Attenuated Partial Internal Reflection Infrared Spectroscopy

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A new method for the spectroscopic study of absorbing films is proposed. In contrast to the well-established methods that take advantage of the attenuation of total internal reflection (ATR) to obtain spectra, we intentionally arrange the optics to permit partial internal reflection from the sampling prism face. Attenuated partial internal reflection (APR) spectroscopy is introduced through theoretical calculations and experimental demonstrations. The calculated APR spectra in the infrared region were obtained. APR spectra of water films on a NaCl prism were measured. Experimentally, APR spectra of water films on a NaCl prism were obtained. APR is more sensitive than ATR, and can easily distinguish water films at the monolayer level (310 pm). The determination of film thickness from interference fringes in APR spectra is also illustrated. It is shown that APR can be used for film thickness measurements that can span 6 orders of magnitude. The limitations of APR are also discussed.

The change in refractive index across the boundary of two uniform materials causes the propagation of light to alter at the interface, that is, some of the light is transmitted and the rest, reflected.1 Internal reflection results when light propagates from a material that has a larger real refractive index to that with a smaller one. For the same polarization, the proportions of the transmitted and reflected light varies with the angle of its incidence. For incident angles larger than a critical value, all light is reflected, that is, total internal reflection occurs. If the light meets an absorbing material at the boundary, some of the reflected light is lost, and attenuated total internal reflection (ATR) results.2 Attenuated total internal reflection was studied by Isaac Newton,3 and its spectroscopic application began with Fahrenfort4 and Harrick.5 Attenuated total internal reflection spectroscopy has been well-characterized.7 The hydrophilic property of NaCl is easily produced by cleaving a single NaCl crystal in air, and it has been well-characterized. The hydrophilicity of NaCl permits the controlled production of films of water in a continuous range from submonolayer to multilayer thicknesses. Moreover, these films have been studied by traditional transmission infrared spectroscopy.8,9 Following the presentation of calculated spectra of water films on NaCl(001), we provide experimental results. We conclude the paper with a critique of APR spectroscopy.

THEORY OF INTERNAL REFLECTION

Transmission and reflection occur when light irradiates the interface of two materials (Figure 1). Medium 1 is also called the substrate, and medium 2 is often referred to as the sample, which may be either a semi-infinite (thick) or a thin film. For the examples that will concern us, medium 1 is optically dense and medium 2 is optically rare, with the consequence that internal reflection occurs at the interface. The notation for our figures and equations follows closely that of Born and Wolf10 and Fowles.11 Incident light (i) from medium 1 is reflected (r) and refracted (t) at the interface. The incident light is typically plane polarized in one of two ways. The TE wave has its electric field perpendicular to the plane of incidence, that is, perpendicular to the xz plane of Figure 1, and the TM wave has its electric field parallel to the plane of incidence. For nonabsorbing samples, the direction of the transmitted light can be found from Snell’s law:

\[ n_1 \sin \theta_1 = n_2 \sin \theta_2 \]

where \( \theta_1 \) and \( \theta_2 \) are defined in Figure 1 and \( n_1 \) and \( n_2 \) are the real refractive indices of media 1 and 2, respectively.

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The optical response of films on a substrate is described by the Fresnel and Airy equations, which can be derived from Maxwell's electromagnetic wave equations\(^1\). The Fresnel equations are appropriate for light meeting a semi-infinite sample at the boundary. A sample is termed thick when its spectroscopic response is indistinguishable from a semi-infinite medium. The Airy equations apply for a film sample of a finite thickness. A thin film has a spectroscopic response that is independent of its thickness.

