











phase density functional theory (DFT) models have attributed the feature at 3.1 THz to the vibration of the anion, at 5.2 THz to a vinyl C-H torsional mode on the cation, and at 12.3 THz to a phenyl ring mode [24], but fail to predict the other absorption features. DFT models such as these have difficulty reproducing low frequency THz spectra, which are dominated by collective vibrations, since they neglect inter-molecule interactions that are present in the bulk. Modeling THz spectra remains an active area of research [25]. The similar structure of the derivatives of DAST will give them similar absorption features [10]. Though Cherenkov radiation from DAST may avoid phase matching requirements, the absorption features remain present in the emitted spectrum [18]. Estimating the THz properties of DAST by modeling its emission via DFG underestimates the effects of these absorption features [15]. Such techniques are valuable above 15 THz where TDS is difficult. We also identify resonances centered at 1.1, 1.3, 1.6, 2.2, 3, 5.2, 7.2, 9.6 and 11.7 THz for the *b*-axis of DAST. Only the resonances at 1.1, 1.3, and 1.6 have been previously observed [14], though DFT models assign the 11.7 THz feature to the torsional mode of the anion methyl group [24].

Given the optical properties of DAST [3], and THz indices we have determined, we compute the coherence length,  $l_c$ , across the band for various pump wavelengths, Fig. 5. For Ti:Sapphire wavelengths the  $l_c$  is larger for an emitter beam polarized parallel to the *b*-axis than the *a*-axis. This is unfortunate, as the nonlinearity is nearly an order of magnitude larger for *a*-axis emission. Though the emission could be stronger for *a*-axis orientation, the *b*-axis must be used if broad bandwidth is desired. The bandwidth over which there is good phase matching is consistent with the bandwidth seen from a 60  $\mu\text{m}$  thick DAST crystal [16]. The largest component of the nonlinear susceptibility,  $\chi_{111}$ , can be accessed at longer wavelengths. There is good phase matching near 1300 nm for light polarized parallel to the *a*-axis. Unfortunately, the nonlinear susceptibility exhibits dispersion, as the linear absorption bands of DAST are near 500 nm. At longer wavelengths the nonlinearity is no longer resonantly enhanced and will be lower than at shorter wavelengths. Though the coherence length is large at these wavelengths, thick DAST crystals used as THz emitters will show numerous spectral gaps due to phonon absorption. The coherence length is consistent with the near 15 THz bandwidth reported using a 160  $\mu\text{m}$  thick DAST crystal [17].

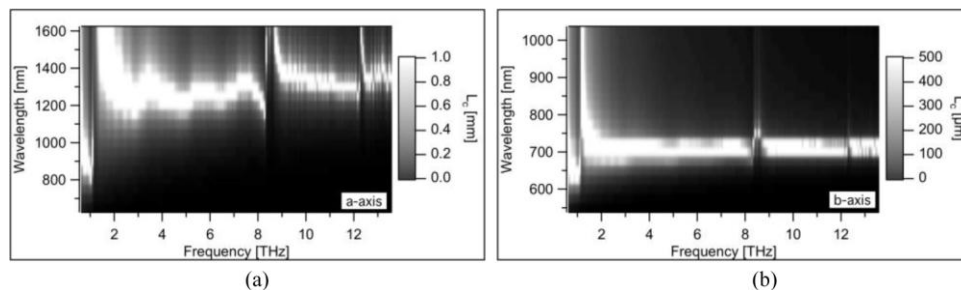


Fig. 5. The coherence length,  $l_c$ , across the THz band of a DAST emitter pumped with (a) *a*-axis or (b) *b*-axis polarized light at relevant wavelengths.

In summary, we have reported the first use of a THz spectrometer based on air-plasma THz generation and FSEOS in a poled polymer. The far infrared properties of DAST are measured from 0.6 to 12 THz, identifying multiple previously unidentified phonon bands and showing their effect on THz emission. Our results are consistent with recent published FTIR spectra [7] and broadband THz emission spectra from DAST [17], and can be used to guide future THz applications.

### Acknowledgements

This material is based upon work supported by the STC program of the National Science Foundation No. DMR 0120967 and a grant from the Air Force Office of Scientific Research No. FA 9550-07-1-0122.