



# Benzoic acid derivatives under pressure: a Raman spectroscopic overview

C MURLI<sup>1,2,\*</sup>, A K VERMA<sup>1,2</sup> and T SAKUNTALA<sup>1,2</sup>

<sup>1</sup>High Pressure and Synchrotron Radiation Physics Division, Bhabha Atomic Research Centre, Mumbai 400 085, India

<sup>2</sup>Homi Bhabha National Institute, Mumbai 400 094, India

\*Author for correspondence (cmurli@barc.gov.in)

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**Abstract.** Benzoic acid derivatives display diverse physical properties depending upon the nature and position of the functional groups. The presence of non-bonded interactions that come into play because of various functional groups in these materials is discussed with the help of density functional theory calculations and Raman spectroscopic studies at ambient conditions and slightly elevated pressures.

**Keywords.** Benzoic acid derivatives; salicylic acid; benzoic acid; o-phthalic acid; Raman; DFT.

## 1. Introduction

Benzoic acid (BA) derivatives are extensively employed in co-crystal engineering for materials research and pharmaceutical applications [1]. Owing to their importance in industries, these compounds have been extensively studied using experimental and computational techniques with a view of understanding the structure–property relations [2], non-bonded interactions that are weaker than the O–H...O hydrogen bonds [3,4], possible polymorphism [5], etc. Introduction of another functional group and its position is found to systematically influence the physical and chemical properties [6] in the substituted BA systems. Among the functional groups, the OH and COOH substituted compounds are widely researched towards understanding several inter- and even intra-molecular interactions. It is often noted that additional non-bonded interactions need to be considered for providing an accurate description of the structure and vibrational properties [7,8]. In this regard, vibrational spectroscopy is very useful in studying the influence of weak interactions in the crystalline phase.

Tuning of interactions in a controlled manner under the application of pressure is often used as a tool to get better insight into various interactions, particularly the weak interactions. Among other pressure-induced effects, polymorphic transitions particularly at very low pressure of less than 1–2 GPa is of particular interest in pharmaceutically relevant compounds, as stresses of this magnitude are often encountered in the process of pelletizing/tableting [9].

Using Raman spectroscopic studies and density functional theory (DFT) calculations, we have studied the high pressure behaviour of the –OH and –COOH substituted BA derivatives with a view to understand the influence of weak, non-bonded interactions in BA derivatives. In this paper, the (ambient) Raman spectra of two of the ortho-substituted BA, namely salicylic acid (SA; 1, 2-hydroxybenzoic acid) and o-phthalic acid (PA; 1, 2-carboxybenzoic acid), are compared and briefly discussed. Results of the high pressure Raman spectroscopic work on PA up to about 1 GPa are presented and compared with those of BA and SA.

## 2. Experimental and theoretical details

Polycrystalline samples of PA, purchased from Sigma-Aldrich Co., with >99.5% purity was loaded in a hole of a diameter of size ~100 μm of a stainless-steel gasket, which was pre-indented to a thickness of ~60 μm in a symmetric type of diamond anvil cell (DAC). Experiments were carried out without a pressure transmitting medium to avoid any interaction of the sample with the medium, and pressure was monitored using ruby fluorescence methods. The Raman spectrum was excited using the 514.5 nm wavelength of Argon (Ar<sup>+</sup>) ion laser. All measurements were recorded in the backscattering geometry using T64000 Raman spectrometer operated in single spectrograph mode along with an edge filter. Quantum mechanical calculations were carried out within the framework of DFT, as implemented in the Quantum-ESPRESSO package [10]. The exchange-correlation energy functional was approximated within the generalized gradient scheme of the Perdew-

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Burke-Ernzerhof (GGA-PBE) [11]. Troullier-Martins norm-conserving pseudopotentials for H, C and O were adopted from the database of the package. Plane-wave basis set was constructed using an energy cutoff of 120 eV. First the crystal structure was fully optimized at chosen pressure and then the optimized structure was used to calculate the Raman spectrum using the density functional perturbation theory, as implemented in the code. The dispersive corrections were treated within the framework of non-local van der Waals (vdW) DFT, as implemented in the code [12–16]. These corrections are known to show significant contributions to the calculated properties of the molecular solids [12–16].

