Abstract—Transmission THz spectroscopy on heterogeneous materials often shows structured spectra due to interference of waves passing through the object along different optical paths. Of special interest is wood with its strong birefringence and pronounced orientation dependent structure. In this paper we show that at specific polarization angles the THz transmission spectra show gaps at distinct frequencies. The frequency changes of these gaps can be used for a fast and accurate determination of the dependency of birefringence on humidity. We present results for spruce and beech with different sample thicknesses and orientations and study and model their optical properties as a function of water content.

Index Terms—Birefringence, wood, water content, humidity, THz spectroscopy.

I. INTRODUCTION

THz radiation is particularly suitable for non-destructive investigation of wood. As illustrated in Fig. 1 wood is a hierarchically organized cellular, fiber-reinforced, orthotropic composite material, and represents one of the oldest and most frequently used construction materials. At macroscopic scale, wood represents a porous material with fiber cells aligned more or less parallel to the trunk. The long axis of the fibre cells is defined as the longitudinal direction (L-direction). On a cross-section, representing the RT-plane (radial-tangential plane) orthogonal to the L-direction, the well-known annual ring structure can be recognized, which consists of the alternating pattern of light coloured, low-density wood and dark coloured, high density wood. The low-density wood with thin walls and large cell lumina is termed earlywood (EW), as it is formed in the early part of the growth season. The high-density wood with thick cell walls and small lumina is termed latewood (LW), as it is produced in the later part of the season and primarily gives mechanical stability. At cell wall level, wood represents a fiber reinforced composite material. The cell wall can be subdivided into different cell wall layers (CWL) with one cell wall layer being dominant. Within such a layer, long chains of cellulose are organized in so-called microfibrils exhibiting crystalline structure. These cellulose microfibrils are embedded in a matrix consisting of the amorphous polymers hemicellulose and lignin. The cellulose microfibrils are oriented parallel to each other and at a certain angle \( \mu \) in respect to the long axis of the fibre cell, which is termed microfibril angle. Hereby an angle of \( 0^\circ \) reflects an orientation of the microfibrils in line with the L-direction (fibre cell direction). For adult spruce and beech wood, the microfibril angle of the dominant cell wall layer is in the range of \( 5^\circ - 15^\circ \). This orientation leads to a helical organisation of the microfibrils within the respective cell wall layer. This specific range of microfibril angles results in the anisotropy of wood making the L-direction the most stress bearing direction, as the cellulose microfibrils are the load bearing elements of the cell wall [6]. Although this hierarchical structure and the specific setup are responsible for excellent mechanical properties, it makes wood challenging for structural analysis. Further complications arise from the fact, that the properties of wood change as a function of moisture content and complicated methods such as neutron scattering [7] are needed to spatially resolve moisture content. Structural features are also spatially variable owing to the biological origin.

It has been shown previously, that some of the challenges of analyzing wood can be tackled with THz spectroscopy. Using a terahertz time-domain spectrometer Koch et al. [8] performed transmission imaging and density profiling with sub-annual ring resolution. A special feature of wood is its strong birefringence [9], [10] combined with diattenuation [11] (also called linear dichroism) at terahertz frequencies. Optical anisotropy in wood originates from both its regular and repetitive fibrous structure in the micrometer range (extrinsic or form birefringence), but also from the regular alignment of partly crystalline cellulose microfibrils along the cell wall at nanometer range (intrinsic birefringence). The coherent superposition of waves with two polarization directions causes frequency dependent constructive and destructive interference effects. Reid et al. [11] described how in principle custom designed \( \lambda/4 \) and \( \lambda/2 \) wave plates can be produced from spruce wood of an optimized thickness. Another consequence is the presence of extinctions ("frequency gaps") at distinct
polarization angles in the THz transmission spectrum [12], which occur when two interfering waves with equal amplitude fully cancel out due to a phase difference of π.

Frequency gaps are caused not only by birefringence but also for example by interference of waves passing partially through latewood and earlywood or by multiple reflections at interfaces. For the determination of optical properties such as refractive index or absorption coefficient one usually tries to avoid such structures by an appropriate experimental design, e.g., by measuring latewood and earlywood samples separately, or in the case of birefringence by measuring only polarization directions parallel and normal to the fiber axis. However, additional information can be extracted by appropriate modeling of these interference effects. In this paper we extract wood properties from transmission spectra as a function of wood orientation and water content. We develop a two-stage model. First we combine the optical properties of cell wall material, air and water based on a geometrical wood model to predict its birefringent optical properties. The second stage consists of modeling interference effects by mixing the spectra of the two polarization directions. We demonstrate, that the positions of frequency gaps can directly be used to monitor humidity dependent properties in a fast and accurate manner.