The Fresnel formulas, eqs 2 and 3, can be used to calculate reflection spectra of a thick sample if its optical constants and that of the substrate are known.\(^1\) When light goes from medium 1 to medium 2, the reflection coefficient of the TE wave, the ratio of magnitude of the reflected electric field to that of the incident, \(r_{12,TE}\), is given by

\[
r_{12,TE} = \frac{n_1 \cos \theta_1 - \hat{n}_2 \cos \theta_2}{n_1 \cos \theta_1 + \hat{n}_2 \cos \theta_2}
\]  

(2)

The reflection coefficient of the TM wave, \(r_{12,TM}\), is

\[
r_{12,TM} = \frac{n_2 \cos \theta_1 - \hat{n}_1 \cos \theta_2}{n_2 \cos \theta_1 + \hat{n}_1 \cos \theta_2}
\]  

(3)

The complex refractive index of medium 1 is \(\hat{n}_1\), with \(n_1\) and \(k_1\) its real and imaginary components and an analogous definition for \(n_2, n_2\) and \(k_2\) of medium 2.

\[
\hat{n}_1 = n_1 + ik_1
\]  

(4)

\[
\hat{n}_2 = n_2 + ik_2
\]  

(5)

The reflectivity from the interface of medium 1 and 2 is

\[
R = |r|^2
\]  

(6)

where \(r\) refers to \(r_{12,TM}\) or \(r_{12,TE}\). For spectroscopic applications, the background is \(R_0\) when medium 2 is vacuum, that is, \(n_2 = 1\). \(R_0\) is 1 for total reflection but is <1 when the incident angle is smaller than the critical angle. Extinction of the reflected light is \(E\), as defined through

\[
E = \log_{10}(R_0/R)
\]  

(7)

It can be seen from eqs 2 and 3 that the spectra of thick samples depend on the incident angle of light, refractive indices of materials, and the polarization of the light, but not on thickness.

In the following paragraph it can be seen that the spectroscopic profile of a thin film also depends on the thickness of the sample.

The reflection spectra of a thin film can be calculated from the Airy equations\(^5,10\) if the optical constants of the materials are known. The model for this equation consists of a thin film with parallel surfaces sandwiched by two thick (semi-infinite) materials (Figure 2). Light from medium 1 may penetrate film 2 and reach medium 3. The reflection coefficient, \(r\), is decided by those of the two interfaces, \(r_{12}\) and \(r_{23}\), the thickness of the film, \(h\), and a dimensionless parameter, \(\beta\),

\[
r = \frac{r_{12} + r_{23}e^{2j\beta}}{1 + r_{12}r_{23}e^{2j\beta}}
\]  

(8)

\[
\beta = 2\pi n h \cos \theta / \lambda_0
\]  

(9)

Equations for stratified layers of films have also been developed.\(^1,11,12\) Although commercial computer codes are available to cast these equations in useful forms for the spectroscopist,\(^12\) we have chosen to develop our own programs.

**CALCULATIONS OF INTERNAL REFLECTION SPECTRA**

Fortran77 programs were written to calculate reflection spectra of either a thick or thin absorbing medium by using equations 1–9.

For internal reflection, the critical value \(\theta_c\) is defined by

\[
n_2 \sin \theta_c = n_2
\]  

(10)

When the incident angle, \(\theta_i\), is greater than \(\theta_c\), total internal reflection occurs; for \(\theta_i\) smaller than \(\theta_c\), the internal reflection is only partial. The example we shall explore in detail is water (or brine) on NaCl. For NaCl, the index of refraction changes


\[^{(12)}\text{Milosevic, M.; Berets, S. L. Appl. Spectrosc. } 1993, 47, 566–574.\]
monotonically throughout the infrared from 1.525 to 1.447. Here we have selected \( n_1 = 1.5 \) as a nominal value for our calculation. Water\(^{14} \) or brine\(^{15} \) has a more varied range of index of refraction. Using \( n_2 = 1.33 \) as a typical value for the thick film of water (or brine), the critical angle is 62.5\(^{\circ} \). With an angle of incidence larger or smaller than 62.5\(^{\circ} \), total internal reflection or partial internal reflection occurs, respectively. In reference to the acronym of ATR, derived from attenuated total internal reflection, we propose APR to identify attenuated partial internal reflection.