### 3. Results and discussion

#### 3.1 Structure and DFT calculations

All three compounds, BA, SA and phthalic acid (PA), crystallize in a centrosymmetric structure. Figure 1 shows the crystal structure and the typical hydrogen bonding. In the case of BA, the linear O–H...O hydrogen bonding between the two molecules leads to a centrosymmetric dimer structure [17]. In the case of SA, the nearly linear O–H...O (179°) h-bond between the two molecules stabilizes the dimer structure; however, this intermolecular h-bonding is weakened by the intra-molecular h-bonding [7]. In addition, two C–H...O interactions also have been identified to be significant. In the case of PA, the COOH groups are not co-planar with the benzene ring; the neighbouring molecules are linked by O–H...O hydrogen bonds to form an infinite zig-zag chain [8]. Interestingly, in PA, besides the h-bonding, several weak interactions (as many as 11) have been identified to contribute to the total crystal energy as well as the crystal structure [8].

Table 1 lists the experimental and computed lattice parameters with and without vdW correction for BA derivatives. It is apparent from the results that GGA-PBE is inadequate to reproduce the lattice parameters accurately and because of the highly anisotropic arrangement of constituent molecules in the crystal lattice, the mismatch between theoretical and experimental values is not uniform. While mismatch of the lattice parameters reduces considerably with the addition of vdW interactions, the persistence

**Table 1.** Experimental and computed lattice parameters with and without van der Waals (vdW) corrections for benzoic acid derivatives.

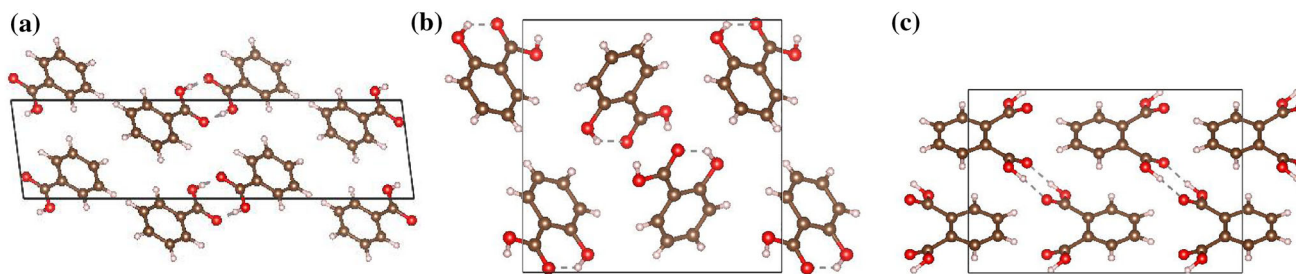
	Experiment	GGA-PBE	GGA-PBE + vdW
<i>Salicylic acid</i>			
<i>a</i> (Å)	11.520	12.623 (+9.6%)	11.647 (+1%)
<i>b</i> (Å)	11.210	11.479 (+2.4%)	11.336 (+1%)
<i>c</i> (Å)	4.920	5.214 (+6%)	4.992 (+1.5%)
$\beta$ (°)	90.83	96.517 (+6.3%)	91.02 (+0.2%)
<i>V</i> (Å <sup>3</sup> )	635.30	750.607 (+18%)	658.97 (+3.7 %)
<i>Benzoic acid</i>			
<i>a</i> (Å)	5.500	5.807 (+5.6%)	5.486 (+0.2%)
<i>b</i> (Å)	5.1570	5.380 (+4.3%)	5.189 (+0.6%)
<i>c</i> (Å)	21.973	23.078 (+5%)	22.261 (+1.3%)
$\beta$ (°)	97.410	94.96 (–2.5%)	97.95 (+0.5%)
<i>V</i> (Å <sup>3</sup> )	619.151	718.278 (+16%)	627.670 (+1.4%)
<i>O-phthalic acid</i>			
<i>a</i> (Å)	5.058	6.091 (+20%)	5.108 (+1%)
<i>b</i> (Å)	14.287	14.314 (+0.2%)	14.441 (+1%)
<i>c</i> (Å)	9.609	10.112 (+5%)	9.788 (+1.8%)
$\beta$ (°)	93.270	100.424 (+7.7%)	93.21 (+0.07%)
<i>V</i> (Å <sup>3</sup> )	693.251	867.09 (+25%)	720.92 (+4%)

of a relatively larger error in the computed volume for SA and PA in comparison to BA reveals that additional interactions have come into play due to the introduction of functional groups in BA. As vdW interactions describe the cell parameters fairly well, the phonon spectrum was computed with vdW corrections.

