



Research article

Wide temperature range studies of the low frequency THz spectrum of benzoic acid using FTIR spectroscopy



Lucia M. Lepodise*

Botswana International University of Science and Technology, Palapye, Botswana

ARTICLE INFO

Keywords:

Spectroscopy
FTIR
DFT
Benzoic acid
Terahertz
Temperature dependence
Engineering
Physics
Materials science
Chemistry

ABSTRACT

Fourier Transform Infrared Spectroscopy was employed to measure the low frequency terahertz transmission spectrum of benzoic acid over a wide temperature range. One broad absorption peak was observed at room temperature but more peaks appeared as the sample was cooled. All the peaks shifted to higher frequencies with the decrease in temperature and they displayed a rate of change in the range of $(2-5.6) \times 10^{-2} \text{cm}^{-1} \text{K}^{-1}$. An anomalous behavior was observed in the peak width and the peak intensity for some absorption peaks and this was attributed to the peaks being composite. There is a good agreement between the model of benzoic acid crystal and the experiment. The QUANTUM ESPRESSO code utilizing the PBEsol functional proved to be slightly better than the GAUSSIAN 03 method which employed NC-PBE functional in predicting the absorption peaks. A comparison was made of these results and the previous studies done using the THz-TDS. These results proved the ability of the FTIR technique in performing low frequency THz measurements.

1. Introduction

The terahertz (THz) frequency range applications have remained scarce. This has been mainly due to lack of powerful sources and detectors of THz radiation which led to a slow advancement of research in this field. This frequency range lies between the microwave and infrared regions of the electromagnetic spectrum. Precisely, 1 THz is equal 4.1 meV of energy and in wavenumbers it is equivalent to 33.3cm^{-1} . Terahertz radiation has the capability of penetrating many materials and therefore has proven to be a valuable tool in the study of a range of materials [1, 2, 3, 4, 5, 6, 7]. Many materials have spectral fingerprints in this frequency range and hence this radiation can be used to detect or even identify different materials for different applications. Characterization and identification of materials is made possible by the ability of THz radiation to probe both the intermolecular and intramolecular vibrations of materials.

THz frequency studies of materials have been dominated by the use of the Terahertz-time domain system (THz-TDS) [8, 9, 10, 11, 12, 13, 14, 15]. This method offers a low frequency range which is not accessible by the conventional Fourier Transform Infrared (FTIR) system. Although the FTIR technique with a combination of appropriate accessories like beamsplitters and detectors can offer the same frequency range, the THz-TDS system remains the commonly used method. To build a strong

and reliable database of materials, it is found indispensable to compare different methods.

For most materials, low temperature measurement studies of the THz spectra have revealed the underlying spectra which are usually concealed at room temperature due to homogeneous broadening. However, the temperature dependence of the absorption peak properties has not been investigated extensively. In majority of the previous low temperature measurements, the samples have been cooled to one particular temperature [16, 17]. This has resulted in the scarcity of studies over a wide temperature range. A few studies that exist do not give a detailed interpretation of the change in line properties (peak width, peak intensity and peak position) with temperature. These studies are however essential in that they can reveal hidden spectra of materials, and therefore avail detailed and precise information about materials which can improve the assignment of absorption peaks.

In this work, the temperature dependence of the THz spectrum of benzoic acid (BA) is studied using the FTIR technique. BA is an example of a small molecule important in a range of research areas and industries. It serves in chemical industries as food additive, medicine and antiseptic [18]. This chemical is also used as antibacterial and antifungal preservative [19]. A thorough understanding of this compound is necessary to improve its applicability. The temperature dependence of the BA spectra was investigated. The changes in peak positions, peak

* Corresponding author.

E-mail address: lepodisel@biust.ac.bw.

