Attenuated total reflection terahertz time-domain spectroscopy: measurement uncertainty and a new scheme for its reduction

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Abstract

Terahertz time-domain spectroscopy (THz TDS) in the attenuated total reflection (ATR) configuration is ideally suited to characterize highly absorptive media. In this article, we analyze the impact of random phase and amplitude errors and prism misalignment on the optical constants extracted from the ATR THz measurements. Analytical models together with empirical data suggest that, among those factors, small prism misalignment has a relatively strong impact on the optical constants. We propose an alternative configuration for ATR THz TDS that significantly reduces the impact of prism misalignment between the reference and sample measurements. As a result, this configuration facilitates repetitive reference and sample scans to mitigate the effect from long-term signal drifts. Based on this proposed method, the measured optical constants of distilled water and pure ethanol have a significantly reduced uncertainty. The presented analysis and method can be used to improve the measurement accuracy in standard ATR THz TDS setups.
1. Introduction

Terahertz time-domain spectroscopy (THz-TDS) is one promising spectroscopic modality developed in the last 25 years for characterization of many materials in the far-infrared band [1], [2]. Compared to traditional spectroscopic methods, THz-TDS has an advantage in that it acquires both the phase and amplitude information, which allows direct determination of the complex refractive index of the sample [3], [4]. To date, several types of samples have been investigated using THz-TDS, ranging from semiconductors [5], [6] to polymers [7]–[10] and liquids [10]–[13]. However, the investigation of samples dissolved in polar liquids, particularly water, has proven challenging given the exceptionally high absorption of those liquids in this frequency range. A standard transmission THz TDS setup is not ideal since the maximum measurable absorption is limited by the system dynamic range [14]. Yet, the study of water dissolved biomolecules such as proteins and nucleic acids with THz radiation can provide important information about both their vibrational and solvation dynamics [15]–[17], [10]. Therefore alternative approaches are desired. In particular, reflection type THz spectroscopy have been considered for these high absorption samples [17].

Attenuated total reflection (ATR) spectroscopy is one of the reflection techniques that have been explored. ATR THz-TDS is the most sensitive method for measuring highly absorbing liquid in the terahertz range [15] and since its first implementation with THz-TDS in 2004 by Tanaka et al. [18], a number of investigations using ATR have been performed in the terahertz band. The samples which have been studied using ATR THz TDS include water [15], [19], heavy water [20], intermolecular stretching and hydration processes [21], [22], monolayer cells [23]. Despite its prevalence, important metrological aspects of ATR THz TDS have not been discussed in detail. In particular, error sources and their impact on ATR measurements have only been partly investigated [24]. In this article the amplitude and phase instability as well as angular deviations in ATR spectroscopy systems will be characterized in the context of their impact on the measurable sample parameters. In addition, an improvement scheme for ATR THz TDS will be proposed in order to increase the measurement accuracy of this technique. Experimental demonstrations with water and ethanol as samples will be discussed.

2. Error sources in ATR THz time-domain spectroscopy
2.1 Standard ATR spectroscopy

As shown in Fig. 1, the core element of an ATR THz TDS setup is a prism. In most cases, the prism is made of high-resistivity silicon (>10 kΩ-cm) that is almost perfectly transparent and non-dispersive across the terahertz band [4]. In order to perform an ATR measurement, a sample is deposited onto the prism base. The prism is inserted into the terahertz path to allow in- and out-coupling of a terahertz beam either with TE or with TM polarization. With a proper prism design, the terahertz beam experiences total internal reflection at the prism-sample interface to create an evanescent field inside the sample close to the reflecting boundary. The minimum thickness of the sample is required to be greater than the penetration depth of the evanescent field [25] to record the spectrum that corresponds to the bulk sample [26]. The method also involves the measurement of a reference pulse in the absence of the sample. In connection with total internal reflection the so-called Goos-Hänchen effect occurs [27]–[29]. This effect will lead to a shift of the beam along the reflecting boundary parallel to the plane of incidence. The incident beam could be assumed as a superposition of plane waves with different incident angles. Each plane wave experiences a different phase shift upon reflection from the boundary. The difference of the phase shift in each reflected plane wave is the origin of the Goos-Hänchen shift. This shift can be estimated by the stationary phase method. This Goos-Hänchen shift is common to both the reference and sample measurements and the path difference is only a few microns, which is much smaller than the wavelength and also much smaller than the silicon lens size of the detector antenna [30]. Hence, it does not have a considerable effect on the accuracy of the measurement or data analysis.
Fig. 1 Terahertz ATR spectroscopy setup. The angle \( \theta_{\text{ATR}} = \theta_r + \alpha \) is required to be larger than the critical angle. The dimension of our prism is mentioned in the sketch.

