Time resolved THz spectroscopy

Our TRTS measurements were done in a traditional transmission configuration, using an optical pump - THz probe setup driven by a femtosecond Ti:Sapphire mJ-class amplifier operating at the central wavelength of 800 nm, and delivering ca. 100 fs – long laser pulses.[1] The samples were optically excited by the fundamental 800 nm pulses or the frequency-double pulses with 400 nm central wavelength (corresponding to 3.1 eV optical energy), and duration of about 100 fs. The precision-delayed single-cycle THz probe pulse, with a total duration on the order of 1 ps, was generated by the optical rectification of 800 nm pulses in a <110> ZnTe crystal.[1] This probe allowed for accurate spectroscopy in the range of ca. 0.3 – 1.6 THz. The divergent THz probe was focused into the sample by a pair of off-axis parabolic mirrors, and subsequently collimated and refocused by another pair of parabolic mirrors onto a second <110> ZnTe crystal. Here the transmitted THz waveforms were measured in the time domain as the temporal evolution of their electric field, using free-space electro-optic sampling, through the polarization rotation of a third, precision-delayed ultrashort 800 nm gating pulse. By varying this gating pulse delay, the entire transmitted THz probe pulse could be mapped out in time. The experiment was repeated as a function of pump-probe delay, which allowed us to measure the temporal evolution of the THz –probed conductivity spectrum of the photoexcited sample at different times after photoexcitation. The data analysis was performed in the frequency domain via Fourier transforms of the measured time traces, see below.

Extraction of the conductivity

We model in frequency the domain the propagation of the THz probe through an air phase of (complex) refractive index n_1 followed by a second phase of refractive index n_2 and thickness l_2, which can be either a cuvette window or another air phase depending on the sample, then the sample of thickness d and refractive index n_3 when unexcited, and n_3^* when photoexcited, then through another window (or substrate) of index n_4 and thickness l_4 into air again. For the transmission through the unexcited and excited sample respectively, we get:

$$T_{unexc}^{calc}(\omega) = T_0(\omega) t_{12} e^{\frac{i\omega n_2 l_2}{c}} t_{23} e^{\frac{i\omega n_3 d}{c}} t_{34} e^{\frac{i\omega n_4 l_4}{c}} t_{41} e^{\frac{-i\omega n_1 (l_2+d+l_4)}{c}} \rho_2 \rho_3 \rho_4$$

and

$$T_{exc}^{calc}(\omega) = T_0(\omega) t_{12} e^{\frac{i\omega n_2 l_2}{c}} t_{23}^* e^{\frac{i\omega n_3^* d}{c}} t_{34}^* e^{\frac{i\omega n_4 l_4}{c}} t_{41} e^{\frac{-i\omega n_1 (l_2+d+l_4)}{c}} \rho_2 \rho_3^* \rho_4$$

so that

$$\frac{T_{exc}^{calc}(\omega)}{T_{unexc}^{calc}(\omega)} = \frac{t_{23}^* t_{34}^*}{t_{23} t_{34}} e^{\frac{i\omega \Delta n d}{c}} \frac{\rho_3^*}{\rho_3}, \quad \Delta n \equiv n_3^* - n_3$$

T_0 is the THz field in the absence of a sample, ω is the angular frequency of the probe (THz) field, c is the speed of light t and t^* are the interfacial Fresnel transmission coefficients, and ρ and ρ^* accounts for multiple reflections within a given region. This correction is necessary when the sample is thin enough that the reflected THz waveforms overlap in time with the transmitted as is the case for the film samples. For the samples dispersed in solvent the optical path length in medium 3 is long enough (1 mm) that the reflected waveforms can be filtered out temporally, and the ρ factors are not included in the analysis. The transmission and reflection factors are given by:[2]

$$t_{23}=\frac{2n_2}{n_2+n_3},t_{23}^*=\frac{2n_2}{n_2+n_3^*}$$

$$t_{34}=\frac{2n_3}{n_4+n_3},t_{34}^*=\frac{2n_3^*}{n_4+n_3^*}$$

$$\rho_3=\left(1+r_{23}r_{34}e^{\frac{2i\omega n_3 d}{c}}\right)^{-1},\rho_3^*=\left(1+r_{23}^*r_{34}^*e^{\frac{2i\omega n_3^* d}{c}}\right)^{-1}$$