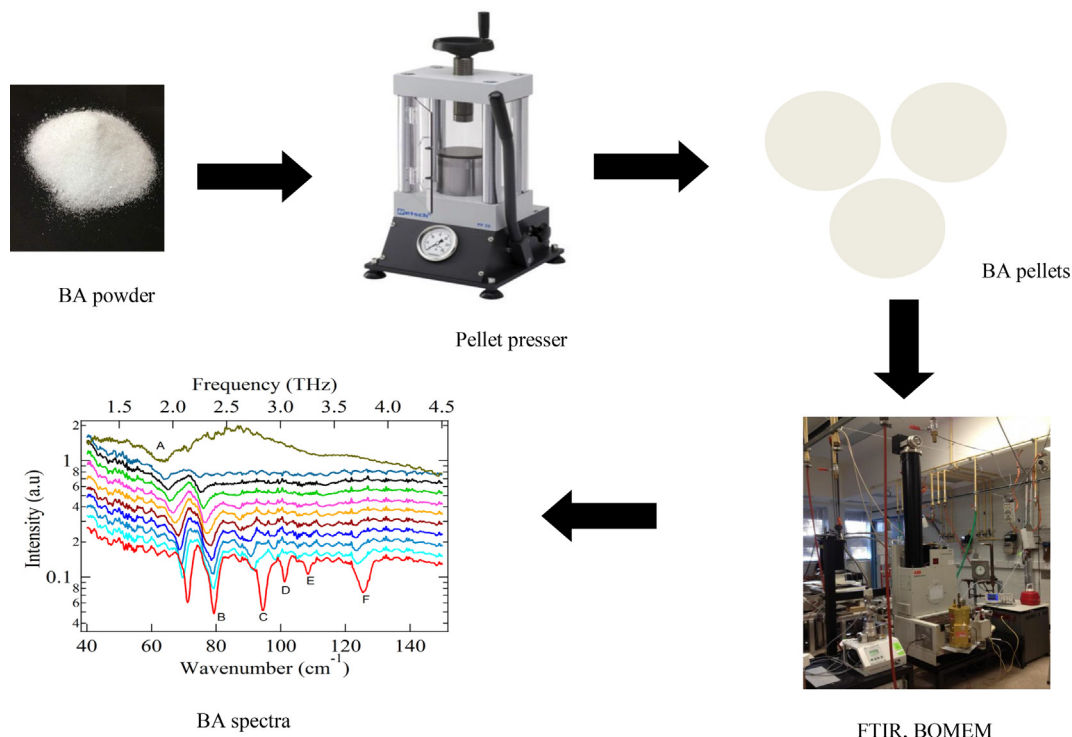


Figure 1. Summary of experimental stages.

widths and peak intensities are presented. A comparison is made of the THz spectrum obtained using the FTIR method and the THz-TDS. Theoretical model of benzoic acid crystal will be used for the interpretation of the obtained experimental spectrum. Furthermore, the accuracy of the theoretical results will be tested by comparing two different modeling programs which are commonly used. This will assist in the choice of a method which will reliably predict the observed absorption peaks in future studies. An attempt to assign the observed absorption peaks was also made.

2. Experiment

Benzoic acid was purchased from Sigma-Aldrich Company. Its purity was 99.5%. The sample was prepared by mixing 5% by weight of benzoic acid powder with a polymer named polyblend 100 XF (a unique mixture of polyethylene and polytetrafluoroethylene (PTFE)) and pressing into a pellet of about 0.5 mm thickness. Pressing was into a die of 13 mm diameter at 1.5 Bar for 2 min. The pellet was measured in the transmission geometry in a FTIR spectrometer. The sample compartment was evacuated at all times to reduce effects of water vapor in the spectra. The sample was cooled in an Oxford Instruments continuous-flow helium cryostat. It was measured over a wide range of temperatures. A globar was used as the source of radiation and the resolution at all times was 0.015 THz. A broadband beamsplitter was employed and a helium cooled bolometer was used as the detector. A ratio of the sample in the beam path to polyblend pellet in the beam path gave the transmission spectrum of the sample. A theoretical model was performed for a of benzoic acid crystal using the QUANTUM ESPRESSO package [20]. The Perdew-Burke-Ernzerhof (PBE)sol Generalized Gradient Approximation, GGA, Density Functional Theory (DFT) functional was used [21]. Norm-conserving scalar-relativistic PBE pseudopotentials were used [22] and the periodic boundary conditions were taken into account. The kinetic energy cut-off for wave functions was 1225 eV and was 4422 eV for charge density. Variable-cell geometry optimization was performed, with van der

Waals correction turned on because of the importance of the bonds between the crystalline planes of benzoic acid [23, 24]. Benzoic acid forms molecular crystals, with hydrogen-bonding between $-\text{COOH}$ groups creating dimers as the basic crystal building blocks. These dimers form crystal planes for a benzoic acid system. A stringent convergence criteria was applied. Figure 1 summarizes the experimental steps.

