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Mendoza-Galvan, A., Mendez-Lara, J. G., Mauricio-Sanchez, R. A., Järrendahl, K., Arwin, H., (2021), Effective absorption coefficient and effective thickness in attenuated total reflection spectroscopy, *Optics Letters*, 46(4), 872-875. <https://doi.org/10.1364/OL.418277>

Original publication available at:

<https://doi.org/10.1364/OL.418277>

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Effective absorption coefficient and effective thickness in attenuated total reflection spectroscopy

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Received XX Month XXXX; revised XX Month, XXXX; accepted XX Month XXXX; posted XX Month XXXX (Doc. ID XXXXX); published XX Month XXXX

Since the introduction of attenuated total reflection (ATR) spectroscopy for the characterization of materials, attempts have been made to relate the measured reflectivity (R) to the absorption coefficient (α) of the absorbing material of interest. The common approach is limited to the low absorption case under the assumption $R \sim \exp(-\alpha d_e)$ where d_e is an effective thickness, which is evaluated for the lossless case. In this letter, a more detailed derivation leads to $R = \exp(-\beta d_p/2)$ enabling the definition of an ATR effective absorption coefficient β and the penetration depth d_p of the electric field in the absorbing material. It is found that $\beta \sim 4\pi\epsilon_2/\lambda$, where ϵ_2 is the imaginary part of the complex dielectric function of the absorbing material and λ is the wavelength. An alternative formulation is $R = \exp(-\alpha d_{ef})$ where d_{ef} is a generalized effective thickness for arbitrary strength of absorption which reduces to d_e in the low absorption limit. Experimental data for water, the biopolymer chitosan, and soda-lime glass prove the reliability of the ATR-effective absorption coefficient in the infrared range. © 2020 Optical Society of America

Total internal reflection is a phenomenon for radiation incident from an optically denser medium with refractive index n_a , impinging the boundary (xy plane) with an optically rarer medium with refractive index $n < n_a$, at an angle of incidence θ larger than the critical angle given by $\theta_c = \sin^{-1}(n/n_a)$. Under these conditions the reflectivity for parallel (R_p) and perpendicular (R_s) polarization both equals unity. However, to satisfy the boundary conditions an evanescent wave exists in the rarer medium with an electric field decaying as $\exp(-z/d_{p0})$ perpendicular (z direction) to the boundary. The penetration depth d_{p0} is wavelength (λ) dependent and given by [1],

$$d_{p0} = \frac{\lambda}{2\pi\sqrt{n_a^2 \sin^2 \theta - n^2}} \quad (1)$$

Sixty years ago, Fahrenfort introduced attenuated total reflection (ATR) to investigate the infrared response of organic compounds [1]. He noticed that for absorbing materials characterized by a complex refractive index $N = n + ik$, where k is the extinction coefficient, the internal reflection spectrum R resembles that obtained in transmission mode in spectral regions where $k \neq 0$. To highlight the application of ATR measurements for quantitative purposes, Fahrenfort introduced the “formal optical density” as $\log R^{-1}$.

Since ATR measurements are very sensitive and particularly advantageous for thick samples for which transmittance measurements are not possible, $\log R^{-1}$ was commonly used as a representation for an

absorption spectrum. For low absorption ($k < 0.1$) Hansen developed a series expansion of R_p and R_s to investigate the range of applicability of the Beer-Lambert law in ATR measurements [2]. The concept of “effective thickness” d_e was introduced for low absorption as the thickness of a film of the same material which would give the same absorption for transmission at normal incidence [3]. That is, if reflection losses are neglected, the transmittance of a film of thickness d and absorption coefficient $\alpha = 4\pi k/\lambda$ has a dependence $T \sim \exp(-\alpha d) \approx 1 - \alpha d$. Analogously, for ATR measurements it was assumed a similar form $R \sim \exp(-\alpha d_e) \approx 1 - \alpha d_e$ where d_e is given by $d_e = (d_{es} + d_{ep})/2$. Here, $d_{e(s)}$ are effective thicknesses calculated [3] for s-polarization,

$$d_{e,s} = \frac{2n_a n \cos \theta}{(n_a^2 - n^2)} d_{p0}, \quad (2)$$

and p-polarization,

$$d_{e,p} = \frac{2n_a n \cos \theta (2n_a^2 \sin^2 \theta - n^2)}{(n_a^2 - n^2)(n_a^2 \sin^2 \theta - n^2 \cos^2 \theta)} d_{p0}, \quad (3)$$

Since it is assumed that $R \sim \exp(-\alpha d_e)$, the ATR-formal optical density (or absorbance) $\log R^{-1}$ is usually corrected by dividing with the effective thickness d_e . Here “correction” means to transform the experimental $\log R^{-1}$ spectrum into a quantity mimicking the absorption coefficient.

