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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 the present 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 the present 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.

Key words: FT-IR; Modulation frequency; MCT detector; Thin film

Introduction: Fourier transform infrared (FT-IR) spectrometer has greatly been improved in the past two decades, and organic ultrathin films represented by Langmuir-Blodgett films¹ 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) detector² 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 ten to fifty 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 the present 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 fifteen 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 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:

$$f_{samp} = 2V\tilde{\nu}_{max} \quad (1)$$

Here, V is the optical velocity, and $\tilde{\nu}_{max}$ is the highest wavenumber for the measurement. For a condition the highest modulation frequency on a NIR measurement at 12000 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.

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 two hours 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 $6.3290\text{ cm sec}^{-1}$, 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 ($\lambda = 1/\tilde{\nu}$) of 632 nm is equipped in the interferometer.⁸ The default “settle time” of 200 ms was used for the present study. The settle time is an implicit parameter controlling a stepping time before the next retardation of the moving mirror.

In the present 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 traveling 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 $3 \times 10^{-4} \text{ M}$ cadmium chloride and $3 \times 10^{-4} \text{ M}$ 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 $18.3 \text{ M}\Omega \text{ cm}$ and the surface tension was 72.8 mN m^{-1} at 25°C , which proved that the water was contamination free.

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 Figure 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

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

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:

$$\text{NEP} = \frac{V_n}{R_v} \quad (3)$$

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 measure low intensity radiation, and it is roughly reciprocal to the signal-to-noise ratio (SNR). Therefore, D^* is a good measure to evaluate the sensitivity of a detector normalized by the detector area A_D . If infrared light having stable and steady power is available for the study, a detector with a higher D^* would have a higher throughput, since the apparatus noise is approximately constant.

The sensitivity of an MCT detector is known to depend on modulation frequency of an FT-IR, which has conventionally been discussed by using the parameter, D^* .² According to a

former report,¹² D^* goes up rapidly when the modulation frequency is increased up to 1 kHz, while it exhibits a gradual increase in the range of 1 kHz—1 MHz, which is, in fact, found in Figure 1 in the range of 20—150 kHz by about only 5%. Since thin film analysis requires high throughput measurements, the observed results indicate that the MCT detector should be used at a high modulation frequency as possible.

The use of an MCT detector at a high modulation frequency has another benefit that the collection time of spectra becomes shorter, which enables us to accumulate more scans in the same period of time to attain a better SNR. For example, multiple-angle incidence resolution spectrometry (MAIRS) that is powerful for thin film analysis⁸⁻¹⁰ requires repeated measurements at several angles of incidence, which spends much time for the measurements.

Then, measurement time of 2000 scans against the modulation frequency was investigated for both spectrometers as plotted in Figure 2. The number of 2000 scans is often employed in our laboratory to obtain spectra of ultrathin films with a good SNR. The results of the two spectrometers are close to each other particularly for a high modulation frequency.

When the moving mirror of Michelson's interferometer is moved at a constant rate of v in a period of time, t , the total running length of the moving mirror, l , is:

$$vt = l \quad (4)$$

Since the modulation frequency, f , is related by Eq. 1 to the mirror velocity, v , at the laser

frequency, $\tilde{\nu}$, the product of f and t becomes a constant as formulated in Eq. 5.

$$ft = 2\tilde{\nu}l \quad (5)$$

In fact, the plot in Figure 2 roughly obeys the inverse proportional relationship. On closer inspection, however, the change in the measurement time becomes little especially above 100 kHz, which is apparently out of Eq. 5. To make the results easier to understand, the same results are re-plotted in Figure 3, in which the measurement time, t , is plotted against the reciprocal mirror velocity, $1/v$.

The open and closed circles are roughly on the dashed and solid lines that are formulated as:

$$(t - a) = \frac{l}{v} \quad (6)$$

where a is the intercept on the ordinate axis. Therefore, the slope of the line corresponds to the total running length of the mirror, l , and a should correspond to the dead time wasted for the smooth mechanical movement of the moving mirror. Judging from Figure 3, l and a are calculated to be 0.516 cm and 0.338 sec for the old spectrometer, whereas they are obtained to be 0.566 cm and 0.270 sec for the new spectrometer, respectively, per scan. No significant difference has been found between the two spectrometers.

