Electronic, NLO, and thermodynamic parameters and frontier molecular orbital investigation of pentafluoro phenol and pentachloro thiophenol with DFT approach

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Abstract. UV-Visible spectra of Pentafluoro phenol (PFP) and Pentachloro thiophenol (PCTP) were estimated with the help of time-dependent density functional theory. Frontier molecular orbital (FMO) approach was used to understand origin of UV-Vis spectra of the molecules. Molecular electrostatic potential (MESP) surfaces were drawn for PFP and PCTP, to establish regions of charge accumulation. Non-linear optical (NLO) parameters (e.g. hyperpolarizability,) were computed. Thermodynamic parameters of these molecules were also calculated.

1. Introduction

We reported results of our investigations on substituted phenols [1, 2] in the past. At present we are engaged with addressing problems associated with structure, vibrational properties, electronic characteristics, frontier molecular orbital (FMO) utility, NLO behavior and thermodynamic parameters using both experimental and theoretical (DFT) tools [3, 4], in addition to anticancer activity. Recently we reported structural and vibrational properties for pentachlorophenol (PCP) [5] and pentabromophenol [6]. However, results of UV-Vis spectra, FMO, NLO and thermodynamic analysis for PFP and PCTP are yet to appear in literature. In this article we report such results.

2. Computational considerations

Necessary calculations were accomplished by employing DFT, incorporated in Gaussian 09 package [7-9]. 6-311++G(d,p) basis set was used. Ultraviolet absorption spectrum arising from electronic transitions was estimated by density functional formalism with suitable modification for time dependence, with 6-311++G(d,p) basis set. Polarizable continuum model (PCM) addressed the effect of solvent, with the integral equation method [10-12] implemented in Gaussian 09 suit of programs. FMO properties and MESP were estimated by using suitable expressions [13-18]. With the help of finite field method [19] and DFT, we calculated the NLO properties of the chosen molecules.

The thermodynamic parameters were computed for PFP and PCTP at the same level of theory. A rigid-rotator harmonic approximation was assumed [20].

3. Results and Discussion
3.1 Electronic Properties

Here we present FMO from the point of view of understanding UV-Visible spectra of both PFP and PCTP. We wish to include MESP also here. Structure of PCTP and PFP determined in earlier articles [5, 6] is made available as Figure 1.

![Figure 1. Optimized molecular structure of PFP and PCTP](image)

3.2 Frontier molecular orbitals (FMO)

FMO is concerned with one electron excitations. Such excitations, for PFP and PCTP are shown in Figure 2. This can conveniently be used to explain UV-Visible spectra of molecules.

3.2.1 Ultraviolet signal

Simulated Ultraviolet signals originating from relevant transition are shown in Figure 3, for PFP and PCTP. As per computations, PFP and PCTP should have one electronic transition each, at $\lambda_{\text{max}} = 238.68$ nm with $f$ (strength of the oscillator) = 0.014, and $\lambda_{\text{max}} = 286.55$ nm with $f = 0.025$, respectively. Frontier molecular orbital study shows that the above simulated bands arise due to HOMO→LUMO transition. On analyzing molecular orbital coefficients, we find that HOMO→LUMO electronic transition corresponds to $n \rightarrow \pi^*$ excitation.

3.3 Molecular electrostatic potential (MESP) surface

MESP plots for both the molecules are shown in Figure 4. This reveals variations in charge distribution between different parts of the molecules. Following usual practice color code is used to indicate such differences. Red is employed to show relatively negative region and Green is used to mark relatively positive region. In PFP and PCTP negative regions occur mainly over F, Cl, O and S atomic sites, attributable to inherent lone pair electrons on them. Positive region is confined to the hydrogen atom.
Figure 2. Frontier molecular orbitals of PFP and PCTP.

Figure 3. Ultraviolet-Visible spectrum of PFP and PCTP

Figure 4. MESP plots for PFP and PCTP
3.4 NLO parameters
Interaction of electromagnetic radiation with NLO material results in a change of important propagation properties, of the incoming radiation (e.g. amplitude, phase, frequency), giving rise to new fields [21]. If these changes are significant then the NLO material may be used for optical-logic, switching, memory and frequency shifting [22 - 24]. NLO effects of a given material are decided by the value of its first order hyperpolarizability.

NLO behavior for a given compound is decided by comparing relevant quantities with those of Urea. For Urea $\beta_0$ is 372.8X10$^{-33}$ cm$^5$/e.s.u and $\mu_0$ is 1.3732 Debye; ($\beta$, hyper polarizability, $\mu$, is dipole moment ) calculated values of $\mu_0$ are 1.0511 and 0.4147 Debye and those of $\beta_0$ are 92.3649 X10$^{-33}$ and 134.738747 X10$^{-33}$ cm$^5$/e.s.u, respectively, for PFP and PCTP. These values are very low in comparison with those of Urea. Therefore, it can be concluded that PFP and PCTP are not useful as NLO compounds.

3.5 Thermodynamic parameters
Common thermodynamic parameters $C_p$, $C_v$ and entropy $S$ (38.81, 44.40; 36.83, 42.41 and 97.25, 112.44), for PFP and PCTP, were estimated, in cal mol$^{-1}$ K$^{-1}$. Zero point vibrational energy (39.99, 31.88 kcal mol$^{-1}$), total thermal energy (46.27, 39.57 kcal mol$^{-1}$) and self-consistent field energy (-803.85 and -2928.60 Hartree) were computed, for PFP and PCTP.

4. Conclusions
Estimated values of UV-Visible spectra, FMO parameters and thermodynamic functions are now available for PFP and PCTP.

5. References
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