Despite the limitation of the zero-absorption assumption, $k=0$ in Eqs. (2) and (3), the effective thickness approach has been successfully applied over the years to investigate the ATR infrared response and structure of proteins, lipids, biological membranes [4-6], depth profiling (taking advantage of the dependence of d_p on n_a and/or θ in Eq. (1)) [7], soft matter at interfaces [8], imaging of biological systems and biopharmaceuticals [9,10]. In most cases, n is assumed to be constant and only in a few applications dispersion is considered [5,11].

However, a long time ago Müller et al. remarked that even for $\theta > \theta_c$ electromagnetic waves propagate in the absorbing medium but with planes of constant amplitude parallel to the interface non coincident with planes of constant phase [12]. Thus, in terms of the dielectric constant of the denser material $\epsilon_a = n_a^2$, and the real ϵ_1 and imaginary ϵ_2 parts of the complex dielectric function $\epsilon = \epsilon_1 + i\epsilon_2$ ($=N^2$) of the sample, the penetration depth is given by [12],

$$d_p = \frac{\lambda}{\sqrt{2\pi} \left[\sqrt{(\epsilon_a \sin^2 \theta - \epsilon_1)} + \sqrt{(\epsilon_a \sin^2 \theta - \epsilon_1)^2 + \epsilon_2^2} \right]}. \quad (4)$$

Notice that Eq. (4) reduces to Eq. (1) for a non-absorbing material, i.e., when $\epsilon_2=0$ and thus also $k=0$. The relevance of Eq. (4) to describe absorption in ATR measurements will be demonstrated.

Other approaches to analyze ATR spectra use either Kramers-Kronig transforms [13-15] or Lorentz dispersion models to determine ϵ or N [16]. However, these procedures require a nearly perfect contact at the interface (complicated to achieve) for accurate determination of optical functions including absorption.

The objective of this letter is to provide a general relationship to describe ATR spectra in terms of fundamental quantities accounting for absorption, i.e., ϵ_2 , k , and/or α . The formalism is applied to experimental data for chitosan, which is a derivative of the biopolymer chitin. The latter is found in the shell of crustaceans, fungi, and the cuticle of beetles [17]. The interest in chitosan is because it has found applications in diverse fields and often it is characterized with ATR in the infrared range [18,19]. Data for water and soda lime glass are also included as contrasting examples of lower refractive index and stronger absorption, respectively.

Assuming unpolarized incident radiation at the interface between two media, one non-absorbing (n_a) and the other absorbing (N), algebraic manipulation of $R=(R_p+R_s)/2$ as shown in Supplement 1 leads to,

$$R = \frac{1-u}{(1+u)^2}, \quad (5)$$

where,

$$u = \frac{2n_a z_1 \cos \theta \sqrt{\epsilon_a \sin^4 \theta + c \cos^2 \theta}}{\sqrt{\epsilon_a \cos^2 \theta + c} \sqrt{\cos^2 \theta (\epsilon_a \sin^2 \theta - c)^2 + c \epsilon_a}}. \quad (6)$$

The expressions for z_1 and c are given in Eqs. (S9) and (S10) in Supplement 1, respectively. As shown in Supplement 1, the natural logarithm of Eq. (5) in combination with relations between $\ln$ and $\tanh^{-1}$ functions lead to an exponential dependence of R on α for arbitrary absorption given by,

$$R = \exp(-\alpha d_{\text{ef}}), \quad (7)$$

where the effective thickness d_{ef} is given by,

$$d_{\text{ef}} = \left(\tanh^{-1} u + \tanh^{-1} \frac{u}{2+u} \right) \frac{n d_p}{z_1}. \quad (8)$$

Both z_1 and d_p depend on ϵ_a and thus also d_{ef} in Eq. (8) which, although undesired, is unavoidable. Furthermore, Eq. (7) can alternatively be viewed in terms of an effective ATR absorption coefficient β defined by,

$$R = \exp(-\beta d_p / 2), \quad (9)$$

where $d_p/2$ is used because R involves measurements of irradiance and the intensity decays as $I \sim \exp(-2z/d_p)$.

