

Evaluation of the Infrared Micro-spectroscopy Beamline

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Abstract

An infrared micro-spectroscopy beamline (SRMS, BL-15) was constructed in the SR center by a JST project (from the fiscal year of 2007 to 2010). The SRMS should have not only higher intensity of infrared (IR) light, but also higher spatial resolution than thermal radiation IR microscopy (TRMS). To evaluate the performance of the SRMS, we applied it to typical examples, polystyrene latex spheres on a mica substrate, onion cells and dehydration process of polymer gels on a Si wafer. Observed images and spectra clearly demonstrate potential applications to material science, bio-science and surface science.

1. Introduction

Infrared micro-spectroscopy (IRMS) is useful for studying local structures of organic materials and biomaterials because it enables us to observe where any specific molecules are distributed in a microscopic region. However, a commercial IRMS using thermal radiation (TRMS) as the light source has a limit of spatial resolution due to lack of high brilliance. Synchrotron radiation is a promising light source with higher brilliance not only for X-rays, but also for infrared region. Then, an infrared micro-spectroscopy beamline (SRMS, BL-15) was constructed in the SR center by a JST project (from the fiscal year of 2007 to 2010) [1,2]. As a result, the SRMS has a higher intensity of infrared light than that of a commercial IR. Also spatial resolution of the microscope has been improved as compared with that of the TRMS. We have to evaluate the SRMS by applying it to some samples as the next step.

Here, we choose three examples to evaluate our SRMS and demonstrate potential for application to material science, bio-science and surface science.

2. Experimental

Using infrared microspectroscope is Nicolet 6700 and Continuum XL (Thermo Fisher Scientific Inc.) equipped at the end of the beamline. The light source of the TRMS for comparison with the SRMS is a glober lamp inside the apparatus.

In section of 3.1 and 3.2, the IRMS measurements were using the transmittance mode and 15x Cassegrain optics. In section of 3.3, it was the reflection mode and 32x Cassegrain optics. The other details of measurement conditions are explained in each section.

3. Examples of measurement

3.1 Polystyrene latexes on a mica

We measured IR absorption spectra of polystyrene (PS) latexes dispersed on a mica to evaluate this beamline [2]. The diameters of the latexes are ca. 2 μm . Fig. 1(a) is a video image of the sample in which dark contrast areas is an assembly of PS latexes and a brighter area is a mica substrate. The sample was scanned in the area of 16 μm x 4 μm shown in Fig. 1(a) and sampling interval is approximately 1 μm . The aperture size of the IR microscope is 7 μm x 5 μm , which is the minimum size in the case of using a 15x Cassegrain optics. Fig. 1(b) shows two IR spectra of the PS latexes measured with the both sources. The absorption spectrum by the SR light source shows two obvious peaks at 2920 and 3020 cm^{-1} , which are attributed to the CH_2 stretching frequency of polymer chain and the CH absorption of aromatic ring, respectively. The spectrum by TR light source also shows two peaks at the same wavenumbers as them by the SR source. However their two peaks are not clear though the number of scans a spectrum of the TRMS is 256 which is the same number as the SRMS. In addition, the signal-to-noise ratio (SNR) of the spectrum of the SR is better than that of the TR. As a result, IR measurements with the TR take more times to make the same quality of

IR measurements with the SR source. Fig. 2 shows the 3d contour maps of the two peaks with both sources. In the case of SRMS, the change of the intensity is gradual toward a PS area to a mica. But in the TRMS, its change is irregular. It is concluded that the spectra measured with SRMS has better SNR than those with the TRMS, even though the aperture size is the minimum.

