Selection of modulation frequency of FT-IR equipped with an MCT detector for thin-film analysis

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ABSTRACT

Optimal modulation frequency (scan rate) of an FT-IR equipped with a mercury–cadmium–telluride (MCT) detector has been investigated for obtaining high quality spectra of a monolayer-level thin film. Since an MCT detector is a semiconductor light device, it does not respond to modulation frequency significantly in comparison to a pyroelectric detector. A very thin film, however, requires high-throughput measurements to have high signal-to-noise ratio. In this study, a balance of throughput and measurement time has been investigated by varying modulation frequency by using two spectrometers that have different sampling frequencies. In this study, the stability of the baseline of absorbance spectra was also investigated depending on modulation frequencies, which suggested that 60 kHz was most suitable for quantitatively reliable transmission measurements of Langmuir–Blodgett films.

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1. Introduction

Fourier transform infrared (FT-IR) spectrometer has greatly been improved in the past two decades, and organic ultrathin films represented by Langmuir–Blodgett films [1] even at a single-monolayer level have become a suitable analyte for FT-IR. The significant progress of FT-IR was realized mainly by technology progress in electronics about a mercury–cadmium–telluride (MCT) detector [2] and the dynamic alignment of interferometer [2]. In early 1990s, measurements of a single-monolayer LB film were a challenging task [3,4] even with a high-sensitive optical geometry such as reflection–absorption spectrometry [5–7]. Multi-layered LB films were therefore fabricated to overcome the analytical limitation. Thanks to the advances in technology, the situation was largely improved, and now a single-monolayer LB film can be measured even with transmission spectrometry.

An MCT detector is a semiconductor light device operated at a liquid-nitrogen cooled temperature, which has characteristics that it significantly responds to weak-intensity light while it does not greatly respond to modulation frequency (scanning rate or mirror velocity) in comparison to a pyroelectric detector [2]. The lowest detectivity limit of a MCT detector can be about 10–50 times greater than a pyroelectric detector such as deuterated triglycine sulfate (DTGS) detector [2]. Therefore, when an MCT detector is coupled with a high-bit analogue-to-digital converter and amplifier, high-resolution measurements of light 'intensity' can be performed, which leads to 'high sensitivity in absorbance.' An MCT detector is thus often used for measurements of infrared spectra of ultrathin films.

Another important improvement is found in the technology of dynamic alignment [2], which proves the stability of interferometer operation. Highly accurate operation of the interferometer in an FT-IR is definitely necessary for quantitatively reliable measurements of interferograms. Due to the development of dynamic alignment by computer-aided mechatronics, the operation has come close to ideal, which made accurate accumulation measurements possible.

In this study, we have found that even a state-of-the-art spectrometer exhibits a theoretically unexpected response to modulation frequency. We have investigated responses of two spectrometers in our laboratory, one of which was assembled about 15 years ago, while the other was made very recently. The old and new spectrometers employ different sampling frequencies of 100 and 500 kHz, respectively, but both are enough above the Nyquist frequency even when mid-infrared measurements at $4000 \, \mathrm{cm}^{-1}$ or lower and the highest modulation frequency (200 kHz) are taken into account. The Nyquist frequency, f_{samp},

in FT-IR is defined as

$$f_{samp} = 2V\tilde{v}_{max} \tag{1}$$

Here, V is the optical velocity, and $\tilde{v}_{max}$ is the highest wavenumber for the measurement. For a condition the highest modulation frequency on a NIR measurement at 12,000 cm^{-1}, for example, the Nyquist frequency is calculated to be 304 kHz. Therefore, if we want to measure NIR spectra with a very rapid scanning rate, the new spectrometer should be chosen. For measurements of ordinary mid-infrared spectra, however, both spectrometers are considered to have no problem as long as only the sampling frequencies are taken into account. In theory, therefore, a very fast scanning can be chosen for mid-infrared measurements, which is expected to play a good role in a long time measurement.

When a very high modulation frequency was chosen, nevertheless, the measurement time has been found to be out of theoretical values largely, and this trend was very common to both the spectrometers. Then, an optimized experimental condition for measurements of ultrathin films has been explored. The modulation frequency was studied with respect to optical throughput, efficiency of accumulations and quantitative stability of absorbance spectra. As a result, the optimization was found to be meaningful to use an FT-IR with high reliability for better analysis of ultrathin films.

2. Experimental

The infrared spectrometers used for the present study were Thermo Fisher Scientific (Madison, WI) Magna 550 FT-IR and Nicolet 6700 both equipped with an MCT/A detector of an identical model that covers a mid-infrared range of 650–4000 cm^{-1}. Measurements were performed after attaining a thermally stable condition of the detector, which was at least 2 h after filling the vacuum bottle on the detector with liquid nitrogen. To make the experimental condition the same as that used for our practical analysis of thin films, 2000 double-sided interferogram patterns were co-added for each measurement. The resolution was 4 cm^{-1}.

