Appendix

Infrared spectroscopy and simulation of spectra

Abstract
Orientational analysis of thin polymer films, such as LB films, can be done by comparing infrared reflection with infrared transmission measurements on the same sample. However, comparison of reflection and transmission spectra must be done with care because of optical effects. In this appendix simulation of spectra is shown to be crucial for a good detailed interpretation of the experimental spectra and the basis of optical effects is explained. It is furthermore shown that simulation of spectra is also very useful to predict maximum sensitivity for the system investigated.
A.1 Introduction

A Langmuir monolayer is an ordered monomolecular layer at the air-water interface. This monolayer can be transferred onto a solid substrate by repeatedly dipping the substrate perpendicularly into the monolayer, forming Langmuir-Blodgett (LB) films.

Vibration levels in molecules can be excited by means of infrared light and vibrations in which the dipole moment changes can be detected. Infrared light can be represented by three vectors: the propagation direction and the electric field- and magnetic field vector. Vibrations will be excited and absorb infrared light only when they have a component of the transition moment in the direction of the electric field vector. No light will be absorbed when the dipole moment is oriented perpendicularly to the electric field vector. This means that it is possible to determine the orientation of molecules in LB films by infrared (IR) techniques. Two widely used infrared techniques are reflection spectroscopy at metallic substrates and transmission spectroscopy.

Reflection spectroscopy at metallic substrates

![Figure A.1](image)

The LB film is transferred onto a reflecting metal layer (Au, Al), see Fig. A.1. When light is reflected at the metallic surface the electric field is enhanced by the metal surface having only a significant component perpendicular to the metal surface. The magnitudes of the electric field vectors in the plane of the substrate $\langle E_x \rangle$ and $\langle E_y \rangle$ are almost zero and will not significantly contribute
to the absorbance. The magnitude of the electric field perpendicular to the metal surface $<E_z^2>$ depends strongly on the incident angle and has its maximum at $\theta = 80^\circ$, as can be seen in Fig. A.2. The optical path length increases with increasing $\theta$ and therefore maximum sensitivity is not found at $\theta = 80^\circ$ but at $\theta = 88^\circ$. However, $\theta = 80^\circ$ is chosen for practical experimental reasons. Thus, reflection spectroscopy at metallic substrates can only detect groups that have a component of the dipole transition moment of the vibration perpendicular to the substrate.

**Transmission spectroscopy**

In case of transmission spectroscopy the LB film is transferred onto a transparent substrate (silicon, ZnS). The specimen is placed perpendicularly to the beam, see Fig. A.3. The electric field vector is oriented can be directed perpendicularly $<E_r^2>$ or parallelly $<E_\theta^2>$ to the transfer direction by means of a polarizer. Thus, transmission spectroscopy can only detect groups that have a component of the dipole transition moment in the direction of the plane of the substrate.

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**Figure A.2.** Magnitude of the electric field component perpendicular to the surface of aluminum at $\lambda = 10.6 \mu m$ as function of the incident angle $\theta$. The magnitude of incident radiation is unity. Adapted from ref 1
However, determination of the orientation of the molecules in a LB film can not be simply done by comparing the measured reflection spectrum of a film with the measured transmission spectrum of the same film, because differences between the spectra are not only caused by orientation but also by optical effects. The cause of these optical effects will be explained in § A.3.

The orientation can be determined by using a simulation program (see § A.2.) that takes into account the optical effects. With this simulation program a non-oriented film in the same experimental setup (material, thickness of the film, angle of incidence, substrate etc.) as the measured one is calculated. Subsequently, the orientation of the film can be determined by comparison of the measured with the calculated spectrum.

The ordered Langmuir film at the air-water interface can also be studied directly using a reflection accessory. In this case the water surface is used as reflecting layer and although water shows a much lower reflectivity compared to a metallic substrate, spectra of a reasonable quality can be obtained. The advantage of this technique is that non-transferable monolayers can also be studied. In contrast to reflection measurements at a metallic substrate, the electric field has not only a component perpendicular to the interface but also a component parallel to the interface. The magnitude of these components depends strongly on the polarization direction and the angle of incidence, see § A.4. Therefore, spectra obtained from reflection spectroscopy at the air-water interface are difficult to interpret. We will show in § A.4 that spectrum simulation, besides elucidation of the orientation, can also be used to determine the maximum sensitivity of a system.

