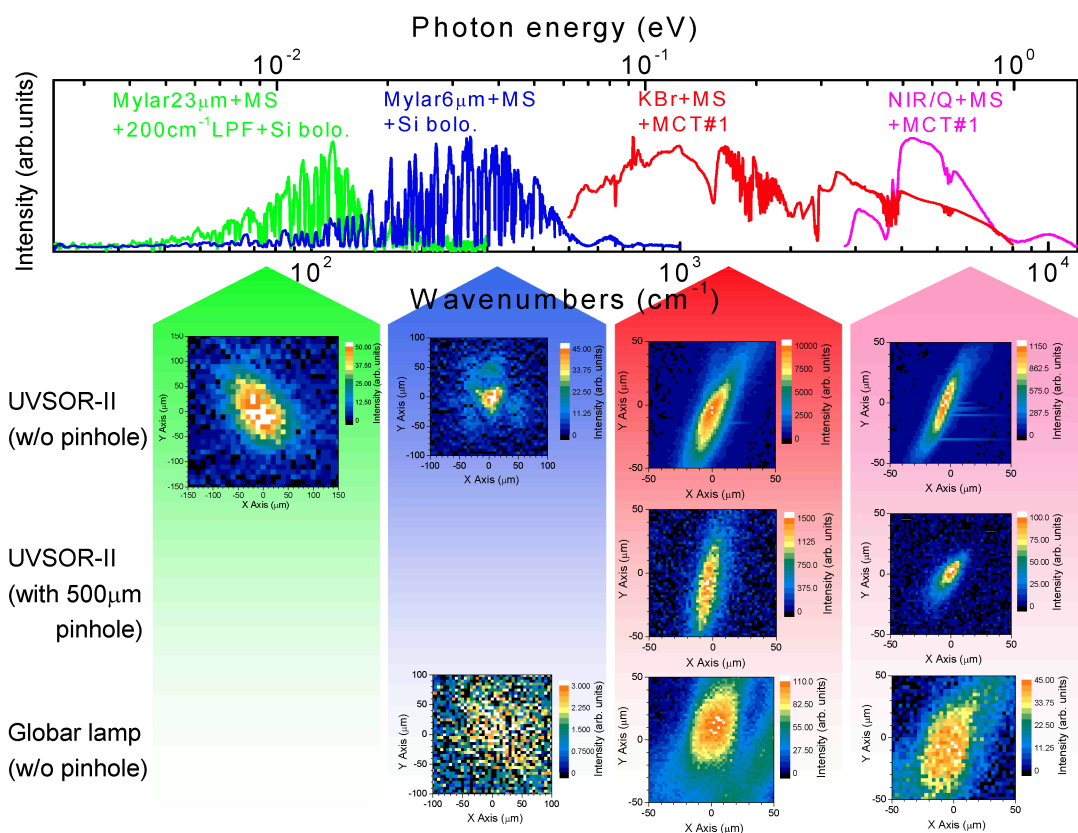
FIGURE 2. Spectral shape and spatial resolution of THz microscope at different wavenumber regions using UVSOR-II compared with a globar lamp. The captions in the top figure indicate the combination of a beam splitter of the FTIR (Bruker 66v/S), a low pass filter and a detector. The caption on the left side indicates the light source and apperture at the another focus of the Schwarzschild mirror. Fine structures in the spectral shapes are due to the absorption of water vapor and can be reduced by nitrogen purge. See the text for detail.

optics chambers by KBr or CsI windows.

Tris-(8-hydroxyquinoline) aluminum (Alq_3) is widely used as an electron transport/light emitting layer in organic light emitting diodes (OLEDs). A typical OLED consists of an indium tin oxide (ITO) as the anode, on which organic thin films are sequentially deposited, with low work function metals finally deposited as the cathode. Since the OLED's performance is affected by the interface, it is important to investigate the interface between the organic thin film and cathode. Up to now, the IRAS study of alkali metal doped Alq_3 in the region of $1000 - 4000$ cm^{-1} using a globar source has been already reported [8]. However, since Al–N and Al–O vibration modes that are expected to be significantly affected by alkali metals appear in the wavenumber region around 400 cm^{-1}. As a matter of fact, the IRAS study below 1000 cm^{-1} of the THz region cannot be reached using the globar source. We measured the alkali metal doping dependence of IRAS spectra of Alq_3 thin films in the THz region using IRSR.

Alq_3 films were prepared by vacuum evaporation onto Ag films deposited on Si substrates. Alkali metals such as potassium, lithium and sodium were evaporated from SAES getter sources. A liquid-helium-cooled Si bolometer was used to detect the THz light. One hundred spectra were recorded with a 2 cm^{-1} resolution and averaged.

