

**AJP**

ISSN : 0971 - 3093

Vol 24, No 5, May, 2015

# ASIAN JOURNAL OF PHYSICS

**An International Quarterly Research Journal**



**ANITA PUBLICATIONS**

FF-43, 1st Floor, Mangal Bazar, Laxmi Nagar, Delhi-110 092, India  
B O : 2, Pasha Court, Williamsville, New York-14221-1776, USA



## Structural and vibrational studies of some pesticides: 2-chlorophenol, 2,4,6-trichlorophenol and pentachlorophenol

V Dixit and R A Yadav\*

*Spectroscopy Laboratory, Department of Physics,  
Banaras Hindu University, Varanasi -221 005, India*

Dedicated to Prof J R Durig

Structural and vibrational investigations of fungicide molecules, namely, 2-chlorophenol (2-CP), 2,4,6-trichlorophenol (TCP) and 2,3,4,5,6-pentachlorophenol (PCP) have been carried out using the DFT (B3LYP) method employing the 6-311++G\*\* basis set available with Gaussian-09 software for the optimized structure of the most stable conformers, if any. The vibrational assignments of the observed IR and Raman bands have been proposed in the light of the results of the DFT computations and the PEDs computed using GAR2PED software. The optimized geometrical structures have overall symmetry as Cs for all the molecules. © Anita Publications. All rights reserved.

**Keywords:** Pesticides, Chlorophenols, Molecular structures, Quantum chemical calculations, Potential energy distributions.

### 1 Introduction

Vibrational (IR and Raman) spectroscopic techniques have become essential tools in modern research fields. These techniques involve wide variety of interesting basic and reasonable concepts, ranging from their applications in material characterization to biomedicines [1, 2]. Because of their fast and non-invasive nature the vibrational spectroscopic techniques have an immediate application in the research fields of biology, material science, agriculture, medicines etc. These techniques provide us easy visualization of the cellular components based on their intrinsic characteristics and the chemical composition, and also result in the potential route to obtain the diagnostic markers for the diseases [3-6].

Sometimes bacteria are able to grow in environments and very often display remarkable biodegradation properties [7]. A large number of bacteria have been isolated that could be used for the bioremediation of the chlorinated compounds [8-10]. Chlorophenols are of widespread environmental concern because of their toxicity, persistence and environmental recalcitrance. In humans, the exposure to phenoxy herbicides, chlorophenols, and dioxins has been linked with excess overall cancer risk and excess risks of soft-tissue sarcoma, non-Hodgkin's lymphoma, and other cancers [11-14]. The evidences, particularly from the case-control studies, have been found inconsistent [15].

The chlorophenols falls in the family of weak acids in aqueous solution. One of the essential factors affecting environmental transport, degradation and toxicity is the degree of dissociation of the material in the natural water [13, 14, 16]. With the acidic nature, chlorophenols exist primarily in the toxic molecular (undissociated) form, while under the basic conditions, the dissociated form predominates. These compounds exist predominately in more active and undissociated form with increasing acidic nature. The proportion of the molecules in the undissociated state increases further, leading to yet higher activity, such as adsorption to suspended solids and sediments and toxicity [16-18]. Chlorophenols are susceptible to photolysis, expected to be a significant process near the surface of the water bodies (especially in the summer) and biodegradation. Photolysis of polychlorinated phenols appears to be higher than for the mono-chlorinated congeners [17-18]. The toxicity of chlorophenols to aquatic organisms increases with increasing degree of chlorination and substitution away from the OH functional group because the close proximity of the ortho-substituted chlorine to the OH group on the molecule appears to shield the OH group, which in turn, interacts with the active site in aquatic organisms, causing the observed toxic effects. The higher toxicity of more chlorinated congeners can be ascribed to an increase in the lipophilicity which leads to a greater potential for the uptake into the

*Corresponding author:*

*e-mail: [rayadav@bhu.ac.in](mailto:rayadav@bhu.ac.in), [ray1357@gmail.com](mailto:ray1357@gmail.com); Tel: +91 542 2368593; fax: +91 542 2368390. (R A Yadav)*

organism [19]. The toxicity of the compounds also depends on the extent of dissociation in the exposure medium of the chlorophenols, the increasing toxicity is observed with decrease in pH value of the compound. This is due to the fact that more toxic non-dissociated form predominates at the lower pH value while at the higher pH values less toxic dissociated form is predominant [16-20].

In the present article DFT calculations have been carried out for the optimized geometries, APT and Mulliken atomic charges, the fundamental vibrational wavenumbers along with their intensities in the IR spectrum, Raman activities and the depolarization ratios of the Raman lines using the B3LYP/6-311++G\*\* method [21-25] available with Gaussian-09 software [26] for the most stable conformer of each of the molecules of interest. The experimental IR and Raman spectral data have been taken from ref. [27] and interpreted in light of the calculated fundamentals and the corresponding PEDs calculated using the GAR2PED software [28]. To compute the PEDs the vibrational problems were set up in terms of the internal coordinates. HOMO–LUMO, total density plots, molecular electrostatic potentials (MEPs) surfaces and corresponding arrays have been analysed and the natural bond orbital (NBO) analysis as well as the analysis of the NMR spectra have also been carried out.

## 2 Computational details

In order to optimize the geometrical structures of the pesticide molecules under the present study we first optimized the benzene molecule using the B3LYP/6-311++G\*\* method available with the Gaussian 09 software as elaborated in ref. [29]. Then replacing one of the H atoms of the ring by OH group, the resulting structure was optimized. Now replacing the H atom of the ortho - position of the OH group in phenol by Cl atom optimization was carried out resulting in the optimized structure of 2-CP which has two different conformers (Fig 1), the conformer C-1 being more stable. By replacing the H atoms at the positions 4 and 6 in the ring of 2-CP by Cl atoms optimized geometry of 2,4,6-trichlorophenol (TCP) was obtained and similarly by replacing the remaining H-atoms in the ring of the TCP by Cl-atoms optimized geometry (Fig 2) of 2,3,4,5,6-pentachlorophenol (PCP) was obtained. Table 1 presents the electronic, different types of thermal and zero point energies of the concerning molecules. PCP is the most stable molecule amongst the molecules under consideration.

Table 1. Energies of the studied molecules.

Energy Type	Unit	2-CP		2,4,6-TCP	2,3,4,5,6-PCP
		C-1	C-2		
E <sub>el</sub>	Hartree (a.u.)	-767.182817	-767.177893	-1686.420146	-2605.642449
	Kcal/mole	-481414.59	-481411.50	-1058244.84	-1635065.67
	eV	-20876.12	-20875.98	-45889.85	-70903.18
E <sub>0</sub>	Hartree (a.u.)	0.094909	0.094691	0.075747	0.056341
	Kcal/mole	59.56	59.42	47.53	35.35
	eV	2.58	2.58	2.061	1.53
E <sub>Th</sub>	Hartree (a.u.)	0.101537	0.101440	0.084845	0.067930
	Kcal/mole	63.72	63.65	53.24	42.63
	eV	2.76	2.76	2.31	1.85
E <sub>En</sub>	Hartree (a.u.)	0.102481	0.102384	0.085789	0.068875
	Kcal/mole	64.31	64.25	53.83	43.22
	eV	2.79	2.79	2.33	1.87
E <sub>Gib</sub>	Hartree (a.u.)	0.063786	0.063431	0.040352	0.017249
	Kcal/mole	40.03	39.80	25.32	10.82
	eV	1.74	1.73	1.098	0.47

	Hartree (a.u.)	-766.820184	-766.815947	-1686.133412	-2605.432054
$E_{\text{Net}}$	Kcal/mole	-481187.03	-481184.37	-1058064.92	-1634933.65
	eV	-20866.25	-20866.14	-45882.049	-70897.45

$E_0$  – Zero point energy,  $E_{e\Gamma}$  – Electronic Energy,  $E_{\text{Th}}$  – Thermal Energy,  $E_{\text{En}}$  – Enthalpy,  $E_{\text{Gib}}$  – Gibb's Free Energy,  $E_{\text{Net}}$  – Net Energy.

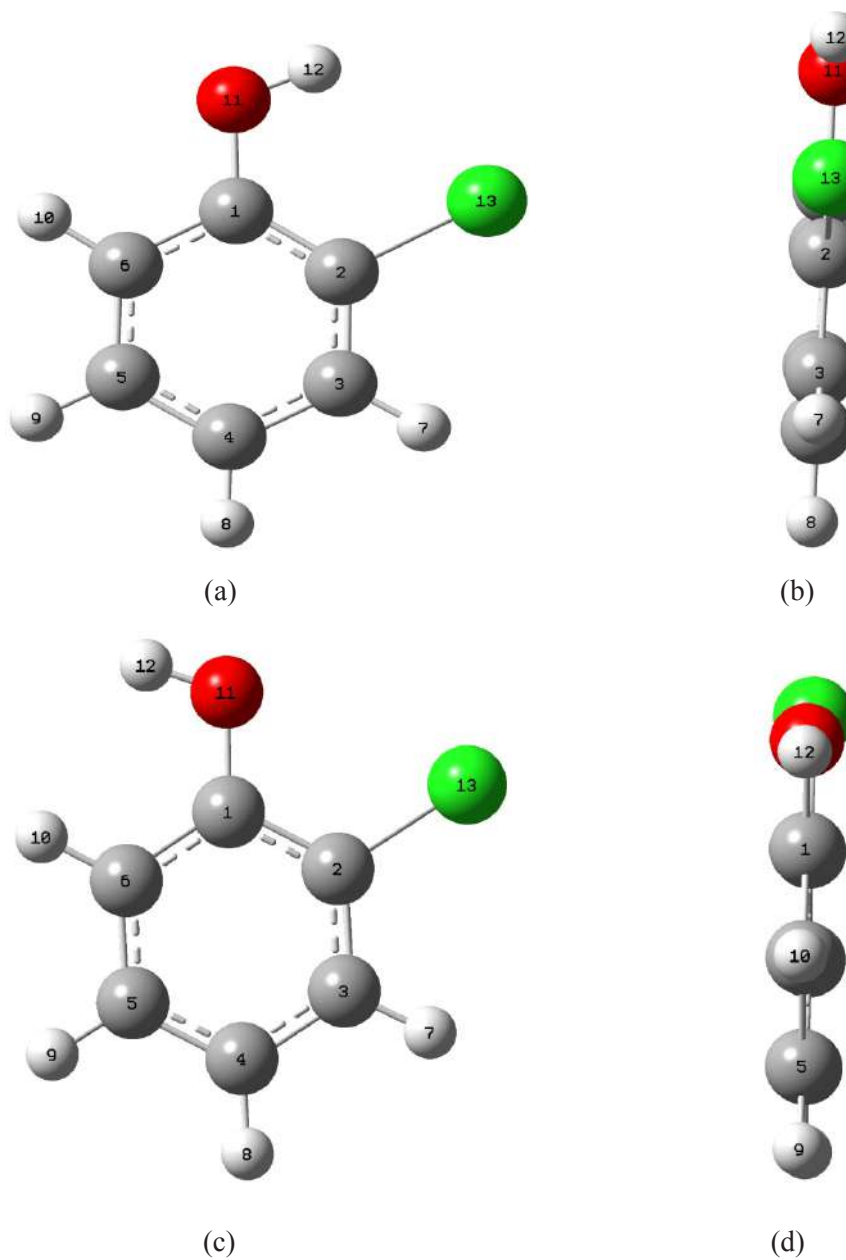


Fig 1. Optimized structures of the two conformers of 2-CP.

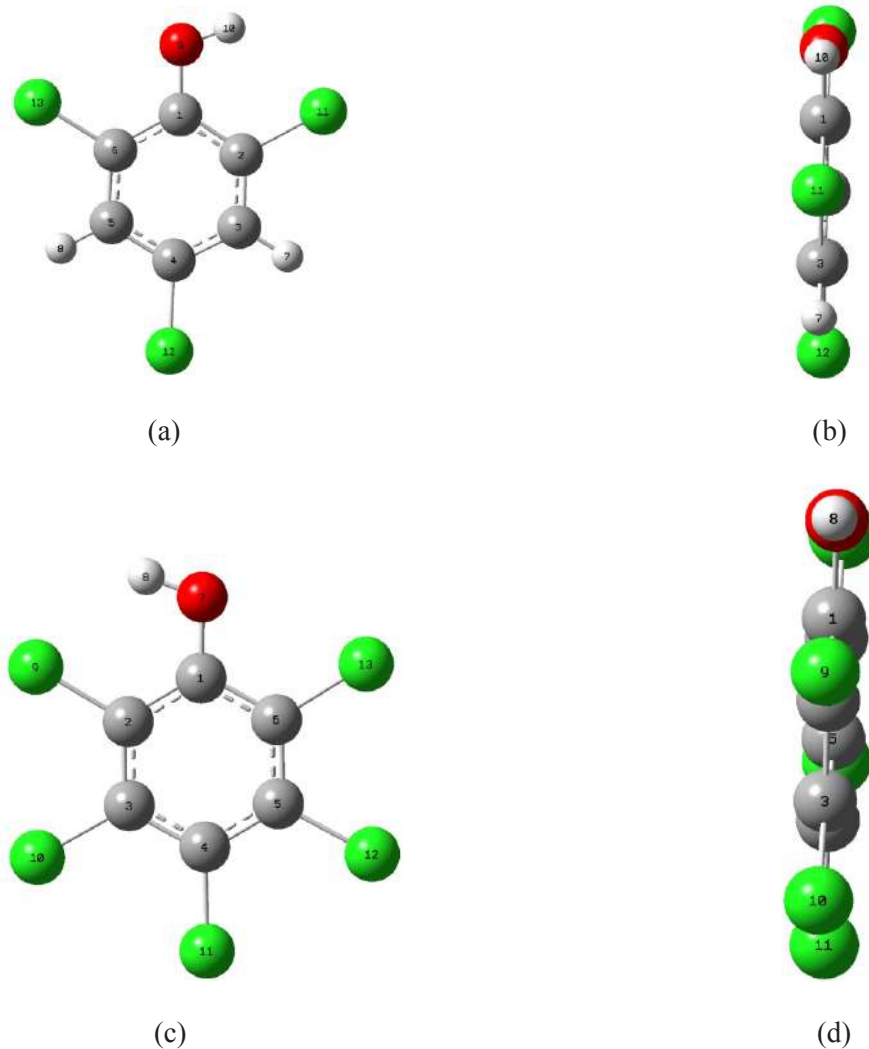


Fig 2. Optimized Structures of TCP and PCP.

### 3 Results and Discussion

#### 3.1. Molecular geometries

The geometrical parameters of 2-CP (C-1 & C-2), TCP and PCP have been computed at the B3LYP/6-311G\*\* level and these are collected in Table 2. The optimized geometrical structures of all the present molecules have overall  $C_s$  symmetry; therefore, all the atoms in a structure of any molecule lie in same plane. All the bond lengths, except  $C_2-Cl_{13}$ ,  $C_4-C_5$  and  $O_{11}-H_{12}$ , are either comparable or shorter in C-1 than those of C-2 of 2-CP. All the bond angles, except  $\alpha(C_2-C_1-O_{11})$  and  $\alpha(C_6-C_1-O_{11})$ , are comparable in the two conformers of 2-CP, while the prior is larger and later is smaller by  $\sim 4.5^\circ$  in C-1 than those of C-2 of 2-CP. Taking into account the above considerations, a signature of intramolecular H bonding appears to occur in the most stable conformer (C-1) of 2-CP.