Since the dependence of d_{ef} (and β) on fundamental quantities in Eq. (8) are complicated, it is convenient to look for a series expansion of $\tanh^{-1}$ as shown in Eqs. (S15) and (S16) in Supplement 1, leading to,

$$\ln R^{-1} = 2u \left[1 + \frac{1}{2+u} + \frac{1}{3}u^2 + \frac{1}{3} \frac{u^2}{(2+u)^3} + O \right], \quad (10)$$

where O stands for terms of higher order (see Eq. (S22) in Supplement 1). The rapid convergence of the series in Eq. (10) makes possible to approximate the calculations with good accuracy by using a first few terms. Indeed, for $u=0.5$ the difference between R calculated as in Eq. (5) and up to the third term in Eq. (10) is only 0.005 (Fig. S3 in Supplement 1), which is within the experimental error. Furthermore, the values of u can be controlled by choosing adequately the experimental settings (n_a and θ) as is shown below. From Eqs. (9) and (10) and $d_p = \lambda/(2\pi z_2)$ we get,

$$\beta = \frac{2 \ln R^{-1}}{d_p} = \frac{4\pi}{\lambda} \epsilon_2 2fs, \quad (11)$$

where $f=u/(2z_1)$ is determined from Eq. (6), s is the summation of the first three terms in brackets in Eq. (10), and $\epsilon_2=2z_1z_2$ (z_2 is given in Eq. (S9) in Supplement 1). Thus, an explicit exponential dependence of R on ϵ_2 has been accomplished which highlights the importance of using Eq. (4). Furthermore, substitution of $\epsilon_2=2nk$ in Eq. (11) leads to the exponential form $R=\exp(-\alpha d_{\text{ef}})$ as in Eq. (7) where the effective thickness is now expressed as,

$$d_{\text{ef}} = 2nfsd_p. \quad (12)$$

Since the derivations above have no restrictions on the strength of absorption, Eq. (12) is a generalization of the effective thickness for low absorption. The relationship between d_e and d_{ef} in the limit $k \rightarrow 0$ ($d_{\text{ef}}|_{k=0}$) is obtained in Eqs. (S24)-(S31) in Supplement 1 leading to,

$$\frac{d_e}{d_{\text{ef}}|_{k=0}} = 1 + \frac{1}{3} \frac{(n/n_a)^2 \cos 2\theta}{\sin^2 \theta - (n/n_a)^2 \cos^2 \theta}. \quad (13)$$

Clearly $d_e=d_{\text{ef}}|_{k=0}$ at $\theta=45^\circ$ regardless of n_a and n . At larger angles of incidence up to 60° , the deviation is smaller than 0.1 for an interface with diamond for common values of the ratio n/n_a . Using a crystal with higher refractive index, e.g., of germanium (Ge), the deviation is even smaller (Fig. S4 in Supplement 1). To illustrate the role of the effective parameters in ATR spectroscopy, experimental data are analyzed for representative liquid, polymeric, and inorganic media as shown below.

Figure 1(a) shows the experimental and calculated (Eq. 10) $\ln R^{-1}$ spectra of deionized water. It is expected that the contact of a liquid with diamond offers an ideal interface. As specified by the supplier (PIKE) of the ATR accessory, the refractive index of the diamond crystal is $n_a=2.4$ and nominal angle of incidence 45° . However, the actual value of θ should be determined because internal mirrors in the accessory must

be routinely adjusted to get the maximum intensity in the background spectrum. In the present case, a good match of the experimental and calculated spectra in Fig. 1(a) was achieved for $\theta=49^\circ$, using reported optical constants of water [20]. This value of θ serve as the calibrated value for further measurements. Figure 1(b) shows the effective ATR absorption coefficient calculated from Eq. (9) using the experimental reflectivity spectrum R_{exp} , i.e., $\beta_{\text{exp}}=2\ln R_{\text{exp}}^{-1}/d_p$. Furthermore, for the experimental settings, the value of u (<0.3) is small enough to approximate the series in Eq. (10) up to the third term (Fig. S5 in Supplement 1). Since the sum of 2nd and 3rd terms as well as f are smoothly dependent on wavenumber, they can be approximated by their mean values 0.49 and 0.383, respectively. Thus, from Eq. (11) $\beta \approx 1.14\beta_0$ where $\beta_0=4\pi\epsilon_2/\lambda$. Figure 1(b) shows that it is indeed a very good approximation. In Fig. 1(b) the difference between β and $1.14\beta_0$ at the maxima which are located at 700, 1640, and 3360 cm^{-1} is 6.4, 2.3, and 7.6 %, respectively.