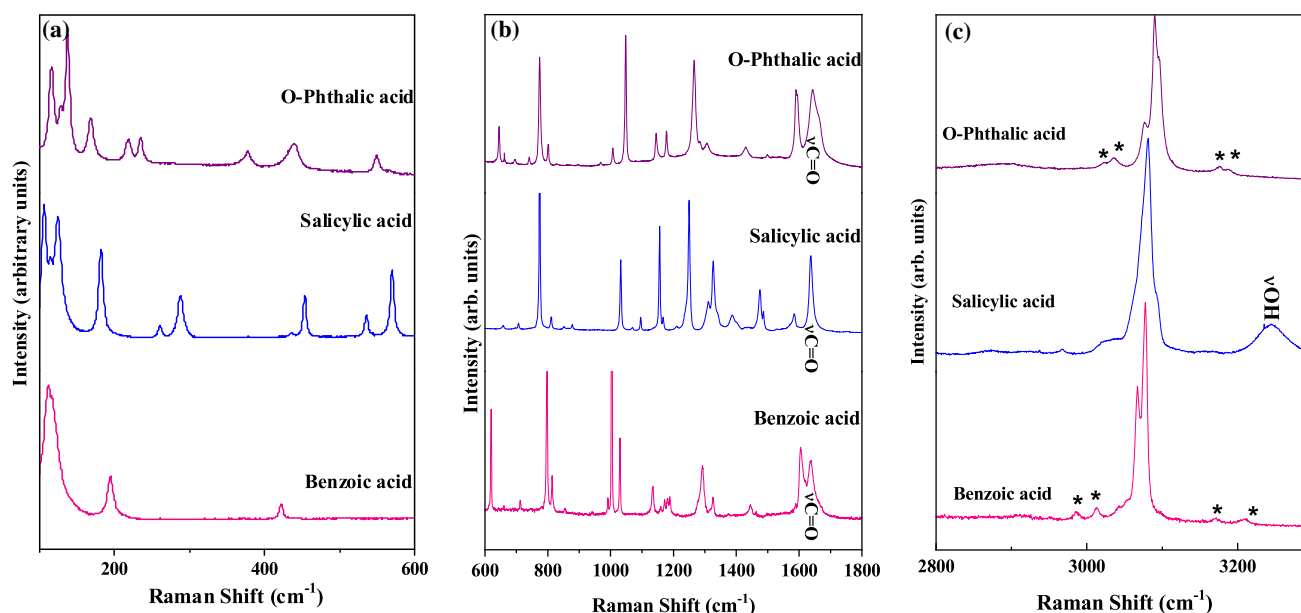
#### 3.2 Vibrational spectrum

The Bravais cell in the case of BA and SA has four molecules per unit cell, while that of PA has 2 molecules per unit cell. Consequently, including acoustic phonons, a total of 180, 192 and 108 phonons are expected in BA, SA and PA, respectively. Due to the mutual exclusion of the Raman and IR modes, nearly half the number of modes is IR active. The mode frequencies and assignment of the Raman spectra of all three compounds in the present work agree well with that reported for BA [18], SA [19] and PA [20].

Figure 2a–c shows the spectrum of the three compounds under ambient conditions. Though a larger



**Figure 1.** Crystal structure of (a) benzoic acid, (b) salicylic acid and (c) o-phthalic acid.



**Figure 2.** Raman spectra of benzoic acid, salicylic acid and o-phthalic acid at ambient conditions: (a) 100–600  $\text{cm}^{-1}$ , (b) 600–1800  $\text{cm}^{-1}$  and (c) 2800–3300  $\text{cm}^{-1}$ . \* denotes combination bands.

number of Raman modes are expected for BA and SA, a much lesser number of distinct modes are actually observed owing to smaller Davydov splitting. This is also confirmed by the DFT calculations, wherein the mode separation was noted to be less than  $2 \text{ cm}^{-1}$ , too close to be observed as a distinct mode. Due to the second functional group, one may note that a number of additional modes in the CH deformational regions are observed in SA and PA as compared to the spectrum of BA [18–20]. As shown in figure 2b, the spectral feature of C=O modes in BA and PA have some similarities, having two overlapping bands with one of them appearing as a rather broad shoulder. In the spectral region of C–H stretching modes ( $\sim 3070 \text{ cm}^{-1}$ ), while only two distinct modes are observed in BA, there are four closely spaced bands in SA and PA, which appear better resolved at lower temperatures. While Raman mode associated with OH stretch is not observable in both BA and PA, in the case of SA, a distinct OH stretch mode (figure 2c) is observed and provides insight into the nature of the intramolecular hydrogen bond.

