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Keywords

thz, frequencies, low, spectroscopy, characterization, raman, material

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Material Characterization at Low Frequencies Using THz and Raman Spectroscopy

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Abstract—We present results from wideband THz, low wave-number Raman, and FTIR measurements on benzoic acid and two of its derivatives. The low energy vibrational modes have been identified and compared with the results from calculations.

I. INTRODUCTION

HYDROGEN bonded carboxylic acid dimers are being extensively studied to obtain a better understanding of systems with intermolecular hydrogen bonds. Hydrogen bonds are strong enough to determine the structure of the compound. Researchers have proposed novel techniques to acquire more information regarding the Fermi resonance in hydrogen bonded compounds by analyzing both low and high frequency vibrational modes of the molecules [1]. A detailed understanding of the spectra at low wave-numbers is necessary to achieve further improvements in this field. Both infrared (IR) active and Raman active spectra are needed to obtain maximum information about the vibrational modes of materials under study.

Conventional Fourier transform IR (FTIR) spectrometers can cover most of the THz region. However, exploring the IR active vibrational modes in the lower THz frequency region is primarily hindered by poor access to the THz frequencies where the most of the vibrational modes related to intermolecular hydrogen bonding have signatures. Developments in highly sensitive Terahertz time-domain spectroscopy (THz-TDS) has provided us with a powerful modality to penetrate into this low energy region.

Benzoic acid crystals are being used extensively for investigating the properties of intermolecular hydrogen bonds. This is because the molecules are planar with a C_s symmetry group that crystallizes into a monoclinic unit cell with a $P2_1/c$ space group that has 4 molecules in the unit cell [2]. The crystalline form consists of two monomers linked by hydrogen bonds leaving a centrosymmetric structure.

Temperature dependent vibrational spectra at low wave-number are considered to be particularly useful in understanding the complex inter- and intra- molecular vibrations and the role of hydrogen interactions. For example, temperature dependent low energy far-IR studies of the vibrational modes in carboxylic acids and benzoic acid by Takahashi *et al.* [3]

showed that there were additional absorption peaks that could not be observed or resolved at room temperature. While THz measurements have been made on 2-hydroxy benzoic acid at 13 K, 80 K, and room temperature [4], there are no reports of temperature dependent Raman spectra in the low energy region.

We report low wave-number Raman and the corresponding IR spectra in the THz region for benzoic acid and two of its derivatives, 2-hydroxy and 3-hydroxy benzoic acids. The experimental data were interpreted using the calculated literature values as well as results from density-functional theory (DFT) calculations at the level of B3LYP/6-31G** using the GAUSSIAN 09 [5] package. An efficient additive to prepare samples for THz spectroscopy is also discussed.

II. EXPERIMENTAL DETAILS

Samples for the THz and FTIR spectroscopy measurements were prepared by mixing 5 - 20 wt% of the crystalline powders with a commercial polymer powder branded as Polyblend 100XF (PB100XF) supplied by Micropowder Inc., USA. Pellets with a thickness of 1.0 to 1.5 mm and a diameter of 9 mm were pressed in a die at 4500 psi for 30 seconds. THz spectra in the 0.5 to 2.5 THz frequency range were collected using a Z-Omega THz system pumped by a Toptica ultrafast fiber optic laser operating at its second harmonic frequency centered at 785 nm. The system was purged with nitrogen to avoid water vapor lines in the spectrum. Far-IR absorption for energies above 80 cm^{-1} were collected using a Nicolet FTIR Spectrometer where the sample space was evacuated.

Samples for Raman spectroscopy were prepared using standard procedures to grow crystals from the compounds in powder form purchased from Sigma Aldrich. The low wave-number Raman spectra of the crystals under study were investigated using a Jobin-Yvon Horiba T64000 triple grating Raman Spectrometer integrated with a confocal microscope with an objective set to 100x. The system was pumped by a He-Ne laser at 633 nm. Low temperature Raman spectra were recorded using the same spectrometer employing a computer controlled cooling system marketed by Linkam scientific instruments that uses cooled nitrogen gas.

III. RESULTS AND DISCUSSION

Structures of the compounds used for this study are shown in figure 1. Benzoic acid and its derivatives generally exist in dimer form in crystals as shown in figure 1(b). Results from the Raman, THz and FTIR spectroscopy for crystalline benzoic acid, 2-hydroxy benzoic acid and 3-hydroxy benzoic acid are shown in figures 2 and 3. The calculated literature values for the vibrational modes reported in the literature and the mode assignments are summarized in Table I along with the results from our calculations using time dependent density functional theory at the level of B3LYP/6-31G** using the package GAUSSIAN 09 [5]. The experimental values show reasonable agreement with the calculated values although there are additional modes that are not predicted in the theoretical model that we used.