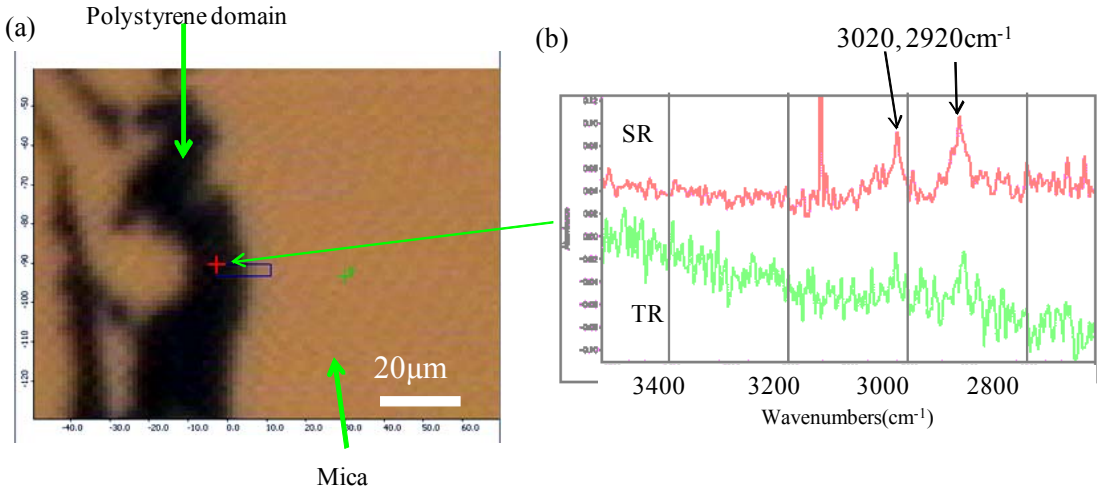


Fig. 1 (a) a video image and (b) IR spectra measured by the SRMS (upper red line) and the TRMS (lower green line) of polystyrene latexes dispersed on a mica substrate. Ring current is 277-189mA.

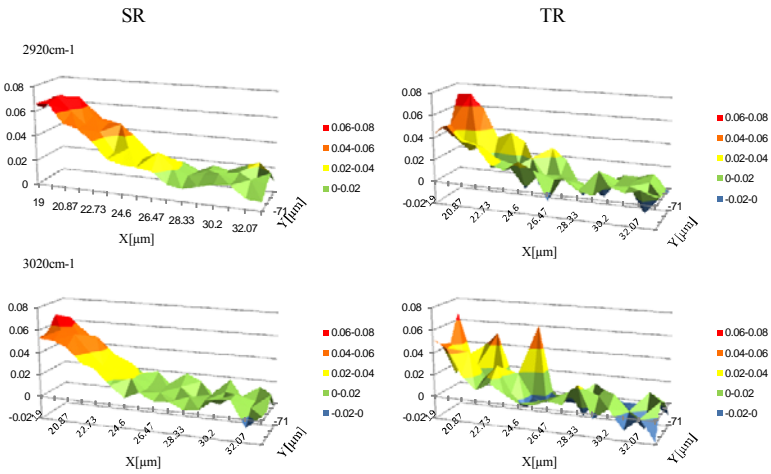


Fig. 2 3-d contour maps of each IR absorbance at 2920(upper), 3020cm⁻¹(lower) observed in Fig. 1 (b). The left column is the mapping by the SRMS and the right column is by the TRMS. Sampling intervals are approximately 1µm.

3.2 Onion cells

We measured IR spectra of a cell in an onion scale leaf. The using sample was dried. The aperture size of the IR microscope is 7µm x 5µm as the PS latexes measurement, but the number of scans is 64. Fig. 3(a) shows a video image of the sample. Figs. 3(b)-(d) are the IR

spectra of the nucleus, the cell wall and the cytoplasm directed by the arrows in the Fig. 3(a). All spectra have the peaks from 2800 cm^{-1} to 3000 cm^{-1} and a broadening peak near 3100 cm^{-1} to 3600 cm^{-1} , which are attributed to C-H stretching of hydrocarbon and O-H stretching, respectively. The spectra of the cell wall and the cytoplasm are nearly identical because cytoplasm is covered with cell wall and then IR beam passed through the cell wall before and after it passed through the cytoplasm. The nucleus is also covered with the cell wall. Any spectrum has the absorption of cellulose which is component of cell wall, at least for that reason. All the spectra measured by the SRMS have better SNR than those by the TRMS. In addition, the IR spectrum of the nucleus by the SRMS has a peak near 3300 cm^{-1} . On the TRMS, however, that peak is difficult to be recognized. This peak is attributed to N-H stretching and can be caused by nucleus acids in the cell. We make distribution maps of the areas of the N-H peaks in a video image (Fig. 4). Sampling intervals are approximately $2\mu\text{m}$. In the map of the SRMS, the domain in lighter contrast is coincident with the nucleus part in the video image as shown in Fig. 4(b). On the other hand, In the case of the IRMS, the contrasts of the nucleus are distributed even out of the nucleus (Fig4. (c)). These results suggest that the SRMS are a useful tool for study of biomaterials.

