

# Combined Infrared and Terahertz Analysis of Amorphous Sorbitol

Juraj Sibik<sup>1</sup>, Timothy M. Korter<sup>2</sup>, and J. Axel Zeitler<sup>1</sup>

<sup>1</sup>Department of Chemical Engineering and Biotechnology, University of Cambridge, Cambridge, UK

<sup>2</sup>Department of Chemistry, Syracuse University, New York, USA

**Abstract**—The nature and formation of the glassy state still lack comprehensive understanding. In this work we present a careful terahertz, FTIR, far-infrared, low frequency Raman and computational analysis using density functional theory on the inter-molecular hydrogen bonding characteristics and how this changes above and below the glass transition temperature in amorphous sorbitol. We show that the changes in inter-molecular bonding are strongly linked to the fast nanosecond-to-picosecond molecular dynamics occurring in the amorphous materials.

## I. INTRODUCTION

DESPITE sustained efforts in research, the physics of glassy matter remains a controversial topic with no universal theory available. Several important pieces of evidence have however already been established [1]. It is well known that the primary relaxation becomes practically immeasurable below  $T_g$ , where liquid turns into a glass, yet some secondary relaxations exist even in the amorphous solid state, in particular the so-called Johari-Goldstein relaxation [2], which involves the motion of the whole molecules, making it a distinctive type of a secondary relaxation compared to the intra-molecular relaxations.

While the glass transition is generally regarded as a physical change in a super-cooled liquid, there is undoubtedly a strong interplay between physical and chemical properties that play a role during the vitrification process. This is immediately obvious given the effect of the glass transition on the different molecular groups as probed by IR vibrational spectroscopy [3].

The part of the IR spectra that is in particular difficult to analyse in this context is the typically very broad –OH stretch mode at 3300–3800  $\text{cm}^{-1}$ . The reason for its width is that the –OH stretch feature often involves multiple types of motions and it can also overlap with other bands, such as the –CH stretch. Upon careful analysis it is possible, in some hydrogen bonding molecules, to resolve contributions of inter-molecular bonding in the –OH stretch mode.

In this work we try to establish several important links between the terahertz spectra and the –OH stretch mode of amorphous sorbitol, both above and below  $T_g$ . We show how the glassy dynamics are linked to the inter-molecular hydrogen bonding structure

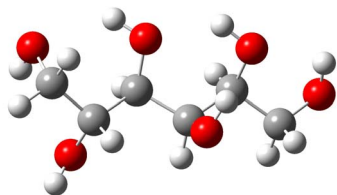


Fig. 1. The molecule of sorbitol  $\text{C}_6\text{H}_{14}\text{O}_6$ . Carbon atoms are shown in grey, oxygen in red and hydrogen in white.

## II. RESULTS

In the case of polyalcohols the –OH stretch is well-separated from other spectral features and hence it is possible to perform a detailed analysis. The –OH stretch in sorbitol is a very broad spectral feature and the data suggest that the peak is originating from several different types of motions. We performed density functional theory calculations on single sorbitol molecules and small clusters that suggest that the modes can be classified in two ways, originating from the terminal –OH groups or from the middle –OH groups.

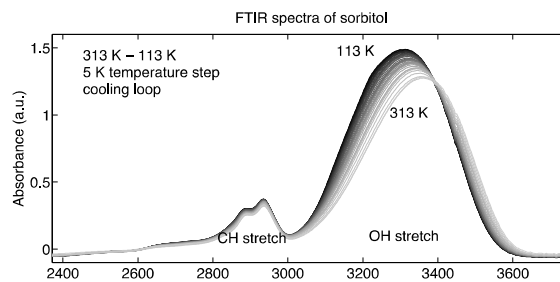


Fig. 2. The FTIR data of sorbitol in the temperature range of 113–313 K, showing –CH and –OH stretch modes.

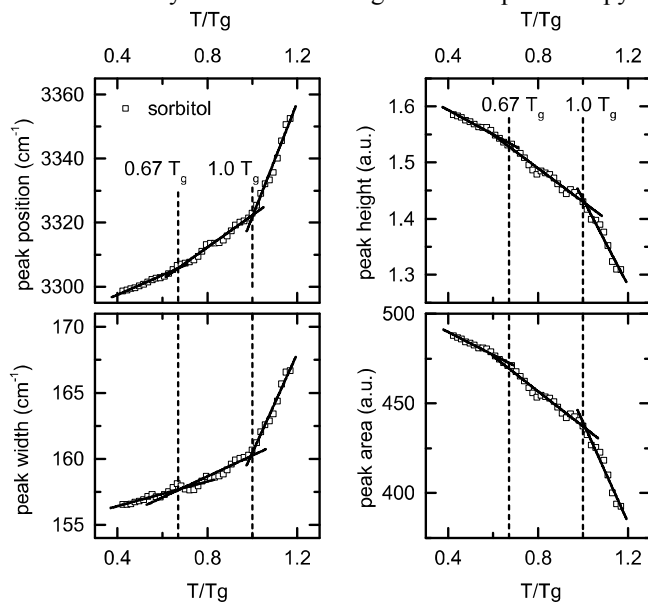
We previously investigated the spectral changes with temperature of sorbitol at terahertz frequencies and observed a change in absorption at  $T_g$ . This change is associated with the vanishing of the global molecular mobility (primary relaxation). At around  $0.67 T_g$ , a second change in absorption is observed where the local inter-molecular mobility (Johari-Goldstein secondary relaxation) vanishes as well [4,5].

In order to gain further insight into the molecular mechanism of these changes in molecular dynamics we investigate the spectral changes of the –OH stretch at infrared frequencies to investigate the role of hydrogen bonding associated with this process. The relevant part of the IR spectra is fitted using a Gaussian line shape in order to better resolve its peak position, width and amplitude (Fig. 3).