The paper is structured as follows: In the next section we describe our modeling of the angular dependence of time signals and spectra as well as the model used to predict spectral properties as a function of water content. This is followed by a section describing experiments on wood samples cut along all the three main directions, on pure water and simultaneous measurements of THz spectra and sample weight during the drying process or during water uptake. Finally, the results are discussed and compared to other published data.

II. Modeling

A. Optical properties

Optical properties of materials can be explained using the electric permittivity $\epsilon_r$ and the magnetic permeability $\mu_r$ relative to the corresponding properties of vacuum $\epsilon_0$ and $\mu_0$. If we assume that the magnetic permeability for a material is $\mu_r = 1$ the refractive index relates to the permittivity according to $n^2 = \epsilon_r$. Refraction and absorption can be modeled using a complex refractive index $\tilde{n} = n + i\kappa$ with $n = c_0/v$ as the ratio between the speed of light in vacuum $c_0$ and the speed of light in the material $v$. $\kappa$ is known as extinction coefficient. The absorption coefficient $\alpha$ is related to the extinction coefficient $\kappa$ by $\alpha = 4\pi\kappa/\lambda$, where $\lambda$ is the wavelength. In the following we will use the notation for a complex quantity e.g. $\tilde{n}$ for the complex refractive index.

B. Extracting optical properties from pulsed THz data

Time domain spectroscopy is a very suitable tool to extract frequency dependent optical properties of materials from pulsed THz data. A good overview is given by Scheller [13]. The complex spectral transfer function $\tilde{H}(\nu)$, defined as the ratio of the Fourier transforms of the sample measurement and the reference measurement, can be written as

$$\tilde{H}(\nu) = \tilde{T}_1(\nu)\tilde{T}_2(\nu)e^{i(2\pi\nu d(n(\nu) - 1))/\nu_0}.$$  \hspace{1cm} (1)

Here $\nu$ is the frequency and $d$ the sample thickness. $\tilde{T}_1 = 2/(\tilde{n} + 1)$ and $\tilde{T}_2 = 2\tilde{n}/(\tilde{n} + 1)$ are the complex transmission coefficients for the amplitudes at the front and back wood-air interface respectively. Note that this formula ignores intensity losses due to diffraction at uneven surfaces as well as at internal structures.

The refractive index $n$ and the extinction coefficient $\kappa$ are under the thick sample approximation ($d \gg \lambda$) [13] and the assumption $n^2 \gg \kappa^2$.

$$n(\nu) = 1 + \frac{\zeta(\tilde{H}(\nu))c_0}{2\pi\nu d}$$ \hspace{1cm} (2)

$$\kappa(\nu) = \frac{c_0}{2\pi\nu d} \ln \left( \frac{\tilde{H}(n(\nu) + 1)^2}{4n(\nu)} \right)$$ \hspace{1cm} (3)

where $\zeta$ denotes the unwrapped phase. We can calculate model time traces and spectra by inverting (2) and (3). With the knowledge of $n(\nu)$, $\kappa(\nu)$ we can determine $H(\nu)$ which can be used to compute for a given reference measurement a modeled time pulse and its spectrum.

C. Modeling optical properties of humid wood

We model the refractive index and absorption of wood based on a structural model on two different length scales using the optical properties of air, water and cell wall material (mixture of cellulose, hemicelluloses and lignin). We start from the model presented in [9]. We use the notation $\parallel$ and $\perp$ for
polarizations parallel and perpendicular to the RT-plane of the wood samples, respectively.

