



# The electric field standing wave effect in infrared transflection spectroscopy



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## ABSTRACT

We show that an electric field standing wave effect is responsible for the oscillations and the non-linear dependence of the absorbance on the layer thickness in thin layers on a reflective surface. This effect is connected to the occurrence of interference inside these layers. Consequently, the absorbance undergoes a maximum electric field intensity enhancement at spectral positions close to those where corresponding non-absorbing layers on a metal show minima in the reflectance. The effect leads to changes of peak maxima ratios with layer thickness and shows the same periodicity as oscillations in the peak positions. These peculiarities are fully based on and described by Maxwell's equations but cannot be understood and described if the strongly simplifying model centered on reflectance absorbance is employed.

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## 1. Introduction

Transflection is an artificial term combined from the words transmission and reflection to signal that the corresponding type of spectroscopy produces spectra similar to transmission spectroscopy while operating in reflection mode. The correlated method is probably better known under the more common term (infrared) reflection-absorption spectroscopy (IRRAS) or reflection-absorption infrared spectroscopy (RAIRS) [1]. Pre-millennial this technique was mostly used for thin films on highly-reflecting substrates as it can have monolayer sensitivity if the measurement conditions are adapted appropriately, i.e. grazing incidence and *p*-polarized radiation [2]. Thick layers can usually be measured either in transmission mode or in reflectance if they are strongly absorbing. In combination with micro-spectrometry, however, which is of particular interest for biomedical spectroscopy and imaging, the use of thick layers together with strongly reflecting substrates can be of advantage. The application of transflection spectroscopy, however, revealed some peculiarities that seemed not to fit to the expected behavior [3–11]. E.g. if the measured quantity, the reflectance, is converted to *reflectance absorbance*, which is defined by  $A = -\lg(R/R_0)$  wherein  $R_0$  is the reflectance of the bare substrate, the absorbance of the peaks shows non-linear dependence on the thickness of the layer. For the non-linear dependence of the reflectance absorbance from the layer thickness an electric field standing wave effect (EFSW) on the surface

of the metal substrate was made responsible [3–11]. This effect is known from films with thicknesses of a few nm and below deposited on metal substrates and responsible for the fact that at normal incidence only very weak vibrational signals of these films are generated [2]. Recently, Lee has shown that “there is no such effect” in transflection for thicker films [11]. Indeed, the non-existence of this kind of effect could have been already deduced from the fact, that while this effect leads to a periodic spatial modulation of the electric field away from the surface of a metal, it does not account for the also observed periodic modulation in frequency [2]. Lee attributed the non-linear dependence of absorption solely to “interferences at the vacuum/sample interface” [11]. While the reasons for the occurrence of the observed effects is still somewhat controversially discussed in the existing literature, there is consensus that an approach based on Maxwell's equations and an optical model consisting of a layer between the incidence medium and the highly reflecting substrate is able to fully explain the existing non-linear relationship between signal strength and layer thickness [3–11]. Recently it was also reported that band shifts can occur in transflection spectra, which would additionally exacerbate chemometric “interpretation” of these kind of spectra [10]. Indeed, such band shifts can also be detected in the spectra of cytosine films in [7] (but were not detected or discussed in this reference). In [10] the question arose if those band shifts can also be attributed to the controversial EFSW. At least, the band shifts can be fully described by the aforementioned approach relying on Maxwell's equations as has been demonstrated already in 2002 by Gunde and Orel who already studied thickness-dependent optical effects in IRRAS spectra on the example of a thick polymer layer in full detail in 2002 [12]. In contrast to the

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strongly simplifying assumptions that lead to Beer's law and the concept of absorbance, the formulas describing the optics of stratified media are comparably complex and seemingly do not allow an intuitive approach to the physics behind. The goal of this work is to show that such an intuitive approach is nevertheless possible. Starting from a simple model employing a perfectly reflecting substrate and a non-absorbing layer we will literally show that there is an electric field standing wave effect. It is not limited to the surface of the substrate or the interface between layer and incidence medium, but it extends within the whole layer and the spectral position at which the effect is particularly strong can be determined by a very simple relationship. Therefore, it is also present in the absence of a substrate [13]. This EFSW effect correspondingly leads to an interference enhanced absorption at these wavenumbers and an interference decreased absorption at others. We will also demonstrate, that while the band shifts are not directly caused by the EFSW they show the same periodic dependence on the thickness of the layer. Furthermore, we will show that interference effects cannot be made responsible for all deviations from Beer's law, as even for situations which allow an incoherent treatment (e.g. thickness variations of the layer on the order of the wavelength and/or periodicity smaller than spectral resolution), deviations from linearity and peak shifts with increasing layer thickness occur.

## 2. Theoretical Considerations

In the following we assume an optical model that consists of a layer sandwiched by two semiinfinite media according to the sequence semi-infinite incidence medium / layer / semi-infinite exit medium. The Maxwell's equation compliant formalism to obtain reflection and transmission is well-known [14]. Here, we just repeat the solutions in its most basic form, as we use the most basic assumption of normal incidence of a plane wave nearly throughout the paper. Furthermore, the exit medium will consist of a metal with a thickness large enough to virtually completely suppress transmission (e.g. for gold thicknesses >200 nm). Therefore  $T = 0$  and  $R + A = 1$ , wherein  $A$  is the absorbance (in italic, in order to distinguish it from the reflectance absorbance  $A$ ). Accordingly, we only provide the equations for the overall reflectance coefficient  $r$  which is given by:

$$r = \frac{r_{12} + r_{23} \exp(2i\phi)}{1 + r_{12}r_{23} \exp(2i\phi)}, \quad r_{12} = \frac{1 - n_2'}{1 + n_2'}, \quad r_{23} = \frac{n_2' - n_3'}{n_2' + n_3'} \quad (1)$$

Here  $r_{12}$  and  $r_{23}$  are the reflection coefficients for the reflections arising from the interfaces between medium 1 and 2 and medium 2 and 3.

