

Terahertz Study of Chiral and Racemic Crystals

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Abstract – We studied far-infrared signatures of various molecules of biological importance using Terahertz Time-Domain-Spectroscopy. Spectral fingerprints in this frequency range are highly sensitive to the inter- and intra-molecular binding and long range order. As a consequence, phonon-like absorption modes differ, depending on whether a chiral or a racemic polycrystalline powder is used. In this contribution, we will present spectra of various chiral and racemic substances and discuss how our measurements could be used to gain a deeper understanding of inter- and intra-molecular binding.

I. INTRODUCTION

It is well known that the molecular structure of a crystal and the binding configuration of the elements with respect to each other govern its far-infrared absorption spectra [1, 2]. In weakly bound crystalline compounds, the energies of phonon-like absorption modes correspond to frequencies in the Terahertz regime. Therefore, a THz Time-Domain-Spectrometer (THz-TDS) is ideally suited to examine subtle differences of inner crystalline configurations. We believe that our technique could also provide a sensitive measure of the density of intermolecular hydrogen bonded networks, since the binding energy, hence the resonance frequency of the phonon-like absorption bands, depends on the distance of the network elements.

II. EXPERIMENT

Powdery polycrystalline chiral and racemic samples of different biological enantiomers were obtained from Sigma-Aldrich and used without further purification. The samples were mixed with PE powder and pressed into pellets of approximately 2 mm thickness, using a hydraulic press. Each pellet contained approximately 30 mg of the sample and 270 mg polyethylene powder as a filling material. The measurements were performed in a THz-TDS at the University of Freiburg. The instrument employs photo-conductive antennas pumped by a 12 fs laser to create the THz pulse and to record the temporal electric field shape. The dynamic range of the experiment ranges from 100 GHz to 3 THz. A detailed description of the setup is given in [3]. Each pellet was examined at different temperatures, using a continuous flow He-Cryostat.

III. RESULTS

All substances studied showed similar characteristic differences between the chiral and racemic form. The lowest phonon-like absorption band of the racemic sample resides at

higher frequencies than the lowest absorption band of the chiral sample. This is taken as indicator that the configuration of the molecular elements and the distance between their centres of mass are different. As an example we show in Figure 1 the absorption spectrum of Cystine. The chiral sample has a distinct low-frequency mode at 0.75 THz. In the racemic sample the low-frequency mode appears at about 0.9 THz.

The reason for the shift might be attributed to the stronger intermolecular binding forces in the racemic crystal. Concurrently the DL-Cystine compound should exhibit higher density than D- Cystine. The explicit behaviour of the

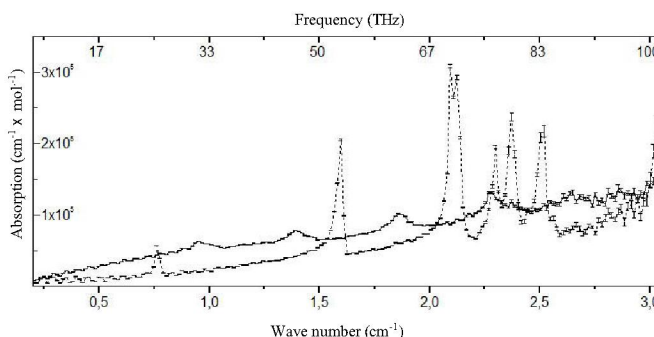


Figure 1. THz-TDS spectrum of chiral D-Cystine (dotted line), and the racemic compound DL-Cystine (solid line), at 13K.

higher-frequency absorption modes is the subject of current study. Of particular importance in this context appears to be the strong disulfid bond in the cystine dimer, which should be investigated in structural calculations. The higher modes could correspond to an additional torsion oscillation of the two cysteine residues with respect to each other.

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