After being recorded, the terahertz waveforms of the reference and sample measurements are Fourier transformed. The frequency-dependent ratio of the two spectra for the \( p \) or TM polarization, defined as the transfer function, is given as

\[
T(\omega) = \frac{E_{\text{sample}}(\omega)}{E_{\text{ref}}(\omega)} = \frac{r^p_{\text{prism-sample}}}{r^p_{\text{prism-air}}},
\]

where \( E_{\text{ref}}(\omega) \) and \( E_{\text{sample}}(\omega) \) are the Fourier transform of the electric field for the reference and sample measurements, and \( r^p_{\text{prism-air}} \) and \( r^p_{\text{prism-sample}} \) are the Fresnel reflection coefficients for the reference and sample measurements, respectively.

As demonstrated in [24], the complex refractive index of the sample, retrieved from this transfer function, is given by

\[
\tilde{n}_{\text{sample}} = \frac{1}{\phi} \sqrt{\frac{1}{2} \left( 1 \pm \sqrt{1 - \left( 2\phi n_{\text{prism}} \sin(\theta_{\text{ATR}})^2 \right)} \right)}.
\]

where \( \phi \) is

\[
\phi = \frac{\cos(\theta_{\text{ATR}})}{n_{\text{prism}}} \left( \frac{1-T^p_{\text{prism-air}}}{1+T^p_{\text{prism-air}}} \right).
\]

In order to comply with energy conservation, the sign of Eq. 2 should be chosen such that the imaginary part of the refractive index remains negative. The same expression for the complex refractive index is applicable to the \( s \) or TE polarization.

2.2 Random errors

For the commonly used transmission geometry, the influence of errors arising from laser power fluctuations [31], electrical noise in the electronic circuitry [32], and delay jitter [33] on the quality of the measured spectra, have been investigated in the past [34]. In this section, the effect
of those error sources on ATR THz TDS will be discussed. In order to study the effect of random fluctuations on the extracted optical parameters, the transfer function in Eq. 1 is re-expressed as

\[ \hat{T}(\omega) = Re^{i\omega \zeta}. \]  

where \( R \) and \( \zeta \) are the amplitude and phase components of the transfer function with the standard deviations \( \sigma_R \) and \( \sigma_\zeta \), respectively.

From the Gaussian error propagation formalism, for the real and imaginary parts of the complex refractive index, i.e.

\[ \tilde{n} = n + i\kappa. \]  

it is possible to show that, to the first order, the standard deviation of the real part is

\[ \sigma_n(\omega) = \sqrt{\left(\frac{\partial n}{\partial \zeta}\right)^2 \sigma_\zeta^2 + \left(\frac{\partial n}{\partial R}\right)^2 \sigma_R^2} \]  

and the standard deviation for the imaginary part is

\[ \sigma_\kappa(\omega) = \sqrt{\left(\frac{\partial \kappa}{\partial \zeta}\right)^2 \sigma_\zeta^2 + \left(\frac{\partial \kappa}{\partial R}\right)^2 \sigma_R^2}. \]

