

Optimum IR measurement conditions for thin layers on dielectric surfaces

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Abstract

The importance of signal-to-noise ratio (SNR) calculations for an optimum Fourier transform-infrared spectroscopy (FT-IR) detection of thin, isotropic layers on dielectric substrates is discussed; some illustrative examples are given. It is found that the SNR increases with increasing refractive index of the substrate whereas the use of p-polarized light is preferable. Optimum measurement conditions for oriented layers were found for a Ge substrate at an angle of incidence of 50–55°. © 1998 Elsevier Science S.A. All rights reserved

Keywords: Fourier transform infrared spectroscopy; Monolayers and dielectric surfaces

1. Introduction

It is well-documented that Fourier transform-infrared spectroscopy (FT-IR) reflection absorption experiments of thin layers on gold often results in high quality spectra, even for submonolayer thickness of the material under investigation. Optimum measurements conditions for this type of experiment are well-known [1–3]. However, samples of interest are often only available on a dielectric support, such as glass. A typical example is the case where one aims to study biological components bound in or at a lipid membrane system. Optimum measurement conditions for detection of thin deposited layers are much less known, although some work has been done in this respect [4–6].

It is the aim of this paper to discuss how IR experiments of such systems should be performed to obtain an optimum signal-to-noise ratio (SNR).

2. Theoretical considerations

The system that we want to consider can be modeled as a thin homogeneous monolayer with a thickness of a few Å and a complex refractive index n_1 deposited on a semi-infinite medium n_2 . The reflectance for such a system with known optical constants (n_1 , n_2) can be calculated using the boundary layer conditions [1]. However, the depth of

an absorption band in the IR spectrum caused by the thin layer is the quantity that we want to measure, rather than the reflectance. This depth of absorption can be defined as follows [2] (Eq. (1)):

$$A = \frac{(R_0 - R)}{R_0} \quad (1)$$

where the value of reflectance of the thin absorbing layer on the substrate, R , is compared with the same system without absorption of the thin layer, R_0 . In the remainder of the paper we will refer to A as the absorption factor.

A hypothetical system that represents an isotropic layer with real and imaginary refractive index, $n_1 = 1.5$ and $k_1 = 0.1$, respectively, on a glass substrate ($n_2 = 1.4$, $k_2 = 3.3 \times 10^{-5}$) at $\bar{\nu} = 3000 \text{ cm}^{-1}$ has been taken as an example. (The optical constants of glass are found by measuring the transmission and reflectance spectra of bare glass.)

The calculated absorption factor of this hypothetical system is given in Fig. 1A, which shows a maximum value of A for s-polarized light at an angle of incidence, $\Theta = 0^\circ$. To rationalize these findings we first note that the absorption of the thin layer is proportional to the electric field at the surface [4]. Now, the phase shift of the reflected s-polarized light relative to the incoming light will be 180° at all angles of incidence [7]. The resulting electric field at the glass/layer interface, which is composed of incoming and reflected light, is maximum at $\Theta = 0^\circ$ because of the low value of reflectance at this angle. There will be no resulting electric field at $\Theta = 90^\circ$ because the reflectance equals 1 at that angle.

For p-polarized light around $\Theta = 55^\circ$ the large values of

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A can be explained by the fact that the reflectance R_0 at the Brewster angle will be zero.

Usually the values of the absorption factor are used to determine the optimum Θ for measurements. However, for best measurement conditions one should find the Θ for which maximum SNR is found rather than maximum A . This can easily be illustrated by inspection of the value of A for the case when p-polarized light at the Brewster angle is applied. A will be high at this angle but the reflectance of the glass layer will be 0. This means that, although A is maximum, the SNR of the signal might not be maximum.

The absorption function is composed of two experimental parameters determined in two separate experiments. In a detector-noise limited spectrometer, which is usually the case [8], the noise is independent from the light intensity. For this situation we propose that for optimum measurement conditions the difference in response between a bare and