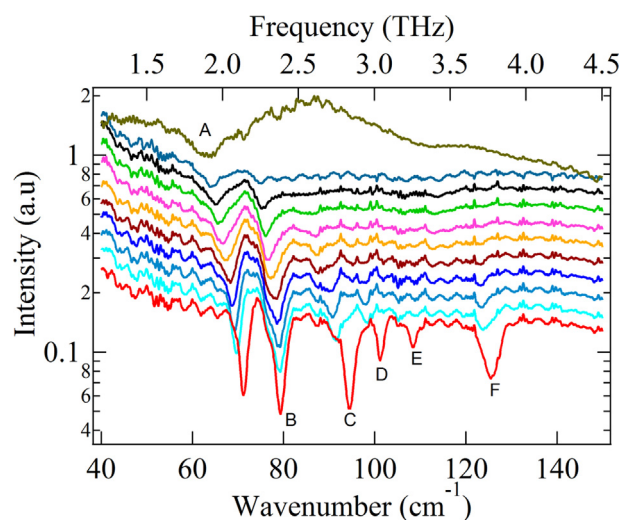


Figure 2. Absorption spectra of benzoic acid measured at different temperatures. Temperature range from top to bottom: 300, 238, 211, 182, 158, 136, 116, 94, 73, 51 and 9.5K. The spectra were offset for clarity.

Table 1. Comparison of the terahertz experimental and theoretical spectrum of benzoic acid.

| Peak Label | Experiment 300K FTIR (THz) | Experiment 9.5 K FTIR (THz) | Theoretical (THz) | THz-TDS [17] 77 K (THz) | THz-TDS [12] 300 K (THz) |
|------------|----------------------------|-----------------------------|-------------------|-------------------------|--------------------------|
| A | 1.89 | 2.14 | 1.81 | 2.07 | 1.89 |
| B | - | 2.38 | 2.29 | 2.38 | 2.38 |
| C | - | 2.83 | 2.75 & 2.76 | 2.68 | - |
| D | - | 3.04 | - | 2.92 | - |
| E | - | 3.25 | 3.26 | - | 3.17 |
| F | - | 3.77 | 3.89 | - | - |

Table 2. Comparison of the theoretical calculations of benzoic acid using different methods.

| Peak Label | Experiment 9.5 K FTIR (THz) | Theoretical PBEsol (THz) | Theoretical NC-PBE [16] (THz) |
|------------|-----------------------------|--------------------------|-------------------------------|
| A | 2.14 | 1.81 | 2.13 |
| B | 2.38 | 2.29 | 2.62 |
| C | 2.83 | 2.75 & 2.76 | 2.78 |
| D | 3.04 | - | 2.84 |
| E | 3.25 | 3.26 | 3.30 |
| F | 3.77 | 3.89 | 5.52 |

3. Results

Figure 2 presents the THz spectra of BA at different temperatures. At room temperature BA exhibit one broad absorption peak denoted A in the considered THz frequency range. As the temperature was lowered, more absorption peaks started developing at different temperatures. The absorption peak denoted B started appearing at 238 K, peak denoted C at 182 K, peak denoted D at 73 K, peak E at 9.5 K while peak F started appearing at 94 K. None of the BA absorption peaks disappeared with cooling and thus this sample does not have any 'hot bands' between 1.2 and 4.5 THz. These measurements were compared with the work of Laman and colleagues [17]. In their study, a THz-TDS system was used and the measurements were performed at liquid nitrogen temperature for a benzoic acid pellet. In the considered frequency range, Laman and colleagues obtained absorption peaks at 2.07, 2.38, 2.68 and 2.92 THz for their pellet measurements. In this study, one absorption peak was observed at 1.81 THz for the room temperature measurements. Additional peaks were observed in the 9.5 K spectrum at 2.38, 2.83, 3.04, 3.25 and 3.77 THz. Absorption peaks appearing at 3.25 and 3.77 THz did not appear in the spectrum by Laman [17]. This shows the necessity of cooling the sample to even lower temperatures to reveal all the details of the particular sample. It has to be however noted that Laman [17] obtained additional peaks using the new waveguide THz-TDS technique. Furthermore a comparison was made between this work and another study by Yan and colleagues [12]. They observed absorption peaks at 1.89, 2.38 and 3.17 THz in the considered frequency range as can be seen in Table 1. All their measurements were done at room temperature and therefore some of the characteristic peaks of benzoic acid were not resolved as per what was observed in this work. In their study they obtained two additional absorption peaks which were not observed in the room temperature FTIR spectrum. However, these absorption peaks were observed in the 9.5 K FTIR measurements showing that the performance of this technique can be enhanced to match that of the THz-TDS by coupling it to cryogenics. A summary of the comparison of the FTIR measurements and the THz-TDS measurements is given in Table 1. The variation in the profile of the room temperature spectrum and the low temperature spectra is attributed to the extra accessory which was used in the low temperature measurements. The low temperature spectra were collected with the use of a cryostat which has extra windows

while on the other hand it was not used for the room temperature measurements.