Table 2. Optimized geometrical parameters of 2-CP, TCP and PCP

Parameters	Values		Parameters	Values	Parameters	Values
	C-1	C-2				
r (C <sub>1</sub> -C <sub>2</sub> )	1.400	1.401	r (C <sub>1</sub> -C <sub>2</sub> )	1.401	r (C <sub>1</sub> -C <sub>2</sub> )	1.400
r (C <sub>1</sub> -C <sub>6</sub> )	1.397	1.397	r (C <sub>1</sub> -C <sub>6</sub> )	1.402	r (C <sub>1</sub> -C <sub>6</sub> )	1.401
r (C <sub>1</sub> -O <sub>11</sub> )	1.357	1.361	r (C <sub>1</sub> -O <sub>9</sub> )	1.349	r (C <sub>1</sub> -O <sub>7</sub> )	1.347
r (C <sub>2</sub> -C <sub>3</sub> )	1.390	1.391	r (C <sub>2</sub> -C <sub>3</sub> )	1.389	r (C <sub>2</sub> -C <sub>3</sub> )	1.397
r (C <sub>2</sub> -Cl <sub>13</sub> )	1.765	1.751	r (C <sub>2</sub> -Cl <sub>11</sub> )	1.758	r (C <sub>2</sub> -Cl <sub>9</sub> )	1.748
r (C <sub>3</sub> -C <sub>4</sub> )	1.392	1.393	r (C <sub>3</sub> -C <sub>4</sub> )	1.389	r (C <sub>3</sub> -C <sub>4</sub> )	1.400
r (C <sub>3</sub> -H <sub>7</sub> )	1.083	1.083	r (C <sub>3</sub> -H <sub>7</sub> )	1.081	r (C <sub>3</sub> -Cl <sub>10</sub> )	1.735
r (C <sub>4</sub> -C <sub>5</sub> )	1.396	1.393	r (C <sub>4</sub> -C <sub>5</sub> )	1.391	r (C <sub>4</sub> -C <sub>5</sub> )	1.404
r (C <sub>4</sub> -H <sub>8</sub> )	1.083	1.083	r (C <sub>4</sub> -Cl <sub>12</sub> )	1.754	r (C <sub>4</sub> -Cl <sub>11</sub> )	1.737
r (C <sub>5</sub> -C <sub>6</sub> )	1.389	1.392	r (C <sub>5</sub> -C <sub>6</sub> )	1.389	r (C <sub>5</sub> -C <sub>6</sub> )	1.398
r (C <sub>5</sub> -H <sub>9</sub> )	1.084	1.084	r (C <sub>5</sub> -H <sub>8</sub> )	1.081	r (C <sub>5</sub> -Cl <sub>12</sub> )	1.735
r (C <sub>6</sub> -H <sub>10</sub> )	1.083	1.086	r (C <sub>6</sub> -Cl <sub>13</sub> )	1.744	r (C <sub>6</sub> -Cl <sub>13</sub> )	1.734
r (O <sub>11</sub> -H <sub>12</sub> )	0.967	0.963	r (O <sub>9</sub> -H <sub>10</sub> )	0.967	r (O <sub>7</sub> -H <sub>8</sub> )	0.968
α (C <sub>2</sub> -C <sub>1</sub> -C <sub>6</sub> )	118.4	118.8	α (C <sub>2</sub> -C <sub>1</sub> -C <sub>6</sub> )	117.2	α (C <sub>2</sub> -C <sub>1</sub> -C <sub>6</sub> )	119.0
α (C <sub>2</sub> -C <sub>1</sub> -O <sub>11</sub> )	123.2	118.5	α (C <sub>2</sub> -C <sub>1</sub> -O <sub>9</sub> )	123.5	α (C <sub>2</sub> -C <sub>1</sub> -O <sub>7</sub> )	122.7
α (C <sub>6</sub> -C <sub>1</sub> -O <sub>11</sub> )	118.3	122.7	α (C <sub>6</sub> -C <sub>1</sub> -O <sub>9</sub> )	119.3	α (C <sub>6</sub> -C <sub>1</sub> -O <sub>7</sub> )	118.3
α (C <sub>1</sub> -C <sub>2</sub> -C <sub>3</sub> )	121.5	120.5	α (C <sub>1</sub> -C <sub>2</sub> -C <sub>3</sub> )	122.5	α (C <sub>1</sub> -C <sub>2</sub> -C <sub>3</sub> )	121.2
α (C <sub>1</sub> -C <sub>2</sub> -Cl <sub>13</sub> )	118.4	119.6	α (C <sub>1</sub> -C <sub>2</sub> -Cl <sub>11</sub> )	117.9	α (C <sub>1</sub> -C <sub>2</sub> -Cl <sub>9</sub> )	117.3
α (C <sub>3</sub> -C <sub>2</sub> -Cl <sub>13</sub> )	120.2	119.9	α (C <sub>3</sub> -C <sub>2</sub> -Cl <sub>11</sub> )	119.6	α (C <sub>3</sub> -C <sub>2</sub> -Cl <sub>9</sub> )	121.6
α (C <sub>2</sub> -C <sub>3</sub> -C <sub>4</sub> )	119.5	120.3	α (C <sub>2</sub> -C <sub>3</sub> -C <sub>4</sub> )	118.4	α (C <sub>2</sub> -C <sub>3</sub> -C <sub>4</sub> )	119.6
α (C <sub>2</sub> -C <sub>3</sub> -H <sub>7</sub> )	119.4	118.9	α (C <sub>2</sub> -C <sub>3</sub> -H <sub>7</sub> )	120.4	α (C <sub>2</sub> -C <sub>3</sub> -Cl <sub>10</sub> )	119.8
α (C <sub>4</sub> -C <sub>3</sub> -H <sub>7</sub> )	121.1	120.8	α (C <sub>4</sub> -C <sub>3</sub> -H <sub>7</sub> )	121.2	α (C <sub>4</sub> -C <sub>3</sub> -Cl <sub>10</sub> )	120.6
α (C <sub>3</sub> -C <sub>4</sub> -C <sub>5</sub> )	119.6	119.6	α (C <sub>3</sub> -C <sub>4</sub> -C <sub>5</sub> )	121.2	α (C <sub>3</sub> -C <sub>4</sub> -C <sub>5</sub> )	119.6
α (C <sub>3</sub> -C <sub>4</sub> -H <sub>8</sub> )	119.8	119.8	α (C <sub>3</sub> -C <sub>4</sub> -Cl <sub>12</sub> )	119.4	α (C <sub>3</sub> -C <sub>4</sub> -Cl <sub>11</sub> )	120.1
α (C <sub>5</sub> -C <sub>4</sub> -H <sub>8</sub> )	120.6	120.6	α (C <sub>5</sub> -C <sub>4</sub> -Cl <sub>12</sub> )	119.4	α (C <sub>5</sub> -C <sub>4</sub> -Cl <sub>11</sub> )	120.3
α (C <sub>4</sub> -C <sub>5</sub> -C <sub>6</sub> )	120.6	120.1	α (C <sub>4</sub> -C <sub>5</sub> -C <sub>6</sub> )	119.3	α (C <sub>4</sub> -C <sub>5</sub> -C <sub>6</sub> )	120.4
α (C <sub>4</sub> -C <sub>5</sub> -H <sub>9</sub> )	120.0	120.4	α (C <sub>4</sub> -C <sub>5</sub> -H <sub>8</sub> )	120.8	α (C <sub>4</sub> -C <sub>5</sub> -Cl <sub>12</sub> )	120.0
α (C <sub>6</sub> -C <sub>5</sub> -H <sub>9</sub> )	119.4	119.5	α (C <sub>6</sub> -C <sub>5</sub> -H <sub>8</sub> )	119.9	α (C <sub>6</sub> -C <sub>5</sub> -Cl <sub>12</sub> )	119.6
α (C <sub>1</sub> -C <sub>6</sub> -C <sub>5</sub> )	120.4	120.7	α (C <sub>1</sub> -C <sub>6</sub> -C <sub>5</sub> )	121.5	α (C <sub>1</sub> -C <sub>6</sub> -C <sub>5</sub> )	120.2
α (C <sub>1</sub> -C <sub>6</sub> -H <sub>10</sub> )	118.1	119.1	α (C <sub>1</sub> -C <sub>6</sub> -Cl <sub>13</sub> )	119.0	α (C <sub>1</sub> -C <sub>6</sub> -Cl <sub>13</sub> )	118.0
α (C <sub>5</sub> -C <sub>6</sub> -H <sub>10</sub> )	121.5	120.2	α (C <sub>5</sub> -C <sub>6</sub> -Cl <sub>13</sub> )	119.5	α (C <sub>5</sub> -C <sub>6</sub> -Cl <sub>13</sub> )	121.7
α (C <sub>1</sub> -O <sub>11</sub> -H <sub>12</sub> )	109.3	109.6	α (C <sub>1</sub> -O <sub>9</sub> -H <sub>10</sub> )	109.3	α (C <sub>1</sub> -O <sub>7</sub> -H <sub>8</sub> )	109.3

# All the dihedral angles are either 0° or ± 180°

The present investigation reveals that the bond lengths of the polar bonds decreased with increasing number of sites of high electronegative atoms in the molecules. The bond angles in the optimized structure of the three molecules are approximately equal with a little difference of the order of 2°, which is obviously due to non-uniformity in charge distribution in different molecules.

### 3.2. APT Charges

The atomic polarizability tensor (APT) charges are the sum of the charge tensor and charge flux tensor, leading to a charge-charge flux model [29, 30]. The APT atomic charges in unit of e, at various atomic sites of the 2-CP (C-1 and C-2), TCP and PCP are collected in Table 3. The ring carbon atoms of both the conformers of 2-CP, namely, C<sub>1</sub>, C<sub>2</sub>, C<sub>5</sub> and C<sub>3</sub>, C<sub>4</sub>, C<sub>6</sub> have alternately positive and negative APT charges with different magnitudes. The APT charges of the ring carbons, connected to the high electronegative atoms in the TCP are positive in nature with sufficient values, while those connected to H atom possess negative APT charges of relatively lower values. In the PCP molecule all the ring carbons are connected to the electronegative atoms, therefore, possess positive APT charges with different magnitudes. All the H atoms in all the geometrical structures have positive APT charges with different magnitudes, while the electronegative atoms, namely, O and Cl atoms in all the molecules and conformers possess negative and different magnitudes of APT charges. The O atom of OH group in all the species possesses the highest magnitude. It is also noticeable that the negative surface charge density is highest in PCP molecule while lowest in 2-CP molecule. It is interesting to note that the H atom of the OH group possesses the highest value of the APT atomic charges for all the H atoms in all the molecules.

Table 3. ATP and Mulliken atomic Charges of 2-CP (C-1 & C-2), TCP and PCP.

Atom	2-Chlorophenol				Atom	2,4,6-Trichlorophenol		Atom	2,3,4,5,6-Pentachlorophenol	
	Conformer-1		Conformer-2			APT	Mulliken		APT	Mulliken
	APT	Mulliken	APT	Mulliken						
C <sub>1</sub>	0.450894	-1.015872	0.447033	-0.771319	C <sub>1</sub>	0.313732	-2.038184	C <sub>1</sub>	0.417748	-2.453269
C <sub>2</sub>	0.273615	1.179517	0.296720	0.776968	C <sub>2</sub>	0.369564	0.903037	C <sub>2</sub>	0.195487	-0.161365
C <sub>3</sub>	-0.042470	-0.323696	-0.040271	-0.387160	C <sub>3</sub>	-0.185056	-0.476798	C <sub>3</sub>	0.306953	0.363459
C <sub>4</sub>	-0.118215	-0.453816	-0.108974	-0.459437	C <sub>4</sub>	0.381965	0.191837	C <sub>4</sub>	0.112503	-0.468538
C <sub>5</sub>	0.032186	-0.124659	0.010534	-0.063758	C <sub>5</sub>	-0.172709	-0.685390	C <sub>5</sub>	0.311769	0.058948
C <sub>6</sub>	-0.098435	-0.271341	-0.102889	-0.096235	C <sub>6</sub>	0.391008	0.532384	C <sub>6</sub>	0.221489	-0.200206
H <sub>7</sub>	0.064508	0.178208	0.063756	0.181358	H <sub>7</sub>	0.091796	0.199999	O <sub>7</sub>	-0.698480	-0.084365
H <sub>8</sub>	0.038332	0.155006	0.038005	0.153919	H <sub>8</sub>	0.091210	0.202129	H <sub>8</sub>	0.335968	0.262522
H <sub>9</sub>	0.042736	0.168795	0.041543	0.166353	O <sub>9</sub>	-0.677735	-0.103858	Cl <sub>9</sub>	-0.266460	0.386734
H <sub>10</sub>	0.056606	0.185736	0.028575	0.122777	H <sub>10</sub>	0.329575	0.257054	Cl <sub>10</sub>	-0.234096	0.643523
O <sub>11</sub>	-0.695364	-0.172830	-0.666144	-0.183994	Cl <sub>11</sub>	-0.315683	0.304156	Cl <sub>11</sub>	-0.226846	0.583595
H <sub>12</sub>	0.318046	0.252415	0.289119	0.268456	Cl <sub>12</sub>	-0.325331	0.364183	Cl <sub>12</sub>	-0.230483	0.669379
Cl <sub>13</sub>	-0.322440	0.242536	-0.297007	0.292072	Cl <sub>13</sub>	-0.292338	0.349450	Cl <sub>13</sub>	-0.245551	0.399583

### 3.3. Mulliken Atomic Charges

Mulliken atomic charges are essential as they play significant roles in the application of quantum chemical calculations to the molecular systems, because these affect the dipole moment, polarizability, electronic structure and much more characteristics of the molecular systems. The Mulliken atomic charges (in unit of e) at various atomic sites of 2-CP (C-1 and C-2), TCP and PCP are collected in Table 3 from which it could be noticed that the carbon atom connected to the phenolic group possesses negative Mulliken

atomic charges with the highest magnitude (TCP and PCP), while in 2-CP the C atom connected to the high electronegative atom, having three electron lone pairs, possesses the highest and positive Mulliken atomic charge (Table 3). A close investigation reveals that the ring carbons, directly connected to the Cl atoms in 2-CP and TCP molecules possess positive Mulliken charge with different magnitudes; while in PCP molecule the C atoms connected to the Cl atoms possess alternately negative and positive Mulliken charge having different magnitudes. The O atom in all the molecules has negative and small magnitude of Mulliken atomic charge (highest in 2-CP and lowest in PCP in magnitude), while the Cl and H atoms in all the molecules possess positive Mulliken atomic charges. The phenolic H atom has the highest value amongst all the other H atoms present in all the considered molecules.

#### 4 Experimental Detail

Raman spectra of the dilute solution in 1-ethyl-3-methylimidazolium-bis-(perfluoroethylsulfonyl) amide [(emim) Beti] of the substances, namely, 2-CP, TCP and PCP purchased from Sigma Aldrich Chemical Co. (USA) were obtained with a SPEX 1404 0.85 m double spectrometer, 13.6 mm back-thinned SPEX CCD chip detector. Raman scattering was excited at 514.5 nm (~ 300 mW laser power) with a Coherent 10 W Argon Ion laser and collected from 2900 to 3400  $\text{cm}^{-1}$ , using a Kaiser Optical system holographic Super Notch filter to modulate the Raleigh line. Raman shifts were calibrated against the laser emission at 514.5 nm. The integration time for each sample was 60 seconds and the accumulations were 120. The integration time and the accumulations were changed to 120 and 30, respectively, when the excitation wavelength was changed to 363.8 nm [27].

Samples for Infrared spectra were dispersed on a KBr pellet. A Bio-Rad Excalibur Spectrophotometer with a DTGS electrically cooled detector and with a KBr extended range beam splitter was used for the analysis. The spectra were collected from 400 to 4000  $\text{cm}^{-1}$  [27].