To further simplify the situation, it was assumed for the derivation of Eq. (1) that the incidence medium is vacuum with an index of refraction  $n_1$  equal to unity, whereas waves in the layer (medium 2) and the exit medium (medium 3) are characterized by having wavenumber-dependent complex refractive indices  $n_2' = n_2 + ik_2$  and  $n_3' = n_3 + ik_3$  to allow for absorption ( $k$  is the imaginary part of the complex refractive index, usually called absorption index).  $\phi$ , the phase, is a function of the wavenumber  $\tilde{\nu}$ , the thickness of the layer  $d$ , and the complex index of refraction function of the wave inside the layer  $n_2'(\tilde{\nu})$  according to:

$$\phi(\tilde{\nu}) = 2\pi\tilde{\nu}n_2'(\tilde{\nu})d. \quad (2)$$

The overall reflectance  $R$  of the system is given by  $R = |r|^2$ .

The media are characterized by scalar and complex dielectric functions  $\epsilon'(\tilde{\nu}) = n'(\tilde{\nu})^2$ : [15,16]

$$\epsilon(\tilde{\nu}) = \epsilon_\infty + \sum_{j=1}^N \frac{S_j^2}{\tilde{\nu}_j^2 - \tilde{\nu}^2 - i\tilde{\nu}\gamma_j} \quad (I)$$

$$\epsilon(\tilde{\nu}) = \epsilon_\infty - \frac{\tilde{\nu}_p^2}{\tilde{\nu}^2 + i\tilde{\nu}\gamma} \quad (II).$$

The first equation (I) in Eq. (3) characterizes a dielectric material in the infrared with  $N$  oscillators, having oscillator strengths  $S_j$ , damping constants  $\gamma_j$  and resonance wavenumbers  $\tilde{\nu}_j$ .  $\epsilon_\infty$  is a constant offset including the contributions of transitions beyond the transparency region in the UV-Vis spectral range. Equation (II) describes a metal in the infrared spectral range with plasma wavenumber  $\tilde{\nu}_p$ , damping constant  $\gamma$  and  $\epsilon_\infty$ , which in particular includes contributions from the intraband transitions. Of some importance in the following is a so-called perfect electric conductor (PEC) for which the optical conductivity  $\sigma = \infty$ . Using Eq. (3) (II), such a perfect conductor is given by  $\tilde{\nu}_p \rightarrow \infty$  while  $\gamma$  remains finite. If we assume that medium 3 consists of such a PEC, based on Eq. (1)  $r_{23} = -1$  and Eq. (1) transforms into:

$$r = \frac{r_{12} - \exp(2i\phi)}{1 - r_{12} \exp(2i\phi)}, \quad r_{12} = \frac{1 - n_2'}{1 + n_2'} \quad (4)$$

## 3. Reflection From a Transparent Layer on a Metal

Transparent layers on metals belong to a class of composite materials that drew already much attention in the 60ies and 70ies of the last century due to their potential use as high-temperature solar absorber surfaces [17,18]. For this use it is advantageous to increase the absorption in the visible, while having an as small as possible emittance in the IR spectral region. For increasing the absorption, it seems on first view a strange concept to combine a non-absorbing layer with a strong reflector like a metal. Indeed, if a transparent material is combined with a PEC (which is, of course, not possible in reality, but an important thought experiment), the absorbance must be zero over the whole spectrum as the reflectance is always unity independent of frequency and the index of refraction of the transparent layer as one would expect. The reason for this behavior may not be immediately obvious, but derives from the fact that  $r_{12}$  and  $\phi$  are both real and, consequently,  $R = |r|^2 = rr^* = 1$ . Therefore, there exists no hint on any EFSW effect in the spectrum of a non-absorbing layer on a PEC. If, however, the electric field is analyzed in the surroundings and inside the layer, an EFSW can readily be noticed (cf. Fig. 1a); the analysis was carried out numerically by the finite difference time domain method (FDTD) using "FDTD solutions" from the company Lumerical. We chose the parameters like mesh size etc. in a way that the numerical solutions, also for  $R$  and  $A$ , agreed with the analytical ones within numerical precision. We note that at the spectral positions where antinodes, i.e. maxima of the electric field strength, occur inside the layer there always exists one antinode centered on the interface between layer and incidence medium. These antinodes build the foundation of the so-called buried metal layer-IRRAS [2], where the spectrum of a nanometer-thin or even monomolecular layer deposited on this interface can be considerably enhanced even for normal incidence (for this application, however, the thickness of the layer is usually minimized in a way that there is only one antinode, namely at the interface between non-absorbing layer and incidence medium in the spectral region of interest). In contrast, at the same spectral positions, a node is always located at the interface between PEC and layer, in line with the fact, that the electric field cannot penetrate into the PEC.

If we exchange the PEC by a real, but highly-conducting metal, e.g. gold, the pattern of the EFSW remains virtually unchanged, in contrast to the reflection spectra which now shows minima (Fig. 1d). The decrease of the reflection at the minima is a function of the optical constants of the metal and the index of refraction of the transparent layer (for Fig. 1 we chose  $n_2 = 4$  to emphasize the effect). The spectral positions of the minima coincide with the strongest variations of the electric field inside the layer. This spectral positions  $\tilde{\nu}_m$  can be described by [17],

$$(2n_2d)^{-1} \left[ \frac{2m+1}{2} - \frac{1}{2\pi} \tan^{-1} \left\{ \frac{2n_1k_2}{(n_1^2 - n_2^2 - k_2^2)^2} \right\} \right] = \tilde{\nu}_m, \quad (5)$$

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