

Optimum Condition of Fourier Transform Infrared Multiple-Angle Incidence Resolution Spectrometry for Surface Analysis

Takeshi Hasegawa,* Lisa Matsumoto, Setsuko Kitamura, Sanae Amino, Shin-ichi Katada, and Jujiro Nishijo

Kobe Pharmaceutical University, Motoyama-kita, Higashinada-ku, Kobe 658-8558, Japan

A novel measurement technique of pure out-of-plane vibrational modes of thin films on a nonmetallic substrate has recently been proposed, which is named multiple-angle incidence resolution spectrometry (MAIRS). Since this technique could not be replaced by other conventional techniques, MAIRS was expected to be a promising tool for analysis of thin soft materials and surface adsorbates. Nevertheless, some experimental conditions have been found to be inappropriate for MAIRS, which yields incorrect results. In the present study, therefore, the problems in the technique have been investigated in terms of optics to improve the accomplishments of MAIRS. The problems have been found to have a strong relationship with optics in FT-IR, which is influenced by refractive index of the sample material and angle of incidence. In particular, optimization of the size matching of the detector surface and the infrared spot at the detector was a key to having MAIRS perform properly. It has been concluded that reliable MAIRS measurements require overfilling of the detector and a substrate with a high-refractive index.

Measurements of pure out-of-plane (OP)-mode spectra of thin films have been a difficult matter for experimental physics, and the only exception is the reflection–absorption (RA) technique, which is very common to infrared spectroscopy.^{1–4} This difficulty is caused by a physical limitation of light: the electric field vector of light has a perpendicular direction to the light path, and no electric field vector that is parallel to the path is available.² In fact, measurements of in-plane (IP)-mode spectra of the thin films are easily performed by use of normal-incidence light that has surface parallel electric fields in the film on a transparent substrate. To generate a surface-normal electric field in the film, reflection optics is used on a metallic surface, which is the RA technique. When an incidental light is irradiated on the metallic surface at a grazing angle, a strong surface-perpendicular electric field is generated

near the surface, and the optically thin film is irradiated in a virtually polarized light that has a surface-normal electric field to the film.³

In this fashion, the OP-mode spectra of adequately thin films can easily be measured by the reflection optical configuration. Nevertheless, this requirement becomes a heavy limitation for various measurements, since the substrate for supporting the thin films must be metallic. This means that IP and OP spectra should be measured on different substrates. For infrared spectroscopy, for example, the substrate for IP-mode spectra should be infrared-transparent materials, such as CaF₂, ZnSe, Si, and Ge. On the other hand, OP-mode spectra are often measured with the use of gold or silver substrates, because of their high reflectivity. Therefore, when we want to compare IP and OP spectra to analyze the film, we have to prepare “nearly identical” films on different surfaces, which are subjected to different spectrometries, transmission and RA techniques. This experimental complexity causes various analytical problems. Among the problems, the chemical influence of the substrate on the film is not ignorable. Since the thin films are molecular adsorbates on the substrate, the film structure depends on molecular conformation that is influenced by the surface free energy of the substrate. This means that the film structure may largely be affected by surface properties of substrates.

To overcome the experimental limitations, a new analytical technique based on a novel physical concept has recently been proposed. This technique employs a classical least-squares (CLS) regression technique^{5–9} to decompose the total light intensity into the two virtual light components: IP and OP components.⁴

$$\mathbf{S} \cong \begin{pmatrix} \mathbf{s}_{\text{obs1}} \\ \mathbf{s}_{\text{obs2}} \\ \vdots \end{pmatrix} = \begin{pmatrix} r_{\text{IP1}} & r_{\text{OP1}} \\ r_{\text{IP2}} & r_{\text{OP2}} \\ \vdots & \vdots \end{pmatrix} \begin{pmatrix} \mathbf{s}_{\text{IP}} \\ \mathbf{s}_{\text{OP}} \end{pmatrix} + \mathbf{E} \cong \mathbf{R} \begin{pmatrix} \mathbf{s}_{\text{IP}} \\ \mathbf{s}_{\text{OP}} \end{pmatrix} + \mathbf{E} \quad (1)$$

Here, $\mathbf{s}_{\text{obs}j}$ is a row vector that represents an observed unpolarized

* Corresponding author. E-mail: hasegawa@kobepharm-u.ac.jp. Fax: +81 78 435 2080.