The three herbicidal molecules are all 13 atomic and so have 33 normal modes of vibration which includes 30 modes corresponding to the benzene ring (12 stretching modes- $\nu$ , 3 planar ring deformation modes - $\alpha$ (R), 3 non planar ring deformation modes - $\Phi$ (R), 6 planar deformation modes - $\beta$ (C-H)/ $\beta$ (C-Cl)/ $\beta$ (C-OH) and 6 non-planar deformation modes - $\gamma$ (C-H)/ $\gamma$ (C-Cl)/ $\gamma$ (C-OH) and the 3 normal modes of OH-group as: OH stretching - $\nu$ (OH), OH torsion - $\tau$ (OH) and C-O-H angle bending, Tables (4-8).

Table 4. Fundamental vibrational frequencies, PEDs and vibrational assignments for the C-1 conformer of 2-CP

Mode S.N.	Computed		Obs. IR	PEDs.	Mode Assignment
	Unscaled	Scaled			
$\nu_1$	156(0,1)0.75	153		$\Phi_2(\text{R})(49) - \Phi_3(\text{R})(19) + \gamma(\text{C}_2\text{-Cl}_{13})(15) + \Phi_1(\text{R})(9)$	$\gamma(\text{C-Cl})$
$\nu_2$	249(3,1)0.69	244		$\beta(\text{C}_2\text{-Cl}_{13})(75) + \beta(\text{C}_1\text{-O}_{11})(15)$	$\beta(\text{C-Cl})$
$\nu_3$	263(1,1)0.75	257		$\gamma(\text{C}_2\text{-Cl}_{13})(32) + \Phi_2(\text{R})(28) + \gamma(\text{C}_6\text{-H}_{10})(11) + \gamma(\text{C}_1\text{-O}_{11})(11) - \Phi_3(\text{R})(8) - \Phi_1(\text{R})(6)$	$\Phi(\text{R})$
$\nu_4$	376(2,4)0.30	368		$\nu(\text{C}_2\text{-Cl}_{13})(27) - \alpha_3(\text{R})(19) - \beta(\text{C}_1\text{-O}_{11})(17) + \alpha_2(\text{R})(16) - \beta(\text{C}_2\text{-Cl}_{13})(9)$	$\alpha(\text{R})$
$\nu_5$	405(109,1)0.75	396		$\tau(\text{C}_1\text{-O}_{11})(92)$	$\tau(\text{C-OH})$
$\nu_6$	449(0,0)0.75	439		$\Phi_3(\text{R})(60) + \gamma(\text{C}_2\text{-Cl}_{13})(24)$	$\Phi(\text{R})$
$\nu_7$	493(12,4)0.44	482		$\beta(\text{C}_1\text{-O}_{11})(57) - \nu(\text{C}_2\text{-Cl}_{13})(16) - \beta(\text{C}_2\text{-Cl}_{13})(11)$	$\beta(\text{C-OH})$
$\nu_8$	545(0,0)0.75	533	516	$\Phi_2(\text{R})(38) - \gamma(\text{C}_1\text{-O}_{11})(28) - \Phi_1(\text{R})(9) + \gamma(\text{C}_4\text{-H}_8)(6) - \Phi_3(\text{R})(6) - \gamma(\text{C}_2\text{-Cl}_{13})(7)$	$\gamma(\text{C-OH})$



v <sub>9</sub>	564(5,10)0.34	552		$\alpha_2(\text{R})(61) + \alpha_3(\text{R})(10) - v(\text{C}_2\text{-Cl}_{13})(6) - v(\text{C}_1\text{-O}_{11})(6)$	$\alpha(\text{R})$
v <sub>10</sub>	685(25,10)0.12	670	608	$\alpha_3(\text{R})(56) + v(\text{C}_2\text{-Cl}_{13})(24) + v(\text{C}_1\text{-C}_2)(10)$	$v(\text{C-Cl})$
v <sub>11</sub>	700(0,0)0.75	685	667	$\Phi_1(\text{R})(64) + \gamma(\text{C}_1\text{-O}_{11})(17) - \gamma(\text{C}_2\text{-Cl}_{13})(11)$	$\Phi(\text{R})$
v <sub>12</sub>	759(73,0)0.75	743	741	$\gamma(\text{C}_4\text{-H}_8)(41) + \gamma(\text{C}_5\text{-H}_9)(22) + \gamma(\text{C}_3\text{-H}_7)(20) + \gamma(\text{C}_6\text{-H}_{10})(11)$	$\gamma(\text{C-H})$
v <sub>13</sub>	843(13,13)0.07	825		$\alpha_1(\text{R})(27) - v(\text{C}_1\text{-O}_{11})(24) - \alpha_2(\text{R})(19) - v(\text{C}_1\text{-C}_6)(10) - v(\text{C}_1\text{-C}_2)(8)$	$\alpha(\text{R})$
v <sub>14</sub>	856(1,0)0.75	838		$\gamma(\text{C}_6\text{-H}_{10})(42) - \gamma(\text{C}_3\text{-H}_7)(26) + \gamma(\text{C}_5\text{-H}_9)(8) - \Phi_1(\text{R})(9)$	$\gamma(\text{C-H})$
v <sub>15</sub>	946(3,0)0.75	926	853	$\gamma(\text{C}_3\text{-H}_7)(41) - \gamma(\text{C}_4\text{-H}_8)(22) + \gamma(\text{C}_6\text{-H}_{10})(20) - \gamma(\text{C}_5\text{-H}_9)(7)$	$\gamma(\text{C-H})$
v <sub>16</sub>	983(0,0)0.75	962		$\gamma(\text{C}_5\text{-H}_9)(46) - \gamma(\text{C}_4\text{-H}_8)(23) - \gamma(\text{C}_6\text{-H}_{10})(13) + \Phi_1(\text{R})(11)$	$\gamma(\text{C-H})$
v <sub>17</sub>	1043(45,27)0.04	996		$\alpha_1(\text{R})(33) + v(\text{C}_4\text{-C}_5)(21) + v(\text{C}_5\text{-C}_6)(13) + v(\text{C}_2\text{-Cl}_{13})(11) + v(\text{C}_3\text{-C}_4)(6) + v(\text{C}_1\text{-C}_6)(6)$	$v(\text{R})$
v <sub>18</sub>	1061(13,3)0.10	1013		$\alpha_1(\text{R})(29) - v(\text{C}_4\text{-C}_5)(15) + v(\text{C}_2\text{-Cl}_{13})(10) + v(\text{C}_3\text{-C}_4)(6) + \beta(\text{C}_3\text{-H}_7)(10) - \beta(\text{C}_6\text{-H}_{10})(9) + v(\text{C}_1\text{-C}_2)(7)$	$\beta(\text{C-H})$
v <sub>19</sub>	1141(5,3)0.24	1090	1093	$v(\text{C}_3\text{-C}_4)(23) + v(\text{C}_2\text{-C}_3)(6) - v(\text{C}_5\text{-C}_6)(9) + \beta(\text{C}_4\text{-H}_8)(12) - v(\text{C}_2\text{-Cl}_{13})(6) + \beta(\text{C}_5\text{-H}_9)(14) - \beta(\text{C}_6\text{-H}_{10})(13)$	$\beta(\text{C-H})$
v <sub>20</sub>	1180(3,3)0.64	1127		$\beta(\text{C}_5\text{-H}_9)(28) - \beta(\text{C}_4\text{-H}_8)(34) - \beta(\text{C}_6\text{-H}_{10})(11) + \beta(\text{C}_3\text{-H}_7)(9) + v(\text{C}_4\text{-C}_5)(10)$	$\beta(\text{C-H})$
v <sub>21</sub>	1210(116,1)0.63	1156	1177	$\alpha(\text{C}_1\text{-O}_{11}\text{-H}_{12})(38) - \beta(\text{C}_6\text{-H}_{10})(12) - \beta(\text{C}_3\text{-H}_7)(10) - v(\text{C}_1\text{-C}_6)(17) - v(\text{C}_1\text{-C}_2)(9)$	$\alpha(\text{C-O-H})$
v <sub>22</sub>	1275(74,10)0.04	1218	1239	$v(\text{C}_1\text{-O}_{11})(31) - v(\text{C}_2\text{-C}_3)(25) - \beta(\text{C}_3\text{-H}_7)(22)$	$v(\text{C-OH})$
v <sub>23</sub>	1324(29,7)0.10	1264	1287	$\beta(\text{C}_6\text{-H}_{10})(15) - v(\text{C}_1\text{-O}_{11})(14) - v(\text{C}_1\text{-C}_2)(17) - v(\text{C}_5\text{-C}_6)(17) + v(\text{C}_2\text{-C}_3)(8) - v(\text{C}_2\text{-C}_3)(7) + \beta(\text{C}_4\text{-H}_8)(7)$	$\beta(\text{C-H})$
v <sub>24</sub>	1366(22,3)0.73	1305	1317	$\alpha(\text{C}_1\text{-O}_{11}\text{-H}_{12})(26) - v(\text{C}_1\text{-C}_6)(8) + v(\text{C}_5\text{-C}_6)(6) - v(\text{C}_2\text{-C}_3)(10) - \beta(\text{C}_3\text{-H}_7)(9) - \beta(\text{C}_5\text{-H}_9)(12) - v(\text{C}_4\text{-C}_5)(10) + v(\text{C}_1\text{-C}_2)(5) + v(\text{C}_2\text{-C}_3)(10)$	$v(\text{R})$
v <sub>25</sub>	1489(4,1)0.31	1422		$\beta(\text{C}_4\text{-H}_8)(30) + \beta(\text{C}_5\text{-H}_9)(14) + v(\text{C}_1\text{-C}_6)(7) - v(\text{C}_2\text{-C}_3)(12) - v(\text{C}_3\text{-C}_4)(7) + v(\text{C}_5\text{-C}_6)(9) - \alpha(\text{C}_1\text{-O}_{11}\text{-H}_{12})(7)$	$v(\text{R})$
v <sub>26</sub>	1510(136,2)0.75	1442	1437	$\beta(\text{C}_3\text{-H}_7)(19) - \beta(\text{C}_6\text{-H}_{10})(16) - v(\text{C}_1\text{-C}_2)(15) - v(\text{C}_4\text{-C}_5)(6) - v(\text{C}_2\text{-C}_3)(8) + v(\text{C}_1\text{-O}_{11})(11) - \beta(\text{C}_5\text{-H}_9)(9)$	$v(\text{R})$
v <sub>27</sub>	1624(15,11)0.73	1551	1548	$v(\text{C}_4\text{-C}_5)(21) + v(\text{C}_1\text{-C}_2)(18) - v(\text{C}_1\text{-C}_6)(15) - v(\text{C}_3\text{-C}_4)(13) + \alpha_3(\text{R})(9) - \beta(\text{C}_4\text{-H}_8)(6)$	$v(\text{R})$
v <sub>28</sub>	1635(39,19)0.68	1561		$v(\text{C}_5\text{-C}_6)(25) + v(\text{C}_2\text{-C}_3)(17) - v(\text{C}_1\text{-C}_6)(11) - v(\text{C}_3\text{-C}_4)(8) - \beta(\text{C}_6\text{-H}_{10})(7) + \alpha_2(\text{R})(10)$	$v(\text{R})$
v <sub>29</sub>	3175(2,52)0.74	3032		$v(\text{C}_5\text{-H}_9)(57) - v(\text{C}_4\text{-H}_8)(28) - v(\text{C}_6\text{-H}_{10})(10)$	$v(\text{C-H})$
v <sub>30</sub>	3188(7,97)0.72	3044		$v(\text{C}_4\text{-H}_8)(42) - v(\text{C}_3\text{-H}_7)(22) - v(\text{C}_6\text{-H}_{10})(22) + v(\text{C}_5\text{-H}_9)(14)$	$v(\text{C-H})$
v <sub>31</sub>	3197(5,60)0.23	3053	3113	$v(\text{C}_6\text{-H}_{10})(59) - v(\text{C}_3\text{-H}_7)(23) + v(\text{C}_5\text{-H}_9)(17)$	$v(\text{C-H})$
v <sub>32</sub>	3203(4,251)0.12	3058	3169	$v(\text{C}_3\text{-H}_7)(51) + v(\text{C}_4\text{-H}_8)(29) + v(\text{C}_5\text{-H}_9)(10)$	$v(\text{C-H})$
v <sub>33</sub>	3766(92,58)0.13	3596	3435	$v(\text{O}_{11}\text{-H}_{12})(100)$	$v(\text{O-H})$

Table 5. Fundamental vibrational wavenumbers, PEDs and vibrational assignments for the C-2 conformer of 2-CP.