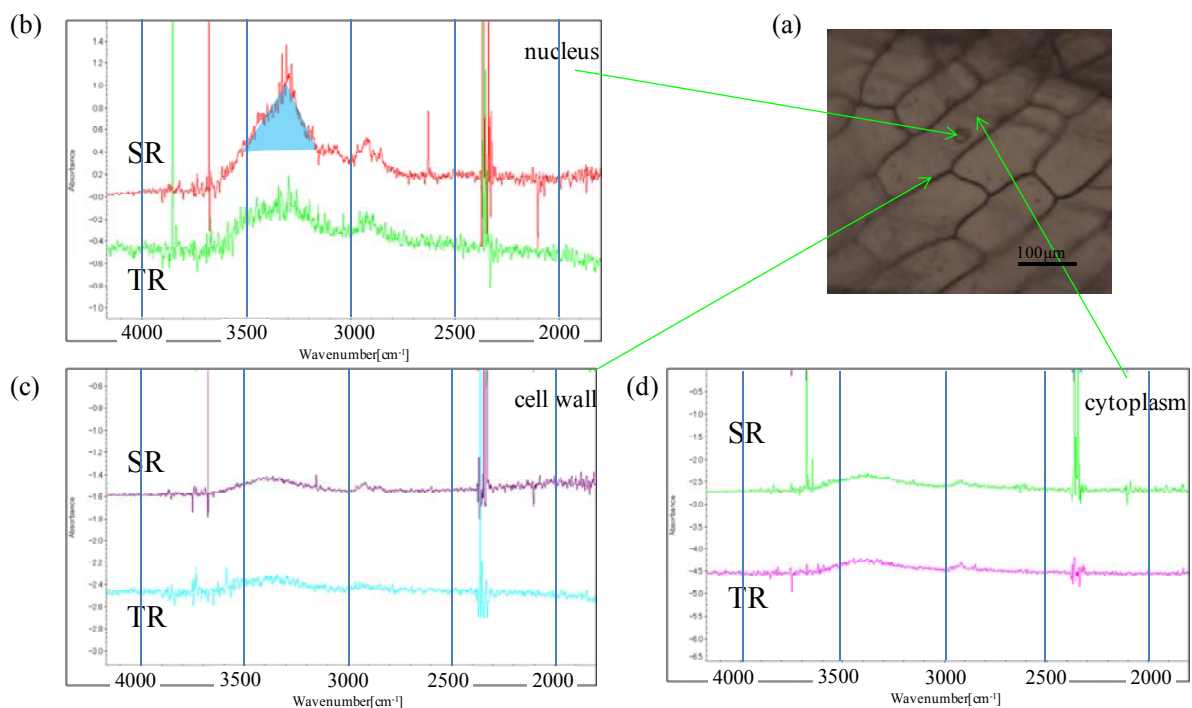


Fig. 3 A video image (a) and IR spectra of an onion scale leaf. The IR spectra are measured at the nucleus (b), the cell wall (c) and the cytoplasm (d) shown by the arrows in (a). Ring current is 173-168 mA.