- (1) Hasegawa, T.; Nishijo, J.; Umemura, J.; Theiss, W. *J. Phys. Chem. B* **2001**, *105*, 11178–11185.
- (2) Ibach, H.; Luth, H. *Solid-State Physics: An Introduction to Principles of Materials Science*; Springer: New York, 1995.
- (3) Umemura, J. In *Handbook of Vibrational Spectroscopy*; Chalmers, J. M., Griffiths, P. R., Eds.; Wiley: Chichester, U.K., 2002; Vol. 2, pp 982–998.
- (4) Hasegawa, T. *J. Phys. Chem. B* **2002**, *106*, 4112–4115.

- (5) Martens, H.; Næs, T. *Multivariate Calibration*; Wiley: Chichester, U.K., 1989.
- (6) Kramer, R. *Chemometric Techniques for Quantitative Analysis*; Marcel Dekker: New York, 1998.
- (7) Hasegawa, T. In *Handbook of Vibrational Spectroscopy*; Chalmers, J. M., Griffiths, P. R., Eds.; Wiley: Chichester, U.K., 2002; Vol. 2, pp 2293–2312.
- (8) Malinowski, E. R. *Factor Analysis in Chemistry*, 3rd ed.; Wiley-Interscience: New York, 2002.

transmission (single-beam) spectrum at an angle of incidence, θ_j . The collection of $\mathbf{s}_{\text{obs}j}$ vectors by the multiple-angle measurements forms the matrix, \mathbf{S} . Of note is that the light intensity can simply be formulated by the two light components and a mixing ratio, since the delivery of electric fields to the surface normal and parallel is adequate. When oriented absorption happens in the film, the anisotropic absorption is also linearly reflected in the series of single-beam spectra by the change of angle of incidence, because the oriented dipole is simply interacted with the delivered electric fields. If absorbance spectra instead were analyzed in a similar way, optical parameters would be necessary, since absorbance is a result of common logarithm of a ratio of transmission spectra, which is basically defined by Beer's law affected by optical parameters.

The "single-beam spectra" matrix can theoretically be related to the pure IP- and OP-mode transmission spectra, \mathbf{s}_{IP} and \mathbf{s}_{OP} , by use of mixing ratios in \mathbf{R} .⁴

$$\mathbf{R} = \left(\frac{4}{\pi}\right)^2 \begin{pmatrix} 1 + \cos^2 \theta_j & \sin^2 \theta_j \tan^2 \theta_j & \tan^2 \theta_j \\ \vdots & \vdots & \vdots \end{pmatrix} \quad (2)$$

The reader may still be concerned that the signal intensity would be influenced by the transmittance or reflectance of the substrate, and optical parameters would be necessary for the evaluation of \mathbf{R} . It is true that the transmission/reflection ratio would reflect the optical parameters. Nevertheless, the ratio would not obey the linear regression model represented by eq 1. Therefore, such complicated factors would be eliminated by the regression calculation, and they would be deposited in the error matrix, \mathbf{E} . As a result, the delivery of the electric fields to the two lights becomes possible.

One of the characteristics of this technique is that the theoretically available matrix, \mathbf{R} , is used as the concentration matrix of CLS. CLS is originally a robust linear regression technique, but it becomes unstable when a concentration matrix that has considerable experimental error is used. In the present technique, the theoretically deduced robust matrix is used, so that the CLS regression would work efficiently.

This idea is of additional importance in terms of chemometrics. Thus far, spectral decomposition has always been performed for the observed "absorbance" spectra. This can schematically be said that "explicit data" is followed by chemometric analysis. In the present technique (multiple-angle incidence resolution spectroscopy; MAIRS), however, collected "implicit data" (single-beam spectra) are subjected to chemometric calculation to yield the explicit data. We can say, therefore, that the novel technique has been realized by changing the position of chemometrics in experimental physics.

As described in the previous paper,⁴ MAIRS was successfully used for the measurement pure OP-mode spectra on nonmetallic surfaces for the first time. Regardless, it has recently been found that some substrates are not suitable for MAIRS. To have MAIRS as a useful physical tool, the problems of this technique must be totally investigated, and they should be solved for practical use.

