# Differentiation of Structurally related Compounds Using Terahertz Spectroscopy

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***Abstract*—Terahertz-Time Domain Spectroscopy (THz-TDS) is a powerfull tool to probe low energy vibrational modes of organic molecules. Three series of structurally related compounds were characterized between 0.1 and 2.5THz. The results obtained shows that THz-TDS enables good discrimination of these compounds. Absorption features were assigned by computational chemistry and fitted to the Lorentz dipole oscillator model.**

## I. Introduction And Background

TERAHERTZ spectroscopy deals with frequency domain covering few gigahertz to few terahertz. Until recently, difficulties to generate these radiations in a convenient manner explain that this part of the electromagnetic spectrum was usually called the terahertz gap. The development of new sources – detectors systems greatly improves availability of THz frequencies, thus leading to an increased interest from scientific community. A lot of papers have been published, covering several fields: label free DNA probing[1], explosives detection[2], and so on.

Some authors previously pointed out that small change in molecular structure leads to dramatic changes in their absorbance spectra. As an example, modification to one of the retinal insaturations from *trans* to *cis* isomer leads to an entirely new spectrum[3], as well as changing the position of the hydroxyl group on the naphthalene ring[4]. We wish to report here the impact on Terahertz signatures of several modifications derived from a unique mother structure.

## II. Results

The mother structure chosen for this systematic study is the cinnamic acid. To avoid loss by scattering, pure cinnamic acids derivatives were carefully ground using a mortar and pestle to yield a fine powder. The samples were next thoroughly mixed with high density polyethylene and pressed into pellets. Seven structurally related compounds derivated from cinnamic acid were characterized. These molecules have been selected to cover three kinds of molecular modification. The first series deals with different aromatic isomers (*ortho*, *meta* and *para*-chlorocinamic acids), the second with three different halogen atom at the same position (*ortho*-chloro, *ortho*-bromo and *ortho*-fluorocinnamic acids) and the last with sodium and potassium salts of *ortho*-chlorocinnamic acids. The three closely related substituted cinnamic acid derivatives can easily be differentiated though their THz signature (figure 1).

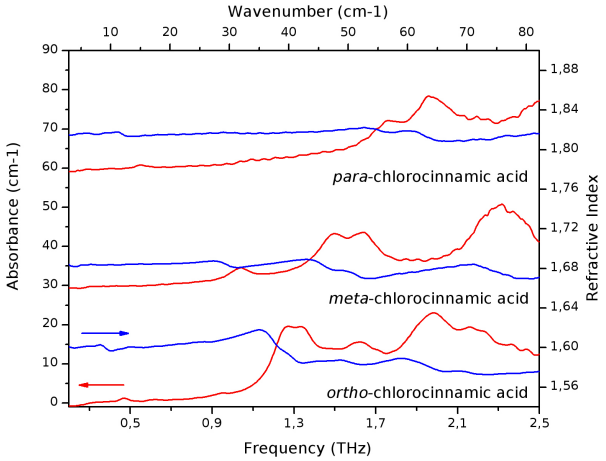


Figure 1: Spectra of the three chlorocinnamic acids. An offset is applied for clarity.

Each absorption peak is correlated to a refractive index variation, therefore assessing without error that these features arises from specific vibrational mode of the studied compounds rather than artifacts or dispersive phenomenon. These results suggest a potential use of THz-TDS for rapid analysis of aromatic halogenations mixtures.

Great differences are also observed for the series obtained by replacing different halogen atoms at the same position on aromatic nucleus (figure 2).

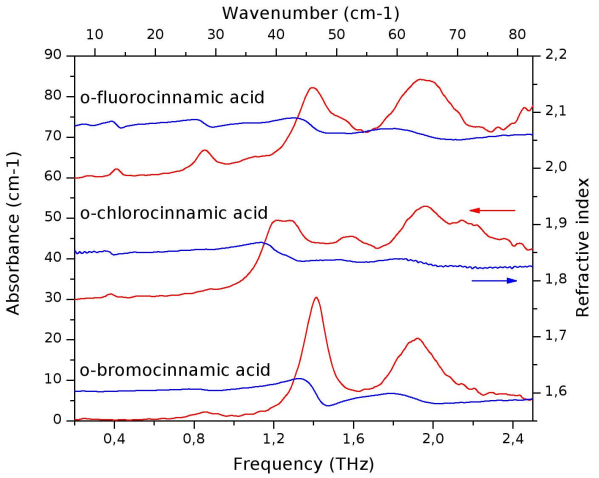


Figure 2: Spectra of the three ortho-halogenocinnamic acids. An offset is applied for clarity

Despite these differences, some common features are noticeable, for example the peak at 1,97 THz. They may arise

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from similar molecular motions that are not involving the halogen substituent.

Anhydrous potassium and sodium salts of ortho-chlorocinnamic acids are also well identified in the THz region, despite the fact that no hydrogen bonds occurs in these products.

Globally, all the differences noticed for the three series of compounds are more markedly noticed in Terahertz range than in mean infrared frequencies, confirming that the observed features arise from collective molecular motions. These vibrations can be well fitted to the Lorentz dipole oscillator model. To assign these vibrational features, *ab-initio* calculations were performed for meta-chlorocinnamic acid. Computational simulation was in good agreement with experimental results, and showed that the cinnamic acids motions arise from symmetric dimer vibrations. All these vibrations involve the whole dimer structure. Work is currently in progress to study other related cinnamic acid derivatives and to analyze absorption peaks shifts with the weight of substituent group.

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