\[ \text{Figure A.3.} \]
A.2 Infrared spectrum simulation

When a substrate with a thin film is radiated with light, the primary beam is partially reflected and transmitted at all interfaces of this optical system, see Fig. A.4. Therefore, only a part of the incident light interacts with the thin film and can be absorbed. The absorbance of the thin film (A) in the transmission or reflection experiment of Fig. A.4 at wavenumber (ν) is determined by:

\[
A \propto n_2^2 \frac{<E_z^2>}{E_2^2} \frac{d}{\cos \theta}
\]

where \(n_2\) is the complex refractive index of the thin film, \(<E_z^2>\) is the electric field with components \(<E_x^2>\), \(<E_y^2>\) and \(<E_z^2>\) in the thin film, d is the thickness of the film, \(\theta\) is the angle of incidence. This complex refractive index (\(n_2\)) is wavelength dependent and determines the optical behavior of the thin film, and is comprised of a real part of the refractive index (\(n_2\)) and an
imaginary part, which describes the absorption characteristics \((k_2)\) of the material.

\[
n_2 = n_2 - ik_2
\]  

(2)

To simulate an infrared absorption spectrum of a non-oriented film of a thickness \((d)\) at an angle of incidence \((\theta)\) in the three-phase optical system (Fig. A.4) the complex refractive index \((n_2)\) and the electric field \((\langle E_2^2 \rangle)\) in the film must be determined. In the infrared spectrum simulation program developed in our group by R.H.G. Brinkhuis and E.J. Vorenkamp \(n_2\) and \(\langle E_2^2 \rangle\) are determined as follows:\(^5\)

As input a transmission spectrum of a freestanding film of the material, with a thickness in the order of magnitude of several microns,\(^1\) is used. See for an example of such a spectrum the transmission spectrum of a freestanding film of prec-DMePPV in Fig. A.5. The interference fringes observed in Fig. A.5 are characteristic for a freestanding film. The thickness \((d)\) of the film together

\(^1\)As input spectrum also a KBr powder spectrum can be used.\(^5\)

Figure A.5. Transmission spectrum of a freestanding film op prec-DMePPV
with the refractive index far from an absorption band ($n_\infty$) can be obtained from the amplitude and wavelength ($\lambda$) of these interference fringes because:

$$2d = \frac{\lambda}{n_\infty} \quad \text{and} \quad \text{Amplitude} \propto n_\infty \quad (3)$$

Subsequently, the absorbance values ($A$) of the transmission spectrum of the freestanding film are converted to $k_2$ values ($k$-spectrum) by:

$$k_2 = A/4\pi dv \quad (4)$$

From this $k$-spectrum the wavenumber dependent $n_2$ ($n$-spectrum) is calculated using the Kramers-Kronig relation (5).

$$n_2 = n(\nu^*) = n_\infty + \frac{2}{\pi} \int_{\nu}^{\nu^*} \frac{k(\nu)\nu}{\nu^2 - \nu^2} d\nu \quad (5)$$

The $k$-spectrum and $n$-spectrum of prec-DMePPV are shown in Fig. A.6. It can be seen that the $n$-spectrum varies enormously at the position of the absorption bands.

Finally, the complex refractive indexes can be determined from the $n$ and $k$ spectrum by using relation (2).

After this the electric field strength $<E_z^2>$ in the thin film is determined using Fresnel coefficients. These Fresnel coefficients take the amount of light (multiply) reflected and transmitted at each interface of the system into account, see Fig. A.4. Therefore, the optical constants of substrate materials must be known. Values used were 2.2 (ZnS), 3.8 (Si) and 9.5-30i (Au). For the optical constants of water wavenumber dependent $n$ and $k$ values taken from the Infrared Handbook were used.

Now all the components of equation (1) are known and the absorption spectra of transmission, reflection or attenuated total reflection (ATR) spectroscopy can be simulated. See for an example of the use of simulated spectra in orientation determination Fig. 3.4 and accompanying text of Chapter 3.
A.3 Understanding optical effects

In this paragraph the basis of optical effects will be demonstrated by means of reflection measurements and electric field strength calculations of a thin cuprous ethyl xanthate film on metallic substrate done by J.A. Mielczarski. We chose this system because the optical effects in this system are very clear.

The k-spectrum and n-spectrum of cuprous ethyl xanthate are shown in Fig. A.7. The transmission and reflection spectra of a non-oriented 10 Å thick film of cuprous ethyl xanthate, obtained using a simulation program, are shown in Fig. A.8. When the calculated reflection spectrum is compared with the calculated transmission spectrum, it can be seen that the band at 1196 cm\(^{-1}\) is shifted to 1204 cm\(^{-1}\), the band at 1124 cm\(^{-1}\) to 1126 cm\(^{-1}\), and the absorbance of the band at 1188 cm\(^{-1}\) is decreased, while the band at 1048 cm\(^{-1}\) is shifted and increased. Both spectra were simulated for a non-oriented film, thus, these significant differences between the spectra of Fig. A.8 are optical effects.
Figure A.7. Optical constants, refractive index (n) and the absorption coefficient (k) of cuprous ethyl xanthate complex, as a function of the wavenumber. From ref. 9.