The characteristic lengths in Eqs. (1), (4), (8) and the average of Eqs. (2) and (3) for the diamond-water interface, decrease from about 2 to 0.36 μm in the spectral range considered as seen in Fig. 1(c). The spectrum of k for water shows three maxima of 0.41, 0.131, and 0.285 at 650, 1640, and 3400 cm^{-1} , respectively. As can be noticed, in most of the spectral range investigated the penetration depths are $d_p \approx d_{p0}$ and $d_e \approx d_{\text{ef}}$ for the effective thicknesses. However, $d_e > d_{\text{ef}}$ in the range 650-900 cm^{-1} as is shown in the insert of Fig. 1(c), indicating the limitation of using Eqs. (2) and (3) in this range. For example, the difference at 650 cm^{-1} is 16.3%. In the insert, that difference is apparently larger because the range of the vertical axis is limited from 1.2 to 2.8 μm .

Fig. 1. (a) $\ln R^{-1}$ spectra of experimental R and data calculated with Eq. (5) at $\theta=49^\circ$ for a diamond-water interface using reported optical constants of water [20]. (b) Effective ATR absorption coefficient $\beta_{\text{exp}}=2\ln R_{\text{exp}}^{-1}/d_p$ compared to $1.14\beta_0=(1.14)4\pi\epsilon_2/\lambda$. (c) Penetration depths from Eqs. (1) and (4), effective thicknesses from Eq. (8) and $d_e=(d_{\text{es}}+d_{\text{ep}})/2$, the average of Eqs. (2) and (3). The insert in (c) shows d_e and d_{ef} in the range 650-900 cm^{-1} .

The second example is ATR measurements on a film of the biopolymer chitosan with thickness $4.32 \pm 0.03 \mu\text{m}$. Its complex dielectric function was determined by combining oblique spectroscopic ellipsometry (IRSE, J. A. Woollam Co., Inc.) and normal incidence transmittance irradiance measurements (Spectrum GX, Perkin Elmer),

as presented in Figs. S1 and S2, respectively, in Supplement 1. The chitosan films were cast following the procedure reported in our previous works [21,22]. Further experimental details are given in Supplement 1.

Figure 2(a) shows experimental and calculated $\ln R^{-1}$ spectra for a chitosan film. The calculated spectrum has been multiplied by 0.74 to put data in the same scale as the experimental spectrum. As is known, in ATR measurements the crystal and solid samples are brought in physical contact. Forcing the contact often improves the quality of ATR spectra. To avoid damage on the crystal, the pressure clamp limits the maximum pressure applied. This affects the optical contact between the crystal and the sample and therefore the magnitude of R . The presence of interfacial roughness creating air gaps decreases the penetration depth to an effective value between that of d_p in Eq. (4) and that of vacuum, d_v in Eq. (1) with $n_a=1$. Other methods to increase the magnitude of an ATR spectrum include the use of index matching liquids or solids [23]. Furthermore, air gaps produce smaller values of ϵ_2 suggesting the use of an effective complex dielectric function. In a first approximation, the overall result is that experimental and calculated $\ln R^{-1}$ data, agree within a scale factor (0.74 in the present case of the diamond-chitosan interface). A rigorous treatment of this subject is beyond the scope of this letter.

Figure 2(b) shows the effective ATR absorption coefficient β_{exp} calculated from Eq. (9) using the experimental reflectivity spectrum. Maxima in ϵ_2 locate resonant frequencies among which the most important are vibrations of the glycosidic ring in range 800-1100 cm^{-1} , the glycosidic bond at 1150 cm^{-1} , amino and amide bands at 1500-1700 cm^{-1} , CH about 2900 cm^{-1} , and O-H stretching modes in the range 3000-3500 cm^{-1} [21]. Substitution of the mean values $s=1.486$ and $f=0.454$ (Fig. S6 in Supplement 1), in Eq. (11) gives $\beta \approx 1.35\beta_0$. As can be seen in Fig. 2(b). At 1077 cm^{-1} the difference between β and β_0 is 22.6%.