In the present study, therefore, details of the measurement techniques have been focused on, and the optics in FT-IR spectrometer have particularly been considered, to determine the optimum conditions to yield good MAIRS spectra.

MATERIAL AND METHODS

For the Langmuir–Blodgett (LB) film deposition technique and the chemical reagents that include stearic acid, cadmium chloride, and solvents, the reader is referred to the literature.⁴ The LB films were adequately dried in a desiccator at least overnight before the MAIRS measurements, so that the recrystallization effect could be ignored. In fact, the spectra of a sample were identical to those taken one week earlier.

Substrates used for the MAIRS measurements, CaF_2 , ZnSe, Si, and Ge, were all purchased from Pier Optics (Gunma, Japan). They have the same size of $40 \times 20 \times 1$ mm (1 mm is the thickness). Each fresh substrate was used after cleaning using a bath-type sonicator in distilled water, ethanol, acetone, chloroform, and dichloromethane, successively.

The FT-IR MAIRS measurements were performed by using a Harrick Scientific Co. (Ossining, NY) Brewster's angle sample holder (BXH-S1G). The angle of incidence was changed manually from 5° to 45° by 5° steps as done in the previous work.⁴ No polarizer is needed for the measurements. The collection of infrared transmission spectra was performed on a Nicolet (Madison, WI) Nexus 670 FT-IR spectrometer equipped with a mercury–cadmium–telluride (MCT) or a deuterated triglycine sulfate (DTGS) detector with a dry airflow in both sample compartment and inside spectrometer. In this spectrometer, the aperture is placed between the light source and the interferometer. Therefore, there is no need to consider the problem of convergence of the infrared light in the sample room. The change of aperture would have influence only on the diameter of the infrared beam spot in the sample room and on the detector. The laser modulation frequencies for the interferogram collections were 60 and 5 kHz for the MCT and DTGS detectors, respectively. The interferogram was accumulated 2000 and 300 times for MCT and DTGS, respectively, to improve the signal-to-noise ratio. The dry air was generated by an AirTech (Yokohama, Japan) AT-35H air drier, and the air purge was performed for ~ 20 min for every measurements.

RESULTS AND DISCUSSION

In the former success of the MAIRS measurements on a Ge substrate, a sample of five-monolayer (ML) LB films deposited on both sides of the substrate was used. For a direct comparison, the same LB film was fabricated on CaF_2 substrate surfaces at the same surface pressure of 30 mN m^{-1} . This LB film was subjected to the same MAIRS analysis by use of the MCT detector. To prevent the saturation of the detector, the aperture was made as small as 30 (full, 150). The analytical results are presented in Figure 1. To enable us to directly compare the IP and OP spectra in terms of absorbance scale, the IP spectrum is doubled in intensity.⁴ It is found that the IP spectrum looks quite similar to an ordinary transmission spectrum measured on CaF_2 , which is presented in Supporting Information. As a matter of fact, the IP spectrum was confirmed to be almost identical to the transmission spectrum directly measured at 0° except that the spectrum by

(9) Massart, D. L.; Vandeginste, B. G. M.; Buydens, L. M. C.; de Jong, S.; Lewi, P. J.; Smeyers-Verbeke, J. *Handbook of Chemometrics and Qualimetrics Parts A and B*; Elsevier Science, Amsterdam, 1997.