Figure A.8. Simulated spectra of a non oriented 10 Å thick film cuprous ethyl xanthate complex; (a) transmission spectrum; (b) reflection spectrum of the film deposited on copper for p-polarization, at $\theta = 80^\circ$. From ref. 9.
The absorbance of a thin film is determined by (1), § A.2. The electrical field plays a predominant role in determining the absorbance. In reflection experiments on a metal surface the electric field has only a significant component in the z-direction, see Fig. A.1. To understand the cause of the optical effects we will focus on the variation of the magnitude of this component of electric field in the thin film, $<E_{z2}^2>$, with the optical constants, i.e. the refractive index ($n_2$) and absorption coefficient ($k_2$). Fig. A.9a shows the $<E_{z2}^2>$ within a hypothetical thin film with $k_2 = 0$ and $k_2 = 0.36$ at $\theta = 80^\circ$ as function of the refractive index. The $<E_{z2}^2>$ is enhanced with respect to the incident light (the electric field strength of incident light is 1) for low refractive indexes, especially for $n_2 < 1.0$, while for $n_2 > 1.5$ the $<E_{z2}^2>$ is decreasing (Fig. A.9).

Fig. A.9b shows the calculated absorbance in the thin film. The absorbance is high at low refractive indexes as was predicted from Fig. A.9a.

**Figure A.9.** Electric field $<E_{z2}^2>$ in the thin film (a) and the calculated absorbance (b) in a reflection experiment of a thin 10 Å thin organic film on a metallic substrate at $\theta = 80^\circ$ and at 1050 cm$^{-1}$ for various refractive indexes of the thin film ($n_2$) and the two values of absorption coefficient $k_2 = 0$ and $k_2 = 0.36$. From ref. 9.
So, the magnitude of electric field in the thin film in a reflection mode is sensitive to changes in the optical properties of the absorbing layer. This is not the case in the transmission mode where the electric field strength in the thin film is constant over the whole spectrum and is not dependent on \( n_2 \) and \( k_2 \). With this knowledge the differences between the transmission and reflection spectra (Fig. A.8), which are the optical effects, can be explained. The shift of the band at 1196 cm\(^{-1}\) to 1204 cm\(^{-1}\) is due to the lowering of \( n_2 \) to 1.05 at 1205 cm\(^{-1}\) (Fig. A.9a). This involves an enormous enhancement of the electric field at this frequency, to near 3.6 (Fig. A.9a), resulting in a strong increase in the absorbance. In contrast, the sharp increase of \( n_2 \) to 2.17 at 1180 cm\(^{-1}\) reduces the electric field to about 0.2 involving a strong decrease in the absorbance of the band on its low-frequency side and also in the intensity of the second component of the band at 1188 cm\(^{-1}\) resulting in low intensity shoulder at this wavenumber. The band at 1124 cm\(^{-1}\) is only shifted 2 cm\(^{-1}\) although the refractive index shows strong dispersion from 1.49 to 2.13. This corresponds well with the relative small changes in the electric field for refractive index values larger than 1.5 (Fig. A.9a). The other differences between the spectra of Fig. A.8 can be explained in the same way.

A.4. Simulation of external reflection measurements at the air-water interface

Spectra obtained from external reflection measurements at the air-water interface are generally very complex and spectrum simulation is needed to interpret these spectra. Based on calculation of the electric field components at the air-water interface in reflection measurements done by J.A. Mielczarski \(^9\) we will explain the reason for the complexity and show that the simulation of spectra is very useful to determine the optimal experimental set-up for these reflection experiments.

Fig. A.10a shows the calculated electric field components for a 10 Å thick organic film with \( n_2 = 1.32 \) and \( k_2 = 0.36 \) at 1050 cm\(^{-1}\). The electric field is calculated in the thin film, and shapes and magnitude are characteristic for organic films at the air-water interface (see for directions of the electric field Fig. A.4). In contrast to what was found for metallic substrates, the electric field vectors parallel to the water surface, \( \langle E_{x2} \rangle \) and \( \langle E_{y2} \rangle \), are not negligible but have even a larger magnitude than the \( \langle E_{z2} \rangle \) component over almost the entire range of incident angles. When the incident light is p-polarized the
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Figure A.10. Electric field $<E_z^2>$ in the thin film (a) and the calculated absorbance components (b) in a reflection experiment of a 10 Å thick organic film ($n_2 = 1.32$, $k_2 = 0.36$) on water ($n_3 = 1.241$, $k_3 = 0.0441$ at 1050 cm$^{-1}$). From ref. 9.