Mode	Computed		Exp. IR	PEDs.	Mode Assignment
	Unscaled	Scaled			
v <sub>1</sub>	152(1,2)0.75	149		$\Phi_2(\text{R})(49) - \Phi_3(\text{R})(20) + \Phi_1(\text{R})(13) + \gamma(\text{C}_2\text{-Cl}_{13})(10)$	$\gamma(\text{C-Cl})$
v <sub>2</sub>	239(2,1)0.75	234		$\beta(\text{C}_2\text{-Cl}_{13})(71) + \beta(\text{C}_1\text{-O}_{11})(17)$	$\beta(\text{C-Cl})$
v <sub>3</sub>	259(17,0)0.75	253		$\Phi_2(\text{R})(26) - (\text{C}_2\text{-Cl}_{13})(26) + \Phi_3(\text{R})(13) + \gamma(\text{C}_1\text{-O}_{11})(9) + \gamma(\text{C}_6\text{-H}_{10})(8) + \tau(\text{C}_1\text{-O}_{11})(7) + \gamma(\text{C}_3\text{-H}_7)(6)$	$\Phi(\text{R})$
v <sub>4</sub>	306(90,2)0.75	299		$\tau(\text{C}_1\text{-O}_{11})(82) + \gamma(\text{C}_1\text{-O}_{11})(7)$	$\tau(\text{C-OH})$
v <sub>5</sub>	381(3,3)0.35	373		$\nu(\text{C}_2\text{-Cl}_{13})(26) - \alpha_3(\text{R})(19) + \beta(\text{C}_1\text{-O}_{11})(17) + \alpha_2(\text{R})(15) - \beta(\text{C}_2\text{-Cl}_{13})(10)$	$\alpha(\text{R})$
v <sub>6</sub>	450(7,0)0.75	440		$\Phi_3(\text{R})(58) + \gamma(\text{C}_2\text{-Cl}_{13})(23) - \gamma(\text{C}_1\text{-O}_{11})(8)$	$\Phi(\text{R})$
v <sub>7</sub>	492(8,4)0.32	482		$\beta(\text{C}_1\text{-O}_{11})(55) - \nu(\text{C}_2\text{-Cl}_{13})(12) - \beta(\text{C}_2\text{-Cl}_{13})(11)$	$\beta(\text{C-OH})$
v <sub>8</sub>	554(1,0)0.75	542	516	$\Phi_2(\text{R})(36) - \gamma(\text{C}_1\text{-O}_{11})(21) - \Phi_1(\text{R})(16) + \gamma(\text{C}_4\text{-H}_8)(7) - \Phi_3(\text{R})(7) + \gamma(\text{C}_2\text{-Cl}_{13})(6)$	$\gamma(\text{C-OH})$
v <sub>9</sub>	566(4,10)0.32	554		$\alpha_2(\text{R})(57) + \alpha_3(\text{R})(12) - \nu(\text{C}_2\text{-Cl}_{13})(7) - \nu(\text{C}_1\text{-O}_{11})(7)$	$\alpha(\text{R})$
v <sub>10</sub>	691(19,10)0.10	676	608	$\alpha_3(\text{R})(54) - \nu(\text{C}_2\text{-Cl}_{13})(25) + \nu(\text{C}_1\text{-C}_2)(11)$	$\nu(\text{C-Cl})$
v <sub>11</sub>	719(5,0)0.75	704	667	$\Phi_1(\text{R})(60) - \gamma(\text{C}_1\text{-O}_{11})(17) - \gamma(\text{C}_2\text{-Cl}_{13})(13) + \gamma(\text{C}_5\text{-H}_9)(7)$	$\Phi(\text{R})$
v <sub>12</sub>	753(77,0)0.75	737	741	$\gamma(\text{C}_4\text{-H}_8)(34) + \gamma(\text{C}_5\text{-H}_9)(20) + \gamma(\text{C}_6\text{-H}_{10})(17) + \gamma(\text{C}_3\text{-H}_7)(11) + \gamma(\text{C}_1\text{-O}_{11})(9) - \Phi_1(\text{R})(7)$	$\gamma(\text{C-H})$
v <sub>13</sub>	840(0,0)0.75	822		$\gamma(\text{C}_6\text{-H}_{10})(43) - \gamma(\text{C}_3\text{-H}_7)(20) - \Phi_1(\text{R})(13) - \gamma(\text{C}_4\text{-H}_8)(11) + \gamma(\text{C}_1\text{-O}_{11})(7)$	$\gamma(\text{C-H})$
v <sub>14</sub>	842(21,12)0.09	824		$\alpha_1(\text{R})(28) - \nu(\text{C}_1\text{-O}_{11})(24) - \alpha_2(\text{R})(19) - \nu(\text{C}_1\text{-C}_6)(9) - \nu(\text{C}_1\text{-C}_2)(7)$	$\alpha(\text{R})$
v <sub>15</sub>	937(2,0)0.75	917	853	$\gamma(\text{C}_3\text{-H}_7)(40) - \gamma(\text{C}_5\text{-H}_9)(29) + \gamma(\text{C}_6\text{-H}_{10})(18) - \Phi_3(\text{R})(7)$	$\gamma(\text{C-H})$
v <sub>16</sub>	974(0,0)0.75	953		$\gamma(\text{C}_4\text{-H}_8)(37) - \gamma(\text{C}_5\text{-H}_9)(30) - \gamma(\text{C}_3\text{-H}_7)(16) - \Phi_1(\text{R})(10)$	$\gamma(\text{C-H})$
v <sub>17</sub>	1055(26,30)0.04	1008		$\nu(\text{C}_4\text{-C}_3)(30) + \nu(\text{C}_5\text{-C}_6)(15) + \nu(\text{C}_3\text{-C}_4)(11) - \nu(\text{C}_2\text{-Cl}_{13})(8) + \alpha_1(\text{R})(19)$	$\nu(\text{R})$
v <sub>18</sub>	1072(25,1)0.25	1024		$\alpha_1(\text{R})(40) - \nu(\text{C}_2\text{-Cl}_{13})(13) + \beta(\text{C}_3\text{-H}_7)(8) + \nu(\text{C}_1\text{-C}_6)(7) - \nu(\text{C}_4\text{-C}_3)(7)$	$\beta(\text{C-H})$
v <sub>19</sub>	1140(77,4)0.08	1089	1093	$\nu(\text{C}_3\text{-C}_4)(20) + \nu(\text{C}_1\text{-C}_2)(8) + \nu(\text{C}_2\text{-C}_3)(7) - \nu(\text{C}_5\text{-C}_6)(7) + \alpha(\text{C}_1\text{-O}_{11}\text{-H}_{12})(13) + \beta(\text{C}_4\text{-H}_8)(13) - \nu(\text{C}_2\text{-Cl}_{13})(10) + \beta(\text{C}_5\text{-H}_9)(8)$	$\beta(\text{C-H})$
v <sub>20</sub>	1182(3,4)0.64	1129		$\beta(\text{C}_5\text{-H}_9)(33) - \beta(\text{C}_4\text{-H}_8)(31) - \beta(\text{C}_6\text{-H}_{10})(10) + \beta(\text{C}_3\text{-H}_7)(9) + \nu(\text{C}_4\text{-C}_3)(8)$	$\beta(\text{C-H})$
v <sub>21</sub>	1187(83,5)0.36	1134	1177	$\alpha(\text{C}_1\text{-O}_{11}\text{-H}_{12})(40) + \beta(\text{C}_6\text{-H}_{10})(15) + \beta(\text{C}_3\text{-H}_7)(9) - \nu(\text{C}_1\text{-C}_6)(10) + \nu(\text{C}_1\text{-C}_2)(8)$	$\alpha(\text{C-O-H})$

$v_{22}$	1285(22,13)0.06	1227	1239	$v(C_1-O_{11})(32) - v(C_2-C_3)(24) - v(C_1-C_6)(6) - \beta(C_3-H_7)(15) + \alpha_1(R)(6)$	$v(C-OH)$
$v_{23}$	1316(78,4)0.10	1257	1287	$\beta(C_6-H_{10})(24) + v(C_1-O_{11})(15) - v(C_1-C_2)(12) - v(C_5-C_6)(11) + v(C_2-C_3)(8) + \beta(C_4-H_8)(7)$	$\beta(C-H)$
$v_{24}$	1353(44,2)0.61	1292	1317	$\alpha(C_1-O_{11}-H_{12})(17) + v(C_1-C_6)(13) - v(C_5-C_6)(11) - v(C_2-C_3)(14) - \beta(C_3-H_7)(11) - \beta(C_5-H_9)(6) + v(C_4-C_5)(10) - v(C_1-C_2)(7) + v(C_2-C_3)(8)$	$v(R)$
$v_{25}$	1478(47,1)0.18	1412		$\beta(C_4-H_8)(26) + \beta(C_5-H_9)(23) + v(C_1-C_6)(11) - v(C_2-C_3)(10) - v(C_3-C_4)(8) + v(C_5-C_6)(6)$	$v(R)$
$v_{26}$	1525(62,3)0.73	1456	1437	$\beta(C_3-H_7)(18) - \beta(C_6-H_{10})(18) - v(C_1-C_2)(11) + v(C_4-C_5)(11) - v(C_2-C_3)(8) + v(C_1-O_{11})(7) - \beta(C_5-H_9)(6)$	$v(R)$
$v_{27}$	1623(13,21)0.74	1550	1548	$v(C_3-C_4)(23) + v(C_1-C_6)(22) + \alpha_3(R)(7) - v(C_4-C_5)(7) - \beta(C_4-H_8)(6)$	$v(R)$
$v_{28}$	1636(28,11)0.60	1562		$v(C_5-C_6)(21) - v(C_1-C_2)(19) - v(C_4-C_5)(16) + v(C_2-C_3)(13) + \beta(C_5-H_9)(8) + \alpha_2(R)(8)$	$v(R)$
$v_{29}$	3152(11,92)0.37	3010		$v(C_6-H_{10})(93) - v(C_5-H_9)(6)$	$v(C-H)$
$v_{30}$	3178(4,75)0.63	3035		$v(C_4-H_8)(48) - v(C_5-H_9)(40) - v(C_3-H_7)(7)$	$v(C-H)$
$v_{31}$	3191(9,97)0.37	3047	3113	$v(C_5-H_9)(46) - v(C_3-H_7)(33) + v(C_4-H_8)(19)$	$v(C-H)$
$v_{32}$	3202(5,196)0.12	3058	3169	$v(C_3-H_7)(59) + v(C_4-H_8)(32) + v(C_5-H_9)(8)$	$v(C-H)$
$v_{33}$	3835(73,107)0.23	3662	3435	$v(O_{11}-H_{12})(100)$	$v(O-H)$

Table 6. Fundamental vibrational frequencies, PEDs and vibrational assignments for TCP.

Mode	Computed Frequency		Exp. IR Freq.	PEDs.	Mode Assignment
	Unscaled	Scaled			
$v_1$	104(0,0)0.75	102		$\Phi_2(R)(73) - \Phi_1(R)(14)$	$\gamma(C-Cl)$
$v_2$	139(0,0)0.75	136		$\gamma(C_4-Cl_{12})(28) + \gamma(C_2-Cl_{11})(20) + \gamma(C_6-Cl_{13})(17) - \Phi_2(R)(14) + \gamma(C_5-H_8)(8) + \gamma(C_3-H_7)(7)$	$\gamma(C-Cl)$
$v_3$	187(0,3)0.75	183		$\beta(C_4-Cl_{12})(54) - \beta(C_6-Cl_{13})(26) - \beta(C_2-Cl_{11})(7)$	$\beta(C-Cl)$
$v_4$	196(0,2)0.75	192		$\beta(C_2-Cl_{11})(50) - \beta(C_6-Cl_{13})(36)$	$\beta(C-Cl)$
$v_5$	210(0,1)0.75	206		$\Phi_3(R)(66) - \gamma(C_2-Cl_{11})(11) + \gamma(C_5-H_8)(8) + \gamma(C_6-Cl_{13})(8) - \gamma(C_3-H_7)(6)$	$\Phi(R)$
$v_6$	296(6,0)0.52	290		$\beta(C_1-O_9)(42) + \beta(C_2-Cl_{11})(17) + \beta(C_6-Cl_{13})(12) + \beta(C_4-Cl_{12})(12) - \alpha_3(R)(9)$	$\beta(C-Cl)$
$v_7$	347(2,0)0.75	340		$\gamma(C_1-O_9)(28) - \gamma(C_2-Cl_{11})(21) + \gamma(C_4-Cl_{12})(19) - \gamma(C_6-Cl_{13})(8) - \Phi_1(R)(12)$	$\gamma(C-Cl)$
$v_8$	372(0,15)0.08	364		$v(C_4-Cl_{12})(28) + v(C_2-Cl_{11})(24) + v(C_6-Cl_{13})(19) + \alpha_1(R)(10)$	$v(C-Cl)$
$v_9$	383(2,3)0.75	375		$\alpha_2(R)(63) - v(C_4-Cl_{12})(13) + v(C_2-Cl_{11})(7) + v(C_6-Cl_{13})(6)$	$\alpha(R)$

$\nu_{10}$	404(96,1)0.75	395		$\tau$ (C <sub>1</sub> -O <sub>9</sub> )(95)	$\tau$ (C-OH)
$\nu_{11}$	433(4,2)0.74	424		$\alpha_2$ (R)(42)+ $\beta$ (C <sub>4</sub> -Cl <sub>12</sub> )(16)+ $\nu$ (C <sub>6</sub> -Cl <sub>13</sub> )(13)- $\nu$ (C <sub>2</sub> -Cl <sub>11</sub> )(11)+ $\beta$ (C <sub>2</sub> -Cl <sub>11</sub> )(7)+ $\beta$ (C <sub>6</sub> -Cl <sub>13</sub> )(6)	$\alpha$ (R)
$\nu_{12}$	508(0,1)0.75	497	517	$\Phi_3$ (R)(47)+ $\gamma$ (C <sub>2</sub> -Cl <sub>11</sub> )(28)- $\gamma$ (C <sub>6</sub> -Cl <sub>13</sub> )(24)	$\Phi$ (R)
$\nu_{13}$	579(11,1)0.72	567		$\beta$ (C <sub>1</sub> -O <sub>9</sub> )(44)- $\beta$ (C <sub>6</sub> -Cl <sub>13</sub> )(14)- $\beta$ (C <sub>2</sub> -Cl <sub>11</sub> )(14)- $\beta$ (C <sub>4</sub> -Cl <sub>12</sub> )(11)	$\beta$ (C-OH)
$\nu_{14}$	580(3,1)0.75	568	612	$\Phi_2$ (R)(36)+ $\gamma$ (C <sub>4</sub> -Cl <sub>12</sub> )(36)- $\gamma$ (C <sub>1</sub> -O <sub>9</sub> )(14)- $\Phi_1$ (R)(12)	$\gamma$ (C-OH)
$\nu_{15}$	715(4,1)0.75	700	683	$\Phi_1$ (R)(52)- $\gamma$ (C <sub>1</sub> -O <sub>9</sub> )(23)- $\gamma$ (C <sub>6</sub> -Cl <sub>13</sub> )(10) - $\gamma$ (C <sub>2</sub> -Cl <sub>11</sub> )(9)	$\Phi$ (R)
$\nu_{16}$	729(83,9)0.08	713	723	$\nu$ (C <sub>4</sub> -Cl <sub>12</sub> )(31)- $\nu$ (C <sub>1</sub> -O <sub>9</sub> )(13)+ $\alpha_2$ (R)(11)- $\nu$ (C <sub>2</sub> -Cl <sub>11</sub> )(10)+ $\alpha_1$ (R)(9)- $\nu$ (C <sub>6</sub> -Cl <sub>13</sub> )(6)	$\nu$ (C-Cl)
$\nu_{17}$	796(74,0)0.45	779	768	$\alpha_3$ (R)(36)+ $\nu$ (C <sub>2</sub> -Cl <sub>11</sub> )(27)- $\nu$ (C <sub>6</sub> -Cl <sub>13</sub> )(27)	$\nu$ (C-Cl)
$\nu_{18}$	866(28,0)0.75	847	793	$\gamma$ (C <sub>3</sub> -H <sub>7</sub> )(67)+ $\Phi_1$ (R)(15)+ $\gamma$ (C <sub>5</sub> -H <sub>8</sub> )(8)	$\gamma$ (C-H)
$\nu_{19}$	870(14,23)0.08	851		$\alpha_2$ (R)(25)- $\alpha_1$ (R)(20)+ $\nu$ (C <sub>4</sub> -Cl <sub>12</sub> )(17)+ $\nu$ (C <sub>1</sub> -O <sub>9</sub> )(12)+ $\nu$ (C <sub>1</sub> -C <sub>2</sub> )(6)	$\alpha$ (R)
$\nu_{20}$	883(6,0)0.75	864	861	$\gamma$ (C <sub>5</sub> -H <sub>8</sub> )(77)- $\gamma$ (C <sub>3</sub> -H <sub>7</sub> )(7)+ $\Phi_3$ (R)(6)	$\gamma$ (C-H)
$\nu_{21}$	1093(2,7)0.09	1044	983	$\alpha_1$ (R)(33)+ $\beta$ (C <sub>3</sub> -H <sub>7</sub> )(11)- $\beta$ (C <sub>5</sub> -H <sub>8</sub> )(10)- $\nu$ (C <sub>6</sub> -Cl <sub>13</sub> )(8)- $\nu$ (C <sub>4</sub> -C <sub>5</sub> )(8)- $\nu$ (C <sub>3</sub> -C <sub>4</sub> )(8)- $\nu$ (C <sub>2</sub> -Cl <sub>11</sub> )(7)	$\nu$ (R)
$\nu_{22}$	1143(4,7)0.08	1092	1097	$\alpha_1$ (R)(23)- $\nu$ (C <sub>4</sub> -Cl <sub>12</sub> )(16)- $\nu$ (C <sub>4</sub> -C <sub>5</sub> )(14)+ $\nu$ (C <sub>3</sub> -C <sub>4</sub> )(12)- $\nu$ (C <sub>6</sub> -Cl <sub>13</sub> )(9)- $\beta$ (C <sub>3</sub> -H <sub>7</sub> )(7)- $\nu$ (C <sub>2</sub> -Cl <sub>11</sub> )(6)	$\beta$ (C-H)
$\nu_{23}$	1178(118,1)0.42	1125		$\alpha$ (C <sub>1</sub> -O <sub>9</sub> -H <sub>10</sub> )(26)- $\beta$ (C <sub>5</sub> -H <sub>8</sub> )(16)+ $\nu$ (C <sub>1</sub> -C <sub>6</sub> )(12) - $\nu$ (C <sub>1</sub> -C <sub>2</sub> )(12)- $\beta$ (C <sub>3</sub> -H <sub>7</sub> )(10)+ $\beta$ (C <sub>1</sub> -O <sub>9</sub> )(6)	$\beta$ (C-H)
$\nu_{24}$	1256(74,1)0.18	1199	1178	$\beta$ (C <sub>3</sub> -H <sub>7</sub> )(16)+ $\nu$ (C <sub>2</sub> -C <sub>3</sub> )(16)+ $\alpha$ (C <sub>1</sub> -O <sub>11</sub> -H <sub>12</sub> )(13)+ $\nu$ (C <sub>1</sub> -C <sub>6</sub> )(10)+ $\nu$ (C <sub>4</sub> -C <sub>5</sub> )(9)+ $\beta$ (C <sub>5</sub> -H <sub>8</sub> )(8)+ $\nu$ (C <sub>1</sub> -C <sub>2</sub> )(7)- $\nu$ (C <sub>3</sub> -C <sub>4</sub> )(6)+ $\nu$ (C <sub>5</sub> -C <sub>6</sub> )(6)	$\nu$ (R)
$\nu_{25}$	1298(33,16)0.10	1240	1223	$\nu$ (C <sub>1</sub> -O <sub>9</sub> )(35)- $\nu$ (C <sub>5</sub> -C <sub>6</sub> )(21)+ $\beta$ (C <sub>5</sub> -H <sub>8</sub> )(11)- $\nu$ (C <sub>3</sub> -C <sub>4</sub> )(8) - $\beta$ (C <sub>3</sub> -H <sub>7</sub> )(7)	$\nu$ (C-OH)
$\nu_{26}$	1352(49,2)0.70	1291	1332	$\alpha$ (C <sub>1</sub> -O <sub>9</sub> -H <sub>10</sub> )(24)- $\nu$ (C <sub>2</sub> -C <sub>3</sub> )(15)- $\nu$ (C <sub>4</sub> -C <sub>5</sub> )(13) + $\beta$ (C <sub>5</sub> -H <sub>8</sub> )(11)+ $\nu$ (C <sub>3</sub> -C <sub>4</sub> )(9)+ $\nu$ (C <sub>5</sub> -C <sub>6</sub> )(8)+ $\nu$ (C <sub>1</sub> -C <sub>2</sub> )(8)- $\nu$ (C <sub>1</sub> -C <sub>6</sub> )(6)	$\alpha$ (C-O-H)
$\nu_{27}$	1423(53,0)0.69	1359	1358	$\nu$ (C <sub>5</sub> -C <sub>6</sub> )(20)- $\nu$ (C <sub>2</sub> -C <sub>3</sub> )(18)+ $\nu$ (C <sub>4</sub> -C <sub>5</sub> )(11)+ $\beta$ (C <sub>3</sub> -H <sub>7</sub> )(13)- $\alpha$ (C <sub>1</sub> -O <sub>9</sub> -H <sub>10</sub> )(9)+ $\beta$ (C <sub>1</sub> -O <sub>9</sub> )(6)	$\nu$ (R)
$\nu_{28}$	1489(257,3)0.50	1422	1478	$\nu$ (C <sub>1</sub> -O <sub>9</sub> )(21)- $\nu$ (C <sub>1</sub> -C <sub>2</sub> )(15)- $\nu$ (C <sub>1</sub> -C <sub>6</sub> )(12)+ $\nu$ (C <sub>3</sub> -C <sub>4</sub> )(12)- $\beta$ (C <sub>5</sub> -H <sub>8</sub> )(13)+ $\beta$ (C <sub>3</sub> -H <sub>7</sub> )(12)	$\nu$ (R)
$\nu_{29}$	1603(45,15)0.73	1531		$\nu$ (C <sub>4</sub> -C <sub>5</sub> )(22)+ $\nu$ (C <sub>1</sub> -C <sub>2</sub> )(20)- $\nu$ (C <sub>1</sub> -C <sub>6</sub> )(14)- $\nu$ (C <sub>3</sub> -C <sub>4</sub> )(12)- $\alpha_3$ (R)(9)+ $\alpha$ (C <sub>1</sub> -O <sub>9</sub> -H <sub>10</sub> )(6)	$\nu$ (R)
$\nu_{30}$	1618(3,23)0.68	1545	1563	$\nu$ (C <sub>2</sub> -C <sub>3</sub> )(21)+ $\nu$ (C <sub>5</sub> -C <sub>6</sub> )(20)- $\nu$ (C <sub>1</sub> -C <sub>6</sub> )(12)+ $\nu$ (C <sub>3</sub> -C <sub>4</sub> )(10)+ $\alpha_2$ (R)(11)- $\beta$ (C <sub>3</sub> -H <sub>7</sub> )(6)	$\nu$ (R)
$\nu_{31}$	3219.8(2,51)0.37	3075	3016	$\nu$ (C <sub>3</sub> -H <sub>7</sub> )(95)	$\nu$ (C-H)
$\nu_{32}$	3220(1,71)0.20	3075	3134	$\nu$ (C <sub>5</sub> -H <sub>8</sub> )(95)	$\nu$ (C-H)
$\nu_{33}$	3760(113,58)0.14	3591	3592	$\nu$ (O <sub>9</sub> -H <sub>10</sub> )(100)	$\nu$ (O-H)