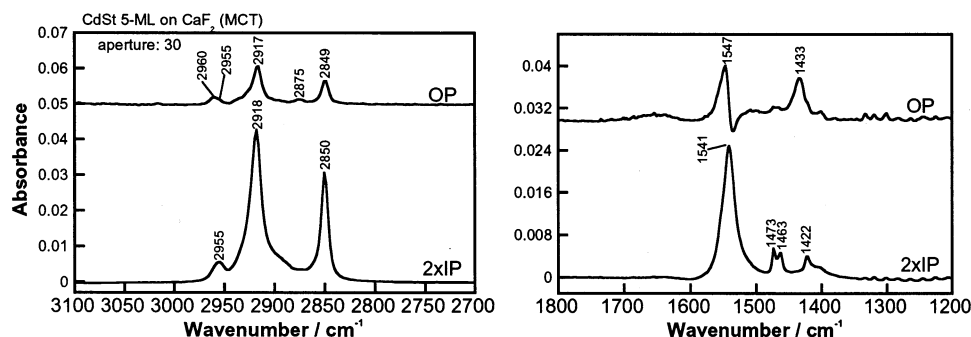


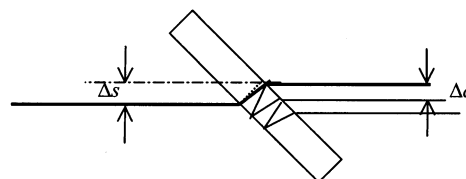
Figure 1. FT-IR MAIR spectra of five-monolayer LB film of cadmium stearate deposited on CaF_2 . An MCT detector was used with an aperture of 30. This corresponds to the underfill condition.

the direct-measurement spectrum slightly contained optical fringelike patterns as found in the previous paper.⁴ By simple consideration, this fringe may come from the multiple reflections in the substrate. Nevertheless, when we take the thickness of the substrate into account, the periodicity of the substrate is evaluated to be 0.6 cm^{-1} , which is apparently less than the band resolution of 4 cm^{-1} . It is possible, therefore, to consider two other reasons: (1) the reflected light from the substrate surface would interfere with the main beam to generate a secondary interferogram,¹⁰ and (2) slightly different interferograms of the sample and the reference would generate a beat signal, which would have larger periodicity and amplitude. Possibility 1 holds when the angle of incidence is perpendicular to the substrate. Since the fringelike pattern was found also for the oblique-angle incidence measurements, possibility 1 may be low. At present, therefore, possibility 2 would be a major candidate to explain the fringelike pattern. At any rate, this removal effect of optical fringelike pattern was reported in the previous paper, and it has been reconfirmed for the CaF_2 substrate.

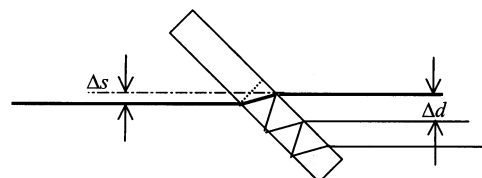
On the other hand, the OP spectrum for the LB film on CaF_2 is very poor. For reference, a RA spectrum of the LB film is also presented in Supporting Information. Both high- and low-wavenumber regions of the OP spectrum exhibit largely different characteristics from the infrared RA spectra of the same LB film measured on a gold surface. Relative intensities of the antisymmetric and symmetric CH_2 stretching vibration bands at 2917 and 2849 cm^{-1} are much stronger than those in the RA spectrum, and the antisymmetric COO^- stretching vibration band at 1547 cm^{-1} is stronger than the symmetric COO^- stretching vibration band at 1433 cm^{-1} , which is improper for RA results.^{1,3} If MAIRS worked ideally, the OP spectrum should be identical to the RA spectrum except for wavenumber dispersion of intensity, which reflects the optical property of the substrate material. Therefore, this large discrepancy between the OP and RA spectra strongly suggests that the MAIR analysis has failed.

When MAIRS was readily performed for the first time in the previous paper, a Ge plate was chosen for the substrate, because the refractive index of the plate is very large for infrared light ($n = 4.0$). Figure 2 presents optical schemes for Ge and CaF_2 plates. Panel a presents an optical path when a parallel infrared beam is irradiated to the Ge plate obliquely, in which the refracted beam is output with an optical shift that is shown by Δs . When a material with a high refractive index is used as the substrate, the

(a) Oblique incidence: Ge



(b) Oblique incidence: CaF_2



(c) Normal incidence

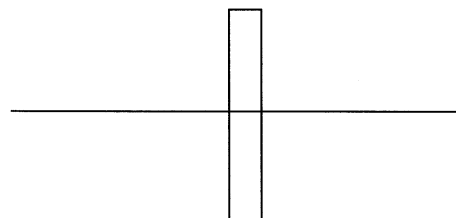


Figure 2. Schemes of optics for (a) Ge and (b) CaF_2 substrates when the angle of incidence is 45° . When the IR beam is irradiated perpendicularly, the optical scheme is represented by (c) irrespective of material. For details, see the text.