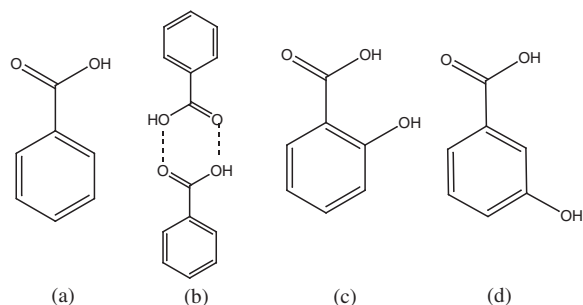


Fig. 1. Structures of the compounds considered for this study; Benzoic acid (a) monomer and (b) dimer, (c) 2-hydroxy benzoic acid, and (d) 3-hydroxy benzoic acid.

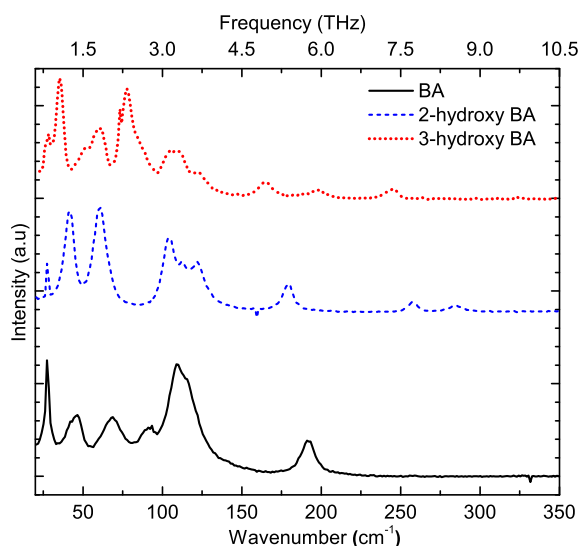


Fig. 2. Raman spectra of benzoic acid, 2-hydroxy benzoic acid, and 3-hydroxy benzoic acid for energies corresponds to the THz region.

The selection of Polyblend 100XF (PB100XF) for preparing samples for THz-TDS and FTIR spectroscopy was motivated by the recent report by Scherger *et al.* [6] that pressed pellets of a mixture of PB100XF can be used to make low-loss THz lenses [6]. Use of PB100XF for sample preparation instead of

conventional additives, such as polyethylene provided sturdy pellets that were relatively less sensitive to moisture. Also, there is no strong absorption or refractive index dispersion for this material in the wider THz frequency range except for a relatively narrow absorption band near 6 THz as shown in figure 3.

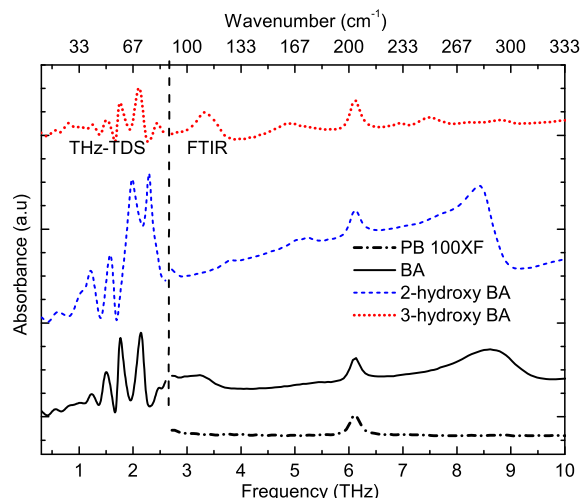


Fig. 3. Infrared absorption spectra of benzoic acid, 2-hydroxy benzoic acid, and 3-hydroxy benzoic acid for the THz region. Also shown is the spectra of PB100XF (dash-dotted curve). Plot of FTIR spectroscopy data translated vertically to match with that of THz-TDS.

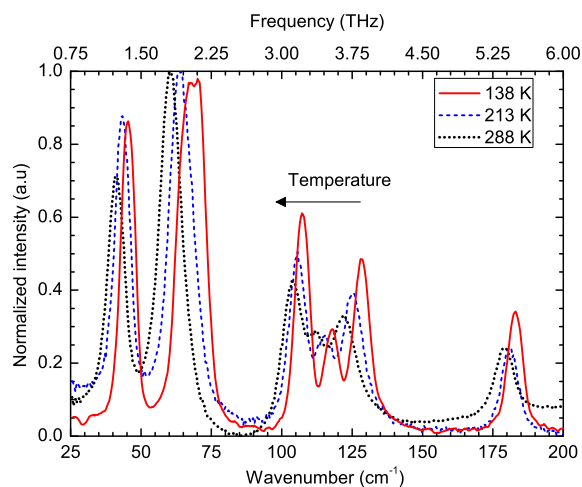


Fig. 4. Raman spectra of 2-hydroxy benzoic acid (Salicylic Acid) for energies in the THz region and at 138 K (solid curve), 213 K (dashed curve), and 288 K (dotted curve). The spectra have been scaled to the same peak height at 68 cm⁻¹.

