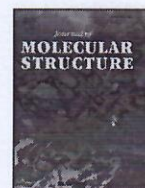




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Experimental and theoretical determination of structural and vibrational properties of pentachlorophenol and pentachlorothiophenol

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ABSTRACT

Fourier Transform Raman (3500–100 cm⁻¹) and Fourier Transform Infrared (4000–400 cm⁻¹) spectra were measured for Pentachlorophenol (PCP). Barrier to internal rotation, optimized geometry parameters, harmonic vibrational frequencies, along with Raman and infrared intensities were computed, for PCP and Pentachlorothiophenol (PCTP), using DFT and employing B3LYP functional with 6–311++G (d,p) basis set. Scaling was used for a better fit between the experimental and predicted frequencies. They agreed with rms error 8.4 and 7.6 cm⁻¹ for PCP and PCTP, respectively. A zero order normal coordinate analysis was made for PCP-OD, which is an isotopomer of PCP, by transferring the optimized force constants from PCP. This resulted in calculated frequencies that agreed with corresponding experimental frequencies with rms error 12.1 cm⁻¹. The vibrational assignments were made with the help of potential energy distribution (PED), eigenvectors, and frequency shifts expected on the basis of PED in PCP, and increased mass of deuterium and sulphur atoms. Geometry optimization was made for dimers of PCP and PCTP in order to lend theoretical support for the existence of bifurcated hydrogen bond in PCP and rule out such possibility for PCTP, at the same level of theory as used for the monomers.

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1. Introduction

Pentachlorophenol (PCP) is one of the nineteen possible congeners of substituted chlorophenols. It is known that PCP is hazardous to human health and ecosystem [1], as it is toxic and carcinogenic. In spite of this it found increasing applications in agriculture and pharmaceutical industries [2–7]. Hence PCP was extensively investigated with regard to nature of hydrogen bonding [8,9], phase transitions [9], vibrational spectra [10–14], and crystal structure [9,15]. It was one of the compounds investigated theoretically to understand the relationship between molecular structure and properties in a series of chlorophenols [16]. However vibrational spectroscopic investigations, reported by earlier investigators, in this regard have several deficiencies, unacceptable theoretical results, and hence not reliable (details are given in

section 5.4 on vibrational assignments). For example, Green et al. [10] and Faniran [11] disagree even on the tentative assignment of several fundamentals of PCP proposed by them on the basis of qualitative considerations; Czarnik-Matusiewicz et al. [13], employing quantum chemical calculations, identified seven C–C stretching vibrations in PCP, instead of six, where as Pawlukojc et al. [14] assigned seven out-of-plane (CCL) wagging modes, instead of five; more over authors of these publications [13,14] preferred to avoid inclusion of numerical values of potential energy distribution (PED), which is the most important result of any normal coordinate treatment, without which it is impossible to draw meaningful conclusions. Further, from a survey of literature on PCP, we found that, computed Raman spectrum is not available; there is no theoretical attempt to substantiate the existence of bifurcated hydrogen bond inferred by Sakurai [15] from an analysis of nuclear quadrupole resonance and X-ray spectra.

Hence we thought that it is worthwhile to revisit experimental and theoretical investigation of PCP to address the above shortcomings. To this end, we propose to

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