The theoretical spectrum of the BA crystal was used for interpreting the experiment. The model revealed absorption peaks which were not

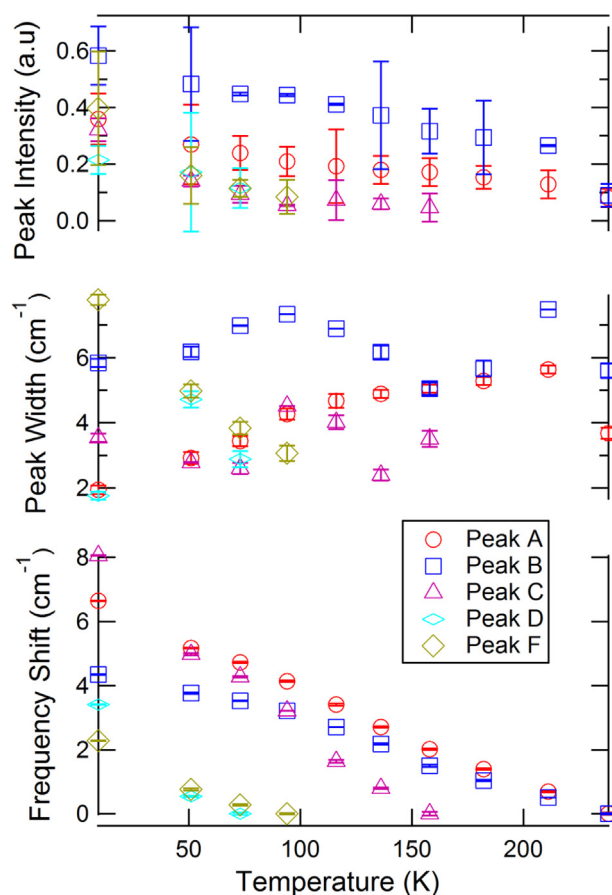
**Figure 3.** Change in peak frequency, width and intensity with temperature for benzoic acid.

Table 3. Approximate descriptions of observed absorption bands.

| Peak Label | Experiment 300 K FTIR (THz) | Experiment 9.5 K FTIR (THz) | Theoretical (THz) | Approximate description of peaks |
|------------|-----------------------------|-----------------------------|-------------------|--|
| A | 1.89 | 2.14 | 1.81 | Wagging of monomers along C1-C4 line |
| B | - | 2.38 | 2.29 | Translational vibrations of monomers |
| C | - | 2.83 | 2.75 & 2.76 | In plane rocking of monomers along C1-C4 line. |
| D | - | 3.04 | - | - |
| E | - | 3.25 | 3.26 | Out of plane rocking of monomers along C1-C4 line. |
| F | - | 3.77 | 3.89 | Tilting of monomers |

apparent at room temperature corroborating the low temperature measurements. Comparison between the theoretical calculations and the experimental spectrum taken at 9.5 K are summarized in Table 1. Despite the shifts in the frequencies which are due to cooling, there is a good agreement between the experiment and the theoretical model. The absorption peak denoted *D* however did not have a matching theoretical peak and this will be further investigated. The theoretical model in this work was compared to the one used by Takahashi and colleagues [16] as shown in Table 2. Absorption peak labeled *A* corresponds well with the Norm Conserving-Perdew Burke Ernzerhof (NC-PBE) calculations. Absorption peaks labeled *B*, *E* and *F* corresponded well with the peaks obtained by the PBEsol method. In addition, there is a better agreement between absorption peak denoted *C* and the NC-PBE absorption peak. In general, the PBEsol functional predicts the spectrum more reliably than the NC-PBE functional.