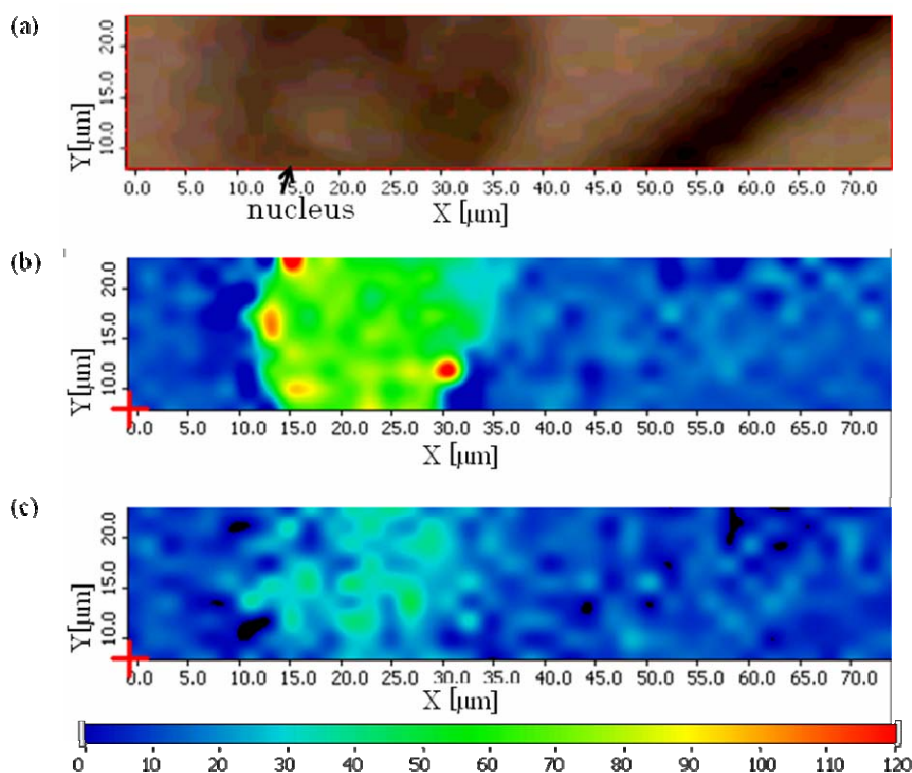


Fig. 4 (a) a video image around the nucleus in Fig. 3(a). (b) is the IR intensity map of (a) for the area of the peak near 3300cm^{-1} (the light blue section shown in Fig. 3 (b)) observed by the SRMS. Ring current is 247-163mA. (c) is that of the TRMS.

3.3 Dehydration process of polymer gels on a Si

Our SRMS has large intensity in the near-IR (NIR) region, compared with TRMS (Fig. 5). Therefore we can study on NIR spectra of water and organic compounds in a microscopic region. The aperture size is $10\mu\text{m} \times 10\mu\text{m}$ with a 32x Cassegrain optics and the number of scans is 32. Figs.6 (a) and (b) show swollen polymer gels which absorbed water and dehydrated polymers on a Si substrate, respectively. We then investigated the change of the spectra of water and the polymer gels under a dehydration process.

Fig.7 shows the reflection spectra of the polymer gels. Two absorption peaks occur

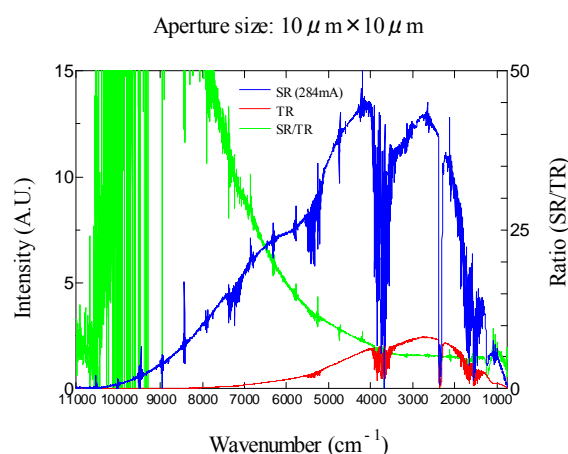


Fig. 5 IR intensity of the SRMS (blue line) and the TRMS (red line). The measurement condition of the microscope is the aperture size of $10\mu\text{m} \times 10\mu\text{m}$ with a 32x Cassegrain optics in a reflection mode. Ring current is 284mA. The green line is a ratio of the intensity of SRMS to that of TRMS. The ratio is five times in the mid-IR (MIR) region.

around 5200 and 7000 cm^{-1} , and a shoulder near 3900 cm^{-1} in the spectra drawn with blue lines. Their absorption bands correspond to those of liquid water [3] and become smaller as water is vaporised. In the mid-IR region, the saturation of absorption occurred. However, the spectrum of the dehydrated polymers (green line) has the two peaks at 1650 and 1550 cm^{-1} , attributed to amide groups in the polymer. The wave-like part in the NIR region of the green spectrum is an interference fringe caused by thickness of the sample. It is difficult to discuss the details of the mechanism on polymer-water interaction only from these results. We will further investigate on interaction between polymer and water. However, it is expected to study on adsorbates on surface and liquid-solid interfaces at a microscopic area.

