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Signature of aromatic carbons in the terahertz spectroscopy of bio-chars

L M. Lepodise
University of Wollongong, lml533@uowmail.edu.au

J Horvat
University of Wollongong, jhorvat@uow.edu.au

Roger A. Lewis
University of Wollongong, roger@uow.edu.au

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Abstract

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Keywords

spectroscopy, bio, terahertz, chars, signature, carbons, aromatic

Disciplines

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Signature of aromatic carbons in the terahertz spectroscopy of bio-chars

L.M. Lepodise, J. Horvat and R.A Lewis
Institute for Superconducting and Electronic Materials, University of Wollongong, Wollongong, New South Wales 2522, Australia

***Abstract*— The potential of terahertz spectroscopy in distinguishing aromatic carbon compounds in bio-chars is demonstrated. Several types of biochar samples were measured and compared with the THz spectra of pure aromatic compounds. Infrared spectra were modeled with B3LYP and mP2PLYP methods. Modeling could not identify accurately each of the absorption lines. However modeling shows that one of the lines close to 500 cm^{-1} is due to vibrations of carbon rings, which can be used for identification of aromatic carbons in biochars.**

I. INTRODUCTION AND BACKGROUND

NUTRIENT poor Amazonian soils were made fertile by burying charred remains of plants, creating the so-called terra preta. While exact skills for re-creating terra preta were lost, significant research has been carried out to produce organic fertilizers based on bio-chars, charcoals obtained through pyrolysis of various organic materials [1]. Whereas encouraging results have been obtained, it still remains unclear what are the essential ingredients in such fertilizers. Some of the bio-char fertilizers work well in specific soils, yet it is not clear why some others are inefficient. Research on soils sampled from the Amazon basin shows that terra preta is much richer in aromatic carbons than the surrounding poor soils [2]. This kind of research typically requires NMR techniques. Significant efforts have been put into development of much simpler and more accessible infrared spectroscopy techniques that can distinguish between different types of carbon.

Here we show on the potential of terahertz spectroscopy in distinguishing the carbon compounds in bio-chars. Terahertz spectroscopy can probe lower energy excitations than infrared spectroscopy [3], which are associated with inter-molecular, together with low-energy intramolecular vibrations. These techniques could shed more light on the effectiveness of bio-chars as organic fertilizers.

II. METHODS

Terahertz transmission measurements were performed using Bomem DA8 Fourier Transform Infrared Spectrometer, measuring between 200 and 500 cm^{-1}. The source of radiation was a globar. A coated broadband beamspliter was employed and the detector was a liquid-helium cooled bolometer. Numerical modeling was performed using Orca *ab initio* package [4]. TZVPP++ base functions were used [5-8] B3LYP [9] hybrid functional and mPW2PLYP [10] double hybrid functional were used, with parameterized-in Van der Waals interaction [11]. The geometries of single molecules were tightly optimized and infrared absorption frequencies calculated in harmonic approximation.

III. RESULTS AND DISCUSSION

Several samples were measured, consisting of bio-chars produced from Eucalyptus saligna and Eucalyptus marginata, mixed with mineral compounds (BMC). Figure 1 shows that all these samples produce absorption peaks at 275, 345, ≈370, 430 and ≈460 cm^{-1}, denoted by number 1-5. There are small differences between the samples: while BMC10 does not show a clear line at 275 cm^{-1}, BMC5 shows an additional line at 395 cm^{-1} and some of the lines do not appear to be shifted in energy. Despite this, there is a good agreement between the measured samples, indicating that all samples contain the same group of compounds. They will be identified by comparison to the terahertz spectra of pure compounds.

The transmission intensities for several aromatic compounds, benzoic acid, hydroquinone, paracetamol and 2,4-dinitrotoluene are compared to BMC5 in figure 2. The positions of the absorption lines 1-5, identified for the biochars in figure 1, are also shown. Absorption lines 2, 4 and 5, obtained for biochars, can be also identified in the spectra of 2,4-dinitrotoluene, benzoic acid and paracetamol. Line 2 is shifted to lower energy for paracetamol and benzoic acid, as compared to the biochars. Further, line 2 is not clearly defined in the spectrum of hydroquinone, even though there is an indication for it in the shape of a broad peak. Line 1 is observed for dinitrotoluene, hydroquinone and benzoic acid, but not for paracetamol. Line 3 is more difficult to define for all the compounds measured. However, each of them has an unassigned line at higher energy than the biochars, which is likely to be line 3 that shifted to higher energies.