Figure 3 shows the temperature dependence of the peak position, peak width as well as the peak strength. All the peaks displayed an expected trend in the change of the frequencies with decreasing temperature. They were all observed to shift to higher frequencies with decreasing temperature. This common behaviour of the THz spectra is as a result of the anharmonicity of the shallow low vibrational potentials associated with the low frequency modes [25]. The rates of change of the frequencies were (2.9, 2.0, 5.4, 5.6 and 2.8) $\times 10^{-2} \text{cm}^{-1}/\text{K}^{-1}$ for lines *A*, *B*, *C*, *D* and *F* respectively. The rates of change are in the linear approximation of temperature change. Some of the absorption peaks show an abnormal behavior in the change of width with temperature. Usually the width of the lines decreases with cooling but a fluctuation in the width is observed for some of the absorption peaks. The strength of the peaks which usually intensifies as the temperature goes down also fluctuates for some of the absorption peaks. This behavior has been previously attributed to absorption peaks being composite [26, 27]. In addition, benzoic acid has been found to undergo transition from one structure to another with change in temperature [28, 29] and thus the anomalous behavior is further attributed to structural transitions. Line *E* appeared only at 9.5 K and hence the analysis done for the other absorption peaks was not plausible. An attempt to describe or assign the observed absorption peaks was made. This task revealed that some of the peaks were composite. Peak denoted *C* was made up of two theoretical peaks which lied at 2.75 and 2.76 THz. These peaks shared the same vibration which is the out of plane rocking of the monomers along C1-C4 line (carbons counted clockwise from COOH). Absorption peak descriptions are presented in Table 3.

4. Conclusion

Temperature dependence analysis of the spectrum of benzoic acid is presented. The observed frequencies display a blueshift with decrease in temperature. The rates of change of the absorption peaks which are in the approximation of linear temperature change lie in the range of (2–5.6) $\times 10^{-2} \text{cm}^{-1}/\text{K}^{-1}$. Some of the absorption peaks displayed an anomalous behavior in the change of both the width and intensity with temperature. This has been attributed to peaks being composite.

Despite slight frequency shifts, there was a good agreement between the theoretical model and the experiment. Model of benzoic acid crystal with PBEsol DFT functional proved to be better than the previously reported model in which NC-PBE DFT functional was used. A comparison was made between this study and another study where the Terahertz -Time Domain System was used. This study showed that the FTIR technique coupled with appropriate accessories is still a suitable tool for investigation of the low frequency THz spectra of materials.

Declarations

Author contribution statement

Lucia Malebogo Lepodise: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Funding statement

This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

Data availability statement

Data will be made available on request.

Declaration of interests statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

Acknowledgements

This work was supported by the Australian research council, the University of Wollongong and the Botswana International University of Science and Technology. Numerical modeling was performed at the University of Wollongong High Performance Computing Centre.

References

- [1] K. Kawase, H. Hoshina, Y. Sasaki, T. Shibuya, Mail screening applications of terahertz radiation, *Electron. Lett.* 46 (2010) 66–68.
- [2] J.B. Federici, B. Schulkin, F. Huang, D. Gary, R. Barat, F. Oliveira, D. Zimdars, THz imaging and sensing for security applications-explosives, weapons and drugs, *Semicond. Sci. Technol.* 20 (2005) S266–S280.
- [3] X.-C. Zhang, J. Xu, Introduction to THz Wave Photonics, Springer Science+Business Media, New York, LLC, 2010.
- [4] A.G. Davies, A.D. Burnett, W. Fan, E.H. Linfield, J.E. Cunningham, Terahertz spectroscopy of explosives and drugs, *Mater. Today* 11 (2008) 18–26.
- [5] M.C. Kemp, P.F. Taday, B.E. Cole, J.A. Cluff, A.J. Fitzgerald, W.R. Tribe, Security applications of terahertz technology, *Proc. SPIE* 5070 (2003) 1–10.