optical shift becomes fairly large, which would result in "mismatch" of the output beam with the infrared detector. This effect would be enhanced when the angle of incidence and thickness of the substrate would be large. Therefore, Ge was considered to be the toughest material for proper MAIRS measurements. In fact, as presented in Figure 2b, Δs would be much smaller for CaF_2 ($n = 1.42$), due to the small refractive index. Regardless, the poor results (Figure 1) have been obtained with the CaF_2 substrate, whereas Ge gave ideal results,⁴ which is unexpected.

To consider this seemingly contradictory issue, the optical scheme in Figure 2 was reconsidered. In the figure, multiple reflections are drawn schematically. It is found that the small refraction angle in the Ge plate due to the large refractive index generates small shifts, Δd , for the multiple reflections in the plate

(10) Griffiths, P. R. *Appl. Spectrosc.* **1982**, *36*, 319.

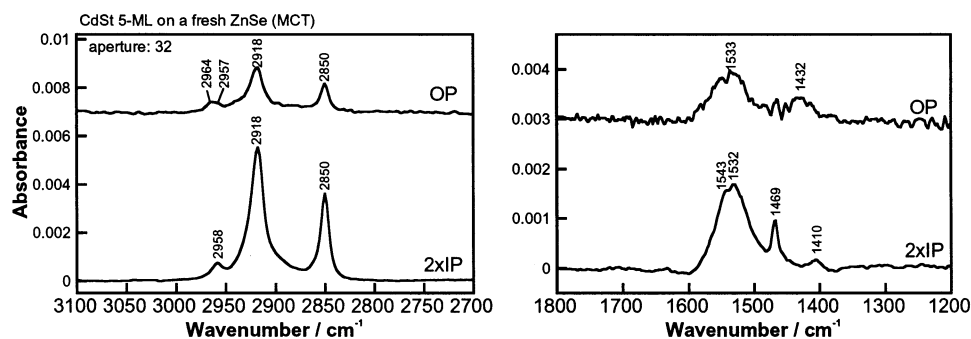


Figure 3. FT-IR MAIR spectra of five-monolayer LB film of cadmium stearate deposited on ZnSe. An MCT detector was used with an aperture of 32. This corresponds to the just-fit condition.

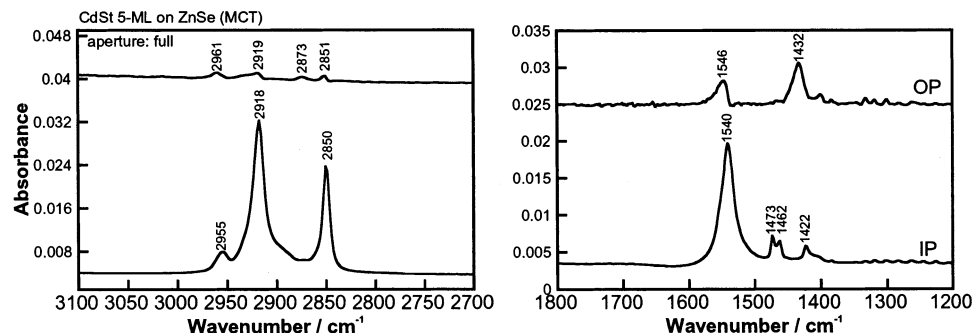


Figure 4. FT-IR MAIR spectra of five-monolayer LB film of cadmium stearate deposited on ZnSe. An MCT detector was used with an aperture of 150 (full). This corresponds to the overfill condition.

(Figure 2a). On the other hand, the large refraction angle in the CaF_2 plate causes large Δd for the multiple reflections (Figure 2b), although Δs is small. As a result, it is suggested that a *high order of multiple-reflection light in a low refractive index material* is considered to *miss the detector* due to the large Δd . When we consider the small sizes of the detector surface of MCT (1-mm i.d.) and DTGS (2-mm i.d.), this Δd effect on the multiple reflections would be crucial.