As expected from Eq. (13), Fig. 2(c) shows that the penetration depths $d_p \approx d_{p0}$ and the effective thickness $d_e \approx d_{\text{ef}}$ in spectral ranges of low absorption. That corresponds to wavenumbers outside the range 900-1100 cm^{-1} of vibrations belonging to the glycosidic ring. The stronger absorption around 1000 cm^{-1} in chitosan produces smaller values on d_p and d_{ef} than on d_{p0} and d_e as calculated with Eqs. (1) and (2) and should be considered for interpretation of data for depth profiling.

Fig. 2. (a) $\ln R^{-1}$ spectra of experimental R and data calculated with Eq. (5) at $\theta=49^\circ$ for a diamond-chitosan interface. The scaling is explained

in the text. (b) Effective ATR absorption coefficient $\beta_{\text{exp}}=2\ln R_{\text{exp}}^{-1}/d_p$. (c) Penetration depths and effective thicknesses from Eqs. (1), (4), (8), and the average of Eqs. (2) and (3). For clarity, data in the range 1800-2500 cm^{-1} are omitted as there are no bands of chitosan in that spectral range.

An example which shows stronger absorption than the two previous examples is ATR measurements on glass. The complex dielectric function of a soda lime glass slide (Corning 2947) was determined by spectroscopic ellipsometry (Fig. S7 in Supplement 1). Figure 3(a) shows the experimental and calculated $\ln R^{-1}$ spectra of the diamond-glass interface in the spectral range of strong absorption in glass 650-1400 cm^{-1} . It can be noticed that there is a very good agreement between the two spectra with scale factor 0.8 accounting for the quality of optical contact. The effective ATR absorption β_{exp} is shown in Fig. 3(b). It can be noticed that as the strength of absorption increases in the order water-chitosan-glass, the larger the deviation of the line shape of $\ln R^{-1}$ and β . For the diamond-glass interface the series approximation of Eq. (10) no longer holds due to the strong absorption. However, using a crystal of larger refractive index as Ge ($n_a=4.0$), the maximum value of u for the Ge-glass interface is about 0.4. This fact makes it suitable to use the three-term approximation in Eq. (11) with mean values $f=0.2$ and $s=1.5$ (Fig. S8 in Supplement 1) and, in good approximation, $\beta \approx 0.6\beta_0$.

As can be seen in Fig. 3(c) the values of d_{p0} and d_e diverge and become indetermined in the range 800-1000 cm^{-1} because $n_a \sin \theta < n$ in Eq. (1). On the other hand, d_p and d_{ef} show a well-behaved spectral dependence because Eq. (4) ensures a smooth behavior with wavenumber and angle of incidence (Fig. S9 in Supplement 1). At about 870 cm^{-1} where glass is weakly absorbing, d_p and d_{ef} reach values of tens of microns.

Fig. 3. (a) $\ln R^{-1}$ spectra of experimental R and data calculated with Eq. (5) at $\theta=49^\circ$ for a diamond-glass interface in the spectral range of strong absorption of glass. The scaling is explained in the text. (b) Effective ATR absorption coefficient $\beta_{\text{exp}}=2\ln R_{\text{exp}}^{-1}/d_p$. (c) Penetration depths and effective thickness from Eqs. (1), (4), (8), respectively, and average of Eqs. (2) and (3).

In summary, we have developed a general description of ATR spectra and shown that the interpretation for bulk materials might be two-fold. One approach is to use an effective absorption coefficient β and the penetration depth d_p for absorbing materials. Another interpretation considers the absorption coefficient and the generalized effective

thickness for arbitrary absorption. Experimental data for the interface of diamond with representative materials (water, chitosan, and glass) have been used to demonstrate the reliability of the approach.

Funding sources and acknowledgments.

Acknowledgments. J. G. Méndez-Lara acknowledges Conacyt the scholarship (#589937) for doctoral studies. K. Järrendahl acknowledges The Swedish Government Strategic Research Area in Materials Science on Functional Materials at Linköping University (Faculty Grant SFO-Mat-LiU 2009-00971). A. B. Domínguez-Gómez is acknowledged for preparation of the chitosan thick sample.

Disclosures. The authors declare no conflicts of interest.

See Supplement 1 for supporting content.

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