Given that

\[ \frac{\partial n}{\partial \zeta} = Re\left(\frac{\partial n}{\partial \zeta}\right), \quad \frac{\partial n}{\partial R} = Re\left(\frac{\partial n}{\partial R}\right), \quad \frac{\partial \kappa}{\partial \zeta} = Im\left(\frac{\partial \kappa}{\partial \zeta}\right), \quad \frac{\partial \kappa}{\partial R} = Im\left(\frac{\partial \kappa}{\partial R}\right), \]

and using the chain rule

\[ \frac{\partial \tilde{n}}{\partial \zeta} = \frac{\partial n}{\partial \phi} \frac{\partial \phi}{\partial \zeta}, \quad \frac{\partial n}{\partial R} = \frac{\partial n}{\partial \phi} \frac{\partial \phi}{\partial R}. \]

The first two terms in Eqs. 8.1 and 8.2 are identical, and are equal to

\[ \frac{\partial \tilde{n}}{\partial \phi} = -\frac{1}{\phi} \left[ \tilde{n} \pm \frac{1}{\tilde{n}} \frac{n^2_{\text{prism}} \sin(\theta_{\text{att}})^2}{1 - (2\phi n_{\text{prism}} \sin(\theta_{\text{att}}))^2} \right], \]

and

\[ \frac{\partial \phi}{\partial \tilde{T}} = -\frac{\cos(\theta_{\text{att}}) 2n^p_{\text{prism-air}}}{n^p_{\text{prism}}} \frac{2r^p_{\text{prism-air}}}{(1+r^p_{\text{prism}})^2} \]

The sensitivity of the refractive index to the phase is
The sensitivity to the amplitude component is

\[
\frac{\partial \bar{n}}{\partial \sigma} = \frac{1}{\phi} \left[ n + \frac{1}{n} \frac{n_{\text{prism}}^2 \sin(\theta)^2}{\sqrt{1 - (2\phi n_{\text{prism}} \sin(\theta))^2}} \right] \frac{\cos(\theta) \frac{2r}{n_{\text{prism}} (1+\sigma)R^2}}{R} \hat{\imath} \omega .
\]

\[ (11) \]

and the sensitivity to the amplitude component is

\[
\frac{\partial \bar{n}}{\partial R} = \frac{1}{\phi} \left[ n + \frac{1}{n} \frac{n_{\text{prism}}^2 \sin(\theta)^2}{\sqrt{1 - (2\phi n_{\text{prism}} \sin(\theta))^2}} \right] \frac{\cos(\theta) \frac{2r}{n_{\text{prism}} (1+\sigma)R^2}}{R} \hat{\imath} .
\]

\[ (12) \]

The numerical models for propagation of the standard deviation in Eqs. 6 and 7 are fully validated with the Monte Carlo method. This numerical models are then adopted in order to quantify the effect of the phase and amplitude error. For this purpose we vary the standard deviations of \( \sigma_{\zeta} \) between 0 and 15 fs (15 steps) and \( \sigma_{R} \) between 0 to 0.05 (5 steps), for the phase and amplitude components, respectively. Figure 2 demonstrates the effect of the phase and amplitude errors on the modelled complex refractive index of distilled water [17]. Based on experimental observations, we estimate typical values \( \sigma_{\zeta} \) of 10 fs and \( \sigma_{R} \) of 0.01. We assume that similar values hold for most THz TDS systems [24]. From these empirical values, the results clearly demonstrate that the phase deviation has a greater impact than the amplitude deviation on both the extracted refractive index and extinction coefficient. It is noted that although the laser stability can be improved to be in the order of sub-femtosecond, the thermal drift of the fibers remains a major factor for the phase instability in the fiber coupled setup.
2.3 Systematic error