We observe that the peak shifts to lower frequencies upon cooling. This can be possibly due to a structural change in the molecular environment of the –OH group, due to change in the anharmonicity of the vibrations in this region, or a combination of these effects. At the same time the peak gets narrower and increases in amplitude upon cooling due to the reduced thermal broadening of the –OH stretch vibration. We also observe that all 3 parameters (peak shift, width and height) deviate from their linear gradient with temperature at  $T_g$  as well as at  $0.67 T_g$ .

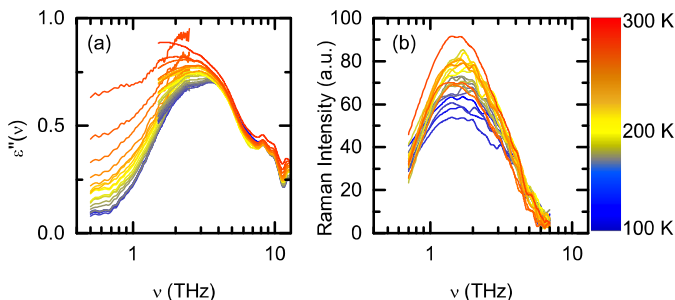
The last point highlights that the previously observed changes in the terahertz spectra are also reflected qualitatively in the mid-infrared –OH stretch vibration. This suggests that

hydrogen bonding plays a significant role in the local molecular mobility as measured using terahertz spectroscopy.



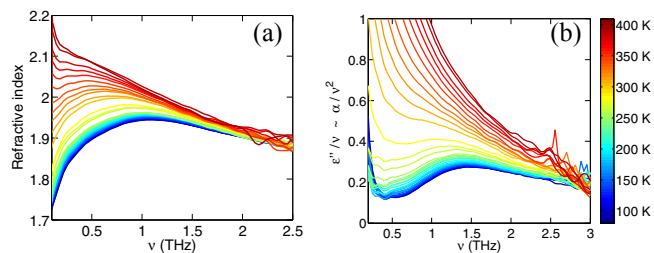
**Fig. 3.** Gaussian fit parameters for the  $-OH$  stretch at different temperatures: peak position (top left), peak height (top right), peak width (bottom left), and peak area (bottom right). The temperature is expressed relative to the glass transition temperature. The solid lines are plotted to guide the eye.

In addition we performed a broadband THz-TDS/ far-IR and low frequency Raman spectroscopy study on amorphous sorbitol in the spectral range 0.2-10 THz and over the temperature range of 80-320 K (Fig. 4). This allowed us to observe the full microscopical peak, originating from the disordered structure in the amorphous systems, together with the first single-molecule vibrations around 9 THz.



**Fig. 4.** (a) THz-TDS dielectric loss spectra and (b) THz-Raman spectra of amorphous sorbitol in the temperature range 100 – 300 K.

Both the infrared and low frequency Raman spectra clearly reveal the microscopical peak, which is comparable between these two techniques. The peaks observed around 9 THz in the far-infrared spectra were however not observed in the low frequency Raman spectra. We assume that these vibrational modes are of symmetric nature and do not exhibit any change in polarizability of sorbitol molecules and hence are Raman inactive.



**Fig. 5.** (a) Refractive index and (b) terahertz density of amorphous sorbitol in the temperature range 100 – 400 K.

Lastly, we derive the vibrational density of states (VDOS) from the broadband terahertz dielectric loss spectra as the terahertz absorption coefficient divided by the square of frequency. VDOS reveals a feature strongly reminiscent of the boson peak as observed both with inelastic neutron scattering and depolarised light scattering studies. A very similar feature is also observed in the terahertz refractive index. Given the nature of the refractive index and comparing the results to a previous inelastic x-ray scattering study [6] it can be argued that such a feature originates from a local structuring on length scales of 10-100 nm.

We provide further insight into dielectric relaxation, Debye density of states and the Boson peak (density of states in excess of the Debye level) contribution to terahertz data of amorphous sorbitol. This compares well with the results from the scattering studies[6] and opens a possibility to replace the expensive and time-consuming scattering experiments with a readily available terahertz spectroscopy.

## REFERENCES

- [1] G. Biroli and J. P. Garrahan, "Perspective: The glass transition," *The Journal of Chemical Physics*, *138*, 12A301, 2013.
- [2] G. P. Johari, "Dielectric Relaxation of Rigid Molecules in Supercooled Decalin". *The Journal of Chemical Physics*, *56*, pp. 4411–4418, 1972.
- [3] P. Papadopoulos, W. Kossack and F. Kremer, "Intra- and inter-molecular dynamics in glass-forming liquids," *Soft Matter*, *9*, 1600, 2013.
- [4] J. Sibik, E. Y. Shalaev and J. A. Zeitler, "Glassy dynamics of sorbitol solutions at terahertz frequencies," *Physical Chemistry Chemical Physics*, *15*, pp. 11931–11942, 2013.
- [5] J. Sibik, S. R. Elliott and J. A. Zeitler, "Thermal Decoupling of Molecular-Relaxation Processes from the Vibrational Density of States at Terahertz Frequencies in Supercooled Hydrogen-Bonded Liquids," *The Journal of Physical Chemistry Letters*, *5*, pp. 1968–1972, 2014.
- [6] B. Ruta, G. Baldi, F. Scarponi, D. Fioretto, V. M. Giordano and G. Monaco, Acoustic excitations in glassy sorbitol and their relation with the fragility and the boson peak. *The Journal of Chemical Physics*, *137*(21), 214502, 2012.