On a first level we assume that wood consists of pores and cell walls with complex refractive indices \( \tilde{n}_{\text{pore}} \) and \( \tilde{n}_{\text{cw}} \), respectively. The two polarization dependent complex refractive indices \( \tilde{n}_{\parallel} \) and \( \tilde{n}_{\perp} \) can be modeled as follows

\[
\tilde{n}_{\parallel}^2 = f_{\text{cw}} \tilde{n}_{\text{cw}}^2 + f_{\text{pore}} \tilde{n}_{\text{pore}}^2 \quad (4)
\]

\[
\tilde{n}_{\perp}^2 = f_{\text{air}}(\tilde{n}_{\text{pore}}^2 \tilde{n}_{\text{pore}}^2 + (1 + f_{\text{cw}})\tilde{n}_{\text{cw}}^2) /

f_{\text{pore}} \tilde{n}_{\text{cw}}^2 + (1 + f_{\text{cw}})\tilde{n}_{\text{pore}}^2 \quad (5)
\]

where \( f_{\text{cw}} \) and \( f_{\text{pore}} \) are the volume fractions of the cell walls and the pores, respectively. If we assume that all water is bound within the cell walls, pores are filled with air only and we can set \( f_{\text{pore}} \approx 1 \).

On a second level we use an effective medium approximation in order to model the optical properties of the cell wall from the properties of its components. An overview of such models is given by Federici [2]. We use the Bruggeman model [14], which is an extension of the Maxwell-Garnett theory [15] enabling to calculate the effective complex refractive index \( \tilde{n}_{\text{eff}} \) of \( N \) components in a mixture solving the following equation

\[
\sum_{j=1}^{N} F_j \left( \frac{\tilde{n}_{\text{eff}}^2 - \tilde{n}_{j}^2}{\tilde{n}_{j}^2 + 2n_{\text{eff}}^2} \right) = 0 \quad (6)
\]

where the volume fractions are constrained by \( \sum_j F_j = 1 \) with \( F_j = f_j / \sum_j f_j \). In our material we combine three components: cell wall material (denoted \( c \)), water (denoted \( w \)) and air (denoted \( \text{air} \)) with optical properties \( \tilde{n}_c, \tilde{n}_w \) and \( \tilde{n}_{\text{air}}, \) respectively, to the effective complex refractive index \( \tilde{n}_{\text{eff}} = \tilde{n}_{\text{cw}} \). For more than two components (6) is solved numerically. Note that this model is similar, but not identical, to the mixture given in [9].

In order to use the model we need to know the fractions and the optical properties of all components. The volume fraction of water \( f_w \) can be determined from the water uptake of dry wood. The volume fraction of the cell wall material can be estimated from

\[
f_c = \frac{w_s / V_s - \rho_w f_w}{\rho_c} \quad (7)
\]

where \( w_s \) is the sample weight, \( V_s \) the sample volume, \( \rho_w \) the density of water and \( \rho_c \) the density of the cell wall material which is around 1.4 g/cm\(^3\) [10]. Note that the density of pure cellulose is in the range of 1.4–1.6 g/cm\(^3\) [16]. The remaining fraction is attributed to air, either within the cell wall or in the pores. The refractive index of water is taken from the literature [17], [18] or from direct measurements. Unknowns are the complex refractive index of the cell wall material, \( \tilde{n}_c \), and the partitioning of air among cell wall \( f_{\text{air}} \) and pores \( f_{\text{pore}} \). In a first step we can use the pore fraction \( f_{\text{pore}} \) as a parameter. For a specific pore fraction we can get two estimates for \( \tilde{n}_{\text{cw}} \) by solving eq. (4) and (5) for \( \tilde{n}_{\text{cw}} \). In a second step the pore fraction \( f_{\text{pore}} \) is optimized to get the best agreement between the two estimates. In a next step \( \tilde{n}_c \) can be determined by solving (6).

D. Modeling interference

A birefringent uniaxial material can be modeled using two polarization dependent complex refractive indices \( \tilde{n}_{\parallel} = n_{\parallel} + ik_{\parallel} \) and \( \tilde{n}_{\perp} = n_{\perp} + ik_{\perp} \). We describe the transmission of a light pulse with respect to the principal axes, by applying the frequency dependent optical properties in the Fourier domain: \( S(\nu) = F T(F(t)) \) where \( F(t) \) is the light pulse without passing through the sample, \( \nu \) the frequency. For a sample with thickness \( d \) we can write

\[
\tilde{S}_{\parallel}(\nu) = \tilde{S}(\nu) \cos\left(2\pi \frac{\nu}{c_0}(n_{\parallel}(\nu) - 1)d\right) e^{-\frac{2\pi}{c_0} \kappa_{\parallel}(\nu)d} \quad (8)
\]

\[
\tilde{S}_{\perp}(\nu) = \tilde{S}(\nu) \cos\left(2\pi \frac{\nu}{c_0}(n_{\perp}(\nu) - 1)d\right) e^{-\frac{2\pi}{c_0} \kappa_{\perp}(\nu)d} \quad (9)
\]