The calculated reflection spectra of a 0.01-\( \mu \)m film of water on NaCl with TE polarization are shown in Figure 3. We have used values of \( n_2 \) and \( k_2 \) for water measured throughout the infrared by Downing and Williams\(^{14} \) together with \( n_1 = 1.5 \) (\( k_1 = 0 \)) for NaCl. The spectra cover a range of incident angles from 0 to 89\(^{\circ} \). Since this range spans the (thick film) critical angle of 62.5\(^{\circ} \), these calculations extend into both APR and ATR regions. It can be seen that although the extinction increases as incident angle becomes smaller, the spectroscopic profiles remain similar. Moreover, comparison with the transmission spectrum of water\(^8 \) would find a qualitative similarity. In other calculations (not shown here) at an incident angle of 30\(^{\circ} \) and for the band maximum near 3400 cm\(^{-1} \), the extinction is linear to within 0.01% with thicknesses below 0.01 \( \mu \)m. Using the molecular density of liquid water at 25 \( ^{\circ} \)C,\(^\text{16} \) we calculate a monolayer thickness of 310 \( \text{pm} \). This monolayer value would find an extinction of \( 10^{-3} \). Since the noise level of a well-tuned FT-IR can approach \( 10^{-5} \),\(^\text{17} \) the detection of thin films even at submonolayer coverage is realizable. We shall demonstrate an experimental monolayer spectrum later in the paper.

Throughout Figure 3, the extinctions in APR spectroscopy are always greater than those in an ATR configuration. In ATR spectroscopy, the extinction arises only because a portion of the evanescent wave is lost to absorption, an inelastic process. In the APR configuration, light can also be lost to absorption. But there is, in addition, another loss. Recall that what is measured in our experiments is the changes in reflected light (see eq 7) at the detector. In APR, some light is transmitted through the film, and even if it is not absorbed, it still does not reach the detector. The reflection loss, an elastic process, then contributes to the APR extinction.

Although Figure 3 demonstrates the greater sensitivity of APR over ATR spectroscopy, APR is also superior to transmission spectroscopy. Using the standard relationships given in Born and Wolf,\(^1 \) we calculated the transmissivity, \( T_0 \), through salt/vacuum and the transmissivity, \( T \), through salt/0.01 \( \mu \)m water/vacuum for an incident angle of \( \theta_1 = 0^{\circ} \). Using the index of refraction of \( n_2 = 1.305 \) and \( k_2 = 0.281 \) for water at 3400 cm\(^{-1} \), we find an absorbance of \( A = \log \left( \frac{T_{0}}{T} \right) = 0.0054 \). This may be compared to the corresponding values of extinction at 3400 cm\(^{-1} \) read from Figure 3 at, say, \( \theta_1 = 30^{\circ} \) of 0.029. In this instance, the response of APR is greater than transmission by a factor of 5.4.

For the special case of an incident angle of \( \theta_1 = 0^{\circ} \), W. L. Schaich\(^\text{18} \) had derived a simple expression relating the absorbance in a transmission experiment to the extinction in an APR experiment given by

\[
E = \frac{2A}{1 - n_2/n_1} \quad (11)
\]

Thus judicious selection of an APR prism with an appropriate index of refraction, \( n_1 \), can favor large values of extinction.

The calculated APR spectra of thicker films of water on NaCl are shown in Figure 4. It can be seen that the spectral profile changes markedly with the thickness of water. At 0.1 \( \mu \)m, the extinction mimics the profile of an absorbance (transmission) spectrum. Here, light penetration of the thin film is principally affected by \( k_2 \), the imaginary index of refraction of water. By contrast, the thick film has an extinction profile largely dictated by \( n_2 \), the real index on refraction. Here, the light is refracted deep into the film and is lost to the detector. This reflection at

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**Figure 3.** Calculated reflection spectra of 0.01-\( \mu \)m water on NaCl with various angles of incidence. TE polarization.

**Figure 4.** Calculated spectra of water of different thickness on NaCl with TE polarization and 45\(^{\circ} \) angle of incidence of light.
the interface then depends not on $k_2$, but on $n_2$ and its similarity to the $n_1$ of the prism.

It is easy to distinguish a 10-$\mu$m-thick film from a semi-infinite (thick) film calculated using the Fresnel equations. Further calculation using the Airy equations for $\theta_i=45^\circ$ and TE polarization shows that only when the thickness of water approaches 300 $\mu$m does the spectrum become nearly indistinguishable from that of a thick sample. By contrast, the calculated ATR spectrum of 3-$\mu$m-thick water (not shown here) is essentially the same as that of the thick sample when the incident angle is 85$^\circ$.