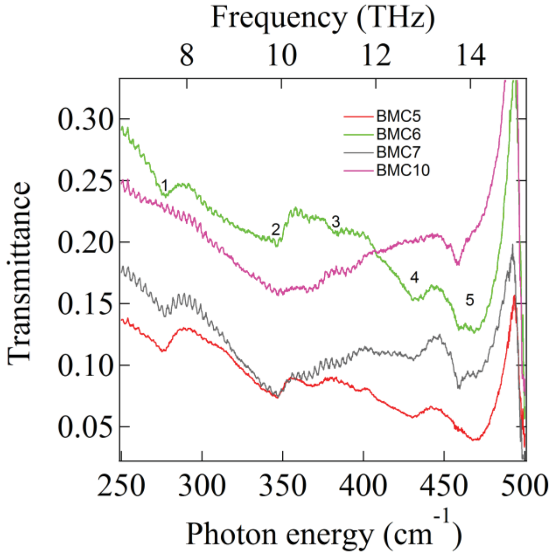

Figure1: Terahertz transmission of different bio-chars.

All of these compounds consist of a benzene ring, to which different functional groups are attached. Therefore, the lines common to all of the compounds must be associated either with vibrations of the benzene ring or the functional groups attached to the rings. Infrared spectra of several aromatic compounds were obtained numerically and these results were compared with the experimental spectra, in an effort to identify the vibration modes for the absorption lines of the measured compounds (fig. 2) . Modeling on hydroquinone with mP2PLYP method gave the absorption lines of significant amplitudes at 163, 329, 356 and 432 cm^{-1} in the measured energy range. These lines were identified as symmetric –OH out-of-plane translation, symmetric –OH out-of-plane rotation, symmetric –OH in-plane translation and C-ring out-of-plane twisting vibrations, respectively. The same modeling with B3LYP method gave the absorption lines with significant amplitudes at 299, 306, 447 and 516 cm$^{-1.}$ They correspond to –OH out-of-plane, –OH in-plane, –OH in-plane and C-ring vibrations, respectively. Apparently, modeling with these methods was not accurate enough to positively identify the measured absorption lines. However, the accuracy of this modeling is expected to be within about 50 cm^{-1}. Therefore, at least some of the observed lines are due to the vibrational modes obtained in the modeling. Since we measured at quite low energies, inter-molecular vibrations could have produced some of the observed lines, which were not taken into account in the modeling.

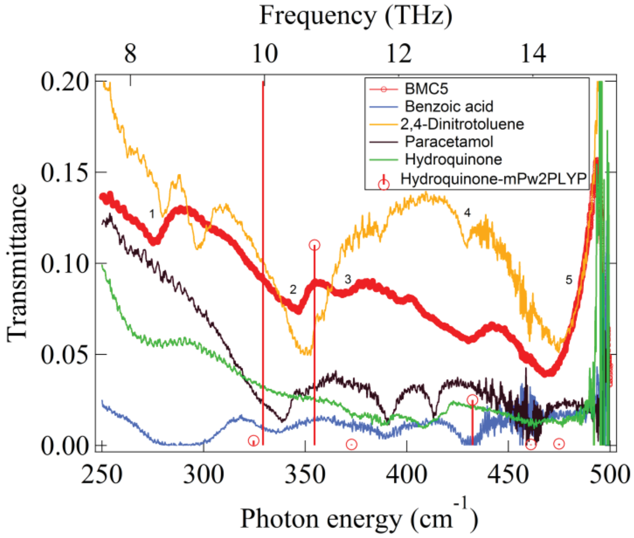

Figure 2: THz transmission of pure aromatic compounds, compared to BMC5 biochar.

IV. CONCLUSIONS

Infrared spectroscopy between 250 and 500 cm^{-1} revealed absorption lines that are common to different biochar samples. These lines were also identified for several pure aromatic compounds, indicating that aromatic compounds are the key components in the biochars. This is consistent with NMR study of biochars [2]. At least one of the observed lines is due to the vibration of carbon rings, which can be used for positive identification of the aromatic compounds in biochars. However, numerical modeling could only show that this must be one of the lines closer to 500 cm^{-1}. More accurate numerical methods are required to single out this line.

V. ACKNOWLEDGMENTS

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