Most of the computed Raman frequencies, particularly those of the ring deformational modes, agreed with the experimentally observed spectrum with less than 1% deviation; however, a larger deviation was noted in the C=O stretching modes. Table 2 shows the experimental and computed values of some of these modes that show larger deviation. As one can see from figure 3 and table 2, the difference in the computed (red-coloured bars) and experimental carbonyl and C–H stretching Raman modes of PA also indicates that more non-bonded interactions

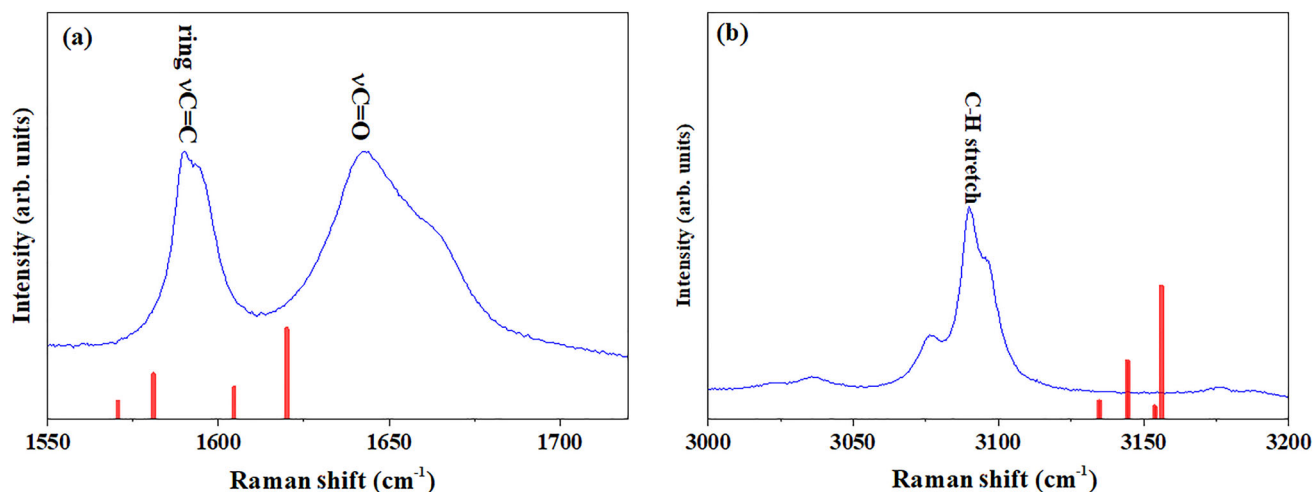
**Table 2.** Comparison of experimental and computed C=O, C=C and C–H stretch modes.

Theory	Experiment	Deviation	Mode
1571	1590	1.2%	$\nu\text{C}=\text{C}$ ring
1581	1594	0.8%	$\nu\text{C}=\text{C}$ ring
1605	1640	2.1%	$\nu\text{C}=\text{O}$
1620	1662	2.59%	$\nu\text{C}=\text{O}$
3135	3078	1.37%	$\nu\text{C}-\text{H}$
3145	3090	1.7%	$\nu\text{C}-\text{H}$
3154	3098	1.77%	$\nu\text{C}-\text{H}$
3156			

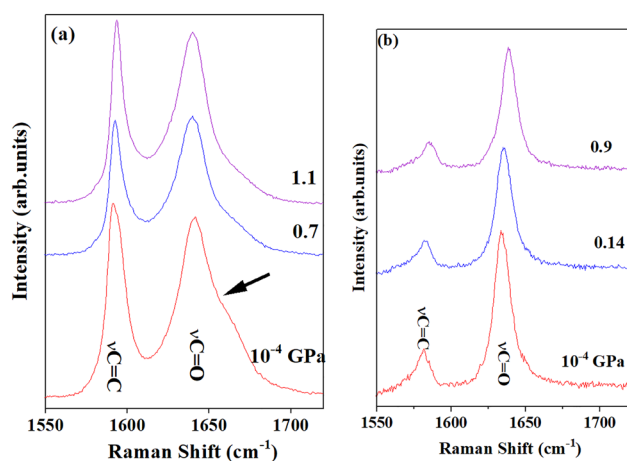
would be needed for a more accurate theoretical modelling.

### 3.3 High pressure behaviour

Figure 4 gives Raman spectra of PA and SA at ambient conditions and at slightly elevated pressures. It is noted that the relative intensity of a shoulder mode of carbonyl stretch and ring C=C stretch as well as C=O stretch reduces considerably at a very low pressure of 0.5 GPa, and at further high pressures it becomes indiscernible. Similar behaviour of carbonyl stretch modes is also noted for BA at comparable pressures [21]. It is of interest to note that such a spectroscopic behaviour of BA has been



**Figure 3.** Experimental and computed Raman modes of o-phthalic acid; (a) 1550–1720  $\text{cm}^{-1}$ ; (b) 3000–3200  $\text{cm}^{-1}$ ; red-coloured bars show theoretical values.