Table 7. Fundamental vibrational frequencies, PEDs and vibrational assignments for PCP

Mode	Computed Frequency		Exp. IR Freq.	PEDs.	Mode Assignment
	Unscaled	Scaled			
$\nu_1$	69(0,0)0.75	68		$\Phi_3(\text{R})(97)$	$\gamma(\text{C-Cl})$
$\nu_2$	75(0,0)0.75	73		$\Phi_2(\text{R})(83)$	$\gamma(\text{C-Cl})$
$\nu_3$	111(0,0)0.75	109		$\Phi_1(\text{R})(36)+\Phi_2(\text{R})(23)+\gamma(\text{C}_2-\text{Cl}_9)(17)+\gamma(\text{C}_6-\text{Cl}_{13})(13)$	$\gamma(\text{C-Cl})$
$\nu_4$	177(0,0)0.75	173		$\gamma(\text{C}_4-\text{Cl}_{11})(18)+\gamma(\text{C}_3-\text{Cl}_{10})(17)+\gamma(\text{C}_5-\text{Cl}_{12})(17)+\gamma(\text{C}_2-\text{Cl}_9)(16)+\gamma(\text{C}_6-\text{Cl}_{13})(13)-\gamma(\text{C}_1-\text{O}_7)(8)-\Phi_1(\text{R})(7)$	$\gamma(\text{C-Cl})$
$\nu_5$	211(0,2)0.64	206		$\beta(\text{C}_6-\text{Cl}_{13})(60)-\beta(\text{C}_2-\text{Cl}_9)(28)$	$\beta(\text{C-Cl})$
$\nu_6$	216(0,1)0.75	211		$\beta(\text{C}_4-\text{Cl}_{11})(36)-\beta(\text{C}_2-\text{Cl}_9)(31)+\beta(\text{C}_3-\text{Cl}_{10})(12)-\beta(\text{C}_6-\text{Cl}_{13})(8)\text{t}$	$\beta(\text{C-Cl})$
$\nu_7$	220(0,1)0.66	215		$\beta(\text{C}_3-\text{Cl}_{10})(41)-\beta(\text{C}_5-\text{Cl}_{12})(37)$	$\beta(\text{C-Cl})$
$\nu_8$	231(0,1)0.75	226		$\beta(\text{C}_5-\text{Cl}_{12})(38)-\beta(\text{C}_4-\text{Cl}_{11})(29)+\beta(\text{C}_3-\text{Cl}_{10})(20)$	$\beta(\text{C-Cl})$
$\nu_9$	310(3,2)0.74	303		$\alpha_3(\text{R})(43)-\beta(\text{C}_1-\text{O}_7)(21)+\nu(\text{C}_6-\text{Cl}_{13})(7)-\beta(\text{C}_4-\text{Cl}_{11})(6)-\nu(\text{C}_2-\text{Cl}_9)(6)$	$\alpha(\text{R})$
$\nu_{10}$	328(1,0)0.75	321		$\gamma(\text{C}_2-\text{Cl}_9)(34)-\gamma(\text{C}_6-\text{Cl}_{13})(27)-\gamma(\text{C}_5-\text{Cl}_{12})(20)+\gamma(\text{C}_3-\text{Cl}_{10})(17)$	$\Phi(\text{R})$
$\nu_{11}$	339(4,4)0.64	332		$\beta(\text{C}_1-\text{O}_7)(30)+\nu(\text{C}_3-\text{Cl}_{10})(13)+\alpha_3(\text{R})(11)+\beta(\text{C}_2-\text{Cl}_9)(10)+\beta(\text{C}_5-\text{Cl}_{12})(6)$	$\beta(\text{C-Cl})$
$\nu_{12}$	341(0,9)0.31	334		$\alpha_2(\text{R})(39)+\nu(\text{C}_5-\text{Cl}_{12})(18)+\nu(\text{C}_3-\text{Cl}_{10})(8)+\nu(\text{C}_2-\text{Cl}_9)(6)$	$\alpha(\text{R})$
$\nu_{13}$	347(0,0)0.75	340		$\gamma(\text{C}_4-\text{Cl}_{11})(30)-\gamma(\text{C}_2-\text{Cl}_9)(18)-\gamma(\text{C}_6-\text{Cl}_{13})(16)+\gamma(\text{C}_1-\text{O}_7)(15)+\Phi_2(\text{R})(6)+\gamma(\text{C}_3-\text{Cl}_{10})(6)$	$\gamma(\text{C-Cl})$
$\nu_{14}$	376(0,16)0.09	368		$\nu(\text{C}_4-\text{Cl}_{11})(28)+\nu(\text{C}_2-\text{Cl}_9)(19)+\nu(\text{C}_6-\text{Cl}_{13})(19)+\alpha_1(\text{R})(10)$	$\nu(\text{C-Cl})$
$\nu_{15}$	423(93,1)0.75	414		$\tau(\text{C}_1-\text{O}_7)(93)$	$\tau(\text{C-O})$
$\nu_{16}$	464(1,9)0.12	454		$\nu(\text{C}_5-\text{Cl}_{12})(17)+\nu(\text{C}_3-\text{Cl}_{10})(17)-\alpha_2(\text{R})(16)-\alpha_1(\text{R})(15)+\nu(\text{C}_1-\text{O}_7)(7)$	$\nu(\text{C-Cl})$
$\nu_{17}$	574(0,0)0.75	562	527	$\Phi_3(\text{R})(37)-\gamma(\text{C}_3-\text{Cl}_{10})(18)+\gamma(\text{C}_2-\text{Cl}_9)(17)+\gamma(\text{C}_5-\text{Cl}_{12})(15)-\gamma(\text{C}_6-\text{Cl}_{13})(11)$	$\Phi(\text{R})$
$\nu_{18}$	618(0,0)0.75	605		$\gamma(\text{C}_4-\text{Cl}_{11})(24)-\Phi_1(\text{R})(22)+\Phi_2(\text{R})(22)-\gamma(\text{C}_5-\text{Cl}_{12})(13)-\gamma(\text{C}_3-\text{Cl}_{10})(13)-\gamma(\text{C}_1-\text{O}_7)(7)$	$\Phi(\text{R})$
$\nu_{19}$	651(17,0)0.50	637	633	$\beta(\text{C}_4-\text{Cl}_{11})(21)+\beta(\text{C}_5-\text{Cl}_{12})(18)+\beta(\text{C}_3-\text{Cl}_{10})(17)-\beta(\text{C}_1-\text{O}_7)(13)+\beta(\text{C}_2-\text{Cl}_9)(9)+\beta(\text{C}_6-\text{Cl}_{13})(9)$	$\beta(\text{C-OH})$
$\nu_{20}$	681(1,1)0.75	666		$\Phi_1(\text{R})(44)-\gamma(\text{C}_1-\text{O}_7)(27)-\gamma(\text{C}_6-\text{Cl}_{13})(11)-\gamma(\text{C}_2-\text{Cl}_9)(7)$	$\gamma(\text{C-OH})$
$\nu_{21}$	694(74,0)0.74	679	674	$\beta(\text{C}_1-\text{O}_7)(22)-\nu(\text{C}_2-\text{Cl}_9)(20)+\nu(\text{C}_6-\text{Cl}_{13})(14)+\nu(\text{C}_5-\text{Cl}_{12})(13)-\nu(\text{C}_3-\text{Cl}_{10})(12)-\beta(\text{C}_6-\text{Cl}_{13})(7)-\beta(\text{C}_2-\text{Cl}_9)(6)$	$\nu(\text{C-Cl})$
$\nu_{22}$	760(83,2)0.08	744	762	$\nu(\text{C}_4-\text{Cl}_{11})(39)+\alpha_2(\text{R})(16)-\nu(\text{C}_6-\text{Cl}_{13})(12)+\nu(\text{C}_2-\text{Cl}_9)(9)$	$\nu(\text{C-Cl})$
$\nu_{23}$	874(0,0)0.75	855	798	$\alpha_3(\text{R})(34)+\nu(\text{C}_5-\text{Cl}_{12})(16)+\nu(\text{C}_3-\text{Cl}_{10})(16)+\nu(\text{C}_6-\text{Cl}_{13})(14)-\nu(\text{C}_5-\text{Cl}_{12})(14)$	$\nu(\text{C-Cl})$
$\nu_{24}$	983(20,4)0.09	962	871	$\alpha_1(\text{R})(18)-\nu(\text{C}_1-\text{O}_7)(17)-\alpha_2(\text{R})(15)+\nu(\text{C}_5-\text{Cl}_{12})(14)+\nu(\text{C}_3-\text{Cl}_{10})(14)-\nu(\text{C}_4-\text{Cl}_{11})(9)$	$\alpha(\text{R})$

v <sub>25</sub>	1129(6,6)0.13	1078	1003	$\alpha_1(\text{R})(43)-\nu(\text{C}_6-\text{Cl}_{13})(14)-\nu(\text{C}_2-\text{Cl}_9)(11)+\nu(\text{C}_1-\text{O}_7)(7)-\nu(\text{C}_4-\text{Cl}_{11})(7)+\nu(\text{C}_1-\text{C}_6)(6)$	$\nu(\text{R})$
v <sub>26</sub>	1218(165,4)0.51	1163	1105	$\alpha(\text{C}_1-\text{O}_7-\text{H}_8)(29)+\nu(\text{C}_1-\text{C}_6)(19)-\nu(\text{C}_1-\text{C}_2)(17)+\nu(\text{C}_4-\text{C}_5)(13)-\nu(\text{C}_3-\text{C}_4)(8)$	$\nu(\text{R})$
v <sub>27</sub>	1278(14,23)0.15	1220	1189	$\nu(\text{C}_3-\text{C}_4)(27)-\nu(\text{C}_1-\text{O}_7)(13)-\nu(\text{C}_4-\text{C}_5)(11)+\nu(\text{C}_5-\text{C}_6)(11)-\nu(\text{C}_3-\text{Cl}_{10})(7)+\nu(\text{C}_4-\text{Cl}_{11})(7)-\nu(\text{C}_5-\text{Cl}_{12})(7)$	$\nu(\text{C}-\text{O})$
v <sub>28</sub>	1304(72,2)0.44	1245	1249	$\nu(\text{C}_2-\text{C}_3)(21)-\nu(\text{C}_5-\text{C}_6)(20)+\nu(\text{C}_4-\text{C}_5)(16)+\nu(\text{C}_3-\text{C}_4)(8)-\alpha(\text{C}_1-\text{O}_7-\text{H}_8)(19)$	$\alpha(\text{C}-\text{O}-\text{H})$
v <sub>29</sub>	1394(189,1)0.34	1331	1328	$\nu(\text{C}_2-\text{C}_3)(20)-\nu(\text{C}_4-\text{C}_5)(16)-\nu(\text{C}_5-\text{C}_6)(10)+\alpha(\text{C}_1-\text{O}_7-\text{H}_8)(11)-\beta(\text{C}_4-\text{Cl}_{11})(7)-\nu(\text{C}_1-\text{O}_7)(6)$	$\nu(\text{R})$
v <sub>30</sub>	1433(180,7)0.43	1368	1353	$\nu(\text{C}_1-\text{O}_7)(25)+\nu(\text{C}_3-\text{C}_4)(19)-\nu(\text{C}_5-\text{C}_6)(12)-\nu(\text{C}_1-\text{C}_2)(10)-\nu(\text{C}_1-\text{C}_6)(8)$	$\nu(\text{R})$
v <sub>31</sub>	1571(36,42)0.74	1500		$\nu(\text{C}_1-\text{C}_2)(30)+\nu(\text{C}_4-\text{C}_5)(15)-\nu(\text{C}_5-\text{C}_6)(11)-\nu(\text{C}_2-\text{C}_3)(10)-\alpha_2(\text{R})(6)$	$\nu(\text{R})$
v <sub>32</sub>	1582(13,23)0.75	1511	1582	$\nu(\text{C}_1-\text{C}_6)(32)+\nu(\text{C}_3-\text{C}_4)(14)-\nu(\text{C}_2-\text{C}_3)(12)-\nu(\text{C}_5-\text{C}_6)(9)-\alpha_2(\text{R})(7)$	$\nu(\text{R})$
v <sub>33</sub>	3747(119,62)0.16	3578	3178	$\nu(\text{O}_{11}-\text{H}_{12})(100)$	$\nu(\text{O}-\text{H})$

Table 8. Comparison of fundamental modes of C-1, C-2, TCP and PCP.

