BL43IR
Infrared Materials Science

1. Introduction

BL43IR is dedicated to infrared (IR) microspectroscopy in the wavenumber region from 10,000 cm^{-1} to 150 cm^{-1}. The beamline has three microscopes: a high-spatial-resolution microscope, a long-working-distance microscope, and a magneto-optical microscope. These microscopes are used with a Fourier transform spectrometer. We are developing new instruments for microspectroscopy not only to upgrade equipment already in operation but also to recruit new users for various sample environments.

2. New sample cells developed on users' request

We often use a temperature control stage (Linkam 10036L) in a range of experiments aimed at investigating the vibrational or structural response of a sample to temperature. Some users desire additional experimental conditions other than temperature to explore responses to multiple conditions. We planned to meet their demands and made new gadgets to put in/on the Linkam stage.

One such gadget we prepared is a "chemical compound vaporizing cell", as shown in Fig. 1, in which some chemicals of interest are vaporized inside the sample cell. The samples are protected from direct contact with the chemicals by putting a mesh cover on the samples and the chemicals are placed on the mesh cover. The cell is closed with two BaF_2 windows. The volume of the sample room is approximately 130 mm^3.

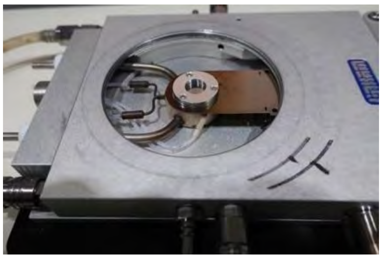

Fig. 1. Chemical compound vaporizing cell (center) on the Linkam stage.

Another cell was planned upon requests for attenuated total reflection (ATR) measurements under various atmospheric conditions. The ATR microscope usually has an ATR probe tip attached to the objective lenses. Therefore, we cannot conduct ATR measurements of a sample in a closed room such as in the Linkam stage. We replaced Linkam's upper lid with the "ATR probe lid" shown in Fig. 2. By screwing on the lid, we can firmly contact the ATR probe to a sample. We then focus the light onto the ATR probe with a non-ATR objective. A preliminary result obtained using the system is shown in Fig. 3. We see a meaningful structure of the sample but in a blurry manner. We need some refinement of the ATR probe housing, which currently does not firmly fix the position of the probe tip, and we are working on a new plan for it.

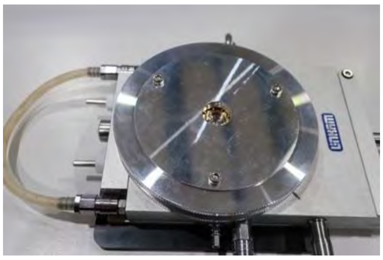

Fig. 2. ATR probe lid on the Linkam stage.

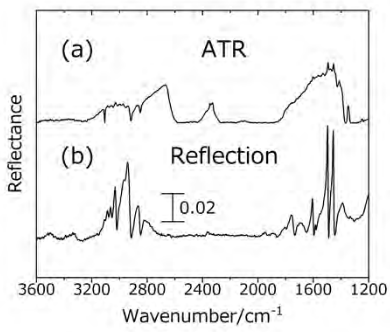

Fig. 3. (a) Reflectance of a polystyrene piece with ATR probe lid. (b) Reflectance of the same sample measured in the reflectance mode with no ATR.

3. Influence of condensation on infrared spectra in low-temperature experiment and countermeasure

OH, stretching vibrations are observed at around 3400 cm^{-1} in the mid-IR region, which is a highly sensitive band. For low-temperature experiments down to liquid helium temperature, a cryostat with a sample space that can be evacuated is used to prevent condensation on the sample. At BL43IR, Cryostat-He (Oxford Cryosystems) is used for the long-working-distance microscopy station and high-spatial-resolution microscopy station, and a Model RC-102 variable temperature continuous flow cryostat (Cryo Industries of America, INC.) is used for the magneto-optical microscopy station. In these cryostats, the sample space is evacuated to the lower half of 10^{-4} Pa at room temperature using turbo- and scroll pumps. This is well below the vacuum recommended for these cryostats. Nevertheless, at low temperatures, ice from condensation may still adhere to the sample surface and affect the infrared spectrum. Figure 4 shows the reflection spectra of a Au mirror measured at the magneto-optical station. The spectra are raw data without corrections for instrument functions and other factors. In curve (b), a band indicated by * is observed at 3300 cm^{-1}, which is not observed in curve (a). The wavenumber of the band is clearly the wavenumber of the OH vibration of the ice (solid phase of water). This band seriously affects the spectra and interferes with the experiments. In the case of Fig. 4, curve (b) was measured at 60 K by decreasing the temperature gradually from room temperature, and curve (a) was measured after curve (b) by increasing the temperature once up to about 220 K and then decreasing it again to 60 K. In our experience, this band is observed below about 180 K, which is consistent with the ice condensation temperature based on the degree of vacuum and water phase diagram. Figure 4 shows a case in which the band disappears when the temperature is increased above 180 K, but after that, it often reappears after some time. We have been exploring various measures to address this problem, especially with Dr. S. Iguchi of Tohoku University.

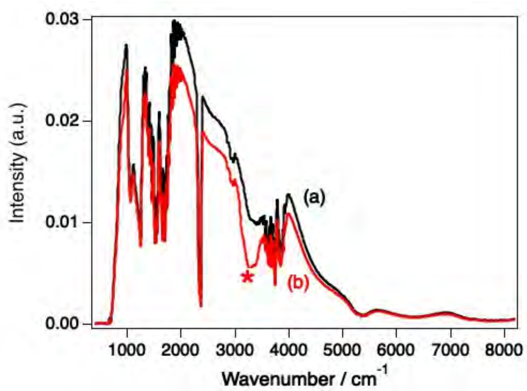

Fig. 4. Reflection spectra of Au mirror measured at 60 K in the magneto-optical microscopy station. The structure marked with * is absent in curve (a) but present in curve (b).

There are two key measures we have found to prevent ice adhesion: (1) improve the quality of the vacuum and (2) prevent atmospheric backflow from the vacuum pump. The cryostats use O-rings, and the degree of vacuum cannot be increased any further because of the structure of the cryostats. Even if the apparent vacuum level is good enough, water molecules adhering to the inner walls of the cryostat, for example, are considered to slowly evaporate and adhere to the sample surface at low temperatures. In this case, the ice band appears in the spectrum within a relatively short time after the temperature is lowered. Countermeasures are as follows. (1) Before the experiment, the cryostat is evacuated for a sufficiently long period of time (about one week), during which time it is baked at a mildly high temperature (about 80°C). (2) When mounting the sample into the cryostat, the inside of the cryostat is warmed with a blower. (3) After mounting the sample, the cryostat should be sufficiently evacuated (about half a day) before lowering the temperature. The second countermeasure is to prevent backflow from the pump. In a scroll pump, which is used as a supplemental pump for a turbopump, water is generated in the pump owing to compression or backflow of air from the exhaust port, and the water may flow into the vacuum layer and become ice. In this case, the ice signal appears sometime (about one day) after the sample has been cooled. The countermeasure is to introduce a flow of dry nitrogen gas through the pump's exhaust port or ballast port. Careful attention should be paid to the flow rate so as not to interfere with the pump's exhaust.

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