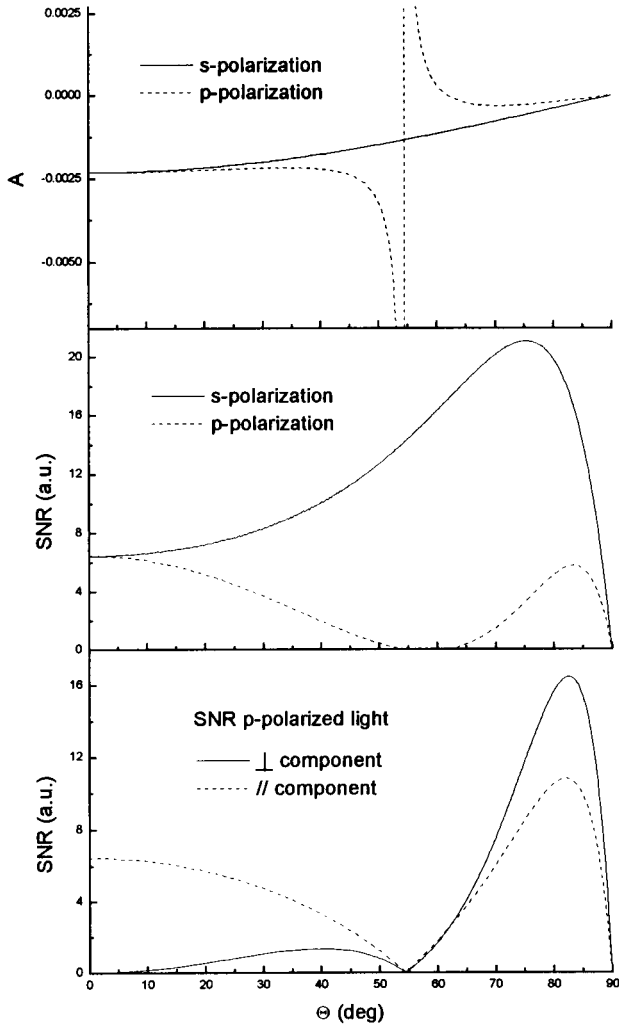


Fig. 1. Calculated absorption (A), SNR of s- and p-polarization (B) and SNR of the \perp and \parallel component of the p-polarization (C) for a 1 nm thick, isotropic layer ($n = 1.5$, $k = 0.1$) on a glass substrate ($n = 1.4$, $k = 3.3 \times 10^{-5}$) at $\bar{\nu} = 3000 \text{ cm}^{-1}$.

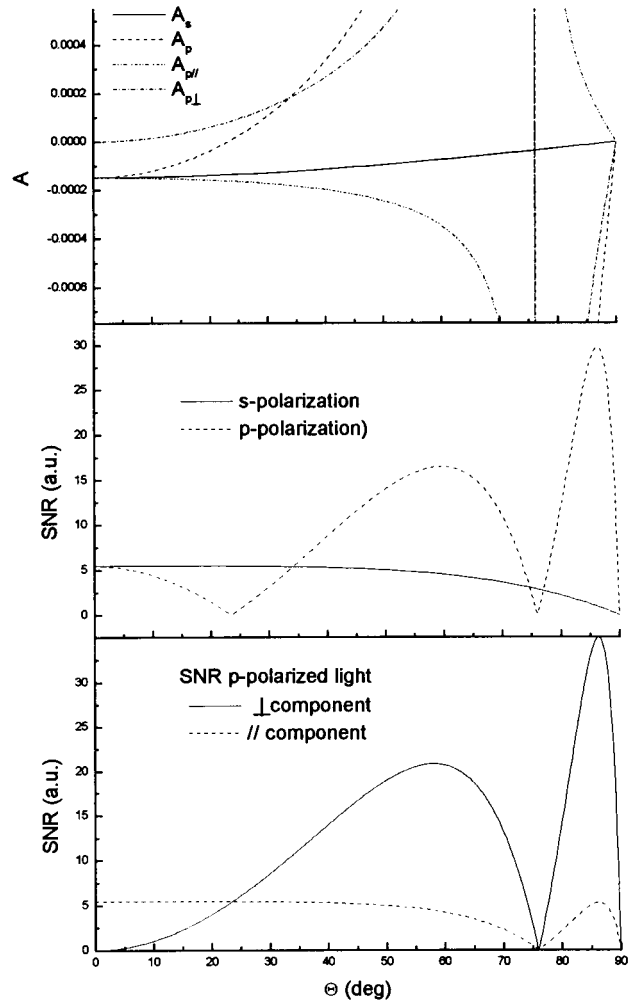


Fig. 2. Calculated absorption and absorption components of p-polarized light (A), SNR of s- and p-polarization (B) and SNR of the \perp and \parallel component of the p-polarization (C) for a 1 nm thick, isotropic layer ($n = 1.5$, $k = 0.1$) on a Ge substrate ($n = 4.01$) at $\bar{\nu} = 3000 \text{ cm}^{-1}$.

coated substrate is optimized as function of Θ . We will call this the signal-to noise ratio of our experiment (Eq. (2)):

$$\text{SNR} = |C \times (R_0 - R)| \tag{2}$$

where C is an instrumental constant.