Scaled wavenumber (cm <sup>-1</sup> )	Scaled wavenumber (cm <sup>-1</sup> )		Scaled wavenumber. (cm <sup>-1</sup> )	Modes
	2-CP	TCP		
C-1	C-2			
153	149	102	68	$\gamma(\text{C}-\text{Cl})$
244	234	183	206	$\beta(\text{C}-\text{Cl})$
257	253	206	321	$\Phi(\text{R})$
368	373	375	303	$\alpha(\text{R})$
396	299	395	414	$\tau(\text{C}-\text{OH})$
439	440	497t	562	$\Phi(\text{R})$
482	482	567	637	$\beta(\text{C}-\text{OH})$
533	542	568	666	$\gamma(\text{C}-\text{OH})$
552	554	424	334	$\alpha(\text{R})$
670	676	364	368	$\nu(\text{C}-\text{Cl})$
685	704	700	605	$\Phi(\text{R})$
743	737	136	73	$\gamma(\text{C}-\text{H})/\gamma(\text{C}-\text{Cl})$
825	824	851	962	$\alpha(\text{R})$
838	822	340	109	$\gamma(\text{C}-\text{H})/\gamma(\text{C}-\text{Cl})$
926	917	847	173	$\gamma(\text{C}-\text{H})/\gamma(\text{C}-\text{Cl})$
962	953	864	340	$\gamma(\text{C}-\text{H})/\gamma(\text{C}-\text{Cl})$
996	1008	1044	1078	$\nu(\text{R})$

1013	1024	192	211	$\beta(\text{C-H})/\beta(\text{C-Cl})$
1090	1089	290	215	$\beta(\text{C-H})/\beta(\text{C-Cl})$
1127	1129	1092	226	$\beta(\text{C-H})/\beta(\text{C-Cl})$
1156	1134	1291	1245	$\alpha(\text{C-O-H})$
1218	1227	1240	1220	$\nu(\text{C-OH})$
1264	1257	1125	332	$\beta(\text{C-H})/\beta(\text{C-Cl})$
1305	1292	1199	1163	$\nu(\text{R})$
1422	1412	1359	1331	$\nu(\text{R})$
1442	1456	1422	1368	$\nu(\text{R})$
1551	1550	1531	1500	$\nu(\text{R})$
1561	1562	1545	1511	$\nu(\text{R})$
3032	3010	713	454	$\nu(\text{C-H})/\nu(\text{C-Cl})$
3044	3035	779	679	$\nu(\text{C-H})/\nu(\text{C-Cl})$
3053	3047	3075	744	$\nu(\text{C-H})/\nu(\text{C-Cl})$
3058	3058	3075	855	$\nu(\text{C-H})/\nu(\text{C-Cl})$
3596	3662	3591	3578	$\nu(\text{O-H})$

The calculated and observed [27] vibrational frequencies along with the corresponding PEDs and vibrational assignments for C-1 & C-2 conformers of 2-CP, TCP and PCP are collected in Tables 4-7, respectively. The corresponding modes for all the molecules are compared in Table 8. The observed (ref-27) and calculated IR and Raman spectra of 2-CP, TCP and PCP are reproduced in Figs 3- 6. The normal mode assignments have been discussed under the following sections: (i) The Phenyl Ring Modes (30) and (ii) The OH Group Modes.

#### 3.4.1. Phenyl Ring Modes (30)

The four C-H stretching modes  $\nu(\text{C-H})$  correspond to the frequencies 3058 ( $\nu_{32}$ ), 3053( $\nu_{31}$ ), 3044( $\nu_{30}$ ) and 3032( $\nu_{29}$ )  $\text{cm}^{-1}$  & 3058 ( $\nu_{32}$ ), 3047( $\nu_{31}$ ), 3035( $\nu_{30}$ ) and 3010( $\nu_{29}$ )  $\text{cm}^{-1}$  dominantly correspond to the modes  $\nu(\text{C}_3\text{-H}_7)$ ,  $\nu(\text{C}_6\text{-H}_{10})$ ,  $\nu(\text{C}_4\text{-H}_8)$  and  $\nu(\text{C}_5\text{-H}_9)$ , respectively in the conformers C-1 and C-2 of 2-CP. Also, the two C-H stretching modes  $\nu(\text{C-H})$  in TCP correspond to the frequencies 3075 ( $\nu_{32}$ ), 3075( $\nu_{31}$ )  $\text{cm}^{-1}$ . The C-H stretching vibrations are pure and highly localized modes. These modes were earlier assigned at the frequencies 3196, 3190, 3176 and 3167  $\text{cm}^{-1}$  in phenol [31] and also at 3204, 3196, 3188, 3174 and 3202, 3190, 3178, 3151 in *cis*- and *trans*-chlorophenols, respectively [31]. The four C-H planar deformations,  $\beta(\text{C-H})$  and non-planar deformations,  $\gamma(\text{C-H})$  in each of the conformer C-1 are found to correspond to the frequencies 1264( $\nu_{23}$ ), 1127( $\nu_{20}$ ), 1090( $\nu_{19}$ ), and 1013( $\nu_{18}$ ) & 962( $\nu_{16}$ ), 926( $\nu_{15}$ ), 838( $\nu_{14}$ ) and 743( $\nu_{12}$ )  $\text{cm}^{-1}$  and for C-2 of 2-CP are found to correspond to the frequencies 1257( $\nu_{23}$ ), 1129( $\nu_{20}$ ), 1089( $\nu_{19}$ ) and 1024( $\nu_{18}$ ) & 953( $\nu_{16}$ ), 917( $\nu_{15}$ ), 822( $\nu_{13}$ ) and 737( $\nu_{12}$ )  $\text{cm}^{-1}$  dominantly correspond to the modes  $\beta(\text{C}_6\text{-H}_{10})$ ,  $\beta(\text{C}_4\text{-H}_8)$ ,  $\beta(\text{C}_3\text{-H}_7)$ ,  $\beta(\text{C}_5\text{-H}_9)$ ,  $\gamma(\text{C}_5\text{-H}_9)$ ,  $\gamma(\text{C}_3\text{-H}_7)$ ,  $\gamma(\text{C}_6\text{-H}_{10})$  and  $\gamma(\text{C}_4\text{-H}_8)$ , respectively. Also, the modes  $\beta(\text{C}_5\text{-H}_9)$ ,  $\beta(\text{C}_3\text{-H}_7)$ ,  $\gamma(\text{C}_5\text{-H}_9)$  and  $\gamma(\text{C}_3\text{-H}_7)$  dominantly correspond to the frequencies 1125( $\nu_{23}$ ), 1092( $\nu_{22}$ ), 864( $\nu_{20}$ ) and 847( $\nu_{18}$ )  $\text{cm}^{-1}$ , respectively in the TCP molecule. These modes are coupled with many other modes. These modes were observed at the frequencies 1499, 1368, 1190 and 1176  $\text{cm}^{-1}$  in phenol [31] and also at 1240, 1170, 1072 and 1021  $\text{cm}^{-1}$  in *N*-(phenyl)-2,2-dichloroacetamide [32]. The modes  $\nu(\text{C-Cl})$  present in each of the 3 molecules under investigation, occur dominantly at wavenumber 670( $\nu_{10}$ ) and at 676( $\nu_{10}$ )  $\text{cm}^{-1}$  in C-1 and C-2 of 2-CP, respectively. These are slightly coupled with  $\alpha_3(\text{R})$ ,  $\beta(\text{C}_1\text{-O}_{11})$ ,  $\alpha_2(\text{R})$  and  $\beta(\text{C}_2\text{-Cl}_{13})$  modes. The C-Cl stretching modes in PCP, namely,  $\nu(\text{C}_5\text{-Cl}_{12})$ ,  $\nu(\text{C}_4\text{-Cl}_{11})$ ,  $\nu(\text{C}_2\text{-Cl}_9)$ ,  $\nu(\text{C}_3\text{-Cl}_{10})$  and  $\nu(\text{C}_6\text{-Cl}_{13})$  are also present.

Cl<sub>13</sub>) dominantly correspond to the wavenumbers 855( $\nu_{23}$ ), 744( $\nu_{22}$ ), 679( $\nu_{21}$ ), 454( $\nu_{16}$ ) and 368 ( $\nu_{14}$ )  $\text{cm}^{-1}$ , respectively and the 3 modes in TCP, i.e.,  $\nu(\text{C}_2\text{-Cl}_{11})$ ,  $\nu(\text{C}_4\text{-Cl}_{12})$  and  $\nu(\text{C}_6\text{-Cl}_{13})$  dominantly correspond to the wavenumbers 779( $\nu_{17}$ ), 713( $\nu_{16}$ ) and 364 ( $\nu_8$ )  $\text{cm}^{-1}$ , respectively.

In dichloronitrobenzene [33] these modes were assigned at wavenumbers 802 and 739  $\text{cm}^{-1}$ , in 2,4-dichlorobenzonitrile [34] at 624 and 407  $\text{cm}^{-1}$ , in the (2,4,5-trichlorophenoxy) acetic acid molecule [35] at wavenumbers 694, 944 and 614  $\text{cm}^{-1}$ , in 1,2-di-chlorobenzene at 770  $\text{cm}^{-1}$ , in 1,4-di-chlorobenzene at 772  $\text{cm}^{-1}$ , in 1,2,3-tri-chlorobenzene at 774  $\text{cm}^{-1}$ , in 1,2,3,4-tetra-chlorobenzene at 765  $\text{cm}^{-1}$ , in 1,2,4-tri-chlorobenzene at 773 and 780  $\text{cm}^{-1}$  and in 1,2,4,5-tetra-chlorobenzene at 640 and 705  $\text{cm}^{-1}$  by Dwivedi *et al* [36]. These modes occur in association with many other modes. The 5  $\nu(\text{C-Cl})$ ,  $\beta(\text{C-Cl})$  and  $\gamma(\text{C-Cl})$  & in PCP are found to correspond to the wavenumbers 332( $\nu_{11}$ ), 226( $\nu_8$ ), 215( $\nu_7$ ), 211( $\nu_6$ ), and 206 ( $\nu_5$ ) & 340( $\nu_{13}$ ), 173( $\nu_4$ ), 109( $\nu_3$ ), 73( $\nu_2$ ) and 68 ( $\nu_1$ )  $\text{cm}^{-1}$  with dominant contributions from the  $\beta(\text{C}_4\text{-Cl}_{11})$ ,  $\beta(\text{C}_5\text{-Cl}_{12})$ ,  $\beta(\text{C}_3\text{-Cl}_{10})$ ,  $\beta(\text{C}_2\text{-Cl}_9)$  and  $\beta(\text{C}_6\text{-Cl}_{13})$  &  $\gamma(\text{C}_4\text{-Cl}_{11})$ ,  $\gamma(\text{C}_3\text{-Cl}_{10})$ ,  $\gamma(\text{C}_6\text{-Cl}_{13})$ ,  $\gamma(\text{C}_2\text{-Cl}_9)$  and  $\gamma(\text{C}_5\text{-Cl}_{12})$ , respectively. The 3,  $\beta(\text{C-Cl})$  in TCP are found to occur at wavenumbers 290 ( $\nu_6$ ), 192( $\nu_4$ ), 183( $\nu_3$ ) and 3  $\gamma(\text{C-Cl})$  at 340( $\nu_7$ ), 136( $\nu_2$ ) and 102 ( $\nu_1$ )  $\text{cm}^{-1}$ . The planar (C-Cl) deformations dominantly correspond to the  $\beta(\text{C}_2\text{-Cl}_{11})$ ,  $\beta(\text{C}_6\text{-Cl}_{13})$ ,  $\beta(\text{C}_4\text{-Cl}_{12})$  while the non-planar (C-Cl) deformations dominantly correspond to the  $\gamma(\text{C}_4\text{-Cl}_{12})$ ,  $\gamma(\text{C}_2\text{-Cl}_{11})$ ,  $\gamma(\text{C}_6\text{-Cl}_{13})$ , respectively.

The  $\beta(\text{C-Cl})$  and  $\gamma(\text{C-Cl})$  in C-1 and C-2 of 2-CP correspond to the wavenumbers 244( $\nu_2$ ), 153 ( $\nu_1$ )  $\text{cm}^{-1}$  and 234( $\nu_2$ ), 149 ( $\nu_1$ )  $\text{cm}^{-1}$  which dominantly correspond to the  $\beta(\text{C}_6\text{-Cl}_{13})$ ,  $\gamma(\text{C}_6\text{-Cl}_{13})$  in both the conformers C-1 and C-2, respectively. These modes in all of the conformational forms of molecules appear in association with other modes. The  $\beta(\text{C-Cl})$  modes were found in the 2,4,5-Trichlorophenoxy Acetic acid molecule [35] at wavenumbers 330, 302 and 270  $\text{cm}^{-1}$ , in 2,4-dichlorobenzonitrile [34] at 347 and 198  $\text{cm}^{-1}$  and in dichloronitrobenzene [33] at wavenumbers 433 and 328  $\text{cm}^{-1}$ . Also, the modes  $\gamma(\text{C-Cl})$  were found in the 2,4,5-Trichlorophenoxy Acetic acid molecule [35] at wavenumbers 137, 76 and 59  $\text{cm}^{-1}$ , in 2,4-dichlorobenzonitrile [34] at 171 and 85  $\text{cm}^{-1}$  and in dichloronitrobenzene [33] at wavenumbers 197 and 163  $\text{cm}^{-1}$ . The modes  $\nu(\text{C-OH})$ ,  $\beta(\text{C-OH})$  and  $\gamma(\text{C-OH})$  in C-1 and C-2 of 2-CP occur at wavenumbers 1218( $\nu_{22}$ ) and 1227 ( $\nu_{22}$ ), 482( $\nu_7$ ) and 482 ( $\nu_7$ ), 533( $\nu_8$ ) and 542 ( $\nu_8$ )  $\text{cm}^{-1}$  which dominantly correspond to the  $\nu(\text{C}_1\text{-OH})$ ,  $\beta(\text{C}_1\text{-OH})$  and  $\gamma(\text{C}_1\text{-OH})$  modes, respectively. The modes  $\nu(\text{C-OH})$ ,  $\beta(\text{C-OH})$  and  $\gamma(\text{C-OH})$  in TCP and in PCP occur at wavenumbers 1240( $\nu_{25}$ ) and 1220 ( $\nu_{27}$ ), 567( $\nu_{13}$ ) and 637 ( $\nu_{19}$ ), 568 ( $\nu_{14}$ ) and 666 ( $\nu_{20}$ )  $\text{cm}^{-1}$  which dominantly correspond to the  $\nu(\text{C}_1\text{-OH})$ ,  $\beta(\text{C}_1\text{-OH})$  and  $\gamma(\text{C}_1\text{-OH})$  modes, respectively. These modes are complex and coupled with the other modes of vibration. The modes  $\nu(\text{C-OH})$ ,  $\beta(\text{C-OH})$  and  $\gamma(\text{C-OH})$  were assigned at the wavenumbers 1275, 405 and 509  $\text{cm}^{-1}$  in phenol [31], 1275, 494 and 542  $\text{cm}^{-1}$  in *cis*-chlorophenols [31], 1285, 492 and 548  $\text{cm}^{-1}$  in *trans*-chlorophenols [31].