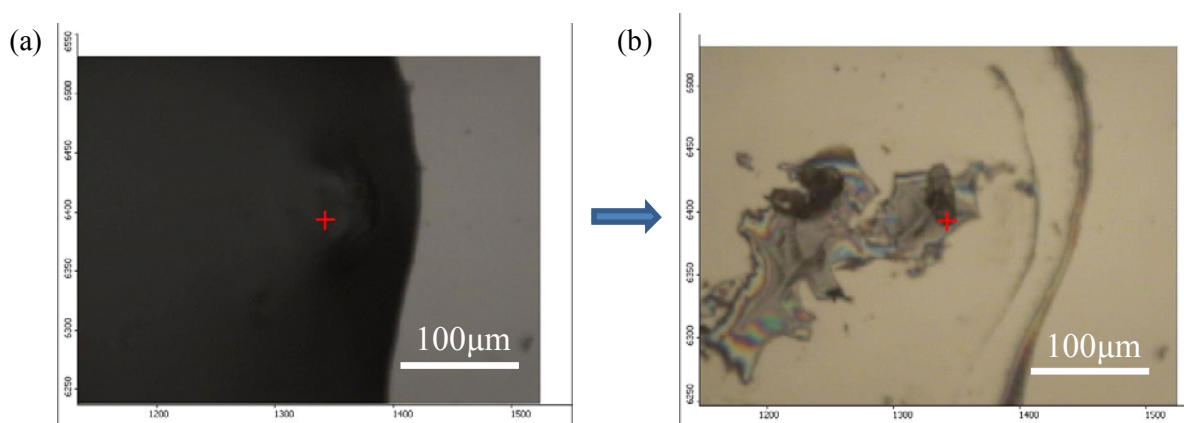


Fig. 6 Video images of polymer gels. After adding a drop of water to the gels, the gels was swollen (a) and was shrank as the water in the gels was evaporated.

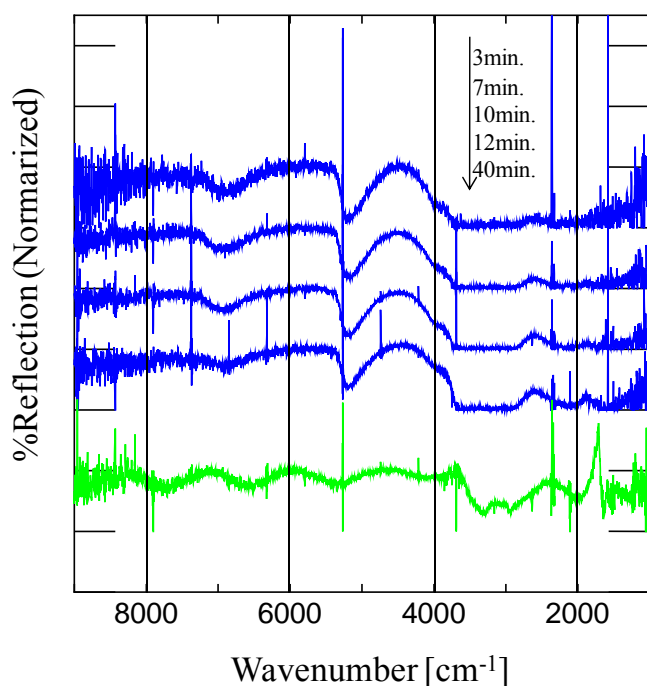


Fig. 7 NIR-MIR spectra of the polymer gels on the swollen polymers (blue lines) and on the dried polymer (green line). The intensities of the spectra are normalized by ring current.

4. Summary

We evaluated the SRMS beamline by observing some samples. Every spectrum measured with the SRMS beamline has better quality than those with the TRMS. Then, we can conclude that our SRMS has potential for application to material science, bio science and surface science.

References

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