The FT-IR has a variation of mirror velocity (v): 0.1581, 0.3165, 0.4747, 0.6329, 0.9494, 1.2659, 1.8988, 2.5317, 3.1647, 3.7974, 4.4303, 4.7468, 5.0632, 5.6961 and 6.3290 cm s^{-1}, which correspond to modulation frequencies (f) of 5, 10, 15, 20, 30, 40, 60, 80, 100, 120, 140, 150, 160, 180 and 200 kHz (refer to Eq. (1)), respectively, since a He–Ne laser with the wavelength ($\lambda = 1/\tilde{v}$) of 632 nm is equipped in the interferometer [8]. The default "settle time" of 200 ms was used for this study. The settle time is an implicit parameter controlling a stepping time before the next retardation of the moving mirror.

In this paper, 'modulation frequency' is used instead of 'mirror velocity' unless otherwise stated, since mirror velocity is often confusing with 'optical path difference (OPD) velocity' or 'optical velocity,' which is defined considering the travelling distance of light between the fixed and moving mirrors.

The standard sample for the absorbance spectra measurements was a five-monolayer LB film of cadmium stearate deposited on a germanium substrate. The refractive index of germanium is extraordinary high, which makes observed band intensities (absorbance) smaller than using a low-refractive-index substrate such as CaF$_2$. Regardless, the germanium substrate is often employed for our purposes, since it is chemically stable especially in an aqueous solution in comparison to materials of ionic salt, which is suitable for fabrication of LB films. Another reason to choose the germanium substrate is that the MAIRS technique requires a high refractive-index substrate [8–10].

The LB deposition was performed at a surface pressure of 30 mN m^{-1} on a subphase surface. The water subphase for the LB deposition was comprised of 3×10^{-4} M cadmium chloride and 3×10^{-4} M sodium hydrocarbonate, so that pH should be ca. 7.3, with which the stearic acid monolayer would fully be reacted to be cadmium salt at the subphase surface. Water used for the subphase was prepared by purification of tap water by a Millipore (Molsheim, France) Elix UV-3 pure-water generator and a Yamato (Tokyo, Japan) Autopure WT100U water purifier, which is a compatible model with Milli-Q. The resistivity of the product water was 18.3 MΩ cm and the surface tension was 72.8 mN m^{-1} at 25 °C, which proved that the water was contamination free.

3. Results and discussion

Single-beam spectra of air (with no sample) were collected at various modulation frequencies in the range of 5–200 kHz. Intensity variations of the single-beam spectra measured at 2600 cm^{-1} for the sampling frequencies of 100 and 500 kHz are plotted in Fig. 1. Since the measurements were performed on the two spectrometers by using different built-in optical mesh filters to prevent saturation of the detector, the absolute intensities are different from each other. The entire variations are, however, found to be highly similar to each other even for a high modulation frequency region, although the two spectrometers have different sampling frequencies. It is commonly found that the variation exhibits almost no increase when the modulation frequency is less than 20 kHz, whereas it exhibits a linear increase by about 5% until the modulation frequency attains at 150 kHz. The sensitivity of a detector is evaluated by the use of 'specific detectivity', D^*, that is defined as [11]:

$$D^* = \frac{(A_D)^{1/2}}{NEP} \tag{2}$$

where A_D is the detector area, and NEP (noise equivalent power) is a measure of the lowest limit of observable signal, which is comparable to the detector noise. NEP is defined as

$$NEP = \frac{V_n}{R_V} \tag{3}$$

where V_n is the root mean square detector noise voltage, and R_V is the voltage responsibility. NEP should be as small as possible to
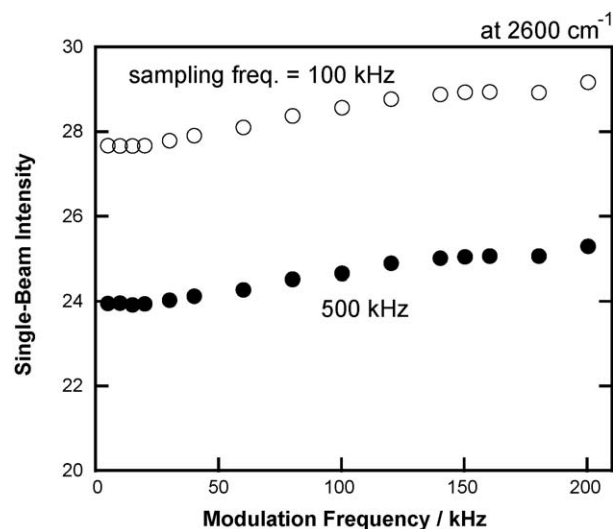

Fig. 1. Intensity variation of single-beam spectra of air measured at 2600 cm^{-1} with an increase of modulation frequency.