There are six C-C stretching modes due to the phenyl ring which are identified as the computed wavenumbers 996 ( $\nu_{17}$ ), 1305 ( $\nu_{24}$ ), 1422 ( $\nu_{25}$ ), 1442 ( $\nu_{26}$ ), 1551 ( $\nu_{27}$ ), 1561 ( $\nu_{28}$ )  $\text{cm}^{-1}$  and 1008 ( $\nu_{17}$ ), 1292 ( $\nu_{24}$ ), 1412 ( $\nu_{25}$ ), 1456 ( $\nu_{26}$ ), 1550 ( $\nu_{27}$ ), 1562 ( $\nu_{28}$ )  $\text{cm}^{-1}$  in C-1 and C-2 conformers, respectively of 2-CP, while the phenyl ring stretching modes correspond to the wavenumbers 1044 ( $\nu_{21}$ ), 1199 ( $\nu_{24}$ ), 1359 ( $\nu_{27}$ ), 1422 ( $\nu_{28}$ ), 1531 ( $\nu_{29}$ ), 1545 ( $\nu_{30}$ )  $\text{cm}^{-1}$  in TCP and 1078 ( $\nu_{25}$ ), 1163 ( $\nu_{26}$ ), 1331 ( $\nu_{29}$ ), 1368 ( $\nu_{30}$ ), 1500 ( $\nu_{31}$ ), 1511 ( $\nu_{32}$ )  $\text{cm}^{-1}$  in PCP. The ring stretching modes were already assigned at wavenumbers 1638, 1610, 1450, 1429, 1292 and 1101  $\text{cm}^{-1}$  in dichloronitrobenzene [33]; 1634, 1624, 1323, 1140  $\text{cm}^{-1}$  in *cis*-chlorophenols [31], 1636, 16 phenol [31]; 1635, 1595, 1508, 1419, 1324, 844  $\text{cm}^{-1}$  in 2,4-dichlorobenzonitrile [34]; 1586, 1493, 1437, 1317, 1285 and 1241  $\text{cm}^{-1}$  in the 2,4,5-Trichlorophenoxy Acetic acid molecule [35]. There are three ring planar deformation modes which are found to occur at wavenumbers 368( $\nu_4$ ), 552( $\nu_9$ ) and 825( $\nu_{13}$ )  $\text{cm}^{-1}$  in C-1 and 373( $\nu_5$ ), 554( $\nu_9$ ) and 824( $\nu_{14}$ )  $\text{cm}^{-1}$  in C-2 of 2-CP, respectively, 375( $\nu_9$ ), 424( $\nu_{11}$ ) and 851( $\nu_{19}$ )  $\text{cm}^{-1}$  in TCP and 303( $\nu_9$ ), 334( $\nu_{12}$ ) and 962( $\nu_{24}$ )  $\text{cm}^{-1}$  in PCP. These modes are coupled with the other modes as is evident from the Tables 4-7. The ring planar deformation modes were found at wavenumbers 629, 602