The pulses \( P_{\parallel}(t) \) and \( P_{\perp}(t) \) can be retrieved using inverse Fourier transforms. \( P_{\parallel}(t) = F T^{-1}(\tilde{S}_{\parallel}(\nu)) \) and \( P_{\perp}(t) = F T^{-1}(\tilde{S}_{\perp}(\nu)) \), respectively.

For a linear polarization at angle \( \phi \) we consider a weighted sum of the intensities of the spectra

\[
\tilde{S}(\phi, \nu) = (\cos^2 \phi) \tilde{S}_{\parallel}(\nu) + (\sin^2 \phi) \tilde{S}_{\perp}(\nu) \quad (10)
\]

and get the corresponding pulse shape upon inverse Fourier transformation \( P(\phi, t) = F T^{-1}(\tilde{S}(\phi, \nu)) \).

As this is a linear system, the knowledge of any pair of independent polarization measurements \( P(\phi_1, t) \) and \( P(\phi_2, t) \) is sufficient to determine \( P_{\parallel}(t) \) and \( P_{\perp}(t) \) from there any \( P(\phi, t) \). Below we will use polarization-frequency \((\phi, \nu)\) maps to illustrate the spectral features caused by interference. These maps may be either taken from a set of measurements or modeled from two spectra with two independent polarizations using (8)–(10).

In polarization-frequency maps we may find extinctions at specific frequencies and polarization angles. Their position can be used to determine birefringence \( \Delta n = n_{\parallel} - n_{\perp} \) and diattenuation \( \Delta \kappa = k_{\parallel} - k_{\perp} \). The distinct frequencies of the extinctions depend on the phase retardance \( \delta = 2\pi c_0 \nu \Delta n d \). Destructive interference occurs at a retardance of \( \delta = \pi(1 + 2m) \) for \( m = 0, \pm 1, \pm 2, \ldots \). From the spectral position \( \nu_m \) of an extinction we can deduce the birefringence:

\[
\Delta n = \frac{1 + 2m}{2\nu_m d} c_0. \quad (11)
\]

At a frequency \( \nu_m \) according to (10) the spectrum is proportional to

\[
S_m \propto (\cos^2 \phi)e^{-\frac{2\pi}{c_0} \nu_m \kappa_{\parallel} d} - (\sin^2 \phi)e^{-\frac{2\pi}{c_0} \nu_m \kappa_{\perp} d} \quad (12)
\]

and vanishes for

\[
\tan^2 \phi = e^{-\frac{2\pi}{c_0} \nu_m (k_{\parallel} - k_{\perp}) d}. \quad (13)
\]

We can therefore retrieve the diattenuation from

\[
\Delta \kappa = -\frac{\ln(|\tan \phi|) c_0}{\pi \nu_m d}. \quad (14)
\]
III. EXPERIMENTAL

A. THz measurements

Experiments were performed with a time-domain spectrometer TeraFlash (Toptica) covering a frequency range of 0.1 – 7 THz. Pulses were collected in a data interval of 70 ps with a time resolution of 0.05 ps. Depending on the expected transmission of the sample 200 – 1000 spectra were averaged, resulting in a total collection time of 12 – 60 s. The time delay between the pump and the first probe pulse was set, so that the maximum of the reference peak falls within the first 5 – 10 ps of the acquisition interval. The inherent polarization direction of the radiation was horizontal corresponding to 0°. The two polarizers (wire grid polarizers G30x10-S from SEMIC RF) before and after the samples allowed for a change of the polarization direction in the range from −60° to 60°. The polarization direction with respect to the sample was changed by either rotating the sample or rotating the two polarizers simultaneously. The samples were measured using a focused beam with a spot size of approximately 2 mm. The experimental setup is shown in Fig. 2.

Fig. 2. Experimental setup for measuring the polarization dependency of wood samples.