The results of SNR calculations as a function of the angle of incidence are given in Fig. 1B; we consider the same hypothetical system as that used in Fig. 1A. Note that all calculated SNR values are given in arbitrary units. However, the SNR values, given in Figs. 1–3 can be mutually compared.

From these calculations it is clear that for s-polarized light maximum SNR is found around 75° instead of the low Θ of the A calculations. For p-polarized light the SNR is maximum at low Θ , and reaches another maximum at 82° . The SNR is about 0 in the region of the Brewster angle, where maximum absorption is expected.

Next, the importance of the refractive index of the substrate was investigated by calculating the response for var-

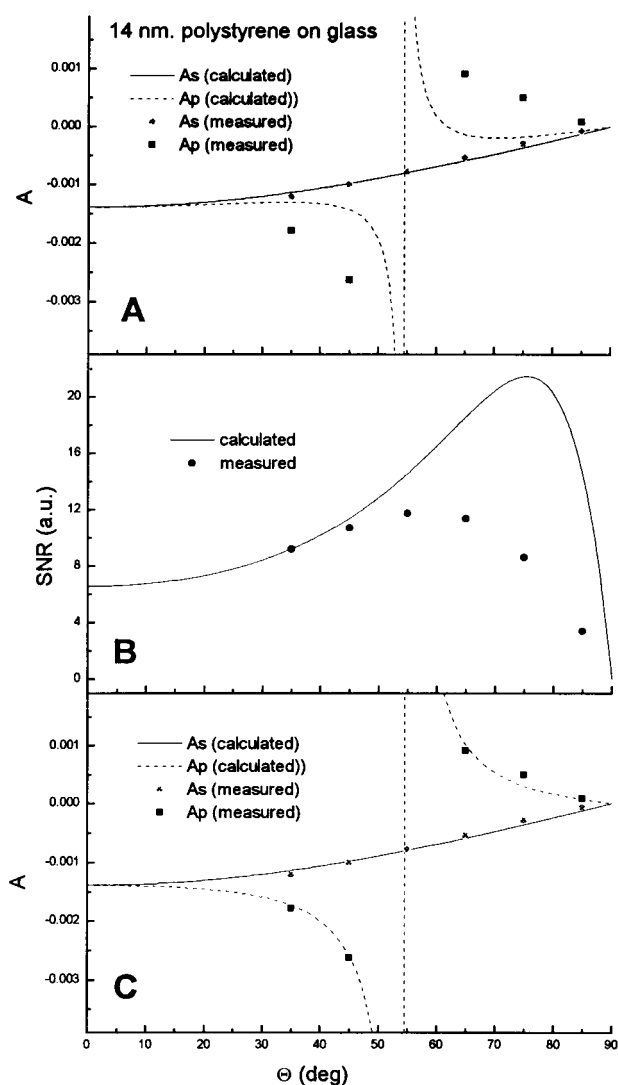


Fig. 3. Measured and calculated (isotropic layer) values of absorption (A), measured and calculated values of the SNR of the s-polarization (B) and measured and calculated (oriented layer) absorption values (C). See text for details.

ious substrate materials, CaF_2 ($n = 1.4$), KBr ($n = 1.54$), ZnSe ($n = 2.43$), Ge ($n = 4.01$). The A and SNR behaviour of a thin layer deposited on CaF_2 is comparable with the case when the substrate consists of glass. For the highest substrate index used in the calculation (Ge) results are depicted in Fig. 2A,B.

Comparison of Fig. 1A and Fig. 2A reveals that A for $\Theta = 0^\circ$ on a Ge substrate is more than one order in magnitude lower than in the case of a glass substrate. The larger value of n in the case of Ge results in a relatively low value of the electric field at the substrate surface. However, SNR for both glass and Ge substrate is comparable because the reflectance, and thus the intensity detected, is much higher for Ge than for glass. Calculations on the various materials show that ZnSe exhibits the highest SNR value at $\Theta = 0^\circ$. SNR will vanish for substrates with even higher refractive indices. SNR for s-polarized light for a Ge substrate remains

almost constant until $\Theta = 50^\circ$ and then decreases to 0 at grazing incidence, see Fig. 2B.

For p-polarized light we note the following. The Brewster angle of Ge is at 76° and the situation around this angle can best be compared with the situation at the Brewster angle of the glass substrate as described above. Fig. 2B shows that SNR is maximum at $\Theta = 87^\circ$ on a Ge substrate; however, SNR will in practice be lower at this angle because intensity is lost in the focus on the Ge substrate. In practice, the maximum at $\Theta = 60^\circ$ might have better SNR. SNR values for a Ge substrate are higher than those for a glass substrate; however more care has to be taken to select the proper angle of incidence.

