

# THz spectroscopy as a versatile tool for investigating crystalline structures

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**Abstract**—Over the last few years it has been shown that, below 3 THz, terahertz signatures of many different biomolecules originate from intermolecular rather than intramolecular vibrations. Whereas this sensitivity to the environment and intermolecular binding forces is a great hurdle for modeling and the assignment of the THz modes, it can be the basis for probing crystallinity and study the weak intermolecular binding forces.

## I. INTRODUCTION

The far-infrared spectra of many biomolecules show very distinct characteristic features. This fingerprint ability of THz-spectra is the basis for many biosensing or security applications [1], [2]. Yet, relatively little is known about the molecular vibrations in this frequency range. While the comparison of the spectra of similar molecules [3] or DFT based calculations [1] can help to assign some of the modes, these approaches often fail due to the intermolecular character of the low-frequency modes. However, the pronounced sensitivity of THz spectra to crystalline structure offers significant potential for applications that probe crystalline configurations.

## II. RESULTS

A direct demonstration of the intermolecular character of the THz signatures is shown in Fig. 1(a), where the absorption spectra of polycrystalline  $\alpha$ -D-glucose and  $\alpha$ -D-glucose monohydrate are compared. Although both samples only differ by the water molecule that is incorporated in the crystalline structure of the monohydrated sample, the spectra are clearly different. Any pure intramolecular modes should, however, appear in both spectra. This also clearly demonstrates that an assignment of modes, based on the calculation of the THz vibrations considering only isolated monomeric atoms, is difficult. Fig. 1(b) shows the absorption spectra of a mixture of enantiopure D- and L-tartaric acid and the DL-tartaric acid racemate. In the racemic crystal, both enantiomers are incorporated in a well defined alternating order. Although both samples consist of the same molecule, the intermolecular order of the enantiomers obviously has a tremendous impact on the far-infrared spectrum. A temperature dependent study of the spectra of these samples reveals that the lowest observed mode of the enantiopure sample shows a unusual redshift upon heating, whereas the lowest mode of the racemic sample follows the usual blueshift upon heating. This further indicates the clear difference in the origin of the modes of the different crystalline forms of the same molecule. A comparison of several other enantiopure and racemic samples will be shown,

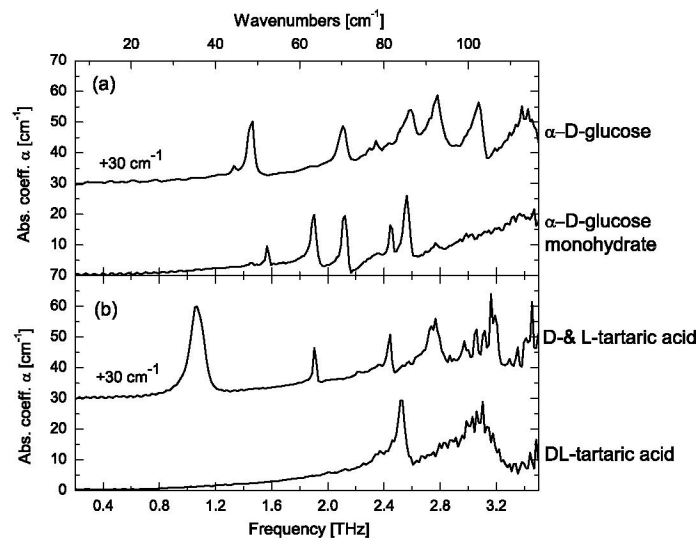


Fig. 1. Absorption spectra of (a) polycrystalline  $\alpha$ -D-Glucose and polycrystalline  $\alpha$ -D-glucose monohydrate and (b) an equimolar mixture of D- and L-tartaric acid compared to DL-tartaric acid.

and an interesting trend between the shift of the modes and the bond parameters of the different structures is observed. The high sensitivity of the THz spectra to the crystalline structure can further be used to detect temperature dependent phase transitions in samples and thus to probe their crystalline configuration.

## III. CONCLUSION

We have shown that the low-frequency modes in the THz spectra of many different biomolecules originate from intermolecular vibrations and thus show a pronounced sensitivity to the crystalline structure.

## REFERENCES

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