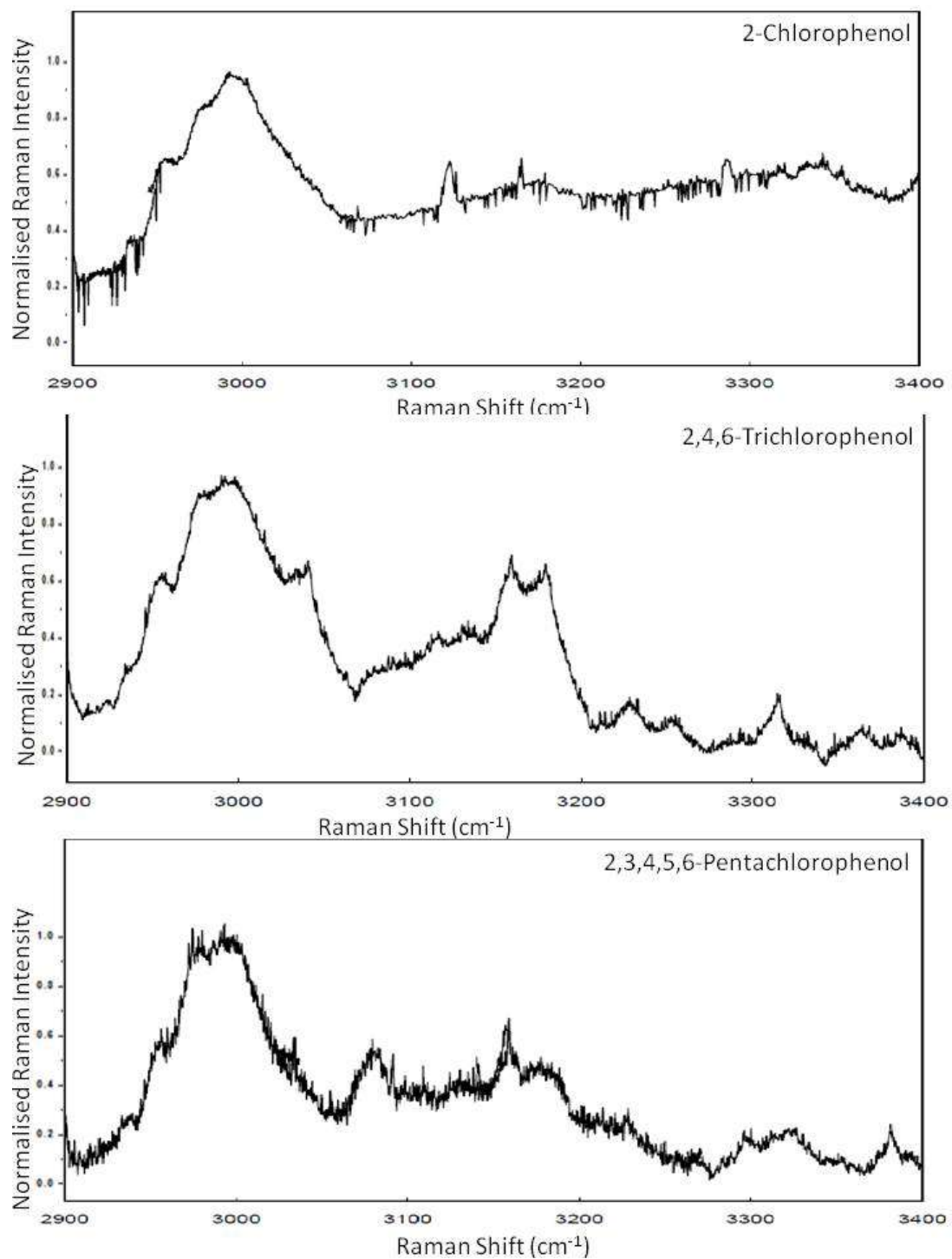


Fig 3. Observed Raman spectra of 2-CP, TCP and PCP

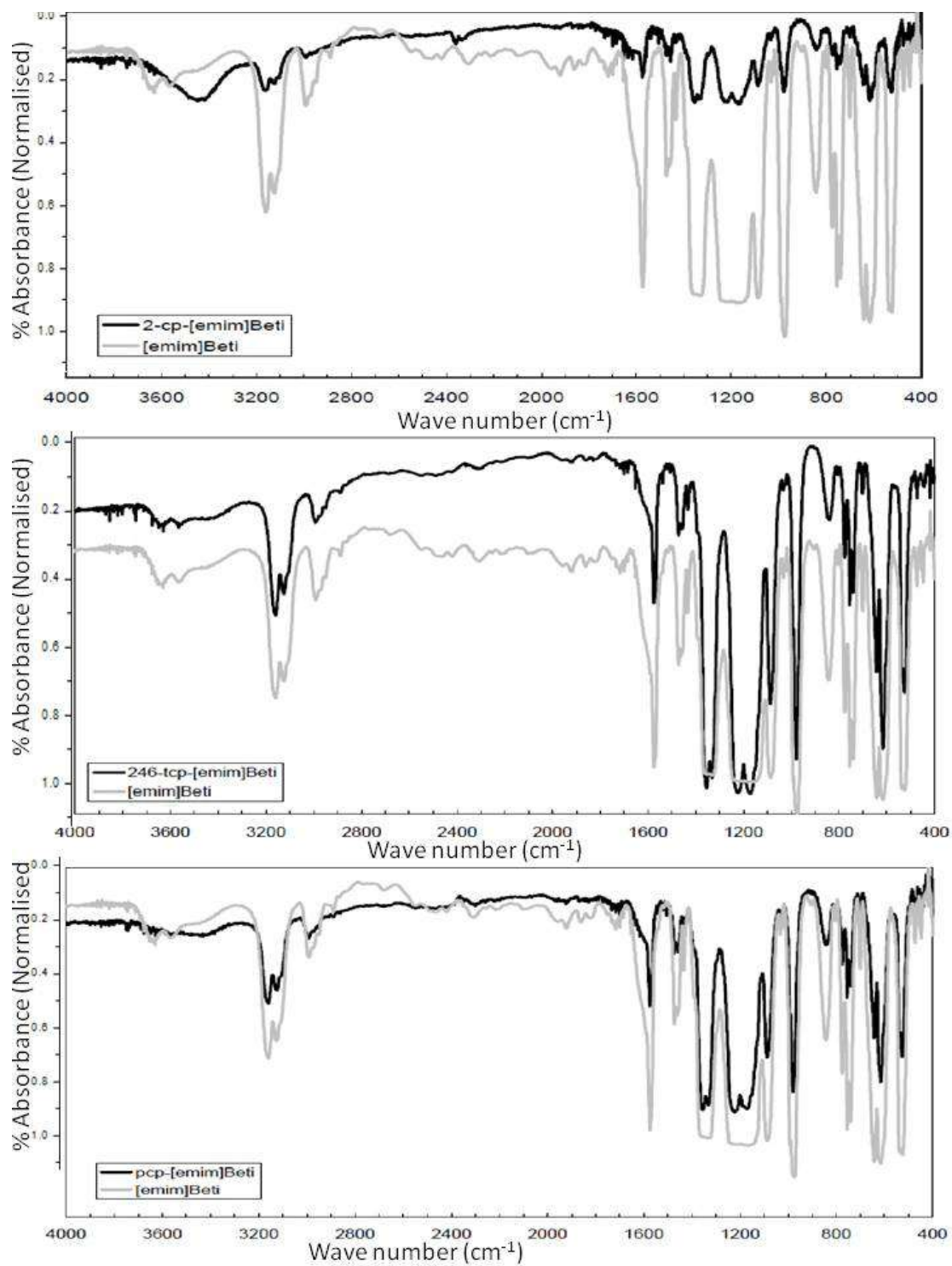


Fig 4. Observed IR Spectra of 2-CP, TCP and PCP

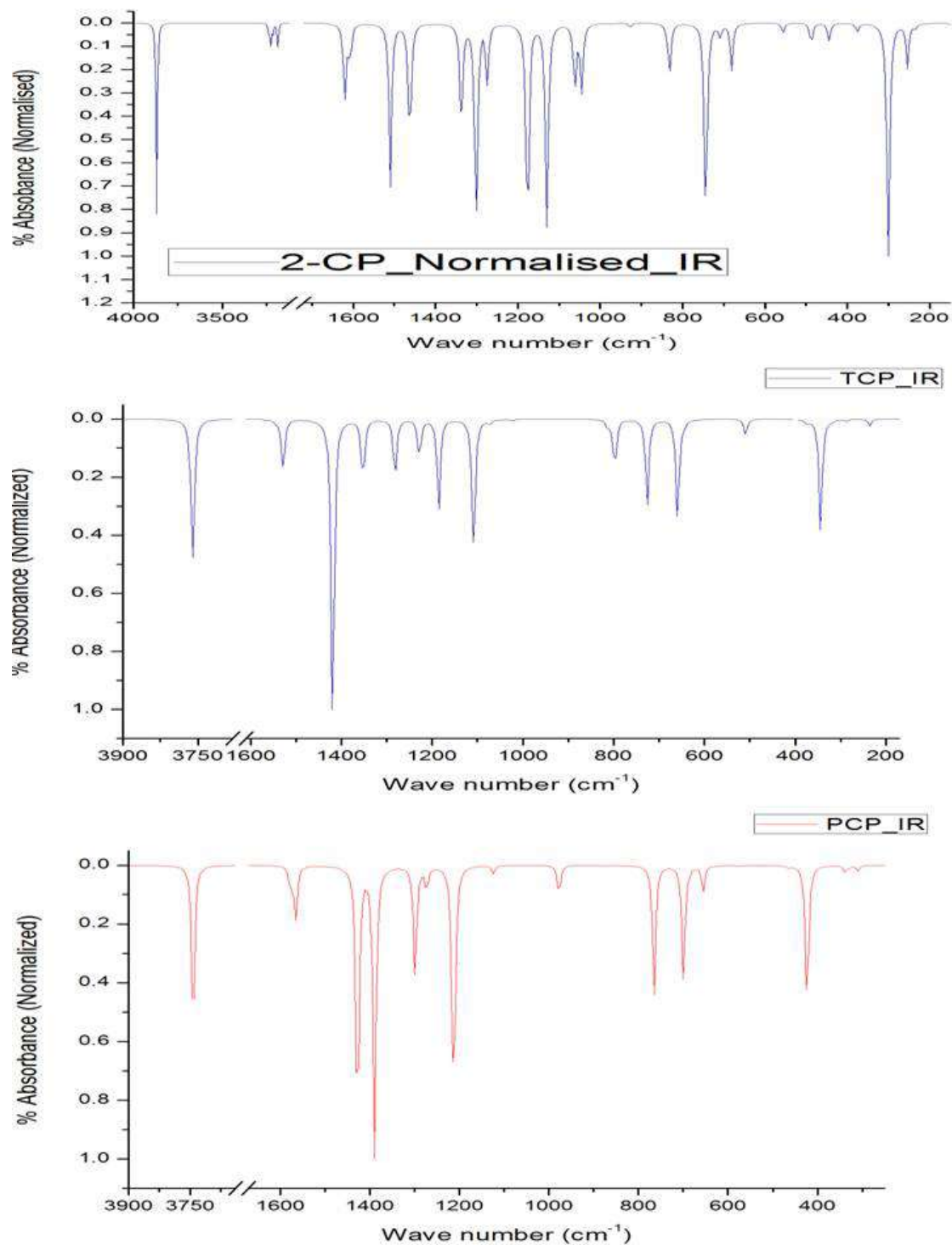


Fig 5. IR spectra of 2-CP, TCP and PCP

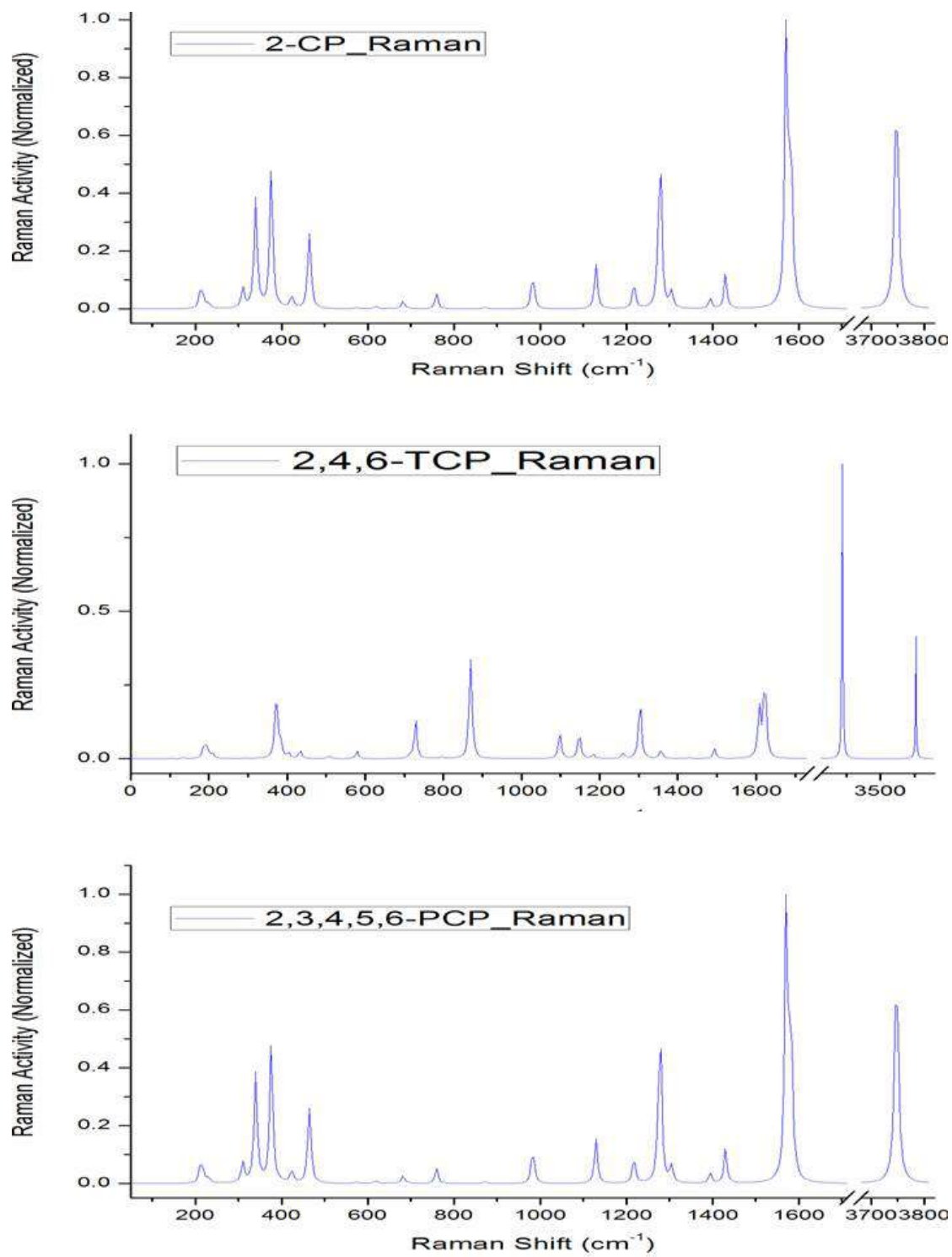


Fig 6. Computed Raman spectra of 2-CP, TCP and PCP

583  $\text{cm}^{-1}$  in the 2,4,5-Trichlorophenoxy Acetic acid molecule [35]; 1074, 705 and 594  $\text{cm}^{-1}$  in 2,4-dichlorobenzonitrile [34], and 1012, 632 and 536  $\text{cm}^{-1}$  in phenol [31]. The three ring non-planar deformation modes are correlated to the wavenumbers 704( $\nu_{11}$ ), 440( $\nu_6$ ) and 149( $\nu_1$ )  $\text{cm}^{-1}$  in both the conformers C-1 and C-2 of 2-CP, 102( $\nu_1$ ), 206( $\nu_5$ ) and 700( $\nu_{15}$ )  $\text{cm}^{-1}$  in TCP and 68( $\nu_1$ ), 73( $\nu_2$ ) and 109( $\nu_3$ )  $\text{cm}^{-1}$  in PCP corresponding to the modes **4** and **16(a,b)** of the benzene molecule. The ring non-planar deformation modes were found at wavenumbers 538, 505 and 460  $\text{cm}^{-1}$  in the 2,4,5-Trichlorophenoxy acetic acid molecule [35], 717, 589 and 431  $\text{cm}^{-1}$  in 2,4-dichlorobenzonitrile [34], 668, 509 and 417  $\text{cm}^{-1}$  in phenol [31].

#### 3.4.2. O-H group modes (3 modes)

The OH stretching mode  $\nu(\text{O-H})$  corresponds to the wavenumbers 3596( $\nu_{33}$ ), 3662( $\nu_{33}$ ), 3591( $\nu_{33}$ ) and 3578( $\nu_{33}$ )  $\text{cm}^{-1}$  in both the conformations of 2-CP, TCP and PCP, respectively. The O-H stretching vibration is a pure and highly localized mode. The O-H stretching vibration mode was assigned at wavenumber 3836, 3768 and 3835  $\text{cm}^{-1}$  in phenol, *cis*- and *trans*-chlorophenols [31], respectively. The torsion of the OH group -  $\tau(\text{C-OH})$  occurs at wavenumbers 396( $\nu_5$ ) and 299( $\nu_4$ ) in C-1 and C-2 of 2-CP and at 395( $\nu_{10}$ ) and 414 ( $\nu_{15}$ )  $\text{cm}^{-1}$  in TCP and PCP molecules, respectively. These modes also are localised and pure. The -  $\tau(\text{C-OH})$  mode was assigned at the wavenumber 409 and 317  $\text{cm}^{-1}$  in *cis*- and *trans*-chlorophenols [31], respectively and at 314  $\text{cm}^{-1}$  in phenol [31]. The C-O-H angle bending - $\alpha(\text{C-O-H})$  mode is found to correspond to the wavenumber 1156( $\nu_{21}$ ), 1134( $\nu_{21}$ ), 1291( $\nu_{26}$ ) and 1245( $\nu_{28}$ )  $\text{cm}^{-1}$  in both the C-1 and C-2 of the 2-CP, TCP and PCP, respectively. These modes are found to be coupled with many other modes. The C-O-H angle bending - $\alpha(\text{C-O-H})$  mode was assigned at wavenumber 1192, 1211 and 1190  $\text{cm}^{-1}$  in phenol, *cis*- and *trans*-chlorophenols [31], respectively.

## 4 Conclusions

From the present investigations of 2-chlorophenol (2-CP), 2,4,6-trichlorophenol (TCP) and pentachlorophenol (PCP) it could be concluded that the bond lengths of the polar bonds decreased with increasing the number of sites of high electronegative atoms in the molecules.

Furthermore, the O atom of OH group in all the species possesses the highest magnitude of APT charge. It is also noticeable that the negative surface charge density is the highest in PCP molecule while it is the lowest in 2-CP molecule. It could also be noted that out of all the H atoms in all the molecules the H atom of the OH group possesses the highest value of the APT atomic charge. A close investigation reveals that the ring carbons, directly connected to the Cl atoms in 2-CP and TCP molecules possess positive Mulliken charges with different magnitudes; while in the PCP molecule the C atoms connected to the Cl atoms possess alternately negative and positive Mulliken charges having different magnitudes. The O atom in all the molecules has negative and small magnitude of Mulliken atomic charge (highest in 2-CP and lowest in PCP in magnitude), while the Cl and H atoms in all the molecules possess positive Mulliken atomic charges. The phenolic H atom has the highest value amongst all the H atoms present in all the considered molecules.

The  $\nu(\text{O-H})$  mode has higher magnitude in the C-1 conformer as compared to the C-2 conformer indicating the presence of a weak intra-molecular hydrogen bonding in C-1. The mode  $\nu(\text{C-OH})$  is unaffected in going from 2-CP to TCP to PCP while  $\alpha(\text{C-O-H})$  has enhanced magnitude for TCP and PCP. The  $\tau(\text{C-OH})$  mode appears to be independent of the number of the Cl atoms on the ring, however it is strongly affected by the juxtra position Cl atom. All the phenyl ring modes are more or less substitution dependent. Noticeable is the mode **12** of benzene which appears at considerably reduced magnitude (825-850  $\text{cm}^{-1}$ ) for mono- and tri-CPs due to its coupling with other modes which disappears in PCP as is evident from its magnitude (962  $\text{cm}^{-1}$ ) much closer to that of benzene (993  $\text{cm}^{-1}$ ).

**References**

1. Diem M, Romeo M, Boydston-White S, Miljkovic M, Matthäus M, *Analyst*, 129(2004)880-885.
2. Singh Bhawana, Gautam Rekha, Kumar Srividya, Kumar B N Vinay, Nongthomba Upendra, Nandi Dipankar, Mukherjee Geetashree, Santosh Vani, Somasundaram Kumaravel, Umapathy Siva, *Current Sc*, 102(2012)232-244.
3. Adele L B, Richard M, *Vib Spectrosc*, 38(2005)107-114.
4. Wu H W, Volponi J V, Oliver A E, Parikh A N, Simmons B A, Singh S, *Proc Natl Acad Sci USA*, 108(2011) 3809-3814.
5. Peter R G, James A de H, *Fourier Transform Infrared Spectrometry*, (Wiley Interscience, Canada), 2007.
6. Prayson R A, Agamanolis D P, Cohen M L, *J Neurol Sci*, 175(2000)33-39.
7. Dercová Katarina, Certík Milan, Mal'ová Anna, Sejáková Zuzana, *International Biodeterioration & Biodegradation*, 54(2004)251-254.
8. Lo K V, Zhu C M, Cheuk W, *Environmental Technology*, 19(1998)91-96.
9. Furukawa K, *Trends in Biotechnology*, 21(2003)187-190.
10. Mannisto M K, Tirola M A, Puhakka J A, *Biodegradation*, 12(2001)291-301.
11. Sithole B B, Williams D T, *J Assoc Off Ana Chems*, 69(1986)807-810.
12. Passivirta J, Heinola K, Humpi T, Karjalainen A, Knuutinen J, Mäntykoski K, Pauku R, Piilola T, Surma-Aho K, Tarhanen J, Welling L, Vihonen H, Särkkä J, *Chemosphere*, 14(1985)469-491.
13. Roberts M S, R.A. R A, Swarbrick J, *J Pharm and Pharmaco*, 29(1977)677-683.
14. Somani S M, Smart T, Khaliq A, *J Toxic & En Health*, 13(1984)787-798.
15. Kogevinas Manolis, Becher Heiko, Benn Trevor, Bertazzi Pier Alberto, Boffetta Paolo, Bueno-de-Mesquita H Bas, Coggon David, Colin Didier, Flesch-Janys Dieter, Fingerhut Marilyn, Green Lois, Kauppinen Timo, Jttorin Margareta L, Lyngelsebeth, Mathews John D, Neuberger Manfred, Pearce Neil, Saracci Rodolfo, *Am J Epidemiol*, 145(1997)1016-1075.
16. Somani S M, Khaliq A, *J Toxic & En Health*, 9(1982)889-897.
17. Exon J H, Koller L D, *Environmental Health Perspectives*, 46(1982)137-140.
18. Korte F, East J M, Condie L W, Borzelleca J F, *Chemosphere*, 7(1978)79-102.
19. Seyler D E, East J M, Condie L W, Borzelleca J F, *Toxico Letts*, 20(1984)309-315.
20. Exon J H, Henningsen G M, Osborne C A, Koller L D, *J Toxic and En Health*, 14(1984)723-730.
21. Seminario J M, Politzer P (Eds.), *Modern Density Functional Theory: A Tool for Chemistry*, vol. 2, Elsevier, Amsterdam, 1995.
22. Becke A D, *J Chem Phys*, 98(1993)5648-5652.
23. Becke B D, *Phys Rev B*, 38(1988)3098-3100.
24. Lee C, Yang W, Parr R G, *Phys Rev B*, 37(1988)785-789.
25. Vosko S H, Wilk L, Nusair M, *Can J Phys*, 58(1980)1200-1211.
26. Frisch M J, Trucks G W, Schlegel H B, Scuseria G E, Robb M A, Cheeseman J R, Scalmani G, Barone V, Mennucci B, Petersson G A, Nakatsuji H, Caricato M, Li X, Hratchian H P, Izmaylov A F, Bloino J, Zheng G, Sonnenberg J L, Hada M, Ehara M, Toyota K, Fukuda R, Hasegawa J, Ishida M, Nakajima T, Honda Y, Kitao O, Nakai H, Vreven T, Montgomery J A (Jr), Peralta J E, Ogliaro F, Bearpark M, Heyd J J, Brothers E, Kudin K N, Staroverov V N, Kobayashi R, Normand J, Raghavachari K, Rendell A, Burant J C, Iyengar S S, Tomasi J, Cossi M, Rega N, Millam J M, Klene M, Knox J E, Cross J B, Bakken V, Adamo C, Jaramillo J, Gomperts R, Stratmann R E, Yazyev O, Austin A J, Cammi R, Pomelli C, Ochterski J W, Martin R L, Morokuma K, Zakrzewski V G, Voth G A, Salvador P, Dannenberg J J, Dapprich S, Daniels A D, Farkas Ö, Foresman J B, Ortiz J V, Cioslowski J, Fox D J, *Gaussian 09, Revision C.01*, Gaussian, Inc., allingford, CT, 2010.
27. Bekou Evangelia, Extraction of organic contaminants using room temperature water-immiscible ionic liquids, M S Thesis, Division of research and advanced studies of the University of Cincinnati, 2002.

28. Martin J M L, Alsenoy C Van, GAR2PED, A Program to Obtain a Potential Energy Distribution from a Gaussian Archive Record, University of Antwerp, Belgium, 1995.
29. Dixit V, Yadav R A, (*Unpublished Work*)
30. Ferreira M M C, Suto E, *J Phys Chem*, 96(1992)8844-8849.
31. Tishchenko Oksana, Kryachko Eugene S, Minh Tho Nguyen, *Spectrochim Acta*, A58(2002)1951-1969.
32. Arjunan V, Mohan S, Subramanian S, Thimme Gowda B, *Spectrochim Acta*, A60(2004)1141-1159.
33. Gayathri R, Arivazhagan M, *Spectrochim Acta*, A81(2011)242-250.
34. Kattan D, Palafox M Alcolea, Kumar S, Manimaran D, Joe I Hubert, Rastogi V K, *Spectrochim Acta*, A 123(2014) 89-97.
35. Karthikeyan N, Prince J Joseph, Ramalingam S, Periandy S, *Spectrochim Acta*, A124(2014)165-177.
36. Dwivedi Y, Thakur S N, Rai S B, *Spectrochim Acta*, A 71(2009)1952-1958.

[Received: 1.10.2014; accepted: 10.11. 2014]