This Δd effect is also influenced by the angle of incidence. An extreme sample is presented in Figure 2c, in which the infrared beam is irradiated on the substrate perpendicularly (the angle is zero). In this case, all of the transmitted multiple-reflection light would reach the detector with no problem, since there is no shift due to the refraction. Of note is that MAIRS employs several transmission measurements with different angles of incidence. When a low refractive index material, such as CaF_2 , is used for MAIRS, therefore, different portions of multiple reflections reach the detector with an increase of the angle of incidence. This is considered to be a major reason for poor MAIRS analysis. Of course the thickness of the substrate should also be as small as possible to reduce the Δd effect.

This discussion suggests that a proper MAIRS analysis largely relies on the refractive index of the substrate and the detector size (or detector choice). Some important results with different combinations of the experimental conditions will be presented with respect to the discussion above.

The most critical material was ZnSe, which has a refractive index of ~ 2.44 in the infrared region. This refractive index is near the middle point of those of CaF_2 ($n = 1.42$) and Si ($n = 3.42$). Figure 3 presents the MAIR spectra obtained with five-monolayer

cadmium stearate LB films deposited on a ZnSe, measured by the MCT with an aperture size of 32. This aperture size was chosen to reduce the infrared light, so that the MCT detector would not be saturated. Since the full aperture size of the FT-IR is 150, 32 is very small. According to an engineer at Nicolet, the aperture size of 32 gives an image size (diameter of the infrared spot at the detector) of 0.94 mm that fits in with the detector diameter (1-mm i.d.). In other words, therefore, the small aperture gave a just-fit size of the infrared spot at the detector. When the transmitted infrared light is slightly shifted through the refraction by the oblique incidence (Δs and Δd), therefore, the “just-fit condition” would be influenced badly. In fact, the spectra in Figure 3, in which the IP and OP spectra are similar to each other, are apparently incorrect, and even the IP spectrum is not identical to the transmission (Supporting Information).

Then, the aperture was fully opened (size of 150), which made the MCT detector “overfilled” with the infrared spot that had a diameter of 1.98 mm. To reduce the infrared light intensity to prevent saturation, a metal plate with small pores was placed in the light path of the incidental beam. Other experimental conditions were not changed, and the collected single-beam spectra for the identical LB film on ZnSe were subjected to the MAIRS analysis again. It is clear that the results in Figure 4 with the full aperture are much better than those in Figure 3: the IP and OP spectra closely correspond to the transmission and RA spectra, respectively. This idea was also applied to the CaF_2 plate, but the results were still poor (data not shown), probably because of the low refractive index. Therefore, the ZnSe may be the lowest limit for the MAIRS measurements with respect to the refractive index.

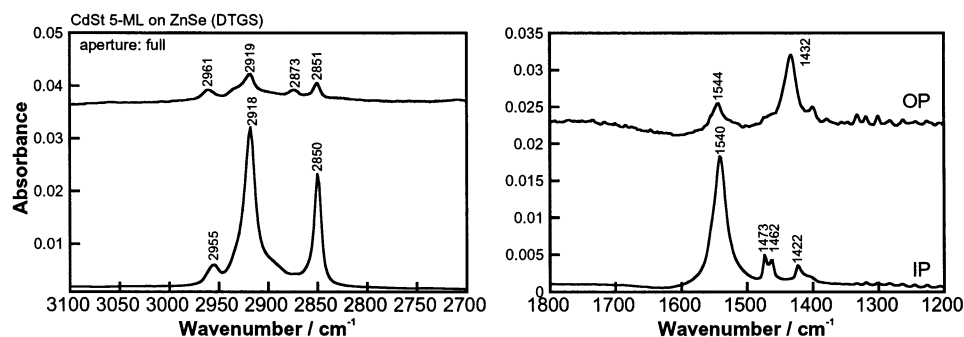


Figure 5. FT-IR MAIR spectra of five-monolayer LB film of cadmium stearate deposited on ZnSe. A DTGS detector was used with an aperture of 150 (full). This corresponds to the just-fit condition.