B. Samples

A set of 20 beech and spruce samples (#1–#20) of different thickness (2, 6, 10 mm) and a diameter of about 40 mm were cut along all three main orientations RT, LR and LT. Sample #19 and #20 were prepared to almost exclusively obtain the latewood or the earlywood part of the annual ring. All samples were kept for several days at ambient humidity of about 50% to dry air. Then the sample was exposed to 100% relative humidity for several days in a storage box with a dry air environment (relative humidity lower than 5%). Measurements were made on the drying process in two steps and one set of polarization map measurements with 5° steps: First measurements were taken from ambient humidity to dry air. Then the sample was exposed to 100% relative humidity for several days and a second set of measurements was taken on drying. For this sample an additional measurement was taken close to an angle where an extinction occurs in addition to each set of -45° and +45° measurements.

C. Polarization mapping

Measurements were conducted in a configuration with parallel polarizers and analyzer (bright field polariscope). LR and LT samples were mounted with a vertical L-direction whereas for the RT samples the R-direction was vertical. They were measured in steps of 5° from 0° to 180°, keeping the polarization of the THz beam horizontal. Reference measurements without sample were taken before and after each set of measurements.

D. Humidity dependency

Three wood samples of thickness 2 mm were used all cut along the LT direction. We used the beech sample #4, and two spruce samples, one cut from late wood (#19) and one cut from early wood (#20). The setup was prepared in a way that terahertz measurements could be taken with a simultaneous weight measurement. Each sample was mounted on the THz spectrometer with a grain orientation of 45°. The sample holder was mounted on a rotation stage to allow easy switching between sample and reference measurement.

Samples #4 and #19 were oven dried for 24 hors at 103 °C, weighted just after removal to determine the oven-dry weight and put into a desiccator for intermediate storage. For each sample THz measurements were taken with a simultaneous weight measurement over a period of 4 hours to follow the changes of the sample while taking up humidity. Two types of measurements were taken: Repeated pair measurements at -45° and +45° corresponding to principal polarization directions and one set of polarization map measurements with 5° steps from -60° to 60°. The same two samples were exposed to 100% relative humidity for several days in a storage box together with water. An equivalent set of measurements as described above was taken to measure the samples during the drying process for a time of 5 hours for sample #4 and 20 hours for sample #19.

For sample #20 a THz experiment was set up in a large box with a dry air environment (relative humidity lower than 5%). Measurements were made on the drying process in two steps: First measurements were taken from ambient humidity to dry air. Then the sample was exposed to 100% relative humidity in a desiccator for several days and a second set of measurements was taken on drying. For this sample an additional measurement was taken close to an angle where an extinction occurs in addition to each set of -45° and +45° measurements.
E. Water properties

Optical properties of water at THz frequencies were reported in a number of papers (see for example [17]–[19]). Nevertheless we have measured the optical properties of water with the same measuring equipment in order to have a consistent base for the wood-water model. The basic measuring concept was the same as reported by Fitzgerald et al. [20]. The liquid samples were held in a polyethylene bag, that was compressed between two slices of Teflon, the distance of which were changed in steps of 5 μm. Difference measurements allowed to eliminate all external influences such as reflections and diffraction from the different interfaces. One even does not need to know the absolute depth of the water which was in the range of 200 – 500 μm.

IV. RESULTS AND DISCUSSION

A. Birefringence

Most of the measured polarization maps exhibit extinctions at specific polarization angles and frequencies. To a first approximation, this behavior was modeled by a weighted superposition of the two signals from the two principal polarization components. Fig. 3 shows typical time signals for the two principal axes and for one critical polarization angle showing a frequency gap. The time signals illustrate the different time delays for the two principal axes, which are caused by birefringence, as well as the mixing of the two pulses at an intermediate angle. The corresponding spectra relative to a reference spectrum taken without sample are given in Fig. 4. Note that the water vapour lines (at 1.2 THz and above 1.6 THz) do not fully cancel out probably due to small variations of humidity between the measurements. The two spectra at 0° and 90° show different slopes which is a consequence of diattenuation. The spectrum for the 55° polarization angle shows a pronounced gap at about 0.8 THz. With the use of (8)–(10) the time signals as well as the spectra can be modeled quite well using two frequency independent refractive indices \( n_\parallel, n_\perp \) and two extinction coefficients \( \kappa_\parallel \) and \( \kappa_\perp \).