The resolution, $\Delta\tilde{\nu}$, is simply related to the maximum retardation of the moving mirror,

$$\Delta_{\max} \propto \lambda^2$$

$$(\Delta \tilde{\nu}) = (\Delta_{\max})^{-1} \quad (7)$$

Since the resolution in the present study is 4 cm^{-1} , $\Delta_{\max}$ is calculated to be 0.25 cm for a double-sided interferogram. Therefore, the observed running distances (0.516 and 0.566 cm) are considered to involve much extra-length (about 0.30 cm) for attaining a mechanical stability. The phenomenon of this time loss of the duty cycles is well known, and the analysis using the reciprocal velocity plot is found to be useful to determine an optimal fastest rapid scan rate.

Of note here is that the observed plots are out of the straight line for both spectrometers when the reciprocal of mirror velocity is less than 0.52 sec cm^{-1} that corresponds to the mirror velocity of $1.8988 \text{ cm sec}^{-1}$ or higher (the modulation frequency is 60 kHz or higher). The plot therefore suggests that if the modulation frequency is increased more than 60 kHz , dead time would also be increased, which means that the efficiency of accumulation would be degraded.

Another issue has come up when absorbance spectra of a thin film were measured with a rapid scan. To investigate the measurement stability of an ‘absorbance spectrum’ of a very thin film, a practical sample of a five-monolayer LB film of cadmium stearate was measured with various modulation frequencies. The background spectra were collected by the use of a germanium substrate with no film. Representative five transmission spectra are presented in Figure 4, in which a whole wavenumber range of spectra measured with an MCT detector is shown. In the C–H stretching vibration region, the anti-symmetric and symmetric CH_2 stretching

vibration bands appear strongly at 2917 and 2850 cm^{-1} , respectively, because of the surface selection rule of the transmission spectrometry for a thin film with a molecular orientation of perpendicular stance.⁷ In the same manner, the anti-symmetric COO^- stretching vibration ($\nu_a(\text{COO}^-)$) band appears strongly at 1540 cm^{-1} . The most significant characteristic of the spectra is that the spectrum measured with a modulation frequency of 200 kHz is largely influenced by fringes.

When a low wavenumber region is magnified as in Figure 5, the intensity of the $\nu_a(\text{COO}^-)$ band is found to be quantitatively influenced by the fringe. In this figure, the five spectra are overlaid with each other, so that the peak tops of the $\nu_a(\text{COO}^-)$ band match each other. Only the spectrum with the modulation frequency of 200 kHz has a shifted baseline to a higher value than those of the rest spectra. As a result, the band intensity is made decreased by about 5 % when 200 kHz is employed. The reason the fringes appear is not clear, but it may be caused by mechanical instability with the very high scan rate irrespective of the sampling frequency considering the Nyquist frequency. In this manner, the highest modulation frequency is not suitable for measurements of spectra having minute absorbance, although it is suitable for time resolved measurements of spectra of quick phenomena.

Conclusion: Optimization of modulation frequency has proved to be necessary for better reliable measurements of spectra for very thin films. In the present case of the old and new spectrometers,

the modulation frequency of 60 kHz has been found most useful in terms of both high throughput and efficient accumulation, although the spectrometers have different sampling frequencies. In addition, instability of single-beam measurements with a too high modulation frequency was revealed by finding fringes on an absorbance spectrum. Even for using a time-consuming technique such as MAIRS¹⁰⁻¹² for molecular orientation analysis in a thin film, a higher frequency near 100 kHz would be employed as the highest possible. With the rapid scan condition, 163 sec can be saved for 2000 scans, which saves 16 min more for a MAIRS analysis using six angles of incidence. A higher frequency than 100 kHz would not work well because of the dead time on scanning.

Although the matter of unpleasant long scanning time can be overcome by reducing settle time, in the present paper, characteristics of FT-IR measurements for thin film analysis with respect to scanning rate have been discussed at the default settle time.

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Figure captions:

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

Figure 2: Measurement time needed for 2000 scans at various modulation frequencies, a part of which is magnified and presented in the inset.

Figure 3: The measurement time data in Figure 2 are re-plotted against the reciprocal of mirror velocity. The theoretically explainable part is represented by the dashed line.

Figure 4: Representative five transmission absorbance spectra of a five-monolayer LB film of cadmium stearate on a germanium substrate. For an easy comparison, the base lines of the spectra are shifted.

Figure 5: A part of the spectra in Figure 4 is re-plotted. In this figure, the peak tops of the $\nu_a(\text{COO}^-)$ band are matched, so that the baseline shift would clearly be recognized.

Figure 1 T. Hasegawa et al.

Figure 2 T. Hasegawa et al.

Figure 3 T. Hasegawa et al.

Figure 4 T. Hasegawa et al.

Figure 5 T. Hasegawa et al.