Temperature dependent Raman measurements were made on one of the compounds used in this study, 2-hydroxy benzoic acid (salicylic acid). The Raman spectra at 138 K, 213 K, and 288 K are shown in figure 4. It can be seen that there is a shift in the Raman peaks to lower wave-numbers as the temperature is increased. This was also observed in a recent THz study at 13 K, 80 K, and 295 K [4]. There is also a broadening of the vibrational modes at higher temperatures that makes it

difficult to see some of the modes. For example, the 288 K peak at 112 cm^{-1} corresponds to hydrogen bond shearing and it is difficult to see because of the more intense 106 cm^{-1} (hydrogen bond shearing) and 126 cm^{-1} (hydrogen bond stretching) peaks. The temperature dependent broadening of vibrational modes can be attributed to a change in the length and strength of hydrogen bonding with temperature due to the symmetry induced breakdown of the Born-Oppenheimer approximation as discussed in detail in [7] and references therein. Broader peaks were also observed at room temperature from THz measurements on polycrystalline salicylic acid samples [4] where more peaks were observed at 13 K. However, the temperature dependent broadening is not as dramatic in our Raman data when compared with the THz data. This may be due to the use of single crystals in our study when compared with powders in the THz study.

TABLE I
SUMMARY OF THE EXPERIMENTAL AND CALCULATED¹ (IN BRACKETS)
VIBRATIONAL MODES OF BENZOIC ACID DERIVATIVES.

BA (cm^{-1})	2-OH-BA (cm^{-1})	3-OH-BA (cm^{-1})	Approximate description	Active in
17 (21)	20 (21)	18 (21) [‡]	butterfly	IR
27 (21)	27 (21)	27 (21) [‡]	butterfly	Raman
34 (32)	34 (32) [‡]	34 (32) [‡]	torsion 'twist'	IR
41 (40)	40 (40) [‡]	41 (40) [‡]	mr 'op'	IR
47 (45)	42	35	mr 'op'	Raman
49 (51)	52	49	$\nu(\text{OH}\cdots\text{O})$	IR
58 (59)	66 (68) [‡]	58 (59) [‡]	cogwheel	IR
68 (68)	50 (68) [‡]	61 (60) [‡]	cogwheel	Raman
71 (68)	76	71	cogwheel	IR
82 (85)	–	82 (85)	τ (-COOH)	IR
91 (87)	–	–	$\nu(\text{OH}\cdots\text{O})$ 'ip'	Raman
108 (103)	–	109 (103)	$\delta(\text{OH}\cdots\text{O})$	Raman
109 (105)	106 (103) [‡]	105 (105)	$\delta(\text{OH}\cdots\text{O})$	IR
114 (111)	112 (111) [‡]	–	$\delta(\text{OH}\cdots\text{O})$	Raman
121 (122)	126 (126) [‡]	122 (122) [‡]	$\nu(\text{OH}\cdots\text{O})$	Raman
–	163 (168) [‡]	162 (168) [‡]	$\gamma(\text{Ph}\cdots\text{COOH})$	IR
–	174 (175) [‡]	–	$\gamma(\text{Ph}\cdots\text{COOH})$	IR
–	179 (175) [‡]	–	$\gamma(\text{Ph}\cdots\text{COOH})$	Raman
–	–	165 (170)	$\nu(\text{CH})$	Raman
191 (196)	–	198 (196) [‡]	τ (CC)	Raman
–	257(336)	245(336)	τ (CC)	Raman
–	284 (283) [‡]	–	$\nu(\text{CO}\cdots\text{O})+\beta(\text{CC})$	Raman
288(283)	–	295 (283)	$\nu(\text{CO}\cdots\text{O})+\beta(\text{CC})$	IR

¹The calculated values were obtained from our DFT calculations (indicated with a [‡]) and literature values [1], [2], [8]–[10]. The modes are assigned based on the simulation as well as the available literature values. (mr: monomer rocking, τ : torsion, ν : stretching, 'ip': in-plane, 'op': out-of-plane. δ : shearing, β : in-plane bending, γ : out-of-plane bending)

IV. CONCLUSIONS

In conclusion, low energy Raman, THz, and FTIR spectra of benzoic acid and benzoic acid derivatives were measured and the data were compared to the theoretical and literature values. The energies of the experimentally measured vibrational modes are found to agree with the DFT calculated values. The Raman spectra were measured down to 138 K

and we find that there is broadening of the vibrational modes when approaching room temperature. This is consistent with a previous temperature dependent THz study. However, the Raman spectra are not as broadened by temperature when compared with the THz spectra, which is likely to be due to the use of single crystals in our study. This shows one advantage of low energy Raman studies. We find that that PB100XF is an efficient, cost effective and stable additive for sample preparation for THz spectroscopy.

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