Fig. 10 shows polarization-frequency maps taken from spectra of samples #1 - #18 normalized to the reference spectrum. This corresponds to the modulus of the complex spectral transfer function \( \tilde{H}(\nu) \), see (1). All LT samples show one or more paired gaps with a mirror symmetry with respect to the 90° polarization. Samples with a thickness of 6 and 10 mm show two or more pairs. For both wood types the frequency of the gap is inversely proportional to the sample thickness as expected from (11). With increasing frequency the angular positions deviate more from \( \pm 45° \), which is due to an increased diattenuation with higher frequency, see (14). Note that for the LT samples the annual ring structure is along the transmitted beam, thus the measurement is little sensitive to the beam position. For the interpretation of the polarization-frequency maps of the RT and LR samples we have to take into account that the rotation of the sample may cause small shifts of the wood area probed by the THz beam. Thus the annual ring structure may cause interference effects in addition to probing its birefringence. The 2 mm RT samples show only little dependency on the polarization angle. This is expected as the microfibrils causing birefringence are almost parallel to the incident beam. For thicker RT samples however structures with generally low mirror symmetry show up which can be attributed to structural features due to the annual rings. Finally polarization-frequency maps of LR samples show both pairs of gaps and structures caused by the annual rings. In general, gaps show up at lower frequencies compared to the structured parts of the spectra being attributed to time delays caused by passing through different wood areas.

B. Refractive index of water

Optical properties of water were determined from measurements taken through different water depths in the range of 200 – 500 μm. The resulting refractive index \( n \) and extinction coefficient \( \kappa \) are shown in Fig. 5. We have an excellent agreement with the published values [17], [18] as well as with the double Debye model [19]. For extinction values at frequencies above 1.2 THz no data was available for the Debye model.

C. Cell wall material

For our wood model we need a good estimation for the optical properties of the cell wall material which can be
deduced from measured spectral data using the model described in section II.C and reasonable assumptions for the parameter values. For the density of the cell wall material we assume 1.4 g cm$^{-3}$. For water we use the mean of our measured data. For each of the samples (#4 beech, #19 spruce LW and #20 spruce EW) we determine a pore fraction that gives the best agreement in birefringence measured at ambient humidity. The optimized pore fractions $f_{\text{pore}}$ are given in Table II together with all other volume fractions which were deduced from the water content and the density of the samples. The resulting curves for the refractive index and extinction coefficient are shown in Fig. 6. In all we get six estimates for the refractive index and extinction coefficient (three samples with two polarizations each). The refractive index $n$ agrees to within 0.1 over the spectral range of interest. The agreement on the extinction coefficient $\kappa$ is also quite good but shows higher estimates for $\|\,$ polarization than for extraordinary $\perp$ polarization. The larger differences for $\kappa$ are probably due to the fact that we ignored diffraction effects, which are likely to be different among the samples. The refractive index of the cell wall material is in the range of 1.85−1.95 and not much lower than the refractive index of water. The extinction coefficient, however, is much lower than that of water. The obtained refractive index and extinction coefficient is in close agreement with the average dielectric function of the cell wall material $\bar{\varepsilon} = 3.38 + 0.19i$ reported by Inagaki et al. [10]. This value was determined for the frequency range of 0.1 to 0.2 THz from samples of aspen, birch, hemlock and maple wood. This corresponds to a refractive index $n = 1.84$ and $\kappa = 0.05$. The facts that the optical properties for the cell wall material are very similar for all three wood samples and both polarizations and that they agree well with published optical properties for other wood types are strong arguments for our model. For further modeling we used the average from these six data sets (shown in black in Fig. 6). Note, that there is a strong correlation of the refractive index with the assumed density of the cell wall material. An assumed cell wall density of $1.5 \text{ g cm}^{-3}$ instead of $1.4 \text{ g cm}^{-3}$ would result in a refractive index higher by about 0.06 without significantly changing the resulting spectra.