where

$$r_{23}=\frac{n_2-n_3}{n_3+n_2},r_{23}^*=\frac{n_2-n_3^*}{n_3^*+n_2}$$

$$r_{34}=\frac{n_3-n_4}{n_3+n_4},r_{34}^*=\frac{n_3^*-n_4}{n_3^*+n_4}$$

Experimentally we measure in the time domain the THz field transmitted through the unexcited sample $T_{unexc}^{meas}(t)$, and the photoinduced change in the transmitted field $\Delta T_{exc}^{meas}(t)$. By Fourier transformation we obtain the frequency dependent waveforms and calculate the ratio

$$\frac{\Delta T_{exc}^{meas}(\omega)}{T_{unexc}^{meas}(\omega)}=\frac{T_{exc}^{meas}(\omega)-T_{unexc}^{meas}(\omega)}{T_{unexc}^{meas}(\omega)}=\frac{T_{exc}^{meas}(\omega)}{T_{unexc}^{meas}(\omega)}-1.$$

By numerically minimizing the difference between $\frac{T_{exc}^{meas}}{T_{unexc}^{meas}}$ and $\frac{T_{exc}^{calc}}{T_{unexc}^{calc}}$, we can extract the photoinduced change in complex conductivity Δn.

From the corresponding dielectric functions $\varepsilon=(n_3)^2$ and $\varepsilon^*=(n_3^*)^2=(n_3+\Delta n)^2$, the complex photoconductivity can now be found:

$$\sigma(\omega)=(\varepsilon-\varepsilon^*)i\varepsilon_0\omega$$

where ε_0 is the vacuum permittivity.

The parameters used in our analysis are $n_2=1$ for air or $n_2=2.157$ for the quartz windows, $n_3=1.5$ (for TCB), $n_4=2.157$ and $d=1$mm in the case of the cuvette or $d=10$ μm in the case of a film.

Directionally averaged *c* parameter

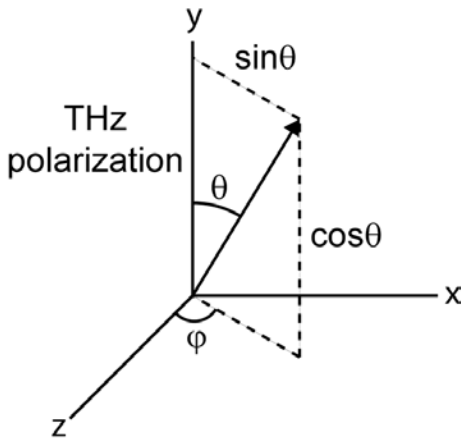

Figure 1 one-dimensional conductor and THz field in spherical coordinate system.

The *c* parameter in the Drude-Smith model denotes the persistence of momentum in a scattering event such that $c = 0$ describes fully momentum randomizing scattering and $c = -1$ describes complete backscattering. We let the polarization of the THz probe field be parallel to the polar axis in a spherical coordinate system and consider an infinite one-dimensional conductor with arbitrary orientation characterized by polar angle θ and azimuthal angle φ, see Figure 1. Taking the component parallel to the THz field to yield $c = 0$, and the perpendicular component to yield $c = -1$, we get the *c* value for a single conductor

$$C = -\sin\theta$$

(for $0 < \theta < \pi$).

In 3 dimensions the directionally averaged *c* value can now be found by integrating over all directions and dividing out the angles, utilizing the differential solid angle $d\Omega = \sin\theta \, d\theta \, d\varphi$:

$$c = \frac{\int C d\Omega}{\int d\Omega} = \frac{\int_0^{\pi} (-\sin\theta) \cdot \sin\theta d\theta \int_0^{2\pi} d\varphi}{\int_0^{\pi} \sin\theta d\theta \int_0^{2\pi} d\varphi} = -\frac{\pi}{4}$$

For a conductors in a 2 dimensional plane which contains the THz polarization direction we simply integrate over the angle θ.

$$c = \frac{\int_0^\pi -\sin\theta d\theta}{\int_0^\pi d\theta} = -\frac{2}{\pi}$$

1. Ulbricht, R.; Hendry, E.; Shan, J.; Heinz, T. F.; Bonn, M. *Rev Mod Phys* **2011,** 83, (2), 543-586.
2. Jackson, J. D., *Classical electrodynamics*. 2 ed.; Wiley: New York, 1975; p xxii, 848 p.