- [6] M.C. Kemp, Explosives detection by terahertz spectroscopy-A bridge too far? *IEEE Trans. Terahertz. Sci. Technol.* 1 (2011) 282–292.
- [7] E.V. Yakovlev, K.I. Zaytsev, I.N. Fokina, V.E. Karasik, S.O. Yurchenko, Non-destructive testing of polymer composite materials using THz radiation, *J. Phys. Conf. Ser.* 486 (2014), 012008.
- [8] P.U. Jepsen, S.J. Clark, Precise Ab-initio prediction of terahertz vibrational modes in crystalline systems, *Chem. Phys. Lett.* 442 (2007) 275–280.
- [9] Z. Zheng, W. Fan, B. Xue, Study on benzoic acid by THz- time-domain spectroscopy and density functional theory, *Chin. Optic Lett.* 9 (2011) S10506–1–S10506-3.
- [10] Y. Ueno, K. Ajito, Terahertz time domain spectra of aromatic carboxylic acids incorporated in nano-sized pores of mesoporous silicate, *Anal. Sci.* 23 (2007) 803–807.
- [11] Y. Kutuvantavida, G.V.M. William, E.M. Pogson, M.D.H. Bhuiyan, K. Radhanpura, R.A. Lewis, Material characterization at low frequencies using THz and Raman Spectroscopy. 37th International Conference on Infrared, Millimeter and Terahertz Waves (IRMMW-THz), University of Wollongong, Wollongong, NSW, Australia, 2012, pp. 23–28. September.
- [12] H. Yan, W.-H. Fan, Z.-P. Zheng, Investigation on terahertz vibrational modes of crystalline benzoic acid, *Optic Commun.* 285 (2012) 1593–1598.
- [13] G. Min, H.-W. Zhao, W.-F. Weng, X.-H. Yu, W.-X. Li, Substituent effects on the low frequency vibrational modes of benzoic acid and related compounds, *Chin. J. Chem.* 25 (2007) 272–277.
- [14] H.R. Zelsmann, Z. Mielke, Far infrared spectra of benzoic acid, *Chem. Phys. Lett.* 186 (1991) 501–508.
- [15] M. Walther, P. Plochocka, B. Fischer, H. Helm, P.U. Jepsen, Collective vibrational modes in biological molecules investigated by terahertz time-domain spectroscopy, *Biopolymers (Biospectroscopy)* 67 (2001) 310–313.
- [16] M. Takahashi, Y. Kawazoe, Y. Ishikawa, H. Ito, Interpretation of temperature dependent low frequency vibrational spectrum of solid-state benzoic acid dimer, *Chem. Phys. Lett.* 479 (2009) 211–217.
- [17] N. Laman, S.S. Harsha, D. Grischkowsky, Narrow-line waveguide terahertz time-domain spectroscopy of aspirin and aspirin precursors, *Appl. Spectrosc.* 62 (2008) 319–326.
- [18] R. Khan, M. Usman, A comparative study of physical and chemical method for separation of benzoic acid from industrial waste stream, *J. Adv. Chem. Eng.* 7 (2016) 1–11.
- [19] A. del Olmo, J. Calzada, M. Nunez, Benzoic acid and its derivatives as naturally occurring compounds in foods and as additives: uses, exposure, and controversy, *Crit. Rev. Food Sci. Nutr.* 57 (2017) 3084–3103.
- [20] P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Gavazzoni, D. Ceresoli, G.L. Chiarotti, M. Cococcioni, I. Dabo, QUANTUM ESPRESSO: a modular and open-source software project for quantum simulations of materials, *J. Phys. Condens. Matter* 21 (2009) 395502.
- [21] J.P. Perdew, A. Ruzsinszky, G.I. Csonka, O.A. Vydrov, G.E. Scuseria, L.A. Constantin, X. Zhou, K. Burke, Restoring the density-gradient expansion for exchange in solids and surface, *Phys. Rev. Lett.* 100 (2008) 136406.
- [22] The pseudopotentials C.pbe-mt_fhi.UPF, O.pbe-mt_fhi.UPF and H.pbe-mt_fhi.UPF, From, <http://www.quantum-espresso.org>.
- [23] M. Dion, H. Rydberg, E. Schroder, D.C. Langreth, B.I. Lundqvist, Van der Waals density functional for general geometries, *Phys. Rev. Lett.* 92 (2004) 246401.
- [24] T. Thonhauser, V.R. Cooper, S. Li, A. Puzder, P. Hyldgaard, D.C. Langreth, Van der Waals density functional: self-consistent potential and the nature of the van der Waals bond, *Phys. Rev. B* 76 (2007) 125112.
- [25] M. Franz, B.M. Fischer, M. Walther, Probing structure and phase-transitions in molecular crystals by terahertz time-domain spectroscopy, *J. Mol. Struct.* 1006 (2011) 34–40.
- [26] L.M. Lepodise, J. Horvat, R.A. Lewis, Collective librations of water molecules in the crystal lattice of rubidium bromide: experiment and simulation, *Phys. Chem. Chem. Phys.* 15 (2013) 20252–20261.
- [27] L.M. Lepodise, Low frequency terahertz spectrum of acetylsalicylic acid over a wide temperature range investigated by FTIR spectroscopy, *Spectrochim. Acta A* 217 (2019) 35–38.
- [28] M.A. Neumann, S. Craciun, A. Corval, M.R. Johnson, A.J. Horsewill, V.A. Bendetskii, H.P. Trommsdorff, Proton dynamics and the tautomerization potential in benzoic acid crystals, *J. Phys. Chem.* 102 (1998) 325–334.
- [29] S. Hayashi, J. Umemura, Disappearances of COOH infrared bands of benzoic acid, *J. Chem. Phys.* 60 (1974) 2630.