In addition to random error which can occur in the amplitude and phase, a parameter that can potentially have a significant impact on the results from ATR spectroscopy is the incidence angle of the terahertz radiation on the prism. The typical measurement procedure runs as follows: first, a reference pulse is recorded. Subsequently the sample, usually a liquid, is placed directly on the top surface of the prism. If the prism is not firmly fixed onto the platform, small mechanical stress induced by sample deposition and cleaning can introduce a very small yet non-negligible variation in the position or angle of the prism. Importantly, this small deviation leads to a change in the system response for the sample and reference measurements. This systematic error can propagate to and adversely affect the estimated complex optical properties of the sample. Let $\gamma$ be the angular displacement of the prism. In this case, the propagation path lengths of the THz beam for the sample measurement ($d'_1 + d'_2$) and for the reference measurement ($d_1 + d_2$) are not equal as depicted in Fig. 3. Additionally, the incidence and total-reflection angles for reference and sample beams are different. By accounting for these factors, the transfer function can be rewritten as

$$T(\omega) = \frac{E_{\text{sample}}(\omega)}{E_{\text{ref}}(\omega)} = \frac{t'_1 e^{-j\beta d'_1} r_{\text{prism-sample}}^p e^{-j\beta d'_2} t'_2}{t_1 e^{-j\beta d_1} r_{\text{prism-air}}^p e^{-j\beta d_2} t_2}. \quad (13)$$
where $t_1', t_2'$ are the transmission coefficients of the air-prism and prism-air interfaces for the sample measurement, and $t_1, t_2$ are the transmission coefficients of the two interfaces for the reference case. In addition, the output THz sample beam from the prism is not parallel to the reference. This implies that the detector might also be imperfectly aligned. Depending on the deviation angle this particular factor might or might not be relevant. Our measurement setup contains four high-density polyethylene (HDPE) 60 mm lenses and the whole terahertz path is 50 cm. The terahertz beam travels 5 cm from the emitter to the first lens, then 14 cm in collimated version to the second lens. The distance between two middle lenses are 13 cm and the prism is located in the middle. The beam travels the last two lenses before being collected by a 5-mm silicon lens into the detector antenna. For 0.05 degree angular deviation of the prism, the maximum beam misalignment on the detector is 150 microns, which is negligible for the 5 mm silicon lens attached to the detector. Yet, for the sake of simplicity, the misalignment between the output beam and the receiver is neglected in the following analysis.

![Figure 3](image)

Fig. 3 Propagation of the THz beam through a tilted prism. The reference measurement is denoted by the black line, and the sample measurement by the blue dotted line. The dimension of the prism is mentioned the sketch.

We numerically estimate the transfer function that accounts for this prism tilting effect by using Eq. 13, and then extract the complex refractive index from this transfer function by using a standard extraction model described in Section 2.1. In Fig. 4 the real and imaginary parts of the refractive index of distilled water are shown as a function of angular deviations $\gamma$ between $-0.05$ and $+0.05$ degrees with a step size of 0.01 degree. Interestingly, such a relatively small angular deviation can have an enormous impact on both the real and imaginary parts of the extracted refractive index, and the effect is enhanced at high frequencies. Hence, we conclude that such a
misalignment can have a significant effect, exceeding effects from phase and amplitude fluctuations. A larger contrast between the refractive indices of the air and the sample (water in this work) enhances the effect of the angular deviation of the prism.

Fig. 4 Refractive index (a) and extinction coefficient (b) of distilled water under the influence of the prism misalignment. The angular deviation of the prism between the reference and sample measurements is varied between -0.05° and 0.05° with a step size of 0.01°.

It should be noted that a large prism size enhances the error from angular deviation. Mathematically, an increment in the size of the prism \( L \) in Fig. 3 increases the difference between \( d \) and \( d' \), and thus enhances the systematic error. Fig. 5 presents the refractive index and extinction coefficient of distilled water for \( \gamma = 0.05 \) degree and a range of the prism size, \( L \), between 260 and 380 mm. The results confirms that by increasing the prism size the error from angular deviation is enhanced.
3. Alternative configuration for ATR THz spectroscopy

3.1 Method description

Fig. 6 Schematic of the proposed configuration for ATR spectroscopy. The prism is divided into two sections and can be translated orthogonally to the beam axis for reference and sample measurements.