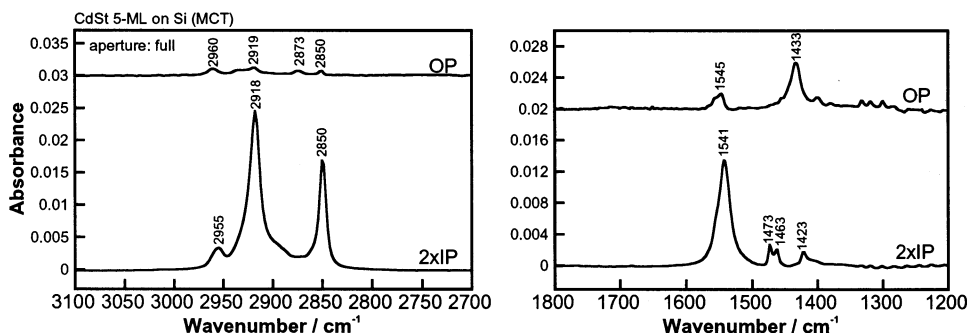


Figure 6. FT-IR MAIR spectra of five-monolayer LB film of cadmium stearate deposited on Si. An MCT detector was used with an aperture of 150 (full). This corresponds to the overfill condition.

This “overfill condition” is a key to getting successful MAIRS measurements. When the aperture is opened fully, the light spot at the focus in the sample compartment of the FT-IR theoretically has a diameter of 10.7 mm. For a ZnSe substrate with 1.0-mm thickness, for example, Δd (see Figure 2) is calculated to be 0.49 mm when the angle of incidence is 45° , which corresponds to be $\sim 5\%$ of the diameter. This shift would correspond to only $40\text{ }\mu\text{m}$ at the MCT detector surface. If we would perform the overfill measurements, therefore, the optical condition would be impervious to the shift, all the transmitted paths would be overlaid, and they would be captured by the detector irrespective of the angle of incidence. On the other hand, if we would perform a just-fit measurement instead, the slight difference would have significant influence on the just-fit condition, which would make the measurements fail. In this manner, the fuzziness of the overfill condition is considered to be suitable for MAIRS measurements.

To confirm this speculation, the same experiments were also performed using the DTGS detector. A significant difference between the DTGS and MCT detectors in this study is that they have different diameters of detector surface. Since the DTGS has a detector surface of 2-mm i.d., the full aperture condition gives the just-fit optical condition (infrared spot at the detector is 1.98-mm i.d.). Although the large detector area is good for collecting infrared beams composed of the direct path and multiple reflections, the just-fit condition would be unstable for the multiple-angle measurements, as discussed above. The analytical results presented in Figure 5 indicate that these are close to ideal results, but it is found that the OP spectrum is little influenced by the IP spectrum by comparing it to the RA spectrum in Supporting Information.

In this manner, it was found that the following two experimental conditions are crucial for proper MAIRS measurements: (1)

overfill condition at the detector and (2) higher refractive index than ZnSe for the substrate.

To confirm this conclusion, the same LB film was prepared on a Si plate with the same thickness, and it was measured by the MCT detector with a full aperture. Since the Si substrate has a larger refractive index than ZnSe, this material satisfies the two optimum conditions above. The analytical results are presented in Figure 6. Both IP and OP spectra are quite satisfying, and in particular, the OP spectrum is even better than that in Figure 4 measured on ZnSe, which is consistent with expectation. It is found that the optimum conditions determined in this paper are of great importance to have MAIRS useful and reliable. Ge was also confirmed to be useful, and it gives results identical to the spectra by Si (data not shown).

The only matter remained for discussion is that a Ge plate gave good results with DTGS in the previous paper.⁴ In the former paper, a small aperture of 50 was used to reduce the light intensity. This aperture size gives a light spot of 1.15-mm i.d., which is an underfill condition for the detector. Therefore, it is considered that almost all the shifted light paths might have been collected by the detector. Nevertheless, it is a problem that the sensitivity of the detector varies depending on the location on the detector surface. Therefore, the overfill condition would be more stable and reliable. The previous good results with DTGS could be realized by the high refractive index of Ge.

It has also been found that the sampling position in the light path is not important for MAIRS. The sample holder was displaced and spectra were collected, but the results were not changed. In this sense, MAIRS is a very stable technique.

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SUPPORTING INFORMATION AVAILABLE

FT-IR transmission and RA spectra of cadmium stearate LB films. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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