### D. Water in wood

The model is now applied to the humidity dependency measurements for beech (sample #4), spruce LW ( #19) and spruce EW ( #20). In Fig. 7 we show the measured and modeled dispersions of the refractive index and the extinction coefficient for samples taken at different moisture contents of wood. Samples were either conditioned close to oven dry condition (very low moisture content), at ambient conditions (moisture content between 5−10%) or to very humid condition (moisture content of the cell wall close to saturation; additional free water might be present in the lumina). We find a good agreement of the simulation with the data for all three samples at dry and ambient conditions. The model performs better for the refractive index $n$ than for the extinction coefficient $\kappa$. A strength of the model is, that it predicts refractive index and extinction coefficient using the same set of parameters for different wood types. For both polarization directions the general spectral trends are reproduced: Whereas the dry samples

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**TABLE II**

<table>
<thead>
<tr>
<th>sample</th>
<th>wood type</th>
<th>$f_c$</th>
<th>$f_w$</th>
<th>$f_{\text{air}}$</th>
<th>$f_{\text{pore}}$</th>
<th>water weight %</th>
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<tr>
<td>#4</td>
<td>beech</td>
<td>0.392</td>
<td>0.039</td>
<td>0.111</td>
<td>0.458</td>
<td>7.1%</td>
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<tr>
<td>#19</td>
<td>spruce LW</td>
<td>0.316</td>
<td>0.028</td>
<td>0.182</td>
<td>0.474</td>
<td>6.4%</td>
</tr>
<tr>
<td>#20</td>
<td>spruce EW</td>
<td>0.176</td>
<td>0.014</td>
<td>0.086</td>
<td>0.724</td>
<td>5.5%</td>
</tr>
</tbody>
</table>

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Fig. 5. Experimental refractive index $n$ and extinction coefficient $\kappa$ of water compared to literature [17]–[19].

Fig. 6. Refractive index $n$ and extinction coefficient $\kappa$ for cell wall material extracted from three wood samples using both polarizations. The averaged curves (black) are used in the wood model.
show a very small spectral dependency, with increasing water content, \( n \) increases more at low frequencies than at higher ones, which is caused by the spectral characteristics of water. For wet beech (#4) and spruce latewood (#19) the agreement of the model with the measurement is reasonable on a spectral average only. The measured spectral data show slowly varying oscillatory frequency dependencies, which are not reflected by our model. This is an indication of an inhomogeneous distribution of water within the sample, which may be caused by free water being retained in the lumina of the wood cells in the initial phase of drying. Accordingly, this structure was pronounced only in the measurements within the first twenty minutes of the drying experiments and decreased quickly later. It is known that unbound, liquid water in the pores (cell lumen) of fiber cells evaporates rather quickly for a relative humidity below 70–80%, retaining bound water in the cell wall material only. Thus, THz spectroscopy may provide a comparatively easy possibility to resolve the two states of water and its distribution in wood. We did not observe such slow, oscillatory behavior in the spruce earlywood samples. This may be due to the fact, that for this sample the maximum water content at the first measurement was lower than those of the other two samples and did not exceed 20%. In Fig. 8 the refractive index and extinction coefficients at 1 THz are shown as a function of water content. This data representation shows also excellent agreement for water contents below the approximate onset of capillary condensation. For higher contents which were measured during the drying process of the initially wet samples the agreement is not as good. In particular for sample #4 and #19 we see a hysteresis effect. We have to keep in mind, that the measurements were not taken under static conditions, and the portion of bound water in the cell wall and liquid water in the pores may not be the same. The dependency of birefringence on water content is shown in Fig. 9. The model represents the measured trends rather well.
For high water contents the measured birefringence is smaller than the model predictions for the beech sample and to a lesser extent also the spruce latewood sample. We attribute this discrepancy to a water distribution within the sample different from the model assumption. In general we observe the same trends and similar values for the refractive index and the birefringence as reported by Todoruk et al. [9] for maple and fir wood. Note that the agreement between experiment and model is considerably better for our data. Our experimental setup is designed to measure changes in wood structure on a rather short time scale, i.e. within a few seconds or minutes. However, polarization dependent structural measurements to probe birefringence involve several measurements which have to be carried out sequentially. The presence of the gaps allows us to extract accurate birefringence values from only one measurement. This allows a faster data acquisition in cases of monitoring time dependent wood properties such as water content. In Fig. 9 we show, for the spruce earlywood sample, two measured dependencies of the birefringence \( \Delta n \) on the water content, once determined with two measurements at 0° and 90° polarization directions (red circles) and once measured at a polarization angle close to the occurrence of a gap (red crosses). Both methods give consistent results. Note that the measurements need not to be taken at a very accurate polarization angle, as the minimum frequency position of the gap hardly changes within a few degrees.