A possible approach to the reliability improvement of ATR THz TDS is to use a long prism fixed to an optics translation stage as shown in Fig. 6. The top surface is divided into two sections, one for the sample measurement and the other for the reference measurement. A lateral
shift of the prism transversal to the beam axis allows alternating measurements between the sample and reference chambers. Since the sample is pre-deposited on the prism, this setup can mitigate the effects from arbitrary prism tilting upon sample loading. Additionally, without accentuating the effect of prism misalignment, it facilitates alternating reference and sample scans during a long course of measurement in order to reduce the effect of long-term signal drifts [35]. Of course, the translation of the prism is expected to introduce angular misalignment which, as discussed earlier, could be a major source of error for the measurements. However, in this case the angular misalignment is known in priori and can be calibrated via a post-processing step. In order to reduce this effect, spectral calibration curves can be obtained for both the phase and amplitude components in order to compensate the misalignment [36]. The calibration function

\[
F_{\text{calibration}}(\omega) = \frac{E_{\text{sample}}(\omega)}{E_{\text{reference}}(\omega)}
\]

(14)

can be obtained by dividing the sample spectrum in the absence of a sample by the reference spectrum on both prism positions. An example of such a function is presented in Fig. 7.

![Calibration Function](image)

Fig. 7 Amplitude (left) and phase (right) profiles of the calibration function in Eq. 14. This empirical function can be used to correct the effect from misalignment of the prism between the reference and sample measurements.

The correction to the reference measurement is therefore given by

\[
E_{\text{corrected}}^{\text{ref}} = E_{\text{measured}}^{\text{ref}}(\omega) \times F_{\text{calibration}}(\omega).
\]

(15)
By loading the sample onto one side of the prism, the relative misalignment between the sample and reference sides is maintained, and this correction factor remains valid. Additionally, the calibration function can account for the angular tolerance of the prism (±0.5 degree for our prism).

3.2 Experimental results

In order to verify the validity of the method proposed in Section 3.1, we performed ATR measurements on distilled water and ethanol. The spectrometer we used is described in Ref. [24] as system B. Firstly, we performed a measurement on distilled water at room temperature. The resulting of refractive index and absorption coefficient are shown in Fig. 8 along with the values published by two other independent research groups. The results are in general agreement with a difference under 5% across the frequency range of interest. Additionally, two series of measurements on distilled water and ethanol were carried out with the traditional ATR method and the proposed method. Each liquid, interlaced with the reference scanning, was measured 20 times using both methods. The measurable data were used to generate the curves and standard deviations shown in Fig. 9. It is obvious that the standard deviation is in both cases significantly smaller for the proposed method. The uncertainty reduction is as a result of the shortened duration between the reference and sample measurements, and the correction to the angular deviation.

![Graph showing measured refractive index (n) and absorption coefficient (α) of distilled water with the](image)

Fig. 8 Measured refractive index (n) and absorption coefficient (α) of distilled water with the
proposed ATR THz method in comparison to the published data.
4. Conclusion

We discussed the impact of amplitude and phase errors and angular misalignment of the prism on the data extracted from ATR THz-TDS measurements on liquids. A careful analysis shows that a small prism misalignment in the order of a thousandth of a radian can produce a significant deviation in the extracted complex refractive index. This effect is much larger than the deviation introduced by the amplitude and phase errors in typical THz-TDS systems. In addition we proposed an alternative measurement setup in which the prism is translated along its axis between each sample and reference measurement. The method accounts for possible angular deviation of the prism and other alignment imperfections via the frequency-dependent correction factor. This method allows alternate acquisitions of sample and reference pulses with a minimal effect from the prism misalignment. This alternating measurement approach is important for observation of sample progress over a long period of time, for example to monitor chemical processes in aqueous solutions over a few days, without suffering from the effect of slow drifts in temperature, laser power, or other environmental conditions that could affect the measurement results.

Fig. 9 Comparison of the uncertainty for the properties of distilled water (a) and ethanol (b) measured with the proposed method (red) and conventional ATR THz spectroscopy (black).
References


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