A and SNR will also vanish at $\Theta = 24^\circ$ on the Ge substrate. This is caused by the fact that p-polarized light has electric field components both parallel and perpendicular to the substrate surface. Mielczarski and Yoon [6] found some simplified equations for a three-layer system that approximate the absorption factor of the components $A_{p//}$ and $A_{p\perp}$, where $//$ or \perp denote the parallel or perpendicular electric field component respectively, see Fig. 2A. (We note that $A_{p\perp}$ is multiplied by a factor of 2 because of the cylinder-symmetrical or isotropic transition dipole orientation distribution we are assuming).

Up to now we have assumed that the thin layer consists of molecules with their transition dipole moments randomly oriented. In the case of oriented layers the angular dependence of the SNR for s-polarized light will retain its shape; however, for p-polarized light the angular dependence of SNR now depends on the orientation of the transition dipole moment. For glass and Ge substrates this is illustrated in Figs. 1C and 2C.

Fig. 1C clearly shows that SNR on a glass substrate is optimum at $\Theta = 82^\circ$ both for a perpendicular and a parallel orientation of the transition dipole moment; in addition a parallel dipole moment orientation has also sizeable SNR at $\Theta = 0^\circ$.

SNR of a parallel orientation of the transition dipole moment on a Ge substrate is a little worse than that on a glass substrate (see Fig. 2C), however, the SNR remains its maximum value in the range $0^\circ < \Theta < 50^\circ$. The same maximum value of SNR is reached at $\Theta = 86^\circ$, but in practice this SNR value will be lower because of the loss of intensity as mentioned above. SNR for a perpendicular orientation of the transition dipole moment is much larger than in the case of a glass substrate; maxima are found at $\Theta = 57^\circ$ and $\Theta = 87^\circ$.

Measurements of layers with a preferred transition dipole moment orientation should be performed at angles of incidence with optimum SNR for the parallel and perpendicular component.

3. Experimental results

Experiments were done with a polystyrene layer on a

glass substrate. Polystyrene was chosen in view of its large absorption cross section of the C–H stretch bands in the 3000 cm^{-1} region; furthermore it is rather simple to manufacture reasonably uniform polystyrene thin layers.

For the following experiments a polystyrene layer with a thickness of 14 nm was used, obtained by spincasting a polystyrene/toluene solution on the glass substrate. The C–H stretch vibration at 3024 cm^{-1} , measured with a Bio-Rad FTS-60A FT spectrometer, was used to determine A as a function of the angle of incidence.

Calculated A values for s- and p-polarized light were normalized to the measured values by adjusting k at 1.0×10^{-2} . Absorption of the s-polarized light is in agreement with the calculations, see Fig. 3A. From Fig. 3B, where the SNR of the s-polarized measurements is normalized to the calculated values, it appears that the maximum is not very well predicted. This finds an easy explanation in the fact that no diaphragm has been used with this experiments. The intensity of the light on the detector, and with this the SNR, is diminished at higher angles of incidence because of a relative large beam diameter in comparison with the sample dimensions. Calculations show that it is plausible that the loss of SNR is caused by this loss of intensity. From these measurements it is clear that optimum measurement conditions for s-polarized light will be at $\Theta = 60^\circ$.

From Fig. 3A it is seen that the measured p-polarized light absorption systematically deviates from the calculations made for an isotropic thin layer. This can be explained by the fact that the incoming p-polarized light introduces an electric field with two components. These components will introduce a dependence on the orientation of the thin layer when the layer is not isotropic as is assumed in the calculations.

We have done some calculations to correct the absorption of p-polarized light for an orientation of the layer. We assumed that the orientation distribution has cylinder-symmetry, because the layer is spun on the glass substrate. The

orientation of the transition dipole moment can now be found by varying the value of $A_{p\perp}$ in comparison with $A_{p\parallel}$. Optimum results were found for a ratio of 0.25, resulting in an average angle of 27 degrees to the substrate surface for the transition dipole moment of the C-H stretch vibration, see Fig. 3C.

4. Conclusions

It can be concluded that calculation of the SNR is extremely useful in finding the optimum measurement conditions for thin, isotropic layers. Maximum SNR of s-polarized light is found for a glass substrate at $\Theta = 60^\circ$. Best SNR ratio for detection of thin, isotropic layers is found for p-polarized light on a substrate with the highest refractive index possible.

FT-IR reflection absorption spectroscopy at dielectric surfaces can be very useful in finding orientation of transition dipole moments because no reference measurements for optical constants are needed. If the layer does not have a preferred orientation transition dipole, then best measurement conditions are at $\Theta = 50\text{--}55^\circ$ for a Ge substrate.

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