\[ \Delta n \text{ at 1 THz} \]

\[ 0.02 \quad 0.04 \quad 0.06 \quad 0.08 \quad 0.1 \quad 0.12 \quad 0.14 \quad 0.16 \]

\[ 0 \quad 5 \quad 10 \quad 15 \quad 20 \quad 25 \]

\[ \text{Water content (weight %)} \]

\[ \text{birefringence } n \text{ at 1 THz} \]

Fig. 9. Experimental (e) and modeled (m) birefringence \( \Delta n \) as a function of water content. Open circles are results from the wetting process and closed circles from the drying process. For the spruce EW sample we show values as determined from the two polarization directions \( \perp \) and \( \parallel \) (red circles) and from the gap frequency (red crosses).

E. Modeling polarization-frequency map

The model is now applied to the polarization-frequency maps for samples #1–18. For all LT and LR samples a pore fraction is optimized to best match the frequency gaps. The results are given in Table III. In general the pore fractions of spruce are larger than those of beech. This is in line with the higher densities of beech compared to spruce. The pore fraction is basically independent of the sample thickness with exception of the 2mm spruce LR sample. This thin sample had one full portion of late wood, but due to its small thickness only a small portion of early wood. The general differences between LT and LR samples are probably due to the fact that the samples were cut from different regions in the tree resulting in different proportion of latewood and earlywood. The modeled polarization-frequency maps are shown in Fig. 11 and can be compared with the experimental maps, Fig. 10. In general we find a good agreement for the position of gaps caused by birefringence. Other features identified in the polarization-frequency maps can be attributed to a different origin such as structural effects from the annual rings. In the simulations the angular positions of the gaps are further away from \( \pm 45^\circ \) compared to the measurement. We attribute this to diffraction effects which are not included in our model.

\[ \Delta n \text{ at 1 THz} \]

\[ 0.02 \quad 0.04 \quad 0.06 \quad 0.08 \quad 0.1 \quad 0.12 \quad 0.14 \quad 0.16 \]

\[ 0 \quad 5 \quad 10 \quad 15 \quad 20 \quad 25 \]

\[ \text{Water content (weight %)} \]

\[ \text{birefringence } n \text{ at 1 THz} \]

\[ \text{Experimental (e) and modeled (m) birefringence } \]

\[ \text{Fig. 9.} \]

\[ \text{optimized pore fractions } f_{pore} \text{ for LT and LR samples.} \]

<table>
<thead>
<tr>
<th>wood type</th>
<th>thickness</th>
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<th>6mm</th>
<th>10mm</th>
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<tr>
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</table>

TABLE III

V. CONCLUSION

We have shown that THz spectroscopy is a valuable tool for investigating structural properties of wood. Of particular interest are the extraction of spatially varying structural properties from the structures in the THz spectra caused by interference effects. The data presented bear the potential for the extraction of further wood properties in particular in connection with density or humidity variation due to the annual ring structure or the spatial information on water distribution. The model developed to predict optical properties complements the results published earlier, e.g. [9], [10]. Its strength is, that it is based only on a few parameters (pore volume) and models at the same time refractive index and absorption properties. As a further step the model could be extended to include diffraction effects. Using extinction of the two principal polarizations at specific angles and frequencies allows to accurately monitor changes of birefringence. Furthermore, THz spectroscopy has proven to be a suitable means to spatially resolve the water content of wood samples, which has otherwise to be done by far more complex and time consuming methods, e.g. neutron scattering. We have demonstrated this capability of THz spectroscopy on humidity dependent birefringence properties of wood. We have also shown evidence for spectral properties caused by local variation of the water content, which could resolve the two different states of water in wood. This calls for a thorough investigation of the local wood structure using scanning methods.

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Fig. 10. Experimental polarization-frequency maps of spectral transmission (log$_{10}$ scale) in spruce and beech, for sample thickness $d = 2$ (top), 6 (middle) and 10 mm (bottom) and orientations LT (left), RT (middle), and LR (right).

Fig. 11. Modelled polarization-frequency maps of spectral transmission (log$_{10}$ scale) in spruce and beech, for sample thickness $d = 2$ (top), 6 (middle) and 10 mm (bottom) and orientations LT (left), RT (middle), and LR (right).
REFERENCES


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