



Structural and vibrational properties of pentabromophenol and pentafluorophenol: A spectroscopic investigation using density functional theory

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ABSTRACT

Fourier Transform Raman and Fourier Transform infrared spectra were measured in the spectral range 3500–100 cm^{-1} and 4000–400 cm^{-1} , respectively, for Pentabromophenol (PBP) and Pentafluorophenol (PFP). Torsional potentials, optimized structure parameters, harmonic vibrational frequencies, general valance force field, potential energy distribution (PED), along with infrared and Raman intensities were evaluated, for PBP and PFP. DFT was used in conjunction with B3LYP functional with 6–311++G (d,p) basis set, for the computations. Scaling process was employed to get a better fit between the measured and computed frequencies. The rms error between them was 9.7 and 7.0 cm^{-1} , for PBP and PFP, respectively. Unambiguous vibrational assignments were arrived at by using PED and eigenvectors. In order to substantiate the existence of inter-molecular hydrogen bond in these molecules geometry optimization was made for dimers of PBP and PFP, at the same level of theory as used for the monomers.

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1. Introduction

Pentabromophenol (PBP) is finding increasing applications in the fields of agriculture and pharmaceuticals, along with pentachlorophenol [1,2]. However, investigations on PBP, both experimental and theoretical, have been very limited. It was one of the nineteen bromophenols investigated theoretically for understanding molecular structure and property relationships [3]. A tentative account of all vibrational frequencies of PBP was given by Faniran for the first time [4]. He reported the vibrational fundamentals of Pentafluorophenol (PFP) also [5]. The structure of PBP, as determined from X-ray methods, is also available [6]. But no theoretical work on PBP and PFP is available from literature to the best of our knowledge. Hence, as a continuation of our recent work on Pentachlorophenol and Pentachlorothiophenol [7], we undertook this work with the following aims.

- To record FT-IR, and FT-Raman, spectra of PBP and PFP, and
- To perform DFT calculations on the molecules so as to,

- (i) identify the most stable rotational conformer by obtaining torsional potentials for various angles of rotation around the C–O bond,
- (ii) optimize equilibrium geometry for the stable rotational isomer and its dimer, and
- (iii) compute harmonic vibrational frequencies and their IR and Raman intensities.

2. Measurement of spectra

Pure sample of solid PBP was purchased from Tokyo Kasei Kogyo Co. Ltd, Japan, and that of PFP was obtained from Aldrich Chemical Company (USA). They were used, as such, for spectral measurements.

Fourier Transform IR (FT-IR) spectrum of PBP and PFP was recorded, in the spectral range 4000–400 cm^{-1} , using Nicolet-740 single beam spectrometer equipped with liquid nitrogen-cooled Deuterated Triglycine Sulphate (DTGS) detector, by diluting the sample in KBr pellet. As PFP was a liquid at room temperature, its spectrum was measured by squeezing in a thin film of unknown

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