The multiple peaks in the spectrum of the 10-$\mu$m-thick film (Figure 4) are a consequence of the interference of light from reflection within the film. The thin film (Figure 2) should indeed act as a Fabry–Perot etalon. The resulting fringes can be used to determine film thickness from

$$m = \frac{2n_2 h \cos \theta_2}{\lambda_0} = 2h \bar{v}_0 (n_2^2 - n_1^2 \sin^2 \theta_1)^{1/2} \quad \text{(12)}$$

where $m$ is the order of a fringe and $\bar{v}_0$, its frequency in wavenumbers. In a group of fringes, two extinction maxima can be picked to solve for thickness, $h$. Each maximum is associated with a refractive index, $n_2$, and a frequency, $\bar{v}_0$. The difference in the fringe orders, $\Delta m$, is the number of valleys between two peaks. The doublet near 3800 cm$^{-1}$ in Figure 4, where $\Delta m = 1$, was used for calculation, resulting in a thickness of 10 $\mu$m, which is consistent with the photometric value of the calculated spectrum. Another calculation was performed under the same conditions of Figure 4 for a film 100 $\mu$m thick. A segment of this spectrum near 2600 cm$^{-1}$ is shown in Figure 5 that presents a clearly defined sequence of fringes. Taking $\Delta m = 6$ for seven of the most prominent peaks yields 100 $\mu$m for the film thickness. Calculation shows that as films become thicker, their APR spectra resemble more those of a semi-infinite sample. But the occurrence of the Fabry–Perot interference pattern still enables the determination of film thickness. This phenomenon echoes that found in transmission spectra of films.\(^{19}\)

We realize that neat water cannot exist on top of a NaCl crystal without dissolving it. The reason to use water on NaCl as a system for its spectra calculation was that a higher quality of refractive index of water is available than for brine. We shall present a calculated brine spectrum in a following section.

Although we have selected TE rather than TM polarization or depolarized light in our sample calculations and experiments, we could have equally well have offered these other polarizations.\(^{20}\) We have chosen to restrict the polarization in order to keep this paper as concise as possible while consistent with illustrating the principles.

The choice of TM polarization actually presents an interesting special case near the principal angle. Here, there is an enhancement of extinction that offers useful analytical applications. This is discussed elsewhere.\(^{20,21}\)

In the next section, we will demonstrate that APR spectra are available experimentally.

**EXPERIMENT**

The internal reflection apparatus is shown in Figure 6. It consists of a cylindrical sample chamber with a 45$^\circ$ NaCl prism glued to the base plate. Two kinematic mirror mounts are fixed with posts to a plate that sits in the sample compartment of the spectrometer. The light path is the same as that used in a previously described ATR application.\(^{22}\) High vacuum to 5 $\times$ 10$^{-6}$ mbar was obtained with a Turbovac 151 molecular pump backed by a Trivac D5E mechanical pump (Leybold Vakuum, Germany). The pressure was monitored using a Baratron 122AA with a PDR-C-2C power supply and readout (MK S Instruments Inc., Andover, MA) and an ion gauge (Kurt J. Lesker Co., Clairton, PA) with gauge controller 260 (Granville-Phillips).

To start an experiment, a NaCl prism was first glued with Torr Seal (Varian Vacuum Products, Lexington, MA) to the base plate of the sample chamber. The NaCl prism, fabricated by REFLEX Analytical Corporation (Ridgewood, New Jersey), was a single crystal with a (001) surface as its base that extended several millimeters above the base plate. A sharp chisel was then used to cleave the prism in air to generate a fresh (001) face nearly flush with the base plate. This cleaving procedure produces a well-

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\(^{21}\) Zhang, Z.; Schaich, W. L.; Ewing, G. E. to be published.