The spectrum is determined by the $<E_z^2>$, which is perpendicular to the interface, and by the $<E_\text{z2}^2>$ component, which is parallel to the interface. However, the $<E_\text{z2}^2>$ dominates at the lower angles of incidence because here the magnitude of this component is much higher than the $<E_z^2>$ component. When the incident light is s-polarized, the spectrum is determined only by the $<E_\text{z2}^2>$ component which is parallel to the interface. Therefore, in the case of a water substrate, the interpretation of the p-polarized reflection spectra are much more complicated than those in the case of a metallic substrate. Moreover, it appeared from calculations of the absorbance components (Fig. A.10b, $A_x$ dotted line) that the $<E_\text{z2}^2>$ component produces negative absorbance bands$^\text{ii}$ (inversion of the bands) for $\theta < \theta_\text{B}$$^\text{iii}$ and positive absorbance bands for $\theta > \theta_\text{B}$. The opposite is found for $<E_\text{z2}^2>$ (Fig. A.10b, $A_p$ dashed-dotted line). The total

$^\text{ii}$ Absorbance = $-\log R/R_0$. The absorbance is negative as $R > R_0$. $R_0$ = reflectivity from water without thin film. R = reflectivity from water with thin film.

$^\text{iii}$ Brewster angle ($\theta_\text{B}$) is given by $\tan(\theta_\text{B}) = n_2 / n_1$. $\theta_\text{B}$ for water-air interface is 51°.
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absorbance for p-polarization at $\theta < \theta_B$ will be negative (Fig. A.10b $\Lambda_p$ solid curve) because over this range the $<E_{z2}^2>$ is high and the $<E_{x2}^2>$ is low (Fig. A.10a) for $\theta > \theta_B$ positive bands will be obtained due to domination of the $<E_{z2}^2>$ component. Furthermore, $<E_{z2}^2>$ is sensitive to changes in the optical properties of the absorbing layer (Fig. A.11) leading to similar optical effects as found for metallic substrates.

When the incident light is s-polarized, the reflection spectrum is determined by the $<E_{y2}^2>$ component, and negative absorbance bands are produced (Fig. A.11b solid $\Lambda_s$). This component is not sensitive to changes in the optical properties, see Fig. A.11.

Fig. A.12 and Fig. A.13 show the calculated reflection spectra of a 10 Å thick prec-DMePPV film on water for p-polarization and s-polarization, respectively, at different angles of incidence. In Fig. A.12 can be seen, as predicted from Fig. A.10, that the absorbance for p-polarization is, compared to the absorbance of a 10 Å thick film on Au (dashed line Fig. A.12), very strong in the region $\theta$ close to $\theta_B$. Depending on the angle of incidence, positive and negative absorption bands are obtained. However, for practical use the region $\theta$
close to $\theta_B$ for p-polarization is not easy to apply. The amount of energy reaching the detector is very low leading to noisy spectra. Moreover, the p-polarized spectrum of a thin film on water will be dominated, as shown, by the component parallel to the interface. As a consequence, the information obtained will be similar to that for s-polarization. Furthermore, in our experimental set-up, the signal/noise ratio is better in s-polarized spectra than in p-polarized spectra and although the absorbancies at s-polarization are lower than for p-polarization (see dashed line Fig. A.13), the measured spectra are of higher quality. Therefore, we did the reflection studies with s-polarized light. The absorbancies for s-polarization (Fig. A.13) are, as predicted from Fig. A.10 negative and increase with decreasing angle of incidence. The energy reaching the detector at s-polarization decreases with decreasing angle of incidence,

**Figure A.12.** Simulated reflection spectra of a non-oriented 10 Å thick prec-DMePPV film on water at different angles of incidence with p-polarization. The simulated reflection spectrum of a non-oriented 10 Å thick prec-DMePPV on gold (dashed line) is added for comparative purposes. The spectra are moved up or down for clarity but are in the same scale.
resulting in an optimum angle of incidence at s-polarization of 30° in our experiments.

In conclusion, spectrum simulation can be useful to determine maximum sensitivity of the system, but the experimental limitations must also being taken into account.

Figure A.13 Simulated reflection spectra of a non-oriented 10 Å thick prec-DMePPV film on water at different angles of incidence with s-polarization. The simulated reflection spectrum with p-polarization at $\theta = 30^\circ$ (dashed line) is added for comparative purposes. The spectra are moved up or down for clarity but are in the same scale.
References

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