Figure 3(b) shows potassium doping dependence of the IRAS spectra of an Alq_3 film of 20 nm thickness in the wavenumber region of $300 - 500$ cm^{-1}. In the spectrum of pristine Alq_3 film, two strong peaks were observed at 423 and 460 cm^{-1} and respectively assigned to the Al–N stretching and pyramidalization modes [9]. The intensity of these peaks gradually decrease, in addition, three new peaks appear at 435, 441 and 448 cm^{-1} as the evaporation time is increased. The similar behavior was also observed in sodium doping. Considering these behavior, the change is believed to be caused by the charge transfer to the Alq_3 molecule from the alkali atoms. However the additional peaks did not appear in lithium doping. This suggests that the interaction between Li and Alq_3 is different from those of K
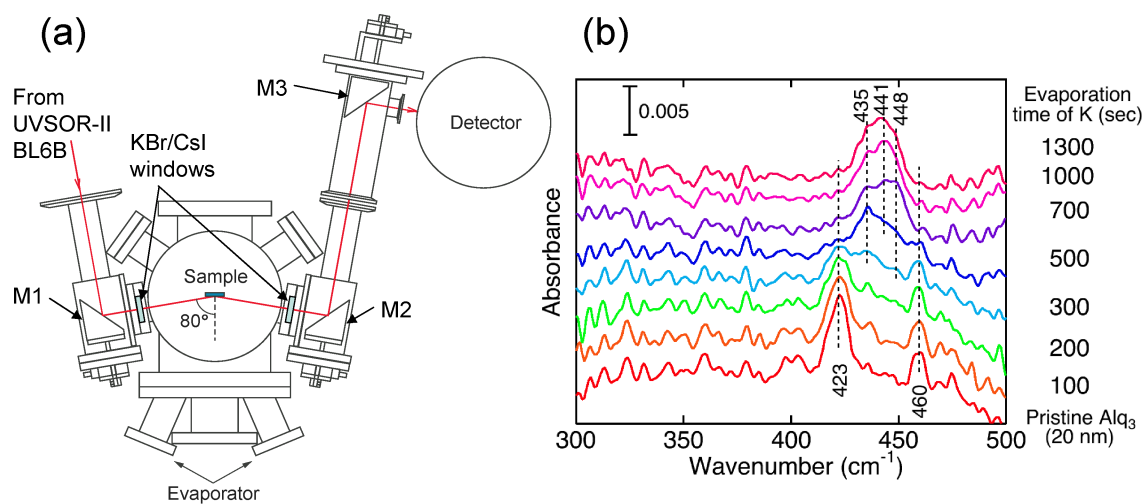
597

FIGURE 3. (a) Top view of the schematic figure of the infrared reflection-absorption spectroscopy apparatus installed at UVSOR-II BL6B. Horizontally polarized parallel IRSR beam is introduced to the off-axis parabolic mirror (M1, focal length: 152.4 mm) to focus on the sample with the incident angle of 80 degree relative to the surface normal. The reflected IR beam is gathered by the second off-axis parabolic mirror (M2, focal length: 152.4 mm) and guided to the third off-axis parabolic mirror (M3, focal length: 101.6 mm) to focus on the detector. The ultra-high vacuum of sample chamber to the low vacuum of the M1 and M2 mirror chambers is separated by KBr or CsI windows. (b)Changes in IRAS spectra of an Alq_3 film with potassium deposition.

and Alq_3 and Na and Alq_3. The investigation of the origin of the different behavior in doping materials is in progress using other method.

CONCLUSION

In conclusion, the outline and performance of the terahertz microspectroscopy and infrared reflection-absorption spectroscopy apparatuses at UVSOR-II were reported. Both of these apparatuses have excellent performance compared with the conventional ones using a globar light source.

This work was a joint study program of Institute for Molecular Science.

REFERENCES

1. T. Nanba, Y. Urashima, M. Ikezawa, M. Watanabe, E. Nakamura, K. Fukui, and H. Inokuchi, *Int. J. Infrared and Millimeter Waves* **7**,1769 (1986).
2. M. Katoh, M. Hosaka, A. Mochihashi, J. Yamazami, K. Hayashi, Y. Hori, T. Honda, K. Haga, Y. Takashima, T. Koseki, S. Koda, H. Kitamura, T. Hara, and T. Tanaka, *AIP Conf. Proc.* **705**, 49 (2004).
3. S. Kimura, E. Nakamura, J. Yamazaki, M. Katoh, T. Nishi, H. Okamura, M. Matsunami, L. Chen, and T. Nanba, *AIP Conf. Proc.* **705**, 416 (2004).
4. S. Kimura, H. Kimura, T. Takahashi, K. Fukui, Y. Kondo, Y. Yoshimatsu, T. Moriwaki, T. Nanba, and T. Ishikawa, *Nucl. Instrum. Meth. A* **467-468**, 437 (2001).
5. H. Okamura, T. Michizawa, T. Nanba, S. Kimura, F. Iga, and T Takabatake, *J. Phys. Soc. Jpn.* **74**, 1954 (2005).
6. S. Kimura, E. Nakamura, T. Nishi, Y. Sakurai, K. Hayashi, J. Yamazaki, and M. Katoh, *Infrared Sci. Tech.* (2006) in press.
7. Y. Ikemoto, T. Moriwaki, T. Hirono, S. Kimura, K. Shinoda, M. Matsunami, N. Nagai, T. Nanba, K. Kobayashi, and H. Kimura, *Infrared Phys. Tech.* **45**, 369 (2004).
8. Y. Sakurai, Y. Hosoi, H. Ishii, Y. Ouchi, G. Salvan, A. Kobitski, T. U. Kampen and D. R. T. Zahn, and K. Seki, *J. Appl. Phys.* **96**, 5534 (2004).
9. M. Cölle, S. Forero-Lenger, J. Gmeiner and W. Brütting, *Phys. Chem. Chem. Phys.* **5**, 2958 (2003).