\(^{22}\) Harrick, N. J. Appl. Spectrosc. 1983, 37, 573–575.
defined and largely atomically flat (001) surface. The base plate with prism was attached to the sample chamber immediately after the cleaving and pumped to high vacuum. The positions of the sample chamber and the mirror mounts were adjusted with the aid of the laser beam of the spectrometer so that the signal intensity was optimized at the chosen 45° angle of incidence. Water vapor was admitted into the sample chamber through the vacuum line at a controlled pressure for preparation of a monolayer thin film. For thick film preparation, a saturated brine solution was introduced from the top of the sample chamber with a couple of small pieces of NaCl crystals beside the prism to minimize prism dissolution.

IR spectra were obtained using a Nicolet Magna 550 spectrometer equipped with a MCT (mercury–cadmium telluride) detector. Resolution was set at 4 cm⁻¹ with 100 scans to obtain both background and sample signals. The signals were processed with triangle apodization and without zero filling. The sample compartment was purged with dry nitrogen. A ZnSe polarizer (International Crystal Laboratory, Garfield, NJ) was used to obtain polarized IR light.

RESULTS AND DISCUSSION

Figure 7 shows the experimental spectrum (dashed line) of several millimeters of saturated brine on NaCl(001) with TE polarization of light and an angle of light 45° at room temperature (22 °C). The calculated thick film spectrum (solid line) of 5 M brine, the optical constants of which are known, is in excellent agreement with the measured spectrum. This example demonstrates that APR can be used to measure the optical response of a thick sample, and the measured spectra can be quantitatively simulated.

Figure 8 shows the measured spectrum (solid line) of thin film water on NaCl(001) in equilibrium with 15.5 mbar water vapor at 22 °C with TE polarization and an angle of incidence of 45°. Also shown are calculated spectra of neat water and 5 M brine on NaCl for a thickness of 400 pm with the same optical conditions used in the experiment. The agreement in extinction between the observed and calculated spectra suggests the apparent thickness of the water is 400 pm, or 1.3 layers. We note that for this monolayer spectrum, the signal-to-noise is near 10:1, indicating that the great sensitivity of APR is capable of exploring submonolayer thicknesses.

We can make a quantitative comparison between the water coverage extracted from Figure 8 and the results of Peters and Ewing taken at the same pressure and under similar temperature conditions (24 °C). They give a coverage of 2.0 water layers on the basis of a Na⁺ adsorption site density of 6.4 × 10¹⁸ ions m⁻² on the NaCl(001) surface. Our coverage estimate of 1.3 is based on the average surface density of water of 10.4 × 10¹⁸ molecules m⁻², as calculated from its liquid properties. Scaling the Peters and Ewing coverage value of 2.0 by the ratio of the two reference surface densities, we find 1.2 layers in reasonable agreement with the 1.3 value extracted from Figure 8.

Sharing the same advantage with ATR, APR spectroscopy is suitable for measuring the spectra of thin films with high vapor pressures, because the molecular density in the gas phase above the film is typically 3 orders of magnitude lower than that in the film. Therefore, the absorption of gas-phase molecules is negligible with respect to the film of comparable thickness. But the APR technique is more sensitive than that of the ATR, as shown by the calculations in Figure 3. APR spectroscopy has also been found to have an application in the understanding of the morphology of thin films.

APR does have a disadvantage over ATR for qualitative analysis. The APR spectra of thick samples resemble the real part of the refractive index of the sample (Figure 7). Thus, from a comparison of the APR spectra of a thick sample to the existing transmission spectra, which resemble the imaginary part of the refractive index of the sample, the qualitative identification of the sample will not be obvious. On the other hand, APR spectra of thin films resemble the imaginary part of the index of refraction of a sample (Figure 3) and, therefore, present no disadvantage over ATR.

CONCLUSIONS

This work demonstrates that attenuated partial internal reflection, APR, spectroscopy can be used to measure the spectra of absorbing films.

One advantage of APR over ATR is that it can distinguish much thicker films. Similarly to transmission, interference fringes occur in APR spectra and allow determination of film thickness. APR also gives higher sensitivity for thin film interrogations. A monolayer sample has been detected. A disadvantage of APR is that the spectra of thick samples do not resemble their transmission spectra.

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