**Figure 4.** Raman modes of (a) o-phthalic acid; (b) salicylic acid in the spectral region 1550–1720  $\text{cm}^{-1}$  at various pressures.

investigated extensively using low temperature infrared and neutron diffraction studies, which interpret them to be due to the presence of two O–H–O configurations of the carboxyl dimer that exist only at ambient conditions [22,23]. However, SA does not exhibit such behaviour, as there are no discernable differences in the carbonyl region and thus indicating that the associated spectral changes in this compound are of a different nature [24]. In addition, high pressure spectroscopic studies on SA also indicate a possible transition around 1 GPa. Careful analysis of the evolution of Raman spectra of PA in the spectral region of C–H modes and external modes also show small but definite discontinuities around this pressure, implying a possible subtle transition around this pressure, and similar observations are noted for BA also. A close comparison of the spectral changes of the three systems suggests that the spectral changes observed at a pressure around 0.5 GPa in BA and PA are likely to be associated with the C=O of the  $-(\text{COOH})$ .

#### 4. Conclusion

Raman spectroscopic studies of PA and SA at ambient conditions and at slightly elevated high pressures along with DFT calculations at ambient pressures provide insight into the nature of non-bonded interactions in these materials. Such investigations are of importance for more accurate modelling of these hydrogen-bonded large molecular systems.

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#### References

- [1] Skovsgaard S and Bond A D 2009 *CrystEngComm* **11** 444
- [2] Amborabé B E, Lessard P F, Chollet J F and Roblin G 2002 *Plant Physiol. Biochem.* **40** 1051
- [3] Otero-De-la-Roza A, Johnson E R and Contreras-Garcia J 2012 *Phys. Chem. Chem. Phys.* **14** 12165
- [4] Surov A O, Manin A N, Voronin A P, Churakov A V, Perlovich G L and Vener M V 2017 *Cryst. Growth Des.* **17** 1425
- [5] Crowell E L, Dreger Z A and Gupta Y M 2015 *J. Mol. Struct.* **1082** 29
- [6] Bohm S, Fiedlerb P and Exner O 2004 *New J. Chem.* **28** 67
- [7] Munshi P and Guru Row T N 2006 *Acta Cryst.* **B62** 612
- [8] Zhurov V V and Pinkerton A A 2015 *Cryst. Growth Des.* **14** 5685
- [9] Rychko D A 2020 *Crystals* **10** 81
- [10] Giannozzi P, Andreussi O, Brumme T, Bunau O, Nardelli M B, Calandra M *et al* 2009 *J. Phys. Condens. Matter* **21** 1
- [11] Perdew J P, Burke K and Ernzerh M 1996 *Phys. Rev. Lett.* **77** 3865

- [12] Thonhauser T, Zuluaga S, Arter C A, Berland K, Schröder E and Hyldgaard P 2015 *Phys. Rev. Lett.* **115** 136402
- [13] Thonhauser T, Cooper V R, Shen L, Puzder A, Hyldgaard P and Langreth D C 2007 *Phys. Rev. B* **76** 125112
- [14] Berland K, Cooper V R, Lee K, Schröder E, Thonhauser T, Hyldgaard P *et al* 2015 *Rep. Prog. Phys.* **78** 066501
- [15] Langreth D C, Lundqvist B L, Chakarova-Käck S D, Cooper V R, Dion M, Hyldgaard P *et al* 2009 *J. Phys. Condens. Matter* **21** 084203
- [16] Sabatini R, Küçükbenli E, Kolb B, Thonhauser T and Gironcoli S 2012 *J. Phys. Condens. Matter* **24** 424209
- [17] Feld R, Lehmann M S, Muir K W and Speakman J C 1981 *Z. Kristal.* **157** 215
- [18] Klsusberger G, Furil K and Colombo L 1977 *J. Raman Spectrosc.* **6** 277
- [19] VolovBek V, Colombo L and Furik K 1983 *J. Raman Spectrosc.* **14** 347
- [20] Colombo L, VolovBek V and LePostollec M 1984 *J. Raman Spectrosc.* **15** 252
- [21] Kang L, Wang K, Li X and Zou B 2016 *J. Phys. Chem. C* **120** 14758
- [22] Hayashi S, Oobatake M, Nakamura R and Machida K 1991 *J. Chem. Phys.* **94** 4446
- [23] Wilson C C, Shankland N and Florence A J 1996 *J. Chem. Soc. Faraday Trans.* **92** 5051
- [24] Mishra A K, Murli C, Pandey K K, Sakuntala T, Poswal H K and Verma A